

Short Communication

Electrochemical Behavior of Nb₂O₅ Films Produced by Magnetron Sputtering

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Metallic engineering materials generally form passive films on their surfaces and therefore are prone to localized corrosion, usually characterized by the occurrence of pits. The improvement of surface properties is a requirement for the metallic components used, for example, in petrochemical industry, in fuel cells, and in nuclear plants. The goal of this paper is to investigate the influence of Nb₂O₅ coatings on the electrochemical behavior of AISI 316 stainless steel. The films were deposited for 15, 30 and 50 minutes by using DC magnetron sputtering technique. The corrosion resistance was evaluated by monitoring the open circuit potential (OCP), the electrochemical impedance spectroscopy (EIS) and the linear potentiodynamic polarization (LP) in an aqueous 0.1 M H₂SO₄ electrolyte at 25 °C. Electrochemical tests revealed a more capacitive behavior of the Nb₂O₅-coated specimens when compared to the uncoated one. This fact indicates that the coated samples are less susceptible to corrosion. The deposited films show a protective character and can be used to avoid the degradation of the AISI 316 austenitic stainless steel in aggressive environments containing sulfur ions.

Keywords: stainless steel, Nb₂O₅, magnetron sputtering, corrosion resistance, niobium oxide.

1. INTRODUCTION

Stainless steels are ferrous alloys that have a minimum chromium (Cr) content of 11% in their composition, and nickel (Ni) is also commonly added [1]. In addition to the main elements silicon, manganese, molybdenum, and nitrogen may also be present in stainless steels. The presence of some elements as oxygen (O), phosphorus (P) and sulfur (S) [2] may be undesirable when in large quantities. Cr is the main alloying element and is responsible for the corrosion resistance of these steels. According to the electrochemical series chromium is less resistant to oxidation than iron (Fe). However, when the surface is in contact with an oxidizing medium, a highly stable chromium oxide

layer known as passive film is formed [3]. According to several authors [4-10], the passive film is formed by duplex character layers, and is mainly composed by iron oxides / hydroxides and chromium oxide. According to Milosev [11], the film inner layer, near the metal / film interface, contains mainly chromium oxide, while the outermost layer near the film / medium interface is composed of iron oxides / hydroxides in higher concentrations. Depending on the alloy, other oxides such as nickel and molybdenum are also present, but in smaller quantities.

Special austenitic stainless steels have a minimum chromium content of 17% and high contents of elements such as nickel and molybdenum. Small additions of manganese and nitrogen may partially replace nickel, and act as stabilizers of the austenitic structure. The main element responsible for pitting corrosion resistance is chromium, although molybdenum also increases the corrosion resistance of the alloy from this type of localized attack. Austenitic stainless steels have a face-centered cubic structure (FCC) at low temperatures. This structure confers suitable mechanical properties for application in orthopedic prostheses, besides high resistance to corrosion and absence of ferromagnetic phase [12, 13]. The use of stainless steels for biomedical applications has been done for many decades [14, 15]. The austenitic stainless steel ISO 5832-1 (ASTM F138 / AISI 316L) is the most used material in the manufacture of orthopedic implants due to its mechanical properties, biocompatibility and price [16-21].

Schultze and Lohrengel [22] published a review on the stability, reactivity and breakdown of passive films. One of the points highlighted is the influence of chloride ions on pitting corrosion, which can be explained by two mechanisms. In the first one, the diffusion of chloride ions in the oxide causes its instability, leading to active dissolution. The second mechanism considers that the adsorption of chloride ions causes internal stresses in the film, resulting in its rupture. In both situations, after the passive film breaks, the chloride ions are adsorbed in the metal surface, accelerating the active dissolution.

The breakdown of the passive film can occur in the presence of anions, particularly the halogens [23]. Three different mechanisms of passive film breaking are proposed: mechanical, electronic and ionic. The mechanical process occurs due to the introduction of micro-fractures resulted from the internal stresses during the passive film growth. The passive film breakdown by the electronic mechanism is caused by the electronic current produced in thick films. During the anodic oxidation process, the anions of the electrolyte penetrate the oxide film acting as impurities donors. In thick films, these electrons gain enough energy to be accelerated, causing the localized destruction of the surface oxide [24-29]. The ionic process occurs as a function of the competition between hydroxyl radicals and aggressive anions such as chloride (Cl^-) to be adsorbed at the oxide / electrolyte interface. Cl^- adsorb in the film, dissolving or producing vacancies of metal ions, which migrate to form voids at the metal / oxide interface. These voids can induce sufficient mechanical stresses for the formation of micro cracks, which causes the passive film breakdown [17].

Many stainless steels undergo degradation processes in different media [30, 31]. Nowadays, additions of niobium (Nb) or coatings based on niobium oxides have been used in order to promote superior resistance to corrosion [32-34], mainly in more aggressive media such as sulfuric acid H_2SO_4 [35, 36]. It has been reported that Nb can increase the strength of low alloyed steel due to the formation of a second phase [37, 38]. Niobium oxide films are of great interest in a wide range of

applications, such as sensors, solar cells, aeronautic and nuclear industries, and biomedical purposes due to its high resistance to wear, good stability and high biocompatibility.

The aim of the present work was to evaluate the susceptibility to localized corrosion of Nb₂O₅ coatings, deposited for 15, 30 and 50 minutes by magnetron sputtering, on the austenitic stainless steel AISI 316 in an aggressive 0.1 M H₂SO₄ medium.

2. EXPERIMENTAL

Specimens of AISI 316 austenitic stainless steel with circular shape by 19 mm in diameter, 6 mm- thick, and chemical composition (wt %) presented in Table 1, were ground up to 600 grit using SiC paper. All the specimens were degreased in acetone, washed in deionized water and dried prior to Nb₂O₅ deposition at three different times: 15 min, 30 min and 50 min. The depositions were carried out in a PV600 DC reactive magnetron sputtering by using a high purity niobium target and DC power of 400 W. The atmosphere was composed of argon and oxygen with flows of 100 mL.min⁻¹ and 15 mL.min⁻¹, respectively. The oxygen content was high enough to allow the formation of Nb₂O₅ [39]. Results published elsewhere [32] have shown that for 15 and 30 minutes the compound Nb₂O_{5,35} was formed, and it is independent of the sputtering time. The distance between the target and the samples was 15 cm, and the pressure in the chamber during the deposition was 8.40 x 10⁻² Pa.

Table 1. Chemical composition of AISI 316 stainless steel (wt %).

Element	C	Si	Mn	P	S	Cr	Mo	Ni	Fe
(wt %)	0.076	0.7	1.56	0.028	0.007	17.1	2.1	10.0	balance

The electrochemical behavior of the samples was evaluated by electrochemical impedance spectroscopy (EIS) and linear polarization measurements in a Biologic EC-Lab V10.33 – SP-150 potentiostat - galvanostat in a flat-cell of three electrodes. Nb₂O₅ coated AISI 316 stainless steel with 1.0 cm² of exposed area was the working electrode, the counter-electrode was a platinized platinum wire, and a Saturated Calomel Electrode (SCE) (3M) was the reference. The electrolyte consisted of a 0.1M sulfuric acid (H₂SO₄) solution. The open circuit potential (OCP) was monitored during 1 hour at room temperature (25°C). The anodic polarization tests were performed at a scan rate of 1.0 mVs⁻¹. For comparison uncoated specimens (blank) were tested.

3. RESULTS AND DISCUSSION

The corrosion resistance of AISI 316 stainless steel specimens, with and without Nb₂O₅ coatings was evaluated by different electrochemical methods, analyzing an area corresponding to 1 cm². Each evaluated sample contained six specimens treated with the parameters cited above. The corrosion potential vs. immersion time is shown in Figure 1.

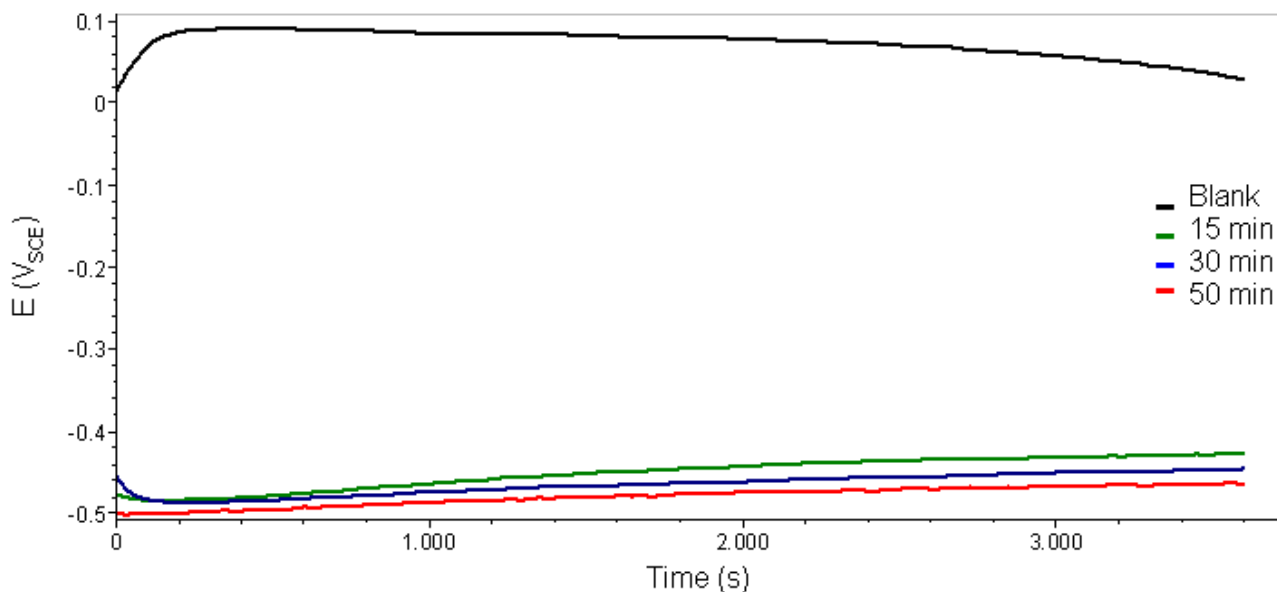


Figure 1. Open circuit potential monitored for blank and coated samples.

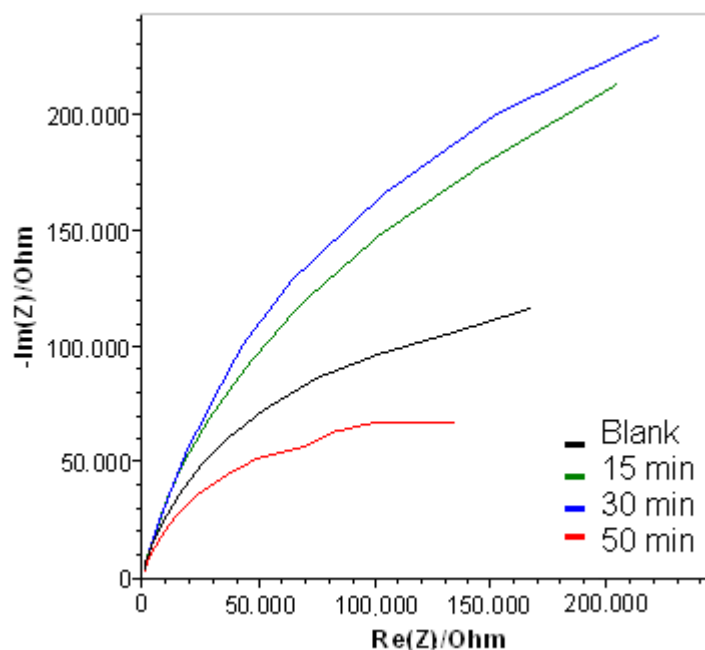


Figure 2. Electrochemical impedance spectroscopy (Nyquist plots) for blank and Nb₂O₅ -coated samples.

The open circuit potential was monitored for uncoated and Nb₂O₅ -coated samples for 1 h. All coated samples presented more negative OCP than the blank. The surface of AISI 316 SS showed a rapid increase of its corrosion potential for the first periods of immersion, then decreasing slightly. The Nb₂O₅-coated samples showed an increasing tendency of the corrosion potential. All the tested samples presented a continuous and homogeneous OCP for 1h of immersion in this electrolyte. This

fact suggests that a stable passive film was formed on these samples. After monitoring, the OCP of the 30 min Nb₂O₅-coated sample was inferior than that obtained for the sample coated for 15 min. Somehow, the OCP for the 50 min coated sample showed the lowest values. Similar tendencies were reported in the literature for Nb₂O₅ films tested in NaCl solution [32].

Nyquist impedance plots for niobium oxide coated samples and blank surface obtained after 1 hour of immersion in 0.1M H₂SO₄ solution are shown in Figure 2. The coatings deposited for 15 min and 30 min presented higher impedance values comparing to the blank sample. These results suggest that in these conditions the Nb₂O₅ coatings promote a corrosion protective behavior on AISI 316 SS surfaces. However, the sample coated for 50 min showed lower impedance than the blank sample. All tested samples showed capacitive character, with high impedance values for the lowest frequencies, indicating that the oxide layer formed on these samples were stable throughout the test [32, 36].

The lowest values obtained for the sample coated for 50 min could be explained by its thickness. It is known that longer sputtering times led to an increasing in coatings thickness, which must reduce the corrosion protection due to the higher porosity and defects formed on these thick films [40, 41]. Another interpretation of the EIS data was obtained by fitting these results using equivalent circuits (ECs). The EC used to simulate the EIS response that best fits all conditions is shown in Figure 3, and the parameters obtained by the fitting procedure are shown in Table 2.

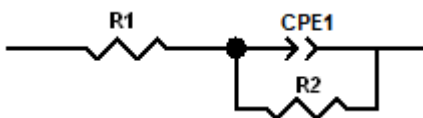


Figure 3. EC used to simulate the EIS experimental data.

Table 2. EIS fitting parameters for the blank and the Nb₂O₅ -coated AISI 316 stainless steel.

Sample	R ₁ (Ωcm ²)	CPE ₁ (cm ² s ⁻ⁿ Ω)	n ₁	R ₂ (Ωcm ²)
Blank	86.1	9.64E-06	0.90	2.19E+06
15 min	101.5	6.80E-05	0.88	4.88E+03
30 min	123.3	6.28E-05	0.88	7.23E+03
50 min	115.8	1.14E-04	0.91	1.73E+03

In the equivalent circuit proposed, R represents the resistance at the interfaces, CPE is a constant phase element and n refers to the power of the CPE. As shown in Table 2, R₁ and CPE₁ values are higher for the Nb₂O₅-coated samples, suggesting that the Nb₂O₅ coatings play a protective role in the arrangement. However, R₂ values are lower for coated samples comparing to the uncoated (blank) samples. This fact implies that these Nb₂O₅ -coatings are not immune to the H₂SO₄ solution penetration [32].

The potentiodynamic polarization behavior of the blank and the Nb₂O₅ -coated AISI 316 SS in 0.1 M H₂SO₄ at 25 °C is presented in Figure 4. The linear polarization curves showed that the passive

current density is lower for the coated samples comparing to the blank. The inferior value was obtained for specimens coated for 30 min, followed by the 50 min and the 15 min.

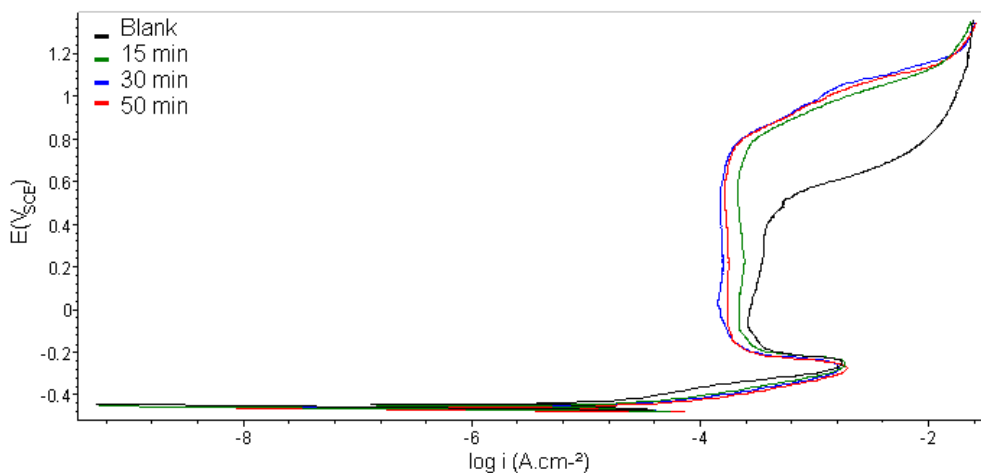


Figure 4. Potentiodynamic polarization curves of the blank and the Nb₂O₅ -coated AISI 316 SS in 0.1 M H₂SO₄ at 25 °C.

All tested samples showed passive current density practically at the same range of passive potentials. The AISI 316 SS samples exhibited breakdown potential (E_b) at about 0.5 V (SCE). No pitting was observed for the niobium coated samples up to 1.3 V (SCE). A fast increase in the current density occurred at potentials below 0.85 V (SCE), which is associated with oxygen evolution. Nb₂O₅ coating affects greatly the anodic behavior of the stainless steel substrate.

The electrochemical values of corrosion potential (E_{corr}), corrosion current density (I_{corr}), Tafel constants (β_a) and (β_c), breakdown potential (E_b) and passive current density (I_p) are shown in Table 3.

Table 3. Electrochemical parameters extracted from the potentiodynamic linear polarization curves of the blank and coated samples.

Sample	E_{corr} (V _{SCE})	I_{corr} ($\mu A.cm^{-2}$)	β_a (mV/decade)	β_c (mV/decade)	E_b (V _{SCE})	I_p ($\mu A.cm^{-2}$)
Blank	-0.450	10.29	82.4	34.0	0.503	3.48
15 min	-0.473	42.19	122.5	35.4	0.783	3.65
30 min	-0.481	68.87	145.2	35.0	0.802	3.79
50 min	-0.485	78.14	144.7	35.1	0.797	3.73

The uncoated AISI 316 SS presented higher corrosion potential (E_{corr}) than the niobium oxide coated samples. The corrosion potential (E_{corr}) for the coated samples decreased with the increasing of the Nb₂O₅ deposition time, and the corrosion current densities (I_{corr}) directly increased as a function of it. Tafel cathodic constants (β_c) obtained for all evaluated samples have presented comparable values, so one can infer that the coatings do not directly affect the cathodic reactions. The AISI 316 SS shows good corrosion resistance due to the presence of the elements Cr, Mo, Ni and Mn in its composition [1-

3, 15]. Comparing the passive range obtained by the Nb₂O₅-coated samples it can be seen that these coatings enhanced the AISI 316 SS breakdown potential for each type of surface evaluated, indicating better resistance to nucleation and propagation of pits.

4. CONCLUSIONS

Electrochemical tests showed that the Nb₂O₅-coated specimens present a more capacitive behavior, and are less susceptible to corrosion than the uncoated specimen. These results suggest that the films obtained by the reactive magnetron sputtering technique have a protective behavior and can be used to avoid the degradation of AISI 316 austenitic stainless steel in aggressive environments containing sulfur ions.

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