

Tribocorrosion Properties of Borided and Al₂O₃-Coated NiTi Material

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Abstract

The purpose of this study was to investigate the tribological properties of NiTi shape-memory alloy that was borided and coated with Al₂O₃ using the electrophoretic deposition (EPD) method. For the study, the sample surface was borided for 1 and 4 h at 800°C with the method of pack boriding, and the surface of the sample that was borided was coated with Al₂O₃ using the EPD method. The tribocorrosion properties of the untreated samples, borided samples, and borided and (duplex) Al₂O₃-coated samples were investigated and characterized using XRD and SEM devices. Accordingly, following the boriding treatment on the NiTi material, Al₂O₃ coating was successfully carried out with the EPD method. In comparison to the untreated samples, the tribocorrosion resistance of the surface-treated samples under a load of 3 N in a 3.5% NaCl solution increased. Additionally, among all samples, those that were subjected to the duplex surface treatment had the best tribocorrosion properties.

Keywords: NiTi, Boriding, EPD, Tribocorrosion

Borlanmış ve Al₂O₃ Kaplı NiTi Malzemenin Tribokorozyon Özellikleri

Özet

Bu çalışmanın amacı, borlanmış ve Elektroforetik biriktirme yöntemi (EPD) ile Al₂O₃ kaplanmış şekil hafızalı NiTi alaşımın tribolojik özelliklerini araştırmaktır. Araştırma için numune yüzeyi kutu borlama yöntemi ile 800 °C sıcaklıkta 1 ve 4 h borlama yapılmış ardından borlanmış numunelerin yüzeyi EPD yöntemi ile Al₂O₃ kaplanmıştır. Daha sonra işlemsiz, borlanmış ve borlanarak ardından Al₂O₃ (duplex) kaplanmış numunelerin tribokorozyon özellikleri araştırılmış, XRD ve SEM cihazı ile karakterize edilmiştir. NiTi malzeme üzerine yapılan borlama işleminden sonra EPD yöntemi ile Al₂O₃ kaplama başarılı bir şekilde gerçekleştirilmiştir. İşlemsiz numuneye göre yüzey işlemi uygulanmış numunelerin %3,5 NaCl çözeltisi içerisinde 3 N yük altında Tribokorozyon direnci artmıştır. Ayrıca duplex yüzey işlemi uygulanmış numunenin diğer numunelere göre en iyi Tribokorozyon özellikler gösterdiği sonucuna varılmıştır.

Anahtar kelimeler: NiTi, Borlama, EPD, Tribokorozyon

1. Introduction

NiTi shape-memory alloys (SMAs) are preferred in various industrial fields thanks to their shape-memory effects, excellent elasticity, and mechanical properties [1]. SMAs are a group of multifunctional metals that have shape memory and superelasticity properties. These properties come from the solid-state phase transition between the phases without diffusion [2]. Due to their properties such as biocompatibility and good compatibility with computed tomography and magnetic resonance applications, NiTi alloys are preferred in biomedical processes. These alloys are also used in several fields from aviation to communication and from automotive to microelectromechanical systems [3-6]. Despite their favorable elasticity properties, NiTi alloys suffer from wear occurring during their usage, as well as their inadequate bending and fatigue strength. To eliminate these shortcomings, surface treatments are applied to the material. While boriding can provide many advantages for the surfaces of materials such as resistance to wear, oxidation, and corrosion, it can also allow the preservation of hardness at high temperatures. The procedure of boriding, which can be applied to iron and non-iron metals, is based on the diffusion of boron atoms on the material's surface. Boriding is a thermochemical surface hardening method. While it can be applied to the material's surface using non-thermochemical methods including ion implantation, DVD, CVD, or plasma spraying, it can also be applied using thermochemical methods such as solid, liquid, gas, and plasma boriding [7-8].

In the colloidal process known as electrophoretic deposition (EPD), charged particles in a suspension are electrophoresed on a working electrode that is negatively charged. EPD has two steps. The first step involves the migration of charged particles suspended in a liquid towards the oppositely charged electrode (electrophoresis). The second step involves the formation of coating by the particles accumulating on the counter electrode (deposition). This method is fast and very cost-effective. Additionally, it is scalable, and intensive coating can be achieved with high purity at room temperature and on objects with complicated geometries. In this method, aqueous or organic suspensions can be used [9-13]. In this study, to improve the tribological properties of a NiTi shape-memory alloy, boriding was applied for 1 and 4 h at a temperature of 800°C using the pack boriding method, and the samples were then coated with Al_2O_3 using the EPD method. Next, the tribocorrosion properties of the untreated samples, borided samples, and borided and (duplex) Al_2O_3 -coated samples were investigated and characterized using XRD and SEM devices.

2. Material and Methods

The material of this study consisted of NiTi alloy samples containing 50.6% Ni whose physical and mechanical properties are shown in Table 1. The samples were cut in dimensions of $15 \times 15 \times 5$ mm. After that, they were progressively polished using sandpaper of 80–1200 grit. They were then polished even more using alumina powders having 0.3 to 0.5 μm particle diameters. To eliminate debris, ethanol was used to clean the produced samples.

Table 1. Comparison between physical and mechanical properties of NiTi alloy and stainless steel

Material	Density ($g\ cm^{-3}$)	Modulus of elasticity (GPa)	Hardness (GPa)	Ultimate tensile stress (MPa)	Recovered elongation (a.u.)
NiTi alloy	6.45	65±3	4.15±0.5	1240	8%

2.1. Boriding Procedure

The samples that were created were placed into ceramic containers loaded with commercial EKABOR II (Bortech) powders and spaced equally from the walls and other objects in the container. Ekrit powder (Bortech) was applied to the tops of the containers to avoid oxidation at high temperatures, and the lid of the programmable box furnace was tightly closed. The samples were borided in the furnace at a temperature of 800 °C for 1 and 4 hours. As soon as the boriding procedure was over, the furnace was opened, and the samples were allowed to cool down to room temperature. To get rid of any powder residue that may have been collected, the sample surfaces were cleaned mechanically.

2.2. Electrophoretic deposition

Dilute solutions containing 1% acetic acid and 99% water were prepared by magnetic stirring at room temperature for 24 h. The suspension containing Al_2O_3 powder at a concentration of 0.6 g/L was prepared by dispersion using a sonicator. Before each deposition process, the suspension was magnetically stirred to prevent particle precipitation and flocculation. The EPD coating was deposited onto the borided NiTi surfaces. This process was carried out using a container and sheet steel electrodes at thicknesses of 0.2 mm. The spacing between the electrodes was kept constant at 10 mm. The potential difference was set at 20 V, and the time was set at 20 min. After the deposition process, the samples were removed from the suspension, rinsed under distilled water, and dried at room temperature for 24 h before characterization.

By using the necessary instruments simultaneously, corrosion and wear tests were performed on the materials to ascertain their tribocorrosion capabilities. Figure 3 depicts the tribocorrosion test apparatus, and Table 2 lists the values of the parameters that were employed throughout the test. Tribocorrosion tests were conducted using a sample holder, using samples with already known surface areas. This area measured 2.54 cm^2 in this holder and in contact with the solution. First, the samples were put through 3600 seconds of Open Circuit Potential (OCP) testing while being loaded. Alumina (Al_2O_3) balls with a 6 mm diameter were employed for the wear tests. The worn track length was changed to 8 mm, and the cycle frequency was set to 1 Hz. A ball-on-disk tribometer (UMT-2, Bruker) instrument linked to a chemical cell with three electrodes submerged in a saltwater solution was used to conduct the tribocorrosion tests at ambient temperature. The tests were carried out using the experimental parameters shown in Table 2 and based on the ASTM G119-09 procedure. The wear and potentiodynamic polarization tests were started simultaneously, and a scan was performed between -1 and 1.5 V. The scanning procedure and the wear testing procedure were ended at the same time.

The data were examined using the Gamry Echem Analyst software package following tribocorrosion testing. At least three more instances of each test and measurement were performed.

Table 2. Tribocorrosion parameters.

Normal load	3 N
Relative wear distance	40 m
Stroke length	8 mm
Sliding velocity	16 mm/s
Alumina ball diameter	6 mm
Electrolyte	3.5% NaCl solution
Temperature	22°C
Reference electrode	Ag/AgCl
Counter electrode	Graphite

Utilizing XRD-GNR-Explorer X-Ray diffractometer with a Co-K α ($\lambda = 1.7903 \text{ \AA}$) source and a 2θ scale between 10° and 100° , the samples' phases were determined at 40 kV and 30 mA. Using a scanning electron microscope (SEM FEI-Quanta 250), the samples' cross-sections and wear surfaces were examined. For the SEM photos of the surface, the surface was cleaned with methanol in a magnetic stirrer for 15 min and subsequently dried to remove contaminations that developed after coating. The samples' roughness and their wear track morphology (width and depth of tracks) after the tribocorrosion tests were examined with the 3-dimensional surface profilometry method (Bruker Contour GT-K1).

3. Results and Discussion

3.1. Characterization of samples

Figure 1 shows the XRD plots of the untreated samples and the samples that were borided for 4 h at 800°C and then coated with Al_2O_3 (duplex). The SEM images of the a) 800°C 4 h, b) 800°C 4 h + Al_2O_3 , c) untreated samples are given in Figure 2. According to the XRD plots, on the surface of the material that was borided at 800°C for 4 h and then coated with Al_2O_3 , NiB_2 , TiB_2 , and Al_2O_3 phases were formed. This result meant that the phases that are likely to occur in the structure could be dispersed homogeneously. This way, stable conditions could be

achieved with the phases that were homogeneously distributed in the microstructure. Moreover, Al_2O_3 coating was successfully achieved with the boriding procedure and the EPD method.

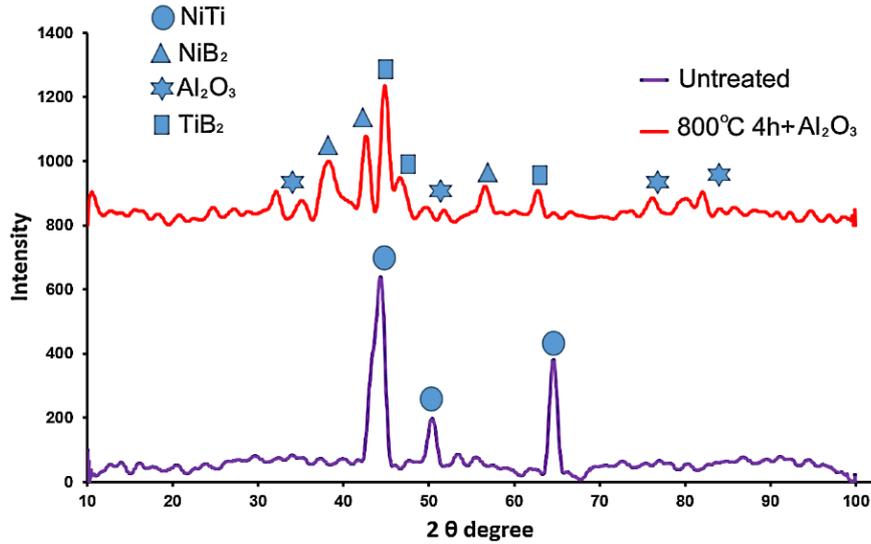


Figure 1. XRD plots of untreated NiTi samples and NiTi samples borided at 800°C for 4 h and coated with Al_2O_3

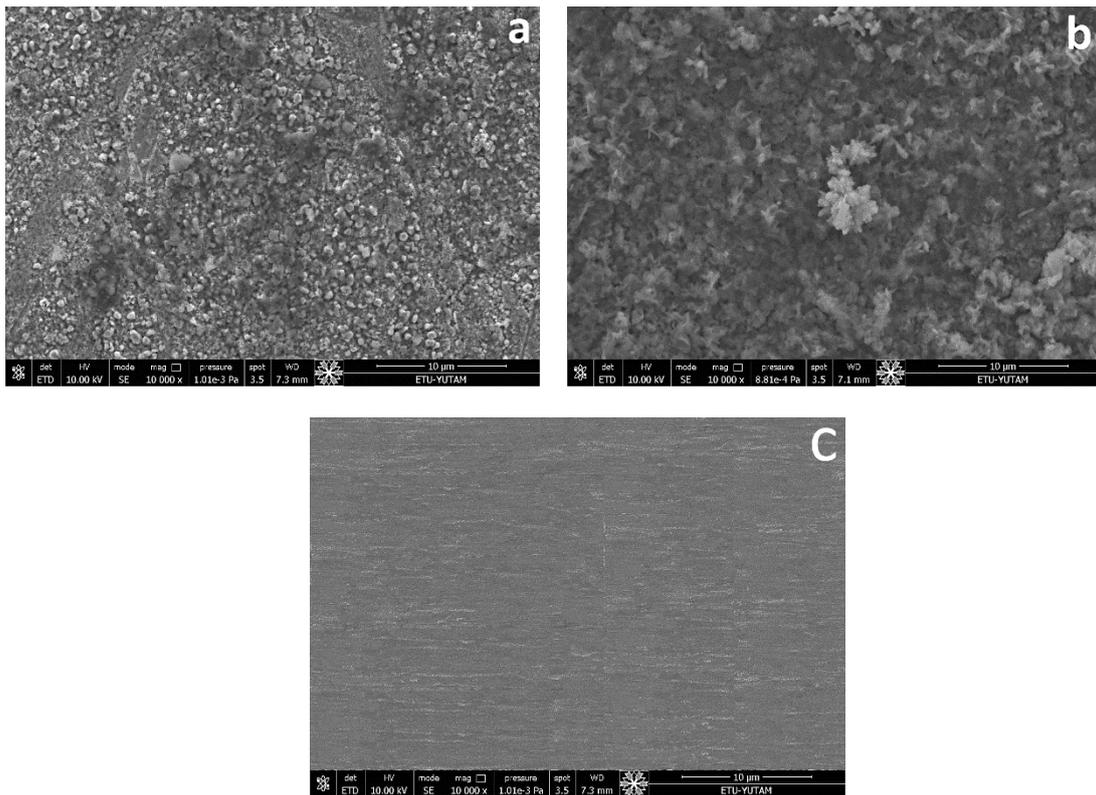


Figure 2. SEM images of a) 800°C 4 h, b) duplex (800°C 4 h + Al_2O_3), c) untreated

3.2. Tribocorrosion properties

Figure 3 presents The SEM images of the untreated samples' worn surfaces and the samples that were borided for 4 h at 800°C and then coated with Al_2O_3 (duplex) after the tribocorrosion tests. Because the structure of the base material contains Ni, and boron has a higher affinity

than Ni in borided samples, B atoms force Ni atoms to move inwards, and this results in a thin boride layer on the surface [14]. The boride layer increases the surface hardness of the NiTi alloy. Additionally, another cause of this increased hardness on the surface is the boride phases created on the surface by the boron with Ni and Ti found in the base metal. The compressive stress that is created with the help of these phases that are likely to be formed plays an effective role in the improvement of the mechanical and wear characteristics of the material [8]. Therefore, the mechanical and tribological properties of the material are enhanced with the help of this layer.

At the start of the wear process in the untreated NiTi sample, a two-body mechanism brings the sample surface and the Al₂O₃ ball into direct contact. The Ti and Ni that form as a result of friction adhere firmly to the ball. As the wear process continues, this adhesion leads to the formation of new wear products, and the surface of the untreated NiTi material transfers material to the surface of the hard abrasive ball. Consequently, the untreated sample's wear behavior persists across the testing period as a mix of the abrasion and plastic deformation mechanisms together with significant adhesive wear.

Treated samples can provide many advantages with the boriding process such as higher wear, oxidation, and corrosion resistance on the surface and the preservation of hardness at high temperatures [15]. Therefore, the Al₂O₃ that is deposited onto the surface with the coating process carried out after boriding leads to an increase in microhardness by increasing the cathodic duty cycle [16-17]. In their study on SiC particles, Luo et al. reported that increasing the concentration of Al₂O₃ initially provides superior mechanical properties including bending strength, fracture toughness, and Vickers hardness [18]. Additionally, uniform Al₂O₃ coating improves mechanical properties and prevents grain growth. However, the hardness and Young's modulus of the coating are strongly affected by the thickness of the coating, its composition, porosity, and microcracks [17]. As seen in the images of the wear surfaces, in this study, it was observed that the untreated samples and the duplex-coated samples showed different wear behaviors due to the aforementioned effects of the surface treatments. Throughout this analysis, wear mechanism damage was far more significant than corrosive damage.

The tribocorrosion behaviors of the untreated samples, the samples that were borided for 1-4 h at 800°C, and the samples that were coated with Al₂O₃ after boriding (duplex) during the sliding test were examined. For this purpose, open circuit potential (OCP) and potentiodynamic polarization tests were conducted. OCP provides information about the state of surface electrochemistry. The polarization curve shows changes in the specimens' ability to withstand corrosion while sliding [19].

Figure 4 presents the friction coefficients of different samples under 3 N load in a 3.5% wt. NaCl solution. As seen in Figure 4, the mean coefficients of friction (COF) for the untreated samples, 800°C 1 h borided samples, 800°C 4 h borided samples, 800°C 1 h borided + Al₂O₃-coated samples, and 800°C 4 h borided + Al₂O₃-coated samples were 0.2, 0.3, 0.4, 0.5, and 0.65, respectively. The fluctuation of COF under a load of 3 N indicates the displacement of the opposing ball along the coating interface [20]. Therefore, this situation shows that the sample has experienced wear. Additionally, as seen in the plot of the 800°C 4 h borided + Al₂O₃-coated

samples, these samples did not show noticeable fluctuations, especially compared to the untreated samples. Hence, the duplex-treated samples did not show much wear under a load of 3 N. This situation is related to the higher density and hardness of the sample surface. Wear on such a sample surface results in minimal loss of volume. High surface hardness values usually go through the phases of high resistance to adhesion, oxidation, and fatigue [21]. As seen in this study, during the sliding test against the Al_2O_3 ball inside the 3.5% NaCl solution, due to the high tendency of the surfaces of the untreated samples to wear, COF values with substantial fluctuations were observed on the surface of this alloy. This indicated the weak tribological behavior of the untreated samples. Among all samples, the course of fluctuations showed a relatively decreasing trend with the thickness of the boriding layer and the coating, and the lowest degree of fluctuations was observed on the duplex-treated surfaces. As seen here, the 800°C 4 h borided + Al_2O_3 -coated surface not only significantly increased the wear resistance of the samples but also affected the COF values during the two-body tribocorrosion test.

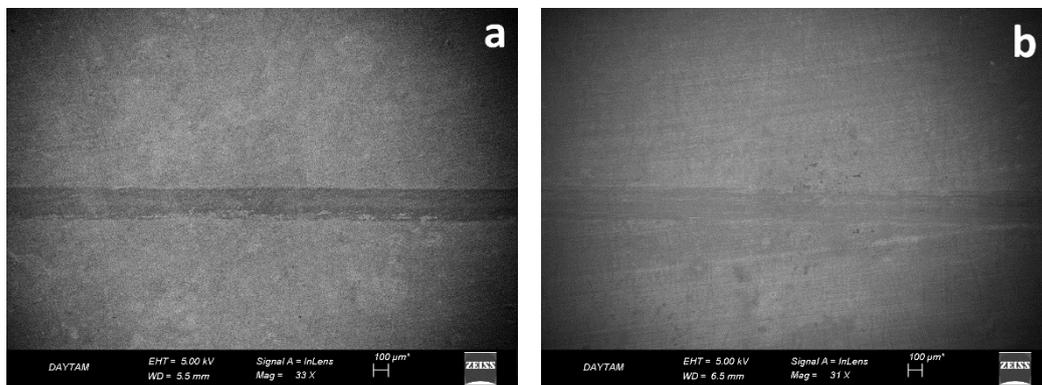


Figure 3. SEM images of wear analysis during tribocorrosion of **a)** Untreated **b)** 800°C 4h + Al_2O_3

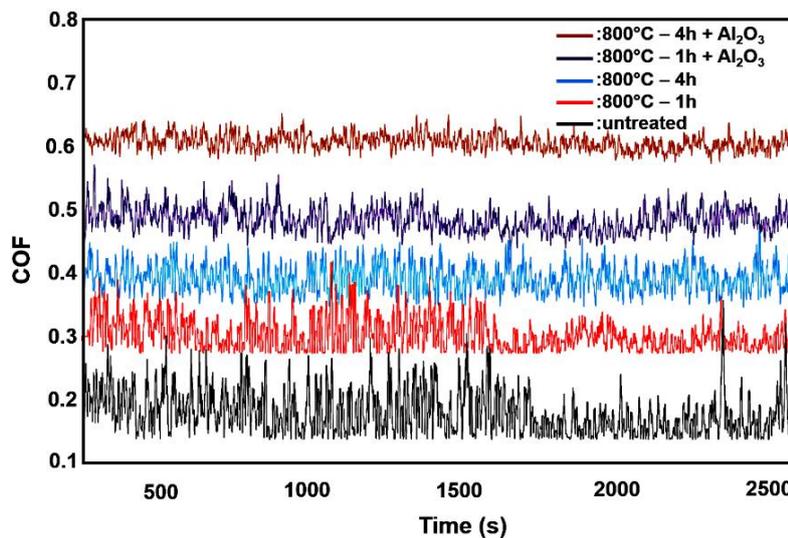


Figure 4. Variation of OCP with time recorded during sliding with the COF values of untreated, 800°C 1 h borided, 800°C 4 h borided, 800°C 1 h borided + Al_2O_3 , and 800°C 4 h borided + Al_2O_3 samples

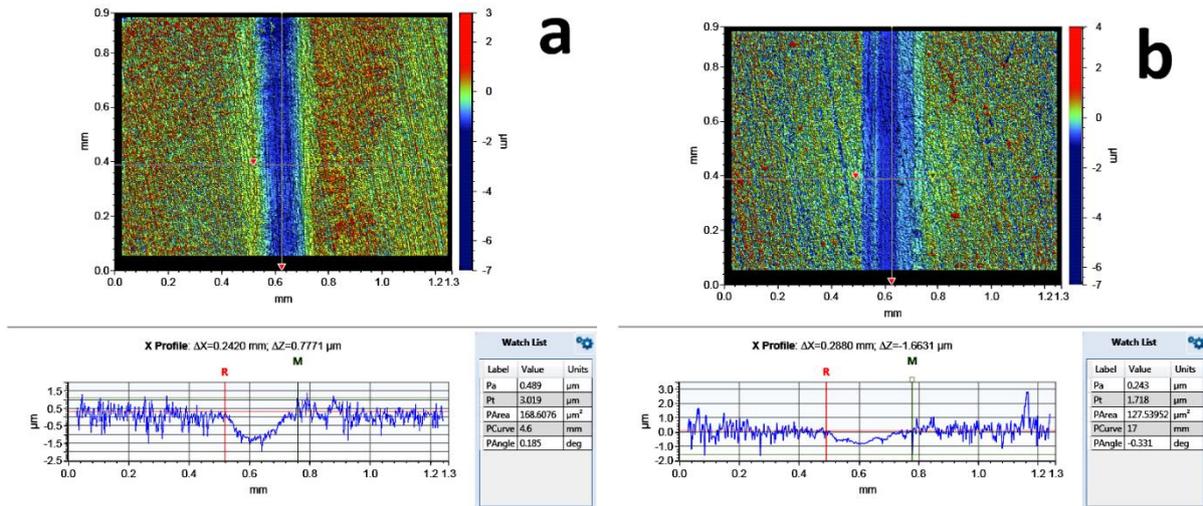


Figure 5. Wear analysis during tribocorrosion of a) Untreated, b) 800°C 4 h + Al_2O_3

Figure 5 displays the cross-sections of the untreated (Figure 5a) and the 800°C 4 h + Al_2O_3 samples, as well as the wear tracks' three-dimensional surface profiles (Figure 5b), respectively (the best and worst experimental conditions are given). It can be observed that the wear depth of the untreated sample was much higher than that of the 800°C 4 h + Al_2O_3 sample due to the lower tribocorrosion resistance of the former. A substantial improvement was seen in the wear behavior of the NiTi alloy during sliding under a load of 3 N in room conditions with the duplex coating treatment. The wear process that started in an adhesive form in the untreated samples gained a micro-abrasive characteristic with the effects of the particles that were released from the material. In the duplex-treated samples, the form of wear was usually adhesive. The surface hardness that increased with the duplex surface treatment led to a decrease in wear by making plastic deformation more difficult. The thicker boron layer that is formed with the prolongation of the boriding time increases the wear rate, although the wear does not reach the base material. For all samples that were examined in terms of COF, Figure 6 shows the potentiodynamic polarization curves during the 3 N sliding test, and Figure 7 displays the voltage-current density curves during the same test. Tribocorrosion causes a mixed potential in OCP. As a result, it demonstrates that the active wear areas and passive wear regions are in a rather steady state [22]. The mechanically passivated portions (anode) and the surrounding passive areas create a galvanic bond as a result of sliding (cathode). As a result, OCP undergoes a severe negative change. After then, the wear track's depassivation and repassivation rates are in balance with one another. This equilibrium brings OCP to a new stable state [19]. In this study, the sliding procedure may have accelerated the corrosion rate of the untreated layer of the NiTi alloy subjected to the corrosive medium inside the 3.5% wt. NaCl solution. This, in turn, may have resulted in a higher i_{corr} value under the 3 N load in the duplex-treated samples compared to the specimens that are untreated.

The OCP data that were obtained in this study showed that the duplex-coated samples had a more positive potential trend compared to the untreated samples. Respectively from the untreated samples to the borided samples, and finally, to the duplex-coated samples, it was seen that the corrosion rates decreased, and accordingly, the corrosion resistance values increased.

As the thickness of the coating on the surface decreased, due to mechanical wear, the potential changes in the negative direction. Additionally, potential is associated with the passive film on the surface [23]. A passive film can be formed during corrosion, it breaks very easily from the worn surface with the effect of mechanical wear, and it separates, which leads to a negative shift in the corrosion potential. As seen in Figure 6, considering that the duplex-treated samples had more positive values and less wear compared to the others, it may be stated that it showed better tribocorrosion properties. As a result, in comparison to the untreated samples, the tribocorrosion resistance values of the surface-treated samples inside the 3.5% NaCl solution under the load of 3 N increased. Furthermore, the samples to which duplex surface treatment was applied showed the best tribocorrosion-related properties among all samples.

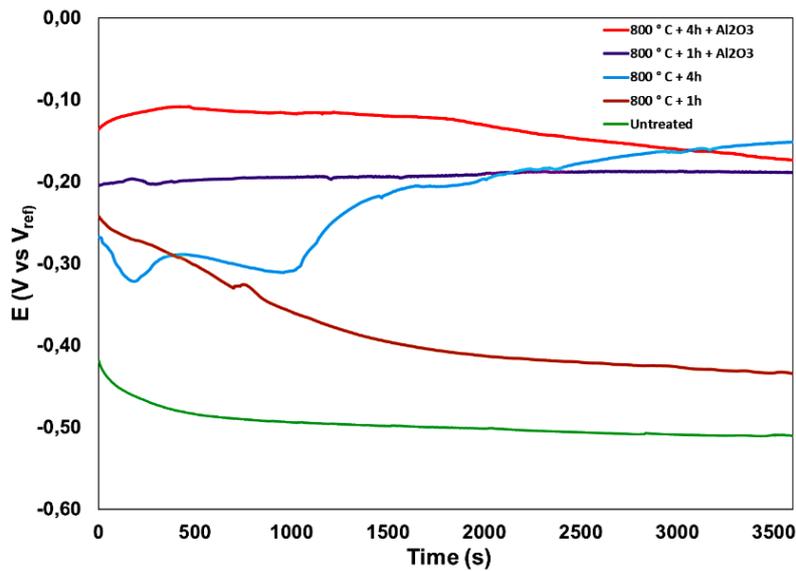


Figure 6. OCP curves of the samples inside the solution.

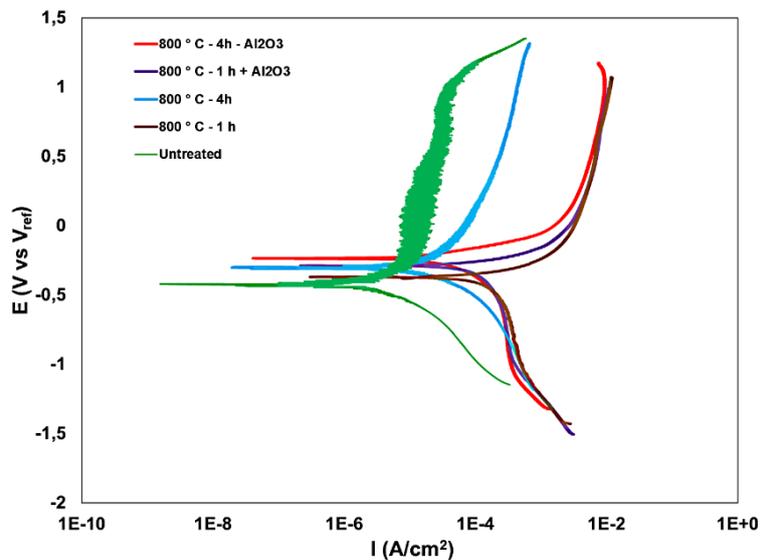


Figure 7. Voltage-current density curves

4. Conclusions

In this study, the tribocorrosion properties of a borided and Al₂O₃-coated NiTi material were investigated, and the results were as follows.

On the surface of the material that was borided at 800°C for 4 h and then coated with Al₂O₃, NiB₂, TiB₂, and Al₂O₃ phases were formed. With the boriding treatment and the EPD method, the Al₂O₃ coating process was successfully implemented. For all samples, the degree of COF fluctuations relatively decreased depending on the increased thickness of the boriding layer and the coating on it, and the lowest degree of fluctuations was found in the duplex-treated samples. In comparison to the untreated samples, the tribocorrosion resistance of the surface-treated samples under the load of 3 N in the 3.5% NaCl solution increased. The duplex-treated samples showed the best tribocorrosion-related characteristics among all samples.

Ethics in Publishing

There are no ethical issues regarding the publication of this study

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