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Improvement of mechanical properties and corrosion resistance of 316L and 304 stainless steel by low temperature plasma cementation

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ABSTRACT

Low temperature plasma carburizing treatment of austenitic stainless steels is a carbon surface diffusion process for a surface hardness and corrosion and wear resistance. The process is carried out by introducing a mixture of carbon-containing gases and through the use of low temperatures the resulting cemented layer usually contains a single phase of supersaturated austenite with carbon – S-phase. For the present investigation, austenitic stainless steels AISI 316L and 304 were plasma cemented for 8 hours in the gas mixture containing 7.5% CH4 in H2, with a pressure of 500 Pa, at temperatures of 375 ºC and 450 ºC. The phases formed were determined by X-ray diffraction. The corrosion resistance was evaluated through immersion tests over time and cyclic voltammetry. The results indicate that there was no formation of compounds (carbides) in the cemented layer for both steels at any of the temperatures and there was a corrosion resistance improvement.

Keywords: plasma carburizing, AISI 304, AISI 316L, corrosion.

1. INTRODUCTION

Austenitic stainless steels have excellent corrosion resistance, high toughness and good workability and are widely used in the chemical, food and automotive processing industries, medical instruments and pharmaceutical equipment [1-3], as well as in orthopedic implants - in the case of AISI 316L steel [4-6]. However, its mechanical properties, especially its hardness and wear resistance, are relatively low, that is, they present low tribological performance, thus limiting their applications, especially those related to friction [2,7].

The field of surface engineering is the process commonly used to design the surface of this type of material in order to improve its surface hardness and wear resistance. Thus, to improve the surface properties, diffusion and thermochemical techniques are used, such as carburizing [8-11], nitrocarburizing [11-13], nitriding [13-15] and ion implantation [16].

However, some of these efforts result in a decrease in the corrosion resistance of the stainless steel surface [17, 18]. Hardening of interstitial solid solution is a technique considered to be effective without causing sensitization and corrosion under stress [19]. Traditional carburizing at temperatures above 900 °C can significantly harden the surface of austenitic stainless steels; however, the inevitable formation of chromium carbides causes a decrease of chromium of the matrix within the hardened layer, deteriorating the corrosion resistance of the alloy [20, 21]. Treatment temperatures maintained below 500 °C can prevent the formation of chromium carbides and nitrides, which sequester the matrix chromium and reduce corrosion resistance [22].

In the present study, the influence of plasma carburizing - performed on an equipment also used for plasma nitriding - in the surface hardness and corrosion resistance of AISI 316L and 304 austenitic stainless steels was investigated using a gas mixture composed of methane in hydrogen at two low treatment temperatures in order to avoid the precipitation of chromium carbides in the cemented layer. Analysis techniques such as metallographic, vickers microhardness, phase determination by X-ray diffraction, immersion tests and cyclic voltammetry were used to characterize the corrosion resistance in simulated physiological solution At the same time, with the characterization and qualification of these layers, the objective is also to obtain suitable plasma carburizing parameters to obtain layers with a maximum depth and with good characteristics of resistance to wear and corrosion, aiming at direct application in the petrochemical industry, food, pharmaceutical, among others.

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2. EXPERIMENTAL PROCEDURE

2.1 Preparation of samples and electrolytic solution

Two austenitic stainless steels were used in this work, AISI 304 and 316L whose nominal chemical composition is presented in Table 1. Samples with dimensions 7 mm in height and 19 mm in diameter were sanded and polished with diamond paste of 4 and 1 μm and then cleaned in an ultrasonic bath (in a total of 10 samples for each steel).

Plasma carburizing was conducted at two different temperatures, 375 and 450 °C, for 8 hours, in a mixture containing 7.5% CH4 in H2. All treatments were performed at a gas pressure of 500 Pa.

Plasma carburizing was performed in a conventional plasma nitriding unit within a reactor under continuous DC power source. The samples were placed on a sample holder inside the 17L carburizing chamber, in which a type K thermocouple was coupled to the temperature measurement.

The characterization of the layers was made by hardness measurements, optical microscopy and X-ray diffraction was used for the determination of phases, using CuKα radiation, in the interval $30º\angle 2\theta \angle 80º$, with an angular pitch of 0.05. Corrosion resistance was assessed by cyclic voltammetry (VC) and immersion tests over time. The VC was conducted with potential scans from 100 mV below the open circuit potential up to 1200 mV and returning to the initial potential using Ringer's solution (Table 2). The immersion tests were carried out in open circuit potential, being maintained the same electrolyte and the same temperature and pH conditions.

Table 1: Chemical composition (wt-%) of the austenitic stainless steels used.

Steel	C	Mn	Cr	Mo	Ni	Si
AISI 316L	0.03	1.65	17.30	2.04	11.52	0.37
AISI 304	0.06	1.63	17.69	0.36	10.07	0.44

Table 2: Chemical composition of the electrolytic solution used in corrosion tests.

Composition of the simulated physiological solution (ASTM F2129-04)	**8.4 g NaCl – 0.33g $CaCl_2$ – 0.3 g KCl Distilled and deionized water**
Temperature	37 ºC
pH	7.3

To facilitate the reading of the treatments performed, the samples were named according to the treatment condition, as described in Table 3.

Table 3: Identification of the samples and their description.

Sample Name	Description
C304	AISI 304
C304_375	AISI 304 cemented to 375°C
C304_450	AISI 304 cemented to 450°C

C316	AISI 316L
C316_375	AISI 316 cemented to 375°C
C316_450	AISI 316 cemented to 450°C

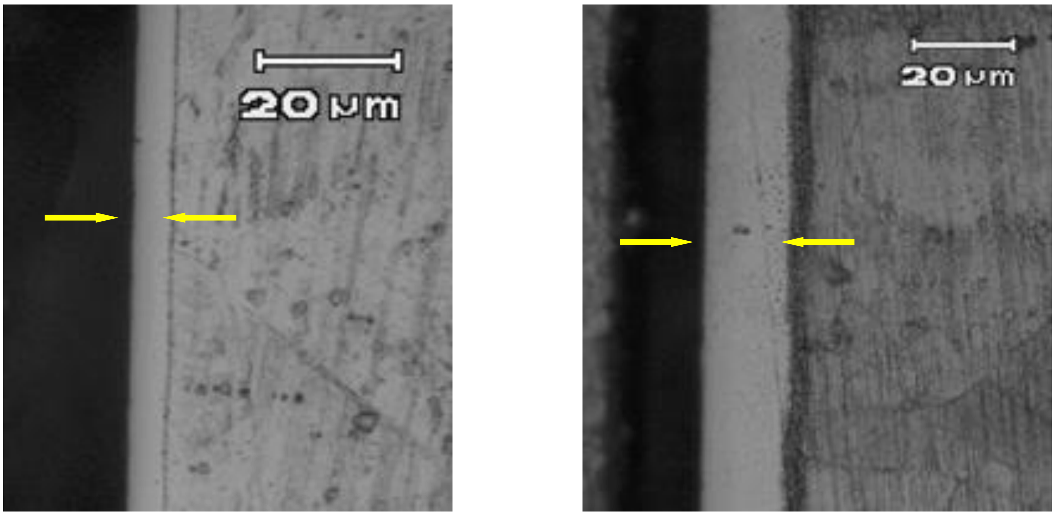
3. RESULTS

3.1 Metallography

Figure 1 and 2 show the cross-sectional micrographs of plasma cemented AISI 304 and AISI 316L steel samples. It can be seen that a continuous layer was produced under both conditions, which has a "white" appearance or color under an optical microscope and after the metallographic development with Marble reagent, which demonstrates the incorporation of carbon in the surface layer. After etching on the Marble reagent, Sun [1] describes that in austenitic steels cemented layers with a white or bright appearance under an optical microscope, after development with Marble reagent, can prevent their superior corrosion resistance on untreated substrates.

The thickness or depth of the carbon penetration layer towards the inside of the samples is dependent on the temperature used for the carburizing process, increasing with increasing treatment temperature, and in the present work the time factor remained constant or invariable. It is also observed that the enriched carbon layer showed uniform appearance (Figures 1 and 2).

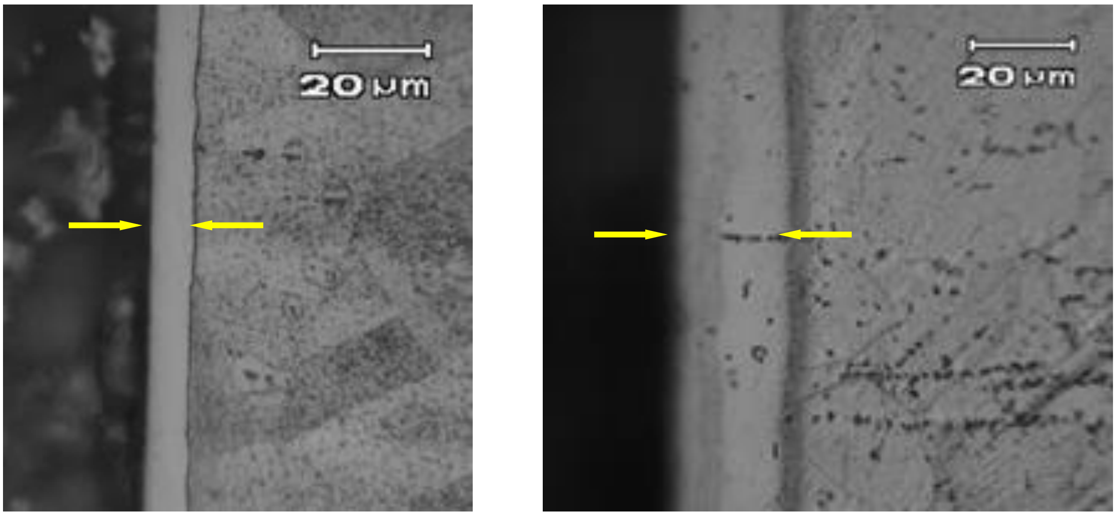
For cemented AISI 304 steel at 375 °C, the obtained layer is approximately 6 µm thick, while at 450 °C the thickness is about 18 µm (Figure 1).



(a) (b)

Figure 1: Micrograph of carburized layers of AISI 304 steel. a) sample *C304_375*. b) sample *C304_450*.

For AISI 316L steel a thickness of approximately 7.5 µm was measured at the carburizing temperature of 375 °C, increasing to a thickness of about 21 µm for carburizing performed at 450 °C (Figure 2).



(a) (b)

Figure 2: Micrograph of carburized layers of AISI 316L steel. a) sample *C316_375*. b) sample *C316_450*.

The thickness results observed in Figures 1 and 2 suggest that the kinetics of the carburizing process is significantly dependent on the substrate material. The thickness of the cemented layer is favored or greater for AISI 316 steel compared to AISI 304 at the same process temperature, and the process time remained constant. The development of the cemented layer can be described by Fick's second law subjected to the fixed surface boundary condition [1]:

$$€ = a\ (Dt)^{0.5} \tag{1}$$

where € is the thickness of the cemented layer, a is a constant (how is it determined?), t is the process time, D is the diffusion coefficient of carbon (which is dependent on process temperature). For example, for the specific cementation temperature of 475 °C the development kinetics of the cemented layer was € = 3.80 + 5.95t0.5 for AISI 316L steels and € = 0.31 + 5.21t0.5 for AISI 304 steel [1]. Thus, AISI 316 steel exhibits the fastest rate of layer growth compared to AISI 304. Moreover, molybdenum (in higher amounts in AISI 316L steel - Table 1) may delay the formation of chromium carbides in steel, particularly at the grain boundaries of austenite [1]. Therefore, this ability to retard the precipitation of grain boundary carbide facilitates the treatment of AISI 316 steel at higher temperatures.

3.2 X-Ray Diffraction

Figures 3 and 4 show the diffractograms of the carburized samples and the uncarburized samples of AISI 304 steel and AISI 316L steel respectively. It is possible to observe that, for both types of steel used, there are no peaks that identify carbides in the layers, both for the treatment temperature at 375 °C and 450 ºC.

During the low temperature carburizing process, the carbon atoms were incorporated in the face-centered cubic austenite (fcc) networks, forming an expanded austenite layer - called the S-phase. This ensures that the chrome remains in free form and thus maintains the corrosion resistance characteristics of stainless steels [23,24]. The diffusion of carbon in the steel matrix is interstitial diffusion [25], where the carbon will occupy the position of the interstitial site. In addition, diffuse carbon has the opportunity to become a solid solution or precipitate with Fe or Cr. This depends on the condition of the carburizing process. Generally, in the low temperature carburizing process the carbon diffuses to form a solid solution. At low temperature, both Fe and Cr are not mobile, therefore it hinders the formation of precipitates [2].

In the carburized samples, the austenite-identifying peaks are shifted to the left, that is, to smaller angles, which implies an expansion of the lattice due to the higher amount of carbon. According to [12], this displacement shows that the S phase is an expanded phase. This is a characteristic of supersaturation phases.

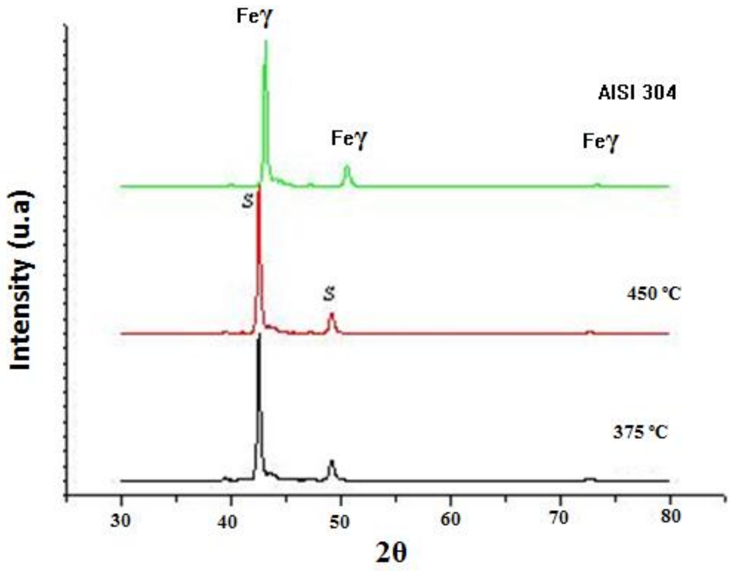


Figure 3: X-ray diffraction analysis for carburized and uncarburized samples of AISI 304 steel.

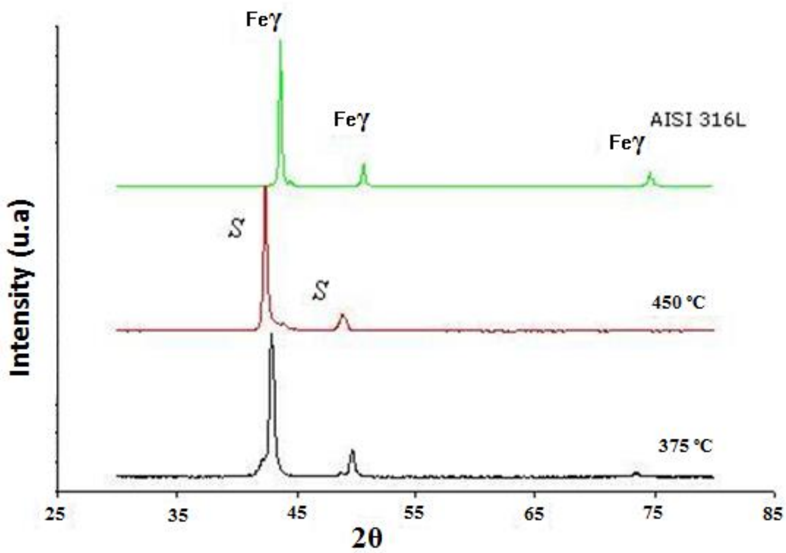


Figure 4: X-ray diffraction analysis for carburized and uncarburized samples of AISI 316L steel.

3.3 Vickers Microhardness

Figure 5 shows the results of the top microhardness measurements of the cemented samples of AISI 304 and 316L steel respectively. Regarding the respective untreated steel, all the samples evidently exhibited a significant increase in surface microhardness, confirming the hardening effect of the process. The microhardness of the base material was, on average, 210 HV0.025 for AISI 304 steel and 196 HV0.025 for AISI 316L steel. The hardness of the samples cemented at 375 ºC for both steels presented lower values than the temperature of 450 ºC. This is mainly due to the influence of the substrate, since the indenter Vickers presents indentation depth of 6/7 diagonal of the impression, that were of approximately 8 μm. Another factor is the fact that the carbon concentration is the maximum at the surface and gradually decreases towards the layer-core interface, thus exhibiting a diffusional type distribution, similar to that found in the worked austenitic stainless steels treated under similar conditions through the profile carbon compositional [1,14,22,26].

The presence of carbon in the matrix of austenitic stainless steels increased their hardness. The hardening of the layer is therefore attributed to the carbon supersaturation and the planar and linear network defects induced in the austenite [1].

For the treatment, temperature of 375 °C the increase was approximately 175% for both steels compared to the untreated samples of the respective steel. On the other hand, in the temperature of 450 ºC the increase was approximately 350%.

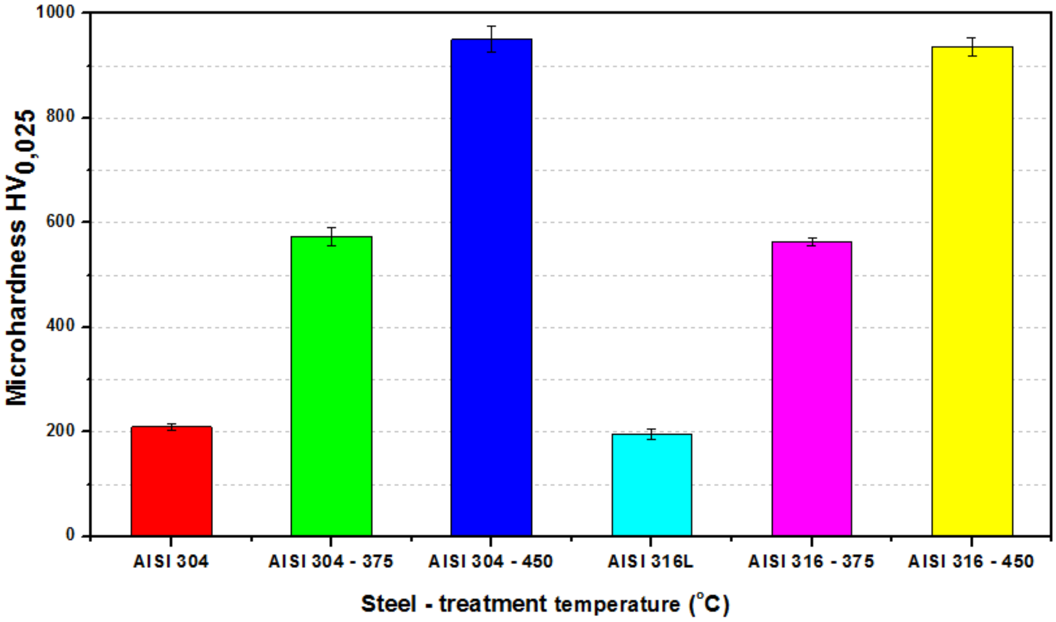


Figure 5: Microhardness measurements HV0.025.

3.4 Corrosion tests

Although the metallographic sections shown in Figures 1 and 2 have already demonstrated the good resistance of the carburized layer to the Marble reagent for both steels, specific corrosion tests were performed, according to the results described below.

3.5 Open Circuit Potential Evaluation

Figure 6 shows the behavior of the samples during immersion tests over time. The samples *C304_450* exhibit the least satisfactory performance with the most negative open circuit potential (E_{ca}) value. The samples cemented at a temperature of 375 °C (*C304_375* e *C316_375*) initially have a much more positive E_{ca} value. This value decreases and stabilizes after 70 hours of immersion. This behavior may be related to a process of oxidation and formation of a surface product. The samples *C304* e *C316* – steels without carburizing process, presented a similar behavior, with potential drop over the immersion time.

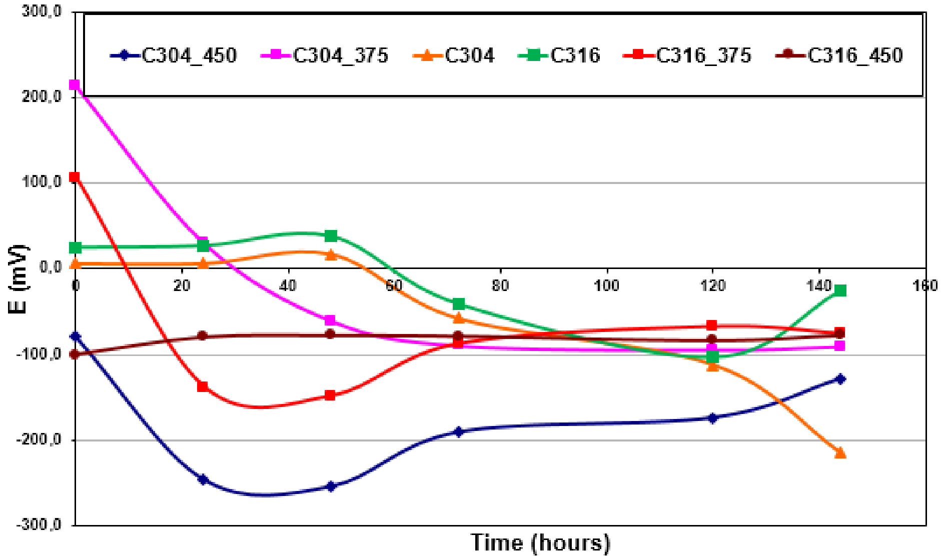


Figure 6: Measurement of open circuit potential over the immersion time for the samples *C304, C304_375, C304_450, C316, C316_375 e C316_450*.

3.6 Cyclic Voltammetry

The electrochemical tests of cyclic voltammetry revealed a different behavior for the samples before and after the treatment. The steel before being cemented (*C304* e *C316*) develops current density (i) characteristics of the localized corrosion process, with a rapid increase in the (i) between 350 and 400 mV (anodic process) (Figure 7). In the cathodic process a (i) is higher, when compared, for a same potential value, with (i) the anodic process. The diagram shows a well defined corrosion process.

When the steel is treated at 375 °C, a significant improvement in corrosion resistance is observed. The values of (i) are much lower than those observed in the untreated sample. AISI 304 steel treated at 375 °C has an anode dissolution peak around 160 mV (i_{peak} = 5 x10^{-4} A.cm^{-2}) (Figure 8).

At the treatment temperature of 450 ° C, it is observed, for both steels, an anodic dissolution peak between 200mV and 400mV and subsequent increase of (i) around 1000mV (Figure 8).

The anodic dissolution peaks present in the cyclic voltammograms of the treated samples (*C304_450*, *C304_375* e *C316_450*) may represent a corrosive process at preferential sites on the sample surface, since the roughness increases with carburizing.

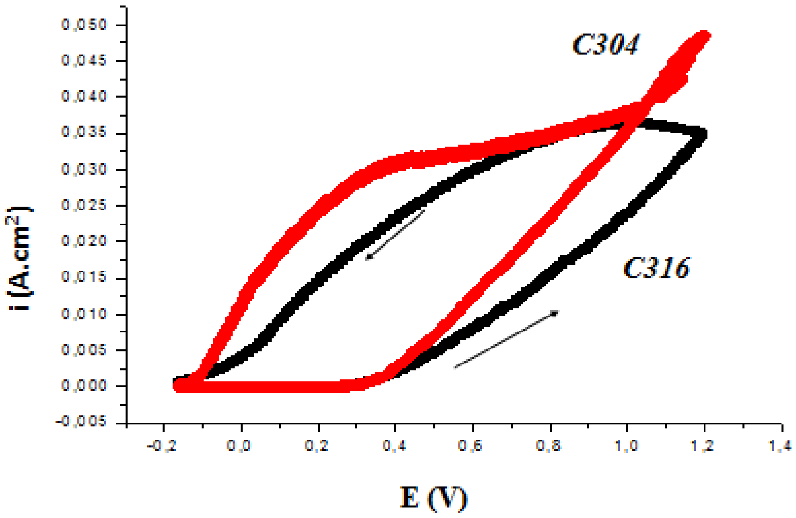


Figure 7: Cyclic voltammetry of AISI 316L and 304 steels in Ringer's solution.

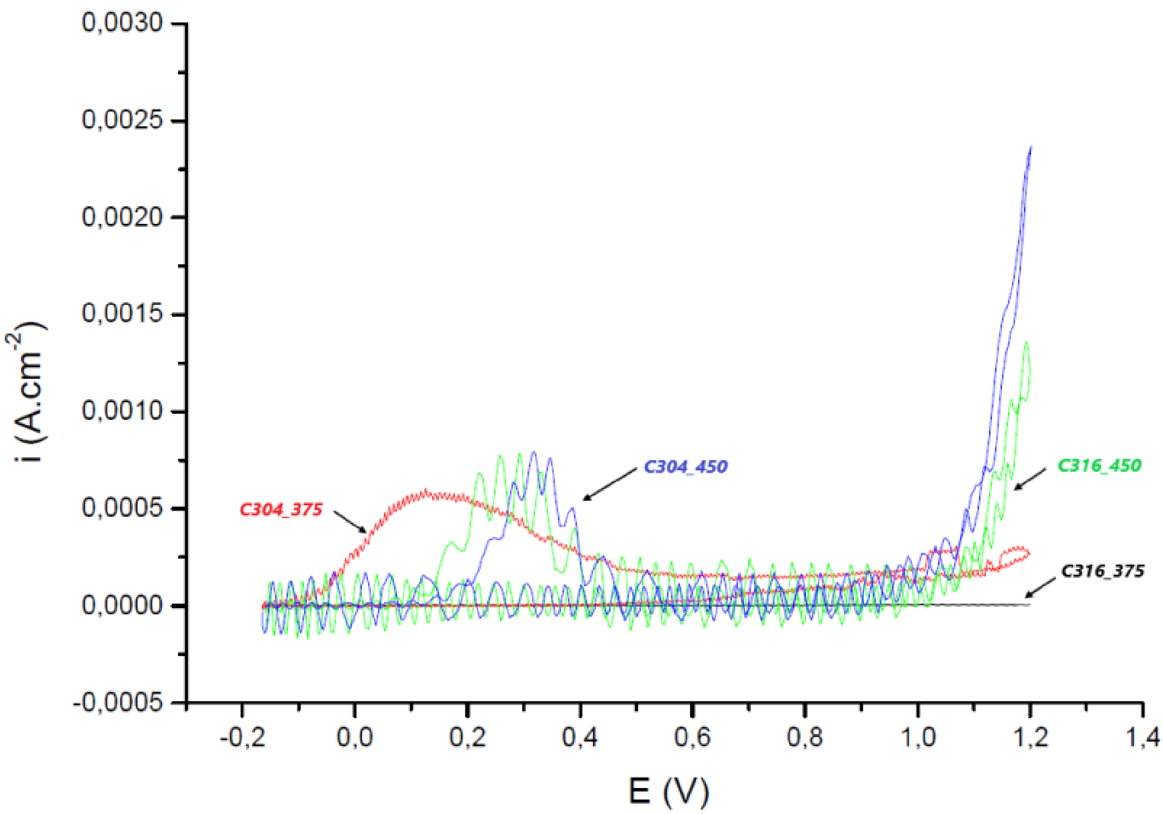


Figure 8: Cyclic voltammetry of samples: C304_375, C304_450, C316_375 and C316_450 in Ringer's Solution.

4. CONCLUSIONS

Through the selected parameters precipitated layers were obtained, free of precipitates, with formation of only S phase, showing higher hardness and higher corrosion resistance for both austenitic stainless steels compared to the untreated material.

The thickness of the cemented layer obtained for AISI 304 steel was 6µm and 18µm at treatment temperatures of 375 and 450 °C respectively; and for AISI 316L steel was 7.5 µm and 21 µm for the treatment temperatures of 375 and 450 °C respectively.

The cyclic voltammetry tests showed that the treated samples had a significant improvement in the corrosion resistance, especially when treated at 375 °C, and the best performance was obtained for the AISI 316L steel at this temperature.

The open circuit evaluation test for the samples treated at 375 °C showed the best performance for both steels compared to untreated steels.

The resulting carburized layer is free of precipitation and has a high hardness with a favorable carbon concentration and hardness gradient, and greatly improved corrosion resistance in the tested solutions as compared to the original molded material.

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