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Electrochemical Corrosion Performance of Hematite-Free Magnetite Layer on AISI 4340 by Duplex Pulsed Plasma Nitriding-Oxidizing Treatment.

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Plasma assisted duplex processes, such as nitriding post-oxidation, has been the focus of recent research publications looking to optimize wear and corrosion performance of several industrial components. High efficiency, process control as well as low energy consumption and clean technologies suggest that these processes are good alternatives for replacing the environmental harmful electrochemical techniques. An important challenge during post oxidation step is to avoid, as much as possible, the formation of hematite (Fe_2O_3) and to produce layers with a high content of high corrosion resistance magnetite (Fe_3O_4). In the present work, pulsed DC plasma post oxidation was used in order to obtain hematite-free magnetite layers on plasma nitrided AISI 4340 steel in order to improve its corrosion resistance. The effect of oxidation time (15, 30 and 45 minutes) on crystalline phases content and electrochemical corrosion performance was evaluated. Rietveld analysis of X ray diffraction data shows an increase in magnetite content and a decrease in Fe_3N content after the post-oxidation period. Corrosion performance of nitrided AISI 4340 steel was significantly enhanced by the smoothest surface and the hematite-free magnetite layer obtained after pulsed post-oxidation process.

Keywords: Pulsed plasma post-oxidation, magnetite, corrosion.

1. INTRODUCTION

AISI grade 4340 is a nickel-chromium-molybdenum alloy steel which is commonly used in the production of piston pins, bearings, and similar parts. Despite its good response to heat treatment and good combination of strength, corrosion resistance is a characteristic to be improved [1]. Recently, research efforts have been focused on duplex processes such as plasma nitriding / nitrocarburizing and post oxidation as alternatives to improve the corrosion resistance of the AISI grade 4340 [2-4].

Nitriding process results in the formation of a compound layer and nitrogen diffusion zone beneath that compound layer. The compound layer is constituted mainly by a combination of iron nitrides ($Fe_{2\text{-}3}N$ and/or Fe_4N) but the diffusion zone is composed of nitrogen saturated ferrite together with dispersed precipitates of iron and alloy element nitrides [5]. The compound layer has a porous structure that limits corrosion resistance of nitrided steels. Post-oxidation treatments produce a thin oxide layer on compound's layer, which covers and seals micropores in the layer and further improves the corrosion resistance of nitrided steel [4,6]. The post-oxidation process has to be controlled to avoid the formation of hematite (Fe_2O_3) and to produce layers with high content of magnetite (Fe_3O_4), which is highly corrosion resistant [2,7].

The production of oxidized layers with the highest magnetite content on low alloy steels has been the focus of several researches that have been recently conducted. After a 3 hour oxidation process in an air furnace (500°C) of plasma nitrided tool steel, Yucel Birol [8] reports nearly 3 µm oxidized layers constituted predominantly of Fe_3O_4. Yang et. al. [7] and M. Ebrahimi et. al. [9] reported the development of oxidized bi-phase layer Fe_2O_3/Fe_3O_4 at temperatures between 350 and 500°C during 1-2 hours of pulsed plasma post-oxidation treatment. Yang et. al. [7] showed that the highest amount of magnetite occurs when oxidation is carried out at 400 and 450°C in an oxygen atmosphere while M. Ebrahimi et. al. [9] reported that nitriding process at 570 and 630°C enhances the formation of magnetite phase in oxidized layers after post-oxidation process. Although these recent researches on duplex nitriding plus post-oxidation treatment have been carried out, process parameters to get layers with the highest magnetite content has not been clearly defined.

N. Yasavol et. Al. [10] reported, in the most recently related work, the effect of temperature and gas mixture, during duplex conventional DC plasma nitriding post oxidation treatment, on the corrosion resistance of AISI 4130 steel. They obtained almost a single-phase magnetite layer with high corrosion resistance using a gas composition of O_2/H_2 1/3 and process temperature of 500 ºC. This high corrosion resistance was attributed to the high magnetite phase content in the oxidized layer.

The aim of the present work is to propose a new method to produce hematite-free magnetite layer on plasma nitrided AISI 4340 low alloy steel in order to improve its corrosion resistance. This method is based on the duplex pulsed DC plasma nitriding post-oxidation process.

2. EXPERIMENTAL

Samples of a commercial Cr-Mo-Ni low alloy AISI 4340 steel (40×40×5 mm), presenting a typical microstructure of tempered martensitic phase, were used in this study. Chemical composition was (weight percent): C 0.38, S 0.017, Mn 0.63, P 0.008, Si 0.19, Cr 0.80, Ni 1.64, Mo 0.20, Cu 0.137, Fe balance. Prior to treatment, the samples surface was ground and polished using a 1 μm diamond suspension and a plasma sputtering cleaning stage was carried out using a gas mixture of 50% Ar and 50% H_2.

The samples were plasma nitrided and post oxidized in a previously described laboratory reactor [11]. Treatments were carried out using, for plasma generation, an IGBT (Insulated Gate Bipolar Transistor) based DC pulsed supply unit which leads precise adjustments of discharge current, pulse frequency and duty cycle. Nitriding process was conducted using the following parameters: Temperature 520 °C, process time 3 hours, work pressure 266 Pa, gas mixture 50 %N_2-50 %H_2, frequency 1000 Hz, duty cycle 30 % and a discharge voltage of 800 V. Immediately after nitriding, plasma oxidation process was carried out for oxidation times at 15, 30 and 45 minutes. Glow discharge was sustained using a gas mixture of $80H_2$ - $20O_2$ volume percent at 200 Pa, frequency of 1 kHz, duty cycle of 50% and temperature of 400°C.

After the duplex process, the samples were sectioned and metallographically prepared to be observed by Scanning Electron Microscopy. Surface hardness measurements were performed for each sample using a Vickers indenter, load of 50g and test time of 10s. Determination of the corrosion performance in chloride ion-rich solutions was done by using the potentiodynamic polarization technique with the test sample as the working electrode (1cm^2 evaluating area) according to ASTM G5 [12]. A calomel electrode was used as a reference and graphite as a counter electrode in 3% NaCl solution in double distilled water as electrolyte at room temperature (26°C). The electrode potential was raised from -1300 mV to -500 mV with the scanning rate of 60 mV/s. Corrosion rate and current values were computed through Tafel extrapolation method.

In order to determine evolution of crystalline phases in plasma nitrided and post oxidized AISI 4340, X ray analysis was carried out. X-ray diffraction patterns (XRD) were collected with an Empyrean PANalytical diffractometer with CuK_α radiation (λ=1.5406 Å) operated at 45 kV and 40 mA and the X'Celerator ultra fast detector based on Real Time Multiple StripTechnology with a Bragg-Brentano geometry. The scans were performed in the 2θ range from 25 to 70° with a step scan of 0.016° and 40 s per step in a continuous mode. Structure refinements and phase identification were performed using the X'Pert HighScore Plus® software, version 3.0d and ICDD PDF-4 database (ICDD-International Centre for Diffraction Data, Newtown Square, PA).

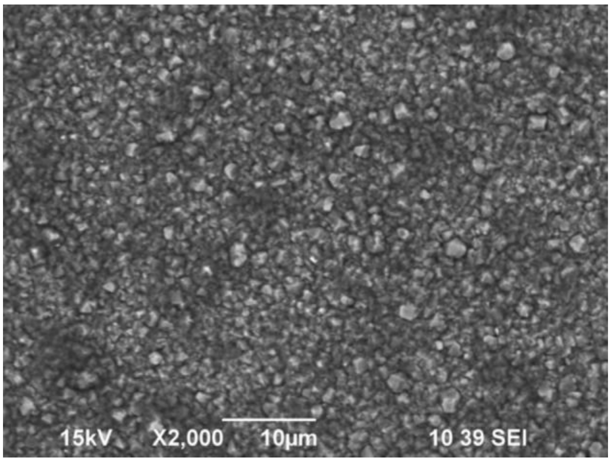
The Rietveld's method was used for quantitative analysis of the crystalline phases. This method is a least squares refinement procedure where the experimental step-scanned values are adapted to theoretical ones [13]. Peak profiles were fitted with the pseudo-Voigt function.

The weight fraction (*Wi*) for each phase was obtained from the refinement relation showed in Equation 1, where *i* is the value of *j* for a particular phase among the umpteenth presents phase, S_j is the refined scale factor, *Z* is the number of formula units per unit cell, *M* is the molecular weight of the formula unit and *V* is the unit cell volume.

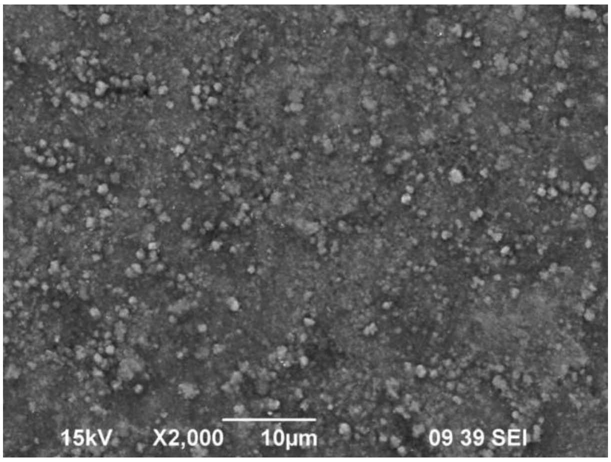
$$W_i = \frac{S_i (ZMV)_i}{\sum_j S_j (ZMV)_j} \quad \text{(Eq.1)}$$

Rietveld refinement has been done by adjusting major parameters such as, scale factor, flat background, zero-point shift, lattice parameters, orientation parameters, peak width parameters (*U*, *V*, *W*), asymmetry parameter and peak shape to obtain a reasonable value of the goodness of fit (GoF), which is an indicative of the fitting quality.

3. RESULTS AND DISCUSSION



a)



b)

Figure 1. Scanning electron microscopy micrographs of the surfaces of treated samples a) plasma nitrided and b) plasma nitrided and post-oxidized during 45 minutes.

Figure 1 shows scanning electron microscopy (SEM) micrographs of plasma nitrided samples and plasma nitrided and post-oxidized samples for 45 minutes. The surface morphology of pulsed plasma nitrided sample is characterized by edged particles and well defined boundaries. This morphology, has been reported for low alloy steels processed by plasma surface treatment as active screen plasma nitriding [14] and it has been related to sputtering phenomenon intensity [15,16]. Figure

1b shows that after post-oxidation process, adherent oxide phases fill and seal the holes between particles, which could have a positive effect on corrosion resistance improvement [17].

A SEM micrograph of the section of pulsed plasma nitrided sample and then post-oxidized at 400°C for 45 minutes is shown in Figure 2. The oxide layer can be identified as a thin region over the white layer. Both white layer and oxide layer are not chemically etched, by Nital reagent, as is the matrix.

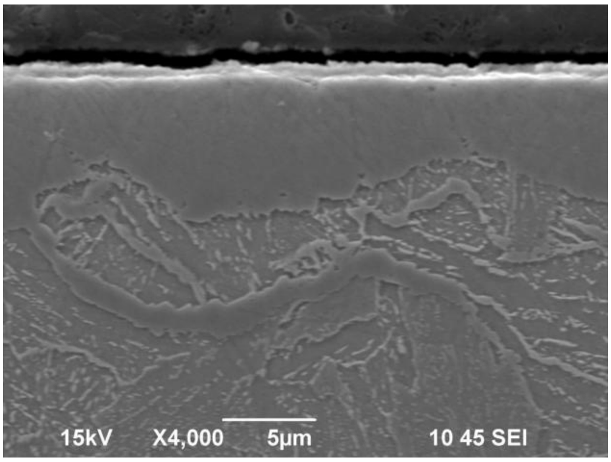


Figure 2. SEM micrograph of the section of nitrided post oxidized samples.

Table 1. Summary of Rietveld´s method analysis.

Sample	Phase Present	Lattice parameter (A) a	b	c	α	β	γ	wt (%)
Untreated	α-Fe	2.87	2.87	2.87	90	90	90	100
Nitrided	α-Fe	2.88	2.88	2.88	90	90	90	6.7
	Fe_4N	3.80	3.80	3.80	90	90	90	93.3
Nitrided Oxidized 15min	Fe_3O_4	8.39	8.39	8.39	90	90	90	6.5
	Fe_4N	3.80	3.80	3.80	90	90	90	57
	Fe_3N	4.67	4.67	4.40	90	90	120	37
Nitrided Oxidized 30 min	Fe_3O_4	8.37	8.37	8.37	90	90	90	9.8
	Fe_4N	3.80	3.80	3.80	90	90	90	69
	Fe_3N	4.67	4.67	4.39	90	90	120	21
Nitrided Oxidized 45min	Fe_3O_4	8.38	8.38	8.38	90	90	90	12
	Fe_4N	3.80	3.80	3.80	90	90	90	77.1
	Fe_3N	4.66	4.66	4.40	90	90	120	10.9

XRD patterns of untreated, nitrided and nitrided post-oxidized samples are shown in Figure 3. The surface layer of the nitrided samples consists mainly of γ′-Fe_4N mono-phasic structure with a weak diffraction peak of α-Fe phase. Presence of this peak is an indicative of penetration of X-ray beyond the compound layer. In the case of nitrided post-oxidized samples, X-ray analysis shows the presence of oxide type magnetite (Fe_3O_4) and ε-Fe_3N phase, in addition to initial γ′-Fe_4N phase.

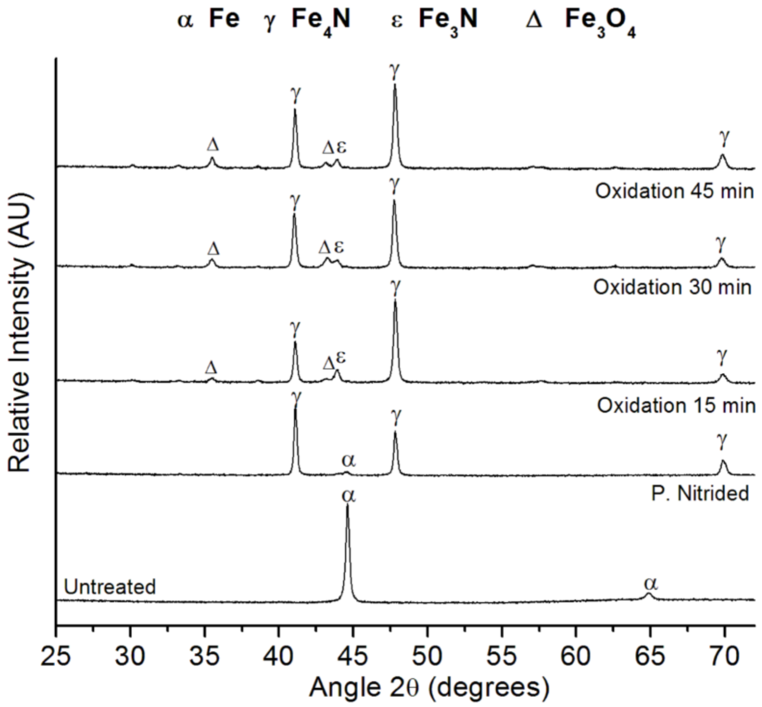


Figure 3. XRD patterns of samples untreated, nitrided, and nitrided post oxidized using different treatment times.

The Rietveld method was used on nitrided post oxidized samples. Magnetite overlayer on nitrided layer constituted by Fe_4N and Fe_3N without evidence of hematite was found. Table 1 lists results of analysis of XRD patterns by Rietveld method for samples nitrided and oxidized with different oxidation times. The lattice parameters of crystalline structures and the quantification (wt%) of phases, are reported.

Presence of magnetite in all analyzed cases, without evidence of undesirable phase hematite, can be related to high hydrogen content on gas mixture used for plasma oxidation process. A.C. Rovani et. al. [18] analyzed the effect of hydrogen content in plasma gas mixture on crystalline phases in plasma post-oxidation process of ferrous alloys. Results show that when the process is carried out at 500°C for 45 minutes, the increase in H_2 concentration from 0 to 25% promotes a generation of oxide layers with high magnetite content. Hydrogen can act as a mandatory chemical agent for rendering a spontaneous reduction of Fe(III) in hematite to Fe(II) in magnetite by a change in Gibbs free energy. In this sense, treatment at 400°C using a hydrogen concentration of 80% results in a magnetite-only layer for all analyzed oxidation times.

Rietveld analysis also shows an increase in magnetite content, from 6.5 to 12 wt %, when oxidation time increases from 15 to 45 minutes; thus confirming evidence of the continuous formation of this phase.

Another important effect of oxidation process is the transformation of a nitrided mono-phase layer γ'-Fe_4N to bi-phase layer constituted by γ'-Fe_4N and ε-Fe_3N phases. Rietvel analysis exhibit that the highest content of ε-Fe_3N phase (37%) occurs when oxidation process is carried out for 15 minutes. However, ε-Fe_3N phase content decreases when oxidation time increases, going as low as 10.9 % when a sample is post oxidized for 45 minutes. As a consequence of the decrease in ε-Fe_3N content, γ'-Fe_4N phase content increases again from 57 % in the sample oxidized during 15 minutes to 77% for the sample treated during 45 min; weight percent relation γ'-Fe_4N / ε-Fe_3N increased from 1.54 to 7.07 respectively.

Results suggest a quick formation of ε-Fe_3N, during the first 15 minutes of oxidation, which could be caused by a chemical reaction of γ'-Fe_4N with oxygen agree with $3Fe_4N+2O_2=3Fe_3N+Fe_3O_4$. A portion of iron in γ'-Fe_4N is removed to react with oxygen and form magnetite, leading to the increase in nitrogen content of nitride phase, thus changing its composition to ε-Fe_3N. However, for oxidation times longer than 15 minutes, the previously formed ε-Fe_3N starts a new transformation process that promotes a decrease in this phase content. As oxidation time increases, the oxidation process continues to consume the iron from the nitrides layer. In this sense, the reaction $Fe_3N+2O_2=Fe_3O_4+N$ which removes Fe from the nitride while releasing N atoms, will occur as a consequence of sputtering and dissociation phenomena during post oxidation process [4], promoting a new relative increase in the Fe_4N content.

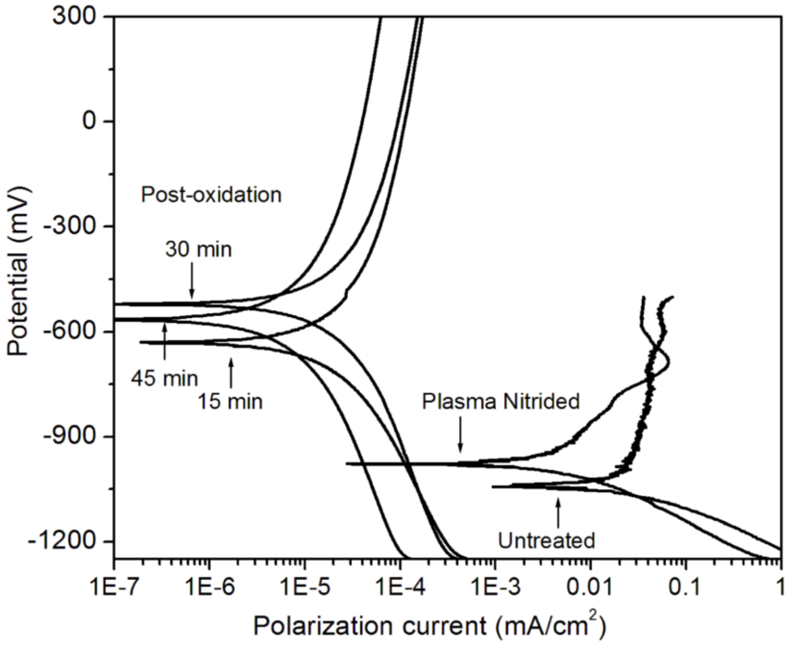


Figure 4. Potentiodynamic polarization curves of untreated, nitrided and nitrided post-oxidized AISI 4340 steel samples.

In the case of corrosion resistance testing, the positive influence of pure magnetite layer on corrosion susceptibility of nitrided post oxidized AISI 4340 steel is evident. Potentiodynamic polarization curves of the untreated, nitrided and nitrided post-oxidized samples are shown in Figure 4. The data extracted from these curves are listed in Table 2.

The results describe that the plasma nitrided samples show lower corrosion current density values I_{corr} (2.60X10^{-3} mA/cm^2) than untreated ones (1.39X10^{-2} mA/cm^2). This behavior has been reported previously [19] and it has been related to high nitrogen content crystalline phases formed on the surface during plasma nitriding. It is also noted that all post-oxidized samples show higher corrosion resistance (lower corrosion current density) than the nitrided samples. It is known that the porous nature of the nitrided layer is a factor that contributes to get higher values of corrosion current density (lower corrosion resistance). In this sense, the formation of the oxide layer after post-oxidation step seals and covers the porous structures of nitrided compound layer [6], which positively affects its corrosion resistance.

Table 2. Surface hardness and corrosion performance of untreated, nitrided and nitrided post oxidized samples.

Sample	Surface Hardness (HV_{25g})	Corrosion Rate (mm/year)	I_{corr} (mA/cm^2)
Untreated	300 (11)	1.61E-1	1.39E-2
Nitrided	1006 (60)	3.01E-2	2.60E-3
Nitrided oxidized 15 min	989 (47)	9.22E-5	7.95E-6
Nitrided oxidized 30 min	1032 (44)	1.634E-4	1.4E-5
Nitrided oxidized 45 min	1012 (37)	1.084E-4	9.35E-6

However, the corrosion resistance of post-oxidized samples is mainly defined by a composition of oxidized layers [2,17]. Thus, considerably lower I_{corr} values of nitrided post-oxidized samples, are associated with obtaining oxidized layers constituted by magnetite which is a dense, compact and adherent oxide with characteristics of high corrosion performance [4].

4. CONCLUSIONS

Hematite-free magnetite layer was obtained on AISI 4340 steel by duplex DC pulsed plasma nitriding post oxidation process.

Rietveld analysis of XRD data confirmed the magnetite increase from 6.5 to 12 wt % when post oxidation time rises from 15 to 45 minutes respectively.

Post oxidation process of monophasic layers γ'-Fe_4N promotes, in addition to the formation of magnetite, a fast transformation of γ'-Fe_4N to ε-Fe_3N in the first minutes of treatment. However content of early formed ε-Fe_3N decreases from 37 to 10.9 %wt when oxidation time changes from 15 to 45 minutes. Consequently, the weight percent relation of γ'-Fe_4N / ε-Fe_3N increased from 1.54 to 7.07 for samples oxidized for 15 and 45 minutes respectively.

Post oxidation process significantly increased the corrosion resistance (decrease in I_{corr} value) of plasma nitrided AISI 4340 steel. While plasma nitrided steel shows an I_{corr} value of 2.60X10^{-3} mA/cm^2, duplex treatment nitriding post oxidation promotes obtaining I_{corr} values of about 1.0X10^{-5} mA/cm^{-2}. Although oxidation time increases the magnetite content on nitrided steel surface, I_{corr} values are very similar for all evaluated oxidation times.

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