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Gas Mixture and Current Density Variation and Their Effect on White-Layer Properties of Nitrided Steel

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The effect of current density and gas mixture on surface properties of low alloy steel processed in a pulsed plasma nitriding system under strictly controlled conditions is evaluated in this work. As current density is a parameter that has not been particularly studied, this study seeks to demonstrate that current density and gas mixture have an important influence on the process and an adequate combination of these two variables is essential to obtain the desired surface properties: hardness, white layer thickness (or absence), and crystalline phases of the modified layer. In this sense, samples processed at low current densities with low nitrogen content in the plasma atmosphere show a diffusive nitrides region which increases the hardness from 250 HV (untreated reference sample) to 400 HV without the presence of the typical white layer that is sometimes undesired due to its fragility and tendency to break. On the other hand, treatment at high current densities and high nitrogen concentrations leads to obtain pieces with a homogeneous single-phase layer (γ-Fe_4N) with an outstanding corrosion performance, diminishing the corrosion rate from 0.160 μm per year in the untreated sample up to 0.050 μm per year.

Keywords corrosion, hardness, plasma nitriding, surface treatment

1. Introduction

Nitrogen has been widely used, along with carbon and boron, as elements introduced in iron and titanium-based alloys to increase the mechanical properties such as hardness, wear resistance, and corrosion resistance (Ref 1). Although there are numerous techniques for doing this, plasma nitriding has become a powerful surface modification technique over other methods owing to several advantages: produces less warping and distortion in the surface, allows processing at low temperature and avoids handling of hazardous and toxic chemicals (Ref 2).

Plasma nitriding is a surface hardening technique which uses a direct current glow discharge to introduce nitrogen to the surface of metallic materials (Ref 3); this surface modification process can be applied in the treatment of several types of iron alloys which are of interest for industrial applications: tool steels (Ref 4), low allow steels (Ref 5), and stainless steels (Ref 6, 7).

In a plasma nitriding process, initial chemical reactions occur at the surface of material when thermal activation from the plasma favors the formation of iron nitrides in a thin compounds layer, usually constituted of γ-Fe_4N/ε-$Fe_{2,3}N$; this layer is hard and increase wear and corrosion resistance (Ref 8, 9). Driven by thermal and concentration gradient effects, nitrogen diffuses towards the core forming very fine nitride particles in a diffusion zone, which promotes hardening of the substrate and increases the fatigue resistance (Ref 10).

Several parameters are involved in the development of the system formed by the compounds and diffusion layers (hereinafter named "system of layers"): work piece temperature, pulse frequency, pulse duration, atmosphere composition, vacuum pressure, etc. (Ref 11, 12). From this assortment of process parameters, there are typical values for the most of them; however, the sensitivity to current density is not clear. In this article, the effect of current density and also the gas mixture on the properties of the system of layers in a nitrided low alloy steel is evaluated.

After treatment, samples were evaluated by metallographic studies using scanning electron microscopy; the existing crystalline phases were determined by X-ray diffraction; microhardness tests were performed and finally, the technique of potentiodynamic polarization curves was used with an aim to evaluate the corrosion performance in comparison with the untreated reference sample.

2. Materials and Methods

Commercial grade AISI 4340 steel was chosen to perform the experiments because of its extensive industrial applications. Chemical characterization showed a composition: 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, and Fe balance (wt.%). As received, the material was in quenching and tempering condition. Samples, cut into pieces of 40 × 40 × 5 mm, were ground by different grades of SiC emery paper (120, 240, 320, 400, 600 progressively) and

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polished with a 6-μm diamond suspension. After that, they were subjected to a cleaning stage in an acetone ultrasonic bath; this step intended to clean the surface from dust or oil.

The nitriding process was performed in the system exhibited in the Fig. 1, previously described in (Ref 12) (own-design), which has the capability to manipulate all the process variables: work piece temperature, atmosphere composition and pressure, discharge current and voltage, pulse duration and frequency. The vacuum vessel is a 42-L cylindrical reactor which is pumped down by means a rotary vane vacuum pump at a base pressure of 10^{-3} Torr. The vacuum chamber contains a central cathode which is negatively biased with respect to the vessel wall by means of a specifically designed high voltage pulsed power supply; an auxiliary heating system affords full control over the sample temperature. The gas inlet system allows a precise control on pressure and gas mixture ratio due to the use of mass flow controllers.

Just before treatment, samples were exposed to a sputtering stage during 0.5 h in a plasma produced at 1.3 Torr in a 50% Ar-50% H_2 atmosphere by a −500 V potential applied as a 1000 Hz pulse train whose duty cycle was fixed at 50% (500 μs). The conditions for nitriding stage were a constant pressure of 2 Torr, pulsed potential of −400 to −700 V (discharge voltage measured between anode and cathode, see Table 1) at a pulse frequency held constant at 1000 Hz and duty cycle at 30% (300 μs). The temperature of each sample was controlled around 500 °C (±10 °C) by means of a dedicated temperature controller, a K-type thermocouple directly attached to the work piece, and a resistive heating element. All of the above conditions strictly controlled during process (Table 1) in order to show the specific effect of the current density and atmosphere composition on the surface properties of the nitride steel. After 4 h, samples were slowly cooled down to room temperature in an inert argon atmosphere.

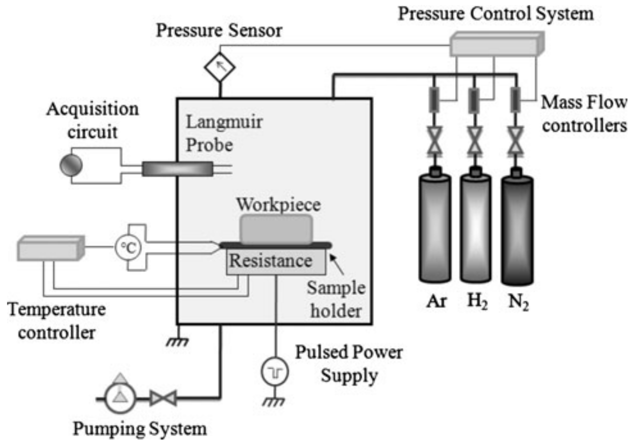

Fig. 1 Schematic diagram of the nitriding system

Table 1 Summary of experimental conditions for the nitriding stage

	Gas ratio N_2%-H_2%		
Current density, J	**75-25**	**50-50**	**25-75**
0.5 mA/cm^2	M1 (400 V)	M2 (400 V)	M3 (450 V)
1.0 mA/cm^2	M4 (480 V)	M5 (500 V)	M6 (550 V)
2.0 mA/cm^2	M7 (550 V)	M8 (600 V)	M9 (700 V)

Discharge voltage for the desired current density is given in parenthesis

3. Results and Discussion

Once the nitriding stage finished, samples were cross-sectioned, polished, and etched with nital for reveal the white layer. Scanning electron microscopy (SEM) was used to measure the thickness of each nitrided layer and results are illustrated in Fig. 2; sample identifier is also included for the different processing conditions, from samples M1 to M9. With an aim to clearly identify the white layer through the difference in the chemical composition, images were taken by using backscattered electrons.

SEM studies showed that white layer increases in thickness as the amount of nitrogen in the mixture raises; this is explainable on the basis of the gradient of nitrogen concentration in the boundary between surface and gas, where a greater number of nitrogen atoms available implies an easier diffusion of some of them through the boundary. Also, current density favors an increase in white layer thickness, attributed to the ionization of the plasma because current density is directly related with the ion density in the plasma (Ref 13) and consequently, the number of charged particles colliding with the surface in each pulse is also bigger.

In contrast, white layer was not visible in samples treated with low nitrogen content and low current density, as occur for the samples M2 and M3 which were treated with 50% N_2-50% H_2 and 25% N_2-75% H_2, respectively, by using a current density of 0.5 mA/cm^2. The latter is a remarkable result because the nitrided work piece can be used without further processing in certain applications where the embrittlement of the surface due to the formation of the white layer must be avoided.

The sequence of micrographs from Fig. 3a-c shows some of the most representative samples to make evident the appearance of the nitrided layer.

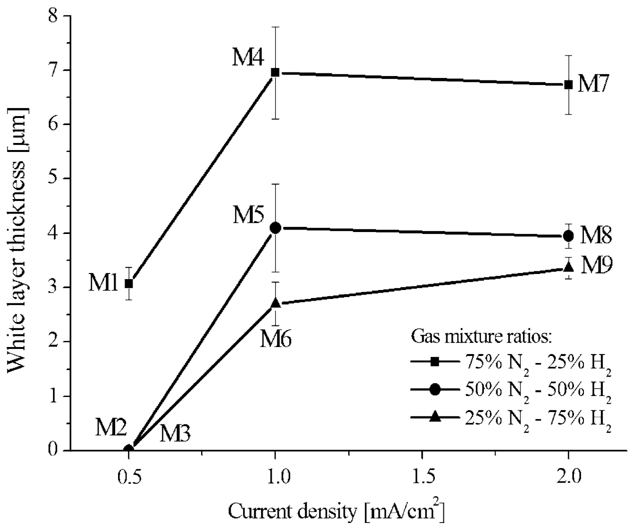

Fig. 2 Evolution of the white layer thickness as a function of nitriding current density and atmosphere nitrogen content

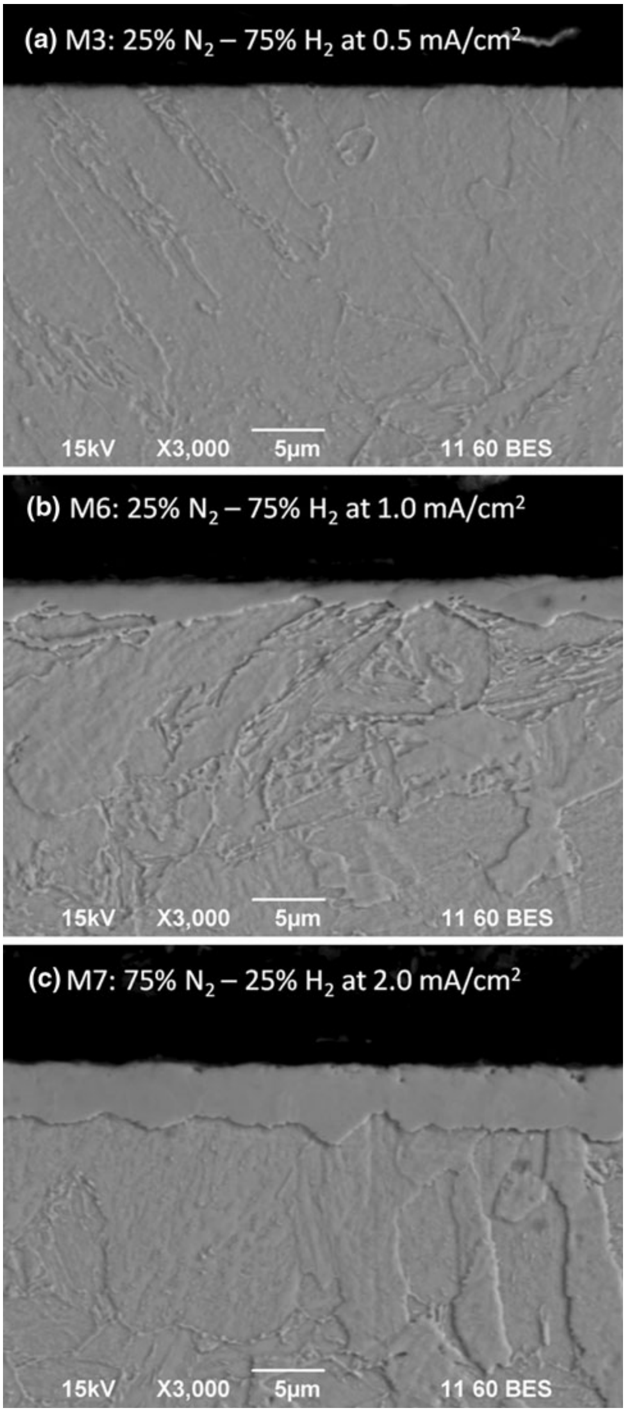

Fig. 3 SEM micrographs of selected samples

Figure 3(a) exhibits sample M3 nitrided with a 25% N_2-75% H_2 gas mixture at 0.5 mA/cm^2; it is clear that no white layer is present, but the typical microstructure of the nitriding zone is noticeable suggesting the existence of a diffusion zone. As the current density increases, the formation of a thin white layer becomes evident, for instance in sample M6 (Fig. 3b) treated with 25% N_2-75% H_2 and 1.0 mA/cm^2. Moreover, when both, current density and nitrogen content in the gas mixture are increased, a well delimited white layer is observed, as shown in Fig. 3(c) for sample M7 treated with 75% N_2-25% H_2 at 2.0 mA/cm^2.

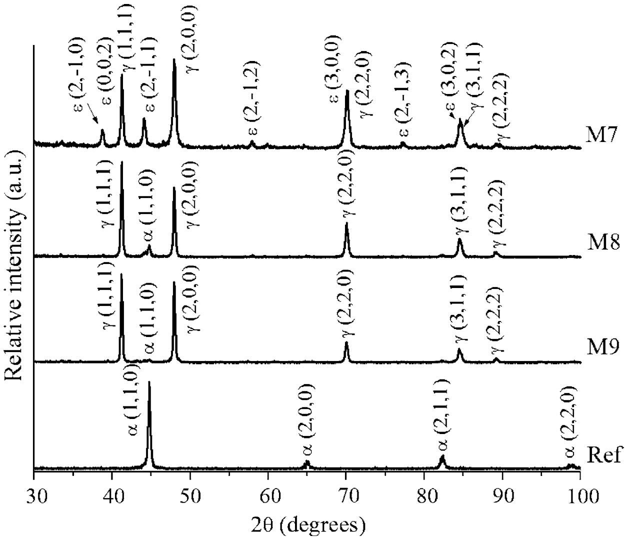

Fig. 4 XRD patterns for selected samples. γ: Fe_4N, ε: Fe_3N, α: Fe

In order to determine the chemical composition of the nitrided layers, representative sections of the samples were characterized through X-ray diffraction analysis (Cu Kα radiation) over a 2θ range from 30° to 100°.

Results in Fig. 4 show that higher nitrogen content in the gas mixture promotes the formation of bi-phase layer containing γ-Fe_4N/ε-Fe_3N (for example in the samples M7 and M4 treated with 75% N_2-25% H_2). On the other hand, samples treated with 50% of nitrogen in the mixture or lower exhibit only the γ-Fe_4N phase, as is suggested by the XRD patterns obtained for samples M8 and M9 treated at 2.0 mA/cm^2 with 50% N_2-50% H_2 and 25% N_2-75% H_2, respectively.

For the samples where white layer was not observed, the XRD analysis does not indicate that the composition of phases was different to the untreated reference sample and only the α reflections of iron were observed, attributed to a low nitrogen content in the diffusion zone.

The achievement of single-phase layers for selected samples is a remarkable result, obtained thanks to the control of processing conditions and an adequate atmosphere composition. The latter is in accordance to other authors which had demonstrated that single-phase γ-Fe_4N layers have better tribological properties in comparison with bi-phase ε-$Fe_{2\text{-}3N}$/γ-Fe_4N layers (Ref 6).

As can be inferred from the exhibited XRD results, the current density has a negligible effect on the obtained phases, because the mechanism of formation of nitrides is mainly affected by the concentration of atomic nitrogen at a constant temperature. Ions in the abnormal glow-discharge plasma play a major role in generating the energetic radicals, but their role in nitriding is minimal (Ref 1). Thus, although the current density affects the ion density in the plasma, it does not modify the amount of neutrals.

Surface hardness measurements were performed to each sample by using a Vickers indenter at 50 gF. Untreated reference sample had a hardness of 250 HV, while the processed samples showed a tendency toward increased hardness as the current density and nitrogen content in the gas mixture are higher, leading into a higher concentration of nitrogen (forming nitrides) in the white layer. The maximum hardness achieved (814 HV) is more than 3 times the original hardness, and even the samples without a white layer report an improved hardness with values up to 400 HV.

Hardening beyond the white layer is the result of the presence of nitrogen towards the core sample; taking advantage of this phenomenon, diffusion zone depth was measured up to the transversal hardness was 10% greater than the substrate hardness (Vickers 50 gF indenter) (Ref 14). Diffusion depth varies directly with the amount of nitrogen in the gas mixture, being 250 to 300 μm for the samples treated at 0.5 mA/cm^2 (M1, M2, and M3) and 350 to 400 μm for the samples treated with 1.0 and 2.0 mA/cm^2 (M4 to M9).

Finally, electrochemical potentiodynamic polarization tests were carried out within a cell containing aqueous NaCl solution (3 wt.%). As shown in Fig. 5 for selected samples, the corrosion potential appears clearly increased while the polarization curves are shifted to the left for the treated samples with reference to the untreated one. These facts point to an improvement in the corrosion performance, and it can be confirmed by the behavior of the corrosion potential plotted in Fig. 6. While the corrosion potential of untreated sample is about −1030 mV, nitrided samples exhibit a higher corrosion potential which tends to increase as the current density rises. That behavior can be linked to the formation of a thicker nitrided layer. Samples without white layer have corrosion potential very similar to the untreated sample. The corrosion rate was estimated for all samples by means the Taffel slope method. Reference untreated sample exhibited a corrosion rate of 0.160 μm per year and this parameter was improved by all treated samples, but especially those treated with higher current densities, achieving an outstanding corrosion rate of 0.050 μm per year in sample M9 (treated at 2.0 mA/cm^2 with 25% N_2-75% H_2). Samples treated by using 0.5 mA/cm^2 also improve, though slightly, the corrosion performance with values about 0.130 μm per year.

It was observed that the corrosion rate does not depend significantly on the nitrogen content in gas mixture, but the current density plays an important role in the formation of a compact and dense layer (such as the sample shown in Fig. 3c) which favors the corrosion performance.

The surface of the samples after the corrosion test was analyzed by SEM. The most characteristic micrographs are shown in Fig. 7 (worst and best cases). The surface of the untreated sample in Fig. 7(a) appears highly affected and exhibits corrosion bi-product deposits. However, the sample M9 which was treated with low nitrogen content (25%) and high current density (2.0 mA/cm^{-2}) in Fig. 7(b) is shown little affected by corrosion.

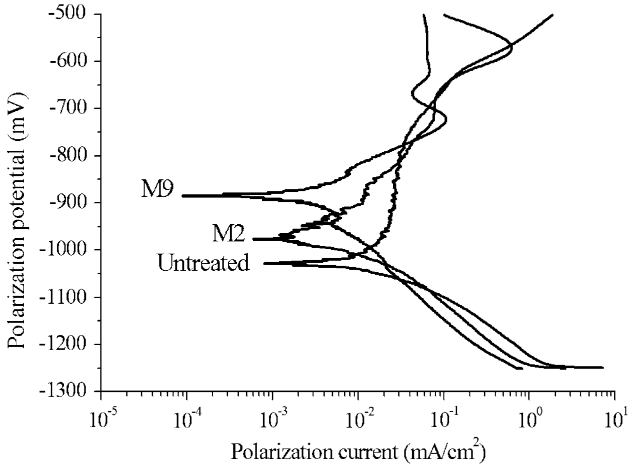

Fig. 5 Potentiodynamic polarization curves for selected samples

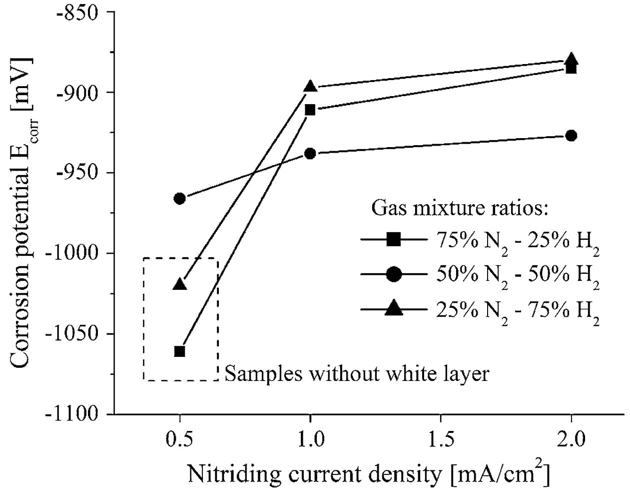

Fig. 6 Corrosion potential as a function of nitriding current density

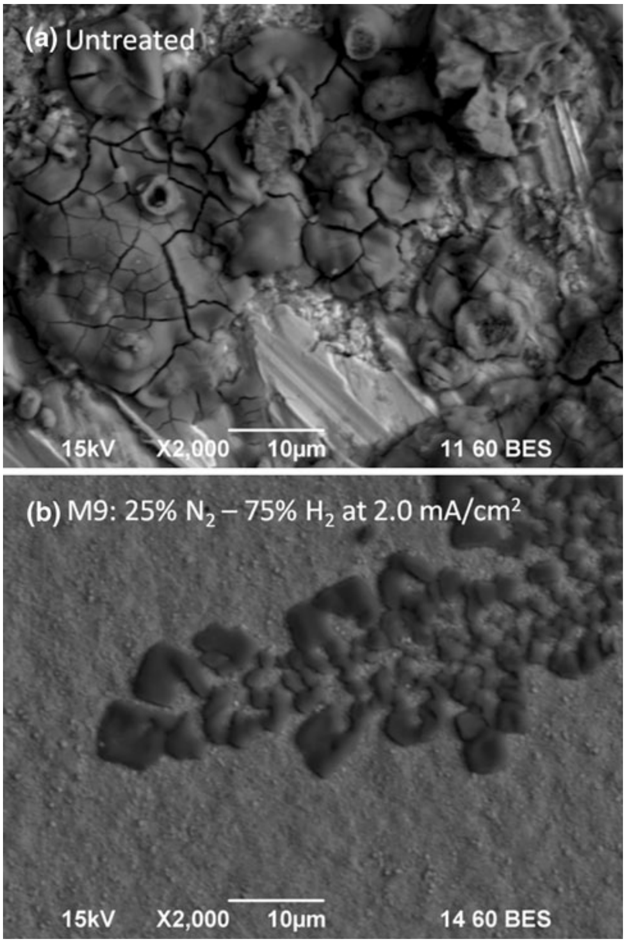

Fig. 7 SEM micrographs of selected samples after corrosion test: (a) worst case (untreated sample) and (b) best case (M9, 25% N_2-75% H_2 at 2.0 mA/cm^{-2})

Concerning to the benefits or disadvantages of the white layer, it is important to note that although the compound layer has a relatively high hardness, the internal stresses make it friable and brittle; in this sense, the width of this layer is often minimized to preserve the sliding wear and fatigue resistance in specific applications (Ref 11). In contrast, the white layer provides the material with good physical characteristics against wearing and rolling friction (Ref 15), being then desirable a homogeneous and thicker compound layer. Moreover, the compound layer was found to act as an intermediate hard layer leading to superior sliding wear properties in plasma nitrided post-hard-coated process (Ref 16). Thus, the thickness of this layer (or its absence) should therefore be determined according to the use of the material and, as can be inferred from the exhibited results, an adequate combination nitrogen and hydrogen in the gas mixture and the current density provide a good method for control the system of layers using specific processing conditions.

4. Conclusions

In this paper, the effect of current density and gas mixture on surface properties of AISI 4340 steel nitrided in a pulsed plasma system was analyzed. These parameters provide control over the compound zone to the extent that is possible to obtain nitrided pieces without white layer by using low-nitrogen mixtures at low current densities.

Also, all treated samples exhibit a noticeable increase in hardness, even the samples without white layer. The corrosion performance is greatly increased when white layer exists, especially in the case of the samples with a homogeneous layer made of a γ-Fe_4N crystalline phase, which can be obtained in a low-nitrogen mixture and using medium to high current densities.

Acknowledgments

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