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Improvement Of The Corrosion Resistance Of The Stainless Steel With The Plasma Nitridingand The Chemical Polishing As Two Different Mechanisms

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ABSTRACT
Two different techniques have been studied to improve the corrosion resistance of the austenitic stainless steel(304L). The first technique is the plasma nitriding using a mixture of N_2-H_2gasesand the second technique is the chemical polishing. The potentiodynamic polarization measurements were used to compare between the effects of the two techniques on the corrosion resistance of the stainless steel. The corrosion potential of thenitridedsampleswasimproved by 61% while in the case of the samples that chemically polished it was improved by 13%. X- ray diffraction (XRD) pattern of the nitride sample confirms the formation of $Fe_{2-3}N$, Fe_4N, and CrNnitridephases and also the formation of the super saturated nitrogen-rich phase "S-phase" which has important role in the improvement of the corrosion resistance. The surface morphology of the two samples confirms the formation of the S- Phase. The grain size of the nitride sample was about 50.25 nm.
Keywords: plasma nitriding, chemical polishing, Corrosion, Stainless steels, metastable phase.

I. INTRODUCTION

Different types of stainless steels have been commonly used in many engineering applications, especially parts in the automotive industry such as crankshaft, gear, pinion, bolt and various machine tool components because they have good mechanical properties and they are easily fabricated. Also, in several services they have been used in corrosive environments such as lubricant, gaseous and liquid environments resulting in reduction of performance and lifetime of those parts. Therefore, the parts require high hardness of surface for increasing corrosion resistance[1].Various Physical and chemicaltechniques were used to improve the properties of the stainless steel. The physical techniques such as Physical Vapor Deposition (PVD), Plasma nitriding, Carbonitriding and Thermal spraying, are widely used to improve their surface in order to achieve better wear, abrasion and corrosion resistance. One the other hand one of the most popular chemical techniques is the chemical polishing.Plasmanitriding is a very promising technique to improve surface mechanical properties of stainless steels[2], and improving their surface corrosion resistance[3].In the present study it has focused on the treatment of the austenitic stainless steel of type (304L) by two different mechanisms; plasma nitriding as a physical techniqueand the chemical polishing as a

chemical one. The treatment by the two techniques was repeated three times to ensure the results and the average has taken. The purpose of this study is to compare between the two mechanisms in the improvement of the corrosion resistance properties and discover the importance of the plasma nitriding technique in the improvement of the surface properties of the stainless steel especially the corrosion resistance.

II. MATERIALS AND METHODS
Materials preparation

The material that is used in the present study is the 304L austenitic stainless steel which was cut into small sheets of dimensions 15x 20 x2 mm. Table1 Shows the chemical composition of the austenitic stainless steel 304L material (in weight percent).

Fe	Cr	Ni	Mo	Co	C	Si	Mn	S
71.5	18.05	7.86	0.3	0.094	0.06	0.05	1.147	0.005

Table 1 The chemical composition of the austenitic stainless steel 304L material (in weight percent).

The surface of the stainless steel samples was mechanically abraded with 400 up to 2000, grit emery papers, rinsed with distilled water, degreased in acetone, absolute ethanol and dried in air.

Plasma Nitriding

Fig. 1 shows the plasma discharge cell which consists of two parallel electrodes enclosed in a cylindrical Pyrex glass tube of 10 cm diameter and 20 cm length. Each electrode consists of a circular disk made of steel of 4 cm in diameter. The distance between the two electrodes is 2cm. The two electrodes are connected to the dc power supply of variable output voltage reaches 1000 volts. Three stainless steel samples were pasted on the cathode by silver paste. The glass tube is evacuated by using a vacuum system to a base pressure about 2×10^{-3}Torr. A mixture of N_2-H_2 gases is entered the tube through needle valves (type Leybold AG 283 40) to control the pressure, and the percentage of the gas mixture inside the reactor. Addition of H_2 to the nitrogen gas causes the cleaning the sample surface and to rise its temperature as it will be shown in the following results.The temperature of the sample is controlled by changing the gas pressure and the percentage of H_2 in N_2-H_2 gas mixture due to the change of the discharge current as it will be shown in Fig. 2.The temperature of the cathode was determined by using a Copper-constantan thermocouple and it was fixed at about 480C^o where the total gas pressure was 5Torr and the percentage of H_2 is 20 %. The discharge current was adjusted to 100 mA.
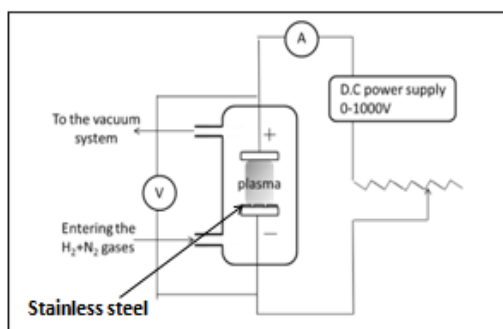

Fig. 1. Plasma nitriding discharge cell.

Chemical Polishing

Another three Stainless steel samples were washed, cleaned and dried with hot air after surface treatment. The samples were immersed in a solution of (12.5 ml HNO_3 + 4 ml HF + 33.5 ml H_2O). The temperature was 30 C^o and the treatment time was 20 min. Unlike electro polishing, chemical polishing can be done without the use of electricity. During chemical polishing, the effect of solution causes the formation of a passivation layer[4].

Electrochemical Measurement

The electrochemical measurement was performed in Potentiodynamic Polarization; the data were obtained in the range of potentials from 1.5 to -1.6 V vs. SCE with the scan rate of 1 mV/s. at 37 C^o. The device used is the workstation Auto lap 302Npotentiostat/galvanostat instrument, Corrosion current density (i_{corr}) which is equivalent to the corrosion rate of the specimens was estimated using Tafel extrapolation.

X-Ray Diffraction Measurements

The structure of the nitrided sample has been studied by using X-ray diffraction technique (XRD). The normal (2θ) scan was taken with CuKα as a target (λ = 1.540560 Å), starting 20°, ending 100°, step: 0.02°, step time 0.5 s, and temperature 27.0 $^\circ$C. X-ray diffraction was used to examine product nitrided phases in the surface layers of the considered samples of (304L) austenitic stainless steel using Siemens x-ray diffractometer and the background noise was subtracted.

Surface Morphology

Surface morphology of nitrided samples were investigated using metallurgical microscope type (inverted Metallurgical Microscope Epiphot 300). This microscope attached with 35 mm camera.

III. RESULTS AND DISCUSSION
Plasma Characterization

Fig. 2.Shows the variation of the discharge current and the cathode temperature with H_2%in the gas mixture.Both the discharge current and the cathode temperature increase by increasing the hydrogen percentage and it reaches its maximum value at about 40% of H_2then decreases again. The similarity between the behavior of the cathode temperature and the discharge current with addition of H_2 is due to the increasing in the ionization probability that causes the increasing in the ion bombardment on the cathode. Further addition of H_2 beyond 50% causes the decreasing in the current and the temperature. This behavior is attributed to the increasing in the mean free bath of the electrons that causes the decrease in the current at constant applied voltage.As it stated in [5], the nitriding temperature affects the formation of the nitride phases. The corrosion resistance can be improved, if plasma nitriding is carried out below a critical temperature to avoid the precipitation of chromium nitrides. This critical temperature is 500 ^{o}C as stated by [6]. The percentage of H_2 in the gas mixture and the discharge current were controlled to avoid reaching the critical temperature (500 ^{o}C). the temperature was fixed at about 480C^o where the total gas pressure was 5Torr and the percentage of H_2 is 20 %. The discharge current was adjusted to 100 mA.
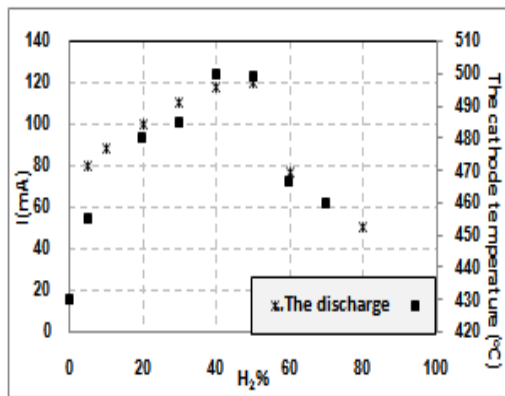
Fig. 2. The discharge current and the cathode temperature as a function of the hydrogen percentage in the gas mixture, at P=5Torr and at V=500 volts.

Potentiodynamicpolarization Measurements

Fig. 3 represents the potentiodynamic polarization curve of the untreated, plasma nitride and chemical polished stainless steel samples. The curves can be divided into several potential domains; the cathodic potential domain, the transition domain, and the anodic potential domain. The intersection between the extrapolation of the cathodic and the anodic domains (the anodic and cathodicTafel slops) determines the current density of corrosion [7].
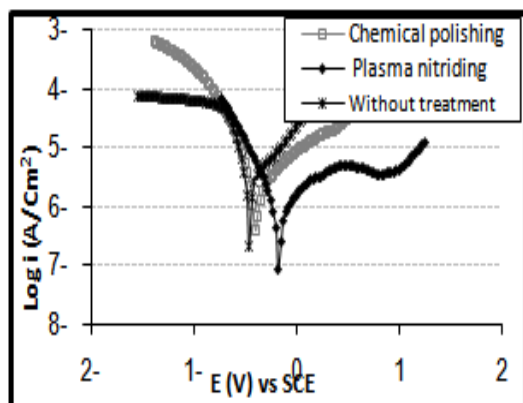

Fig. 3.Potentiodynamic polarization curves of the untreated, plasma nitride and chemical polished stainless steel samples in Hank's solution.

Fig. 4 shows the corrosion rate that was estimated by using Stern-Geary [8]. It can be noticed that the plasma nitride sample has the lowest corrosion rate.
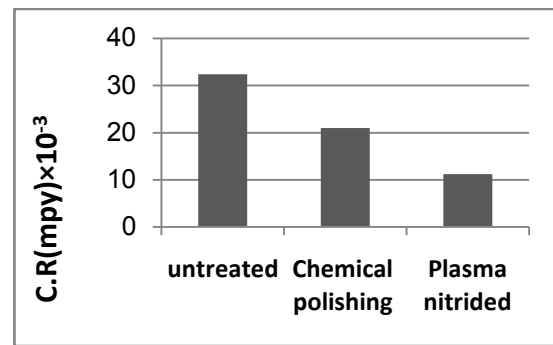

Fig.4 The corrosion rate of the untreated, plasma nitride and chemical polished stainless steel samples.

The corrosion potential (E_{corr}), the corrosion current (I_{corr}) and the corrosion rate (CR) that was estimated by using Stern-Geary, as stated in [9],for the three samples have beentabulated in the table2 [10]:

Treatment	E_{corr} V(SCE)	I_{corr} $\mu A\ cm^{-2}$	CR Mpy 10^{-3}
Untreated	-0.464	1.56	32.39
Plasma nitride	-0.178	0.54	11.21
Chemical treated	-0.403	1.01	20.97

Table 2. The corrosion potential (E_{corr}), the corrosion current (I_{corr}) and the corrosion rate (CR) of the untreated, nitride and chemical polished stainless steel samples.

The corrosion potential of the plasma nitride sample tends to be more positive than that for the samples that treated chemically or that the untreated one. The sharp increase after $E_{corr}$with a very small break in the current and well-defined current plateau after E_{corr} which suggesting the existence of a partially protective film on the alloy surface as stated in [11] [12].

Fig. 5 shows the X-ray diffraction (XRD) pattern of nitrided sample at P = 5Torr, N_2:H_2 = 80:20, and t = 2 hours.The pattern shows the formation of $Fe_{2-3}N$ (ε phase), Fe_4N (γ' phase), and CrN phases. The broadening hump in the peaks of nitrided phases at 2θ angles from 37.4 to 50.6 represents the formation of nitrogen-rich phase denoted by γN andvariously termed "expanded austenite" or the "S-phase" and sometimes is called" the metastable supersaturated austenite" [13] [14]. This phase results from the diffusion of nitrogen atoms and occupying the fcc octahedral sites in the compound layer of the stainless steel until the saturation level is reached [15] [16].
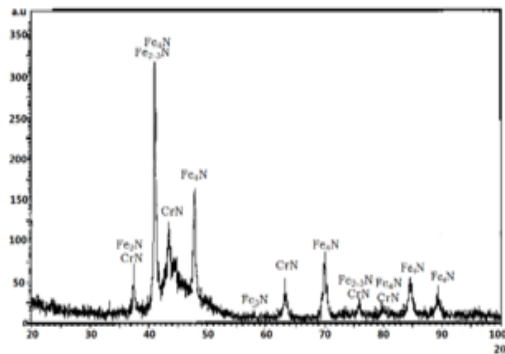
Fig. 5.XRD pattern of nitrided304L austenitic stainless steel sample.

The surface morphology of untreated ASS sample, chemically treated and plasma treated samples respectively are shown in Fig. (6).The grain size of the treated sample is much smaller than the other two samples that confirm the formation of the short-ordered S-phase.The grain size of the crystallites of the nitrided sample was calculated from the X-ray diffraction measurements by using the equation that is stated in [17] to be about 50.25nm. Ionic bombardment, which introduces vacancies and vacancy clusters and therefore increases nitrogen diffusion, has been thought tobe a responsible for this process. The decrease in the grain size of the nitride sample rather than the other ones is the result of the diffusion of nitrogen atoms which leads to the distortion of crystalline structure by inducing a high density of stacking faults.
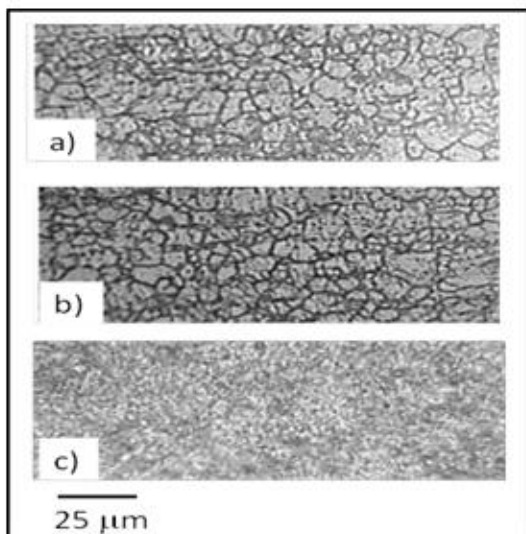

Fig. (6) The surface morphology of the samples: a) the untreated, b) the chemical polished and c) the nitride samples

Above $500^{o}C$, the S-phase decomposes to the most stable products ($Fe_{2-3}N$ and Fe_4N) and

CrN phase precipitates around the grains boundaries. This precipitation of CrN causes the difference in the stress and in turns causes the corrosion. To avoid the precipitation of CrN the temperature should be kept below $500^{o}C$. Moreover, the time is needed to transform the S-phase to the most stable nitrided phases. The importance of the S-phase refers to its high corrosion resistance because of the high concentration of the nitrogen atoms that are physically diffused inside the nitride sample. This high concentration of nitrogen atoms in the S-phase shields the surface from the corrosive environments [18].

IV. CONCLUSION

In the present paper, the Austenitic stainless steel 304L samples were treated by two different mechanisms; the first one is the plasma nitridingin continuous d.c glow discharge plasma reactor in N_2-H_2 gas mixture under pressure of 5 Torr.The second technique is the chemical polishing in a solution of (12.5 ml HNO_3 + 4 ml HF + 33.5 ml H_2O). The purpose of the treatment is to improve the corrosion resistance of the stainless steel and to compare between the two techniques.The results above show that the treatment of the 304L austenitic stainless steel improves its corrosion resistance. The plasma nitriding treatment is more efficient than the chemical one.

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