

An investigation on the passivation behavior of nitrogen enriched AISI 316L austenitic stainless steel

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Abstract

In the present work the effects of plasma nitridization on the passivation behavior of AISI 316L was investigated. To do this; nitriding treatments were carried out at 420°C for 1, 2, 4 and 16 hours. The phase composition and structure of the nitrided layer were studied by Low Angle X-ray diffraction and Scanning Electron Microscopy. The hardness of samples also was evaluated by Vickers microhardness test method. Potentiodynamic Polarization Scan (PDS) and Electrochemical Impedance Spectroscopy (EIS) techniques were used for corrosion studies. The plasma nitridization process produced surface-modified layers essentially composed of a metastable phase called S-phase, for all the nitrided samples, independent of the nitriding time. Surface microhardness measurements revealed that the surface hardness of treated samples was higher compared to that in untreated samples and that it increased with the treatment time. Electrochemical tests demonstrated that plasma nitriding for 4 h is the optimum treatment condition regarding corrosion behavior of nitrided austenitic stainless steels. In addition, nitriding treatment increases passivation current values and decreases charge transfer resistance value of the passive film.

Keywords: AISI 316L, Plasma Nitriding, Passivation, Low Angle XRD, Potentiodynamic Scan, Impedance Spectroscopy.

1- Introduction

The austenitic stainless steels are widely used in many industrial fields because of their very high general corrosion resistance. Nevertheless, they can suffer pitting or crevice corrosion in specific environments¹⁾ and their performance is not as satisfactory in applications in which wear may be responsible for material degradation²⁾. Nitriding is one of the widely used surface engineering technologies to improve the surface hardness and wear resistance of various engineering materials³⁾. Low temperature plasma nitriding has been proved to be an efficient way to form a very hard and corrosion resistant layer on the surface of austenitic stainless steels⁴⁾. Nitriding at lower temperature, about 420°C, produces a nitrogen expanded austenite γ_N , known as S-phase on the surface of an austenitic stainless steel. Due to the superb properties of the S-phase, the low temperature nitrided austenitic stainless steel has a very high surface hardness, wear resistance and more importantly, an excellent corrosion resistance⁵⁻¹⁰⁾. In principle, the low temperature nitriding (LTN)

process can be carried out using liquid, gas or plasma environments. There is an increasing interest in industry in plasma-based nitriding technologies which offer many advantages over traditional gas and bath nitriding, particularly, in terms of reduced gas consumption, reduced energy consumption and the complete removal of any environmental hazard³⁾. It should be mentioned that austenitic stainless steels exhibit passivation behavior in sulphuric acid solutions¹¹⁾. The main purpose of this work is to investigate the passivation behavior of plasma nitrided AISI 316L austenitic stainless steel at different treatment times and its comparison with untreated samples by electrochemical method. The effect of nitriding time on the morphology, microstructure and hardness of these steels are also investigated.

2- Experimental Details

2-1- Sample preparation

The AISI 316L austenitic stainless steel with chemical compositions (in wt %) of 13% Ni, 17% Cr, 67% Fe, 2% Mo, 0.5% Si 0.2% Mn, 0.02% C were used in this study. The samples were cut from a cylindrical bar which was annealed at 900°C for 24 h, and then followed by machining to a 20 mm in diameter and 4 mm in thickness. The samples were, then, ground and mechanically polished (by 1 μ m diamond paste) to a mirror like finish and finally cleaned in methanol for 15 minutes by using ultrasonic method.

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2-2- Nitriding Process

Plasma nitriding is realized using an 800 Hz pulsed DC discharge, with an 0.8 duty cycle ratio (ratio of the pulse duration to the pulse period) in a DC pulse plasma reactor. Normally, the sample is screwed into the substrate holder. An in situ cleaning procedure, intended to remove the native oxide layer and to simultaneously heat the sample to the working temperature, was performed before the nitriding treatment in 50% Ar-50% H₂ plasma under a 200 Pa pressure. The nitriding treatment was then performed in a 90%N₂-10%H₂ gas mixture. The temperature was measured by a thermocouple embedded into the substrate holder. The samples were nitrided at different time intervals: 1, 2, 4, and 16 h and at the end of the normal treatment, they were allowed to cool in vacuum.

2-3- Characterization of plasma nitrided layer

The features of the produced plasma nitrided layers were examined by Scanning Electron Microscopy (SEM). Low Angle X-Ray Diffraction (XRD) analysis was performed to identify the phases present in the surface layers by using Co-K α radiation ($\lambda=1.789$ Å). The microhardness of the surfaces was measured with a microhardness tester ECO M400 in the Vickers mode using a load of 10 gf. The electrochemical behavior of the samples was investigated in 2M H₂SO₄ solution by means of potentiodynamic polarization scan (PDS) and electrochemical impedance spectroscopy (EIS) techniques. The electrochemical tests were performed at room temperature in a flat cell which was a three-electrode set-up consisting of a saturated calomel reference electrode (SCE), a platinum auxiliary electrode and a working electrode (sample). The scanning potential for potentiodynamic polarization test was in the range between -0.5 V (SCE) and +1.2 V(SCE) and the scan rate was 1 mV/s. Polarization scan was carried out using the BHP2063 electrochemical analyzer system, and data logging was achieved by sequencer computer software. Prior to the polarization measurements, the samples were allowed to reach a stationary corrosion potential after a 30-minute exposure to the solution. Electrochemical impedance spectroscopy measurements were carried out in +315 mV_(SCE) anodic potential (passivation potential, extracting from polarization curve) using a Potentiostat/Galvanostat Autolab PGSTAT30 with a frequency response analyzer (FRA). All experiments were carried out at the frequency range from 10⁻² up to 10⁵ Hz by superimposing an AC voltage of 10 mV amplitude. Before starting the impedance measurements, the samples were exposed to the solution for 30 min and simultaneously +315 mV_(SCE) anodic potential was applied to form and stabilize passive layers.

3- Result and Discussion

Fig. 1 shows the X-ray diffraction pattern (incidence angle of 4°) for the untreated sample and nitrided samples at 420°C for 1, 4 and 16 h. In the untreated sample, the peaks of XRD analysis correspond to austenite phase, but for nitrided samples a set of diffraction peaks correspond to the metastable FCC solid solution phase supersaturated in nitrogen, also known as expanded austenite, γ_N phase or S-phase^{6, 12}. As a result, the nitriding process with mentioned conditions, leading to modified layer, consist of single S-phase, independent of any nitriding time. It can also be seen that with an increase the nitriding time, the broad γ_N phase peaks are shifted to lower angles; this means there is a large amount of supersaturation nitrogen in the layer. Therefore, the formed nitrided layers are defect-rich and contain a large amount of stress.

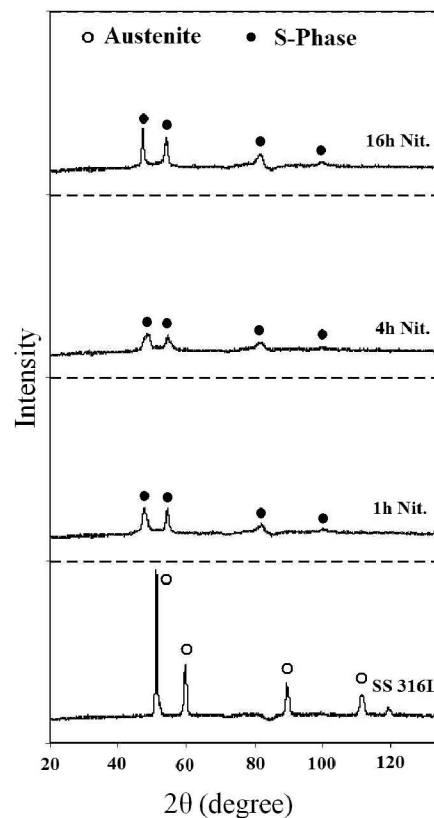


Fig. 1. X-ray diffraction patterns of the AISI 316L substrate and samples nitrided at 420°C for different times, 1, 4, and 16 h. (With Co K α Radiation at the incident angle of 4°).

Table 1. Reflected angles corresponding to different crystallography orientations for untreated and nitrided samples

| Sample | 2 $\theta_{(111)}$ | 2 $\theta_{(200)}$ | 2 $\theta_{(220)}$ | 2 $\theta_{(311)}$ |
|----------|--------------------|--------------------|--------------------|--------------------|
| SS316L | 51.23 | 60 | 90 | 112 |
| 1h Nit. | 47.79 | 54.62 | 82.47 | 101.46 |
| 4h Nit. | 48.45 | 54.74 | 81.66 | 100.53 |
| 16h Nit. | 47.14 | 54.14 | 82.05 | 100.34 |

Table 1 shows the reflected angles corresponding to different crystallography orientations for untreated and nitrided samples. Considering Table 1 and Fig.1, it can be seen that the minimum and maximum shift values are obtained for samples nitrided at 4 h and 16 h, respectively. The atomic planes distance (symbol d) of the (111) orientation were calculated from Bragg's law and the lattice parameters (symbol a) were obtained from the relationship between the a and the d in the cubic systems. Table 2 shows the lattice parameters of the (111) orientation and their expansion values for all samples, it should be noted that the expansion results from incorporation of nitrogen in the interstitial position of the austenite phase Table 3 also shows the lattice parameters calculated by the Nelson-Riley method (by considering the reflected angles of the different orientations (Table 1) and their expansion for all samples¹³). Presence of nitrogen atoms in interstitial sites of austenite lattice (as a solid solution) leads to the formation of a compressive stress in the lattice. Hence, the more the increase in the lattice parameters values, the more the presence of the compressive stress in austenite lattice. Considering Table 2 and Table 3, the 4 h nitrided sample has the smallest lattice parameter and related expansion, while the 16 h nitrided sample has the largest.

Table 2. Lattice parameters and their expansions corresponding to (111) plane orientation for all samples

| Sample | $a_{(111)}(\text{Å})$ | Expansion (%) |
|----------|-----------------------|---------------|
| SS 316L | 3.583720619 | 0 |
| 1h Nit. | 3.824899493 | 6.729845866 |
| 4h Nit. | 3.775874849 | 5.361864124 |
| 16h Nit. | 3.874568965 | 8.115820886 |

Table 3. Lattice parameters calculated from the Nelson-Riley method and their expansions for all samples

| Sample | Lattice Parameter (Å) | Expansion (%) |
|----------|-----------------------|---------------|
| SS 316L | 3.578 | 0 |
| 1h Nit. | 3.8235 | 6.86137507 |
| 4h Nit. | 3.8037 | 6.307993292 |
| 16h Nit. | 3.8295 | 7.029066518 |

As a result, 4 h nitrided sample has the minimum stress and 16 h nitrided sample has the maximum. On the other hand, the 4 h nitrided sample has less stress than the 1 h nitrided sample, in spite of its more treatment time. Compared to the 1 h nitrided sample, unexpected low stress of the 4 h nitrided sample can be interpreted by considering the mutuality of two disparate phenomena: First, stress creation during sputtering action and second, stress reduction during appropriate heat treatment, at enough times. For the 4 h nitrided sample there is enough time for approximate balance between the amount of induced stress and the disappeared stress because of

relaxation phenomenon, at 420°C. For 16 h nitrided sample, increasing operation time caused maximum stress creation. This is due to the dominant effect of stress creation compared to stress relaxation at higher treatment time. The averages of surface microhardness values of untreated sample and nitrided samples at 420°C for different times are shown in Fig. 2.

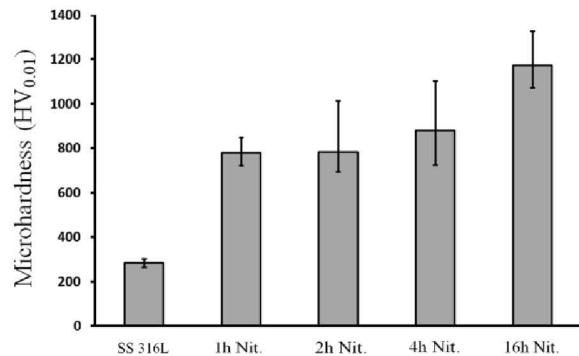


Fig. 2. Surface microhardness values of AISI 316L austenitic stainless steel samples untreated and Plasma nitrided at 420°C for different times.

Nitrided samples show higher hardness than untreated samples. The microhardness values increase with treatment time. In the case of the samples nitrided for 16 h, the microhardness value is about 4 times higher than that of untreated AISI 316L stainless steel sample. Fig. 3 shows the SEM cross-section morphology of 420°C plasma nitrided samples after 1 and 16 h nitridation treatment. As can be seen, the thickness of the modified layers formed on the surface of the samples increases with nitriding time. So, in the longest nitriding treatment, the effect of low hardness of substrate on the measured hardness of surface is more negligible⁸⁾. By increasing the nitriding treatment time which leads to an increase in nitrogen content of the layers, the microhardness values increases. Since the hardness value of S-phase depends on its nitrogen content¹⁴⁾ and increasing in nitrogen content of the nitrided layers leads to more lattice distortion and results large in hardening effects¹⁾. Fig. 4 shows the polarization curves of untreated and plasma nitridation treated (at 420°C for different treatment times) samples, in 2M H₂SO₄ solution. All nitrided samples and the untreated sample exhibit typical behavior of a passive material. Considering Fig. 4, it is seen that all samples show a well defined active-passive transition in anodic range and transpassive behavior. Fig. 5 shows the SEM morphology of the untreated samples surface after polarization test. As can be seen, many pits with various size and depth are formed on the corroded surface. From polarization curve (Fig. 4) it can be seen, at the highest polarization potentials, that the anodic current values for all samples are quite large and are limited only by concentration polarization phenomena¹⁾. It can also be seen that for nitrided samples, the rate of

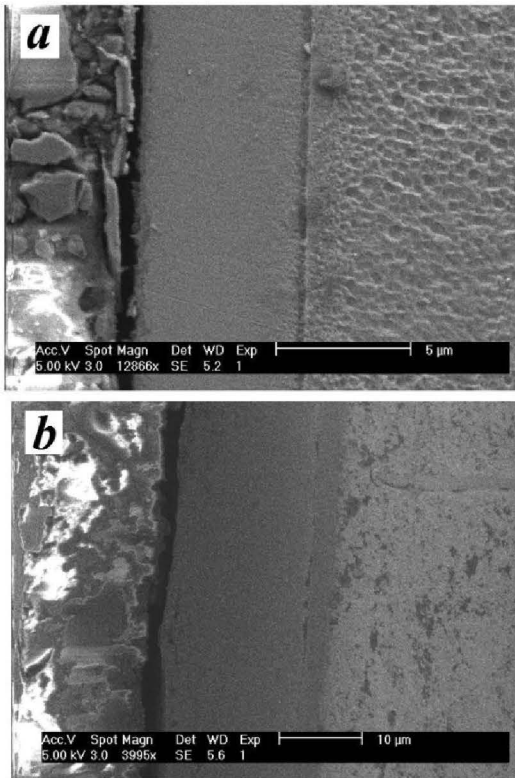


Fig. 3. SEM micrographs of the cross-section of nitrided samples at (a) 1 h, and (b) 16 h.

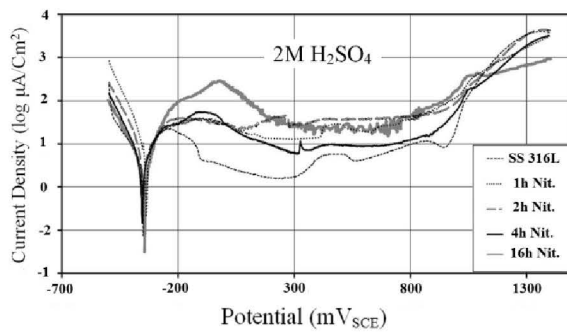


Fig. 4. Polarization curves of AISI 316L austenitic stainless steel samples, untreated and plasma nitrided at 420°C for different times in 2M H₂SO₄ solution.

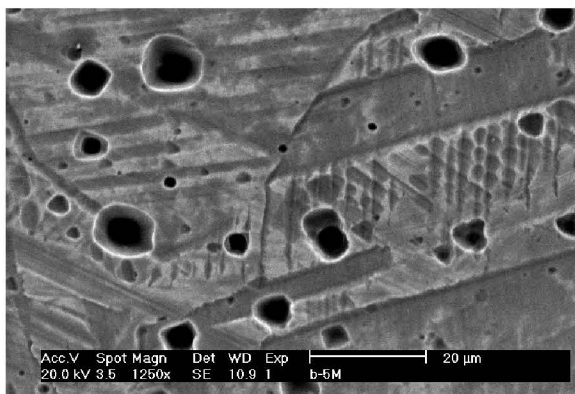


Fig. 5. SEM morphology of the untreated samples surface after polarization test.

increasing the current density at transpassive region is too less than that in untreated sample. It can be deduced that dissolution rate of untreated sample is more severe than nitrided samples. Further gradual increasing of the current at higher potentials for nitrided samples indicates that the reactions are controlled by mass transfer phenomenon. It is also likely that the corrosion product becomes saturated and may stick to the metal surface. According to polarization curves (Fig. 4), the nitrided samples, especially in the case of samples nitrided for a long time, show large amounts of current density fluctuations in passive region of potential in untreated samples. Current density fluctuations can be ascribed as the instability of the passive films under this condition. Thus, nitrided samples in passive condition are more instable passive films in comparison to the untreated stainless steel samples. The sample nitrided for 16 h exhibits maximum fluctuations in current density and therefore has minimum passive film stability. Another fact that can be observed in polarization curves is that the current density values in passive region for untreated sample are much less in comparison to those values for all nitrided samples. The important point is that nitriding treatment changes the surface morphology of samples as can be seen in Fig. 6. In other words, by nitriding, the effective surface of samples in contact with solutions increases. Current density values extracted from the polarization curves in both untreated and plasma nitriding treated samples is also calculated by constant theoretical surface of work electrode exposed to electrolyte. In the treated samples, the effect of the effective surface has been ignored, if this aspect applies to current density calculation, the calculated actual current density values for treated samples becomes very small.



Fig. 6. Surface morphology of sample plasma nitrided at 420°C for 16 h.

Hence, it can be concluded that the corrosion resistance of nitrided samples at passive range is much lower compared to that of untreated sample. According to the polarization curves in the range of passive potentials, the 4 h nitrided sample has minimum passivation current density among nitrided samples. Thus, it has the highest corrosion resistance

in comparison to others in current work conditions. Therefore, the passive layer formed on the 4 h nitrided sample surface in H_2SO_4 is more stable than those formed on other nitrided samples. As described in XRD analysis, the formed nitrided layers are defect-rich and contain a large amount of stress; therefore, the stability of passive layers can be related to the amount of created stress in nitriding treatment. As a result, the 4 h nitrided sample has low residual stress and consequently it becomes more stable than others. Fig. 7 shows the Nyquist and Bode plots of untreated and nitrided samples. The electrochemical impedance measurements for both untreated and plasma nitrided samples with different nitriding times are carried out in potential $+315\text{ mV}_{SCE}$ at the passive

region. Equivalent circuit model for fitting impedance data also is shown in Fig. 7. In the present work, the capacitive loops observed for all the samples showed only a single time constant. All Nyquist plots shows depressed semicircle at high frequencies, attributed to the typical charge-transfer-dominated process in passive layers, with some diffusion control which is believed to be attributed to the film formation coupled in the restricted diffusion process. It should be noted that R_2 represents charge transfer resistance (R_{ct}) or polarization resistance (R_p) in equivalent circuit. In impedance measurement, high R_p value implies good corrosion resistance and low capacitance value signifies long term stability of the passive film [15].

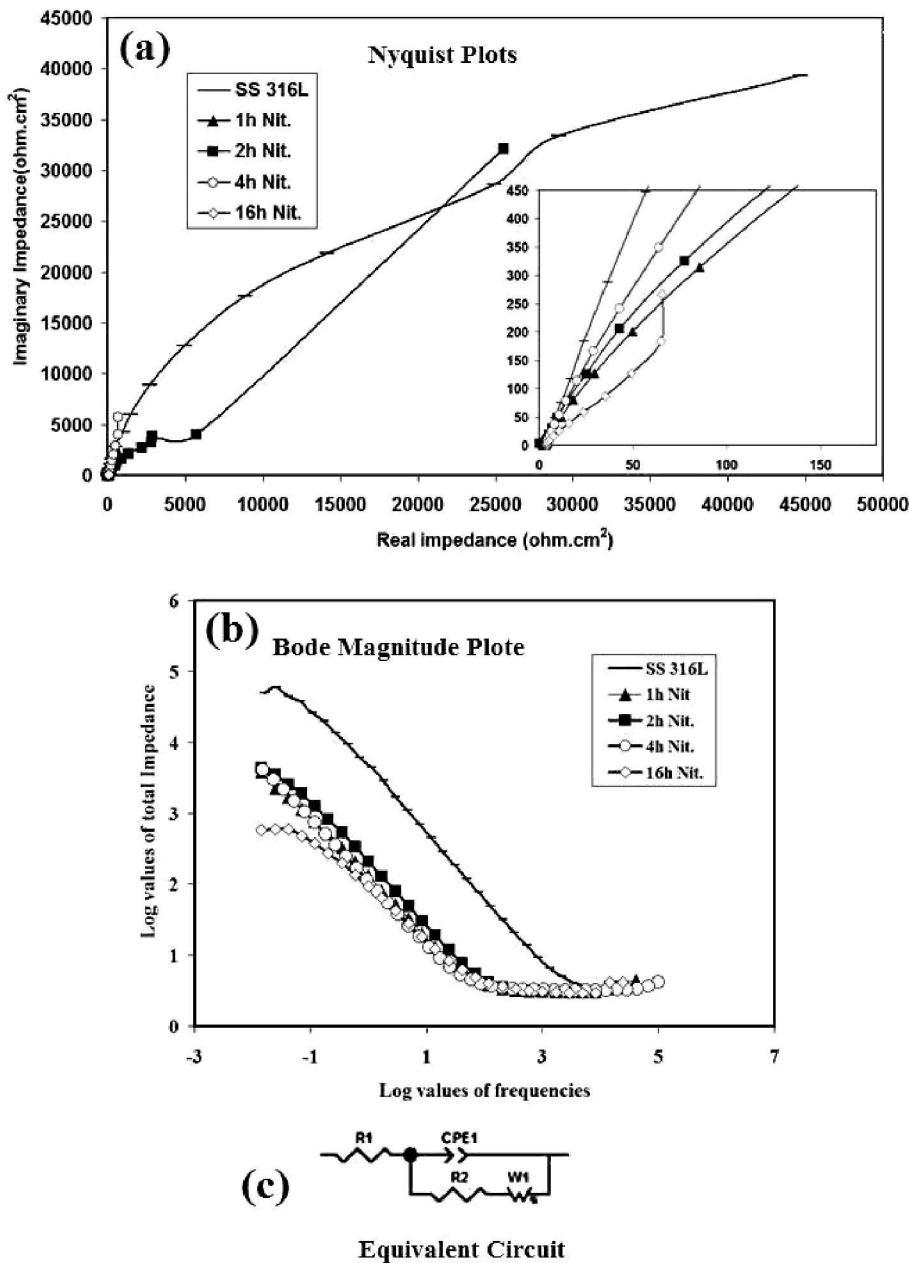


Fig. 7. Nyquist Plots (7-a), Bode magnitude plots (7-b) and Equivalent circuit model (7-c), for untreated and nitrided samples.

A comparison of Nyquist plots between untreated and plasma nitrided samples with different nitriding times revealed that the charge transfer resistance of untreated sample is much higher than nitrided samples. Among the nitrided samples, 4 h nitrided sample has the lowest R_p and 16 h nitrided sample has the highest. The lowest R_p value for 16 h nitrided samples coincides with high passivation current densities and current density fluctuations in polarization curve. The passive film that forms on the surface of 16 h nitrided sample is very instable due to its high amount of stress. Therefore, it is exposed to consecutive break down and reproducing on the surface of the sample. The presence of the Warburg element in equivalent circuit indicated that a diffusion stage is present in the corrosion process of passive films¹⁶. It can be deduced that electron exchange between a metal and electrochemically active species is very rapid and that the corrosion rate is controlled by the rate of electrochemically active species diffusion to a metal surface, or by the rate at those corrosion products which desorb and diffuse away from metal surface. Corrosion process product gas bubbles like hydrogen which can block access of electrochemically active species to a sample surface, thereby restricting hydrogen ion diffusion to the surface thus impeding the overall corrosion reaction rate. In the case of nitrided samples the active places on the surface of samples for electron exchange are increased due to instability of passive films, and thereby the charge transfer resistance of nitrided layers is decreased.

4- Conclusion

- It was observed that the low temperature nitriding process in the condition of this research, produced modified layers consisting of single S-phase on the surface of all nitrided samples, independently of nitriding time.
- The surface microhardness values and the thickness of the hardened layers increase with nitriding time.
- Polarization tests demonstrate that the current density values in passive region for untreated sample are much less in comparison to those values for all nitrided samples. Regarding the surface increasing effect of nitriding treatment, the actual current density values are even much higher than those present in polarization curves for nitrided samples.
- The 4 h nitrided sample has minimum passivation current densities between nitrided samples, in passive range potentials, due to its minimal residual stress, and consequently it is more stable than other films.
- Dissolution rates of nitrided samples in transpassive region are lower than untreated samples. Hence, low temperature plasma nitriding can

relatively improve pitting behavior of austenitic stainless steels.

- Impedance tests showed that charge transfer resistance of untreated sample is much higher than nitrided samples and among nitrided samples; 4 h nitrided sample has the lowest R_p while 16 h nitrided sample has the highest.

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References

- [1] A. Fossati, F. Borgioli, E. Galvanetto, T. Bacci: Surf. Coat. Tech., 200(2006), 3511.
- [2] R. W. Hertzberg: Deformation and Fracture Mechanics of Engineering materials, John Wiley and Sons, (1989).
- [3] C.X. Li, T. Bell: Corr. Sci., 46(2004), 1527.
- [4] T. Bell, Y. Sun: Heat Treatment of Metals, A29(2002), 57.
- [5] L.C. Gontijo, R. Machado, S.E. Kuri, L.C. Casteletti, P.A.P. Nascente: Thin Solid Films, A515(2006), 1093.
- [6] A. Fossati, F. Borgioli, E. Galvanetto, T. Bacci: Corr. Sci., A48(2006), 1513.
- [7] J.H. Liang, C.S. Wang, W.F. Tsai, C.F. Ai: Surf. Coat. Tech., A201(2007), 6638.
- [8] A. Fossati, F. Borgioli, E. Galvanetto, T. Bacci: Surf. Coat. Tech., A200(2005), 2474.
- [9] A. Fossati, F. Borgioli, E. Galvanetto, T. Bacci, G. Pradelli: Surf. Coat. Tech., A200(2005), 5505.
- [10] S. Picard, J.B. Memet, R. Sabot, J.L. Grosseau-Poussard, J.P. Rivière, R. Meilland: Mater. Sci. Eng., A303(2001), 163.
- [11] M.G. Fontana: Corrosion Engineering, 3rd ed. McGraw-Hill Book Company, USA, (1987).
- [12] V. Singh, K. Marchev, C.V. Cooper, E.I. Meletis Surf. Coat. Tech., A160(2002), 249.
- [13] B. D. Cullity: Elements of X-ray diffraction, Wiley USA, (1976).
- [14] L. Wang, S. Ji, J. Sun: Surf. Coat. Tech., A200(2006), 5067.
- [15] N. Padhy, S. Ningshen, B.K. Panigrahi, U. Kamachi Mudali: Corr. Sci., 52(2010), 104.
- [16] W.S. Tait: An Introduction to Electrochemical Corrosion Testing for Practicing Engineers And Scientists, Pair O Does Pubns, USA, (1994).