

Effect of duty cycle on surface properties of AISI 4340 using a pulsed plasma nitriding process

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Plasma nitriding is a glow discharge technique, which is widely used to improve the surface properties of steel and its alloys, such as wear, corrosion resistance and hardness; additionally, it can increase fatigue strength. The aim of this work is to evaluate the effect of duty cycle on the surface properties of AISI 4340 low alloy steel, in a pulsed plasma nitriding process. The effect of duty cycle (applying a 10 – 80 % t_{ON} interval) on the surface hardness, treatment depth, compounds zone width and crystalline phase composition will be discussed. It has been found that for nitriding process at 540 °C in a gas mixture 50 % N_2 – 50 % H_2 at a constant pressure, using a discharge voltage of -800 V, duty cycle has a negligible effect on crystalline phase composition, even though the influence on surface hardness, treatment depth and compounds zone width is evident.

Keywords: Surface modification; Plasma nitriding; White layer control

1. Introduction

Plasma or ion nitriding is a technique of surface hardening which use the direct current (DC) glow discharge phenomena to introduce elemental nitrogen in the surface of metallic pieces for subsequent diffusion process into the crystalline lattice of the material [1]. Typically, glow discharge is generated and sustained by means of a constant direct current power supply; however, the present trend is using a pulsed direct current device which allows better arc control [2].

Ion nitriding is a plasma-activated thermo-chemical method extensively used to increase the fatigue strength, hardness and wear resistance of alloy steels, tool steels and stainless steels [3]. Additionally, it has been used for improve properties such as load bearing capacity of dynamic loaded components [4, 5].

Plasma nitriding process is accomplished in a vacuum chamber where the sample is directly connected to a cathode. High voltage is applied between the cathode and the anode, being the vessel walls acting as the anode, to generate plasma in a gas mixture, usually at rough vacuum (0.75-10 torr) [6]. Ion nitriding process is usually preceded by a cleaning stage by plasmas produced in Ar and H_2 mixtures. Then addition of nitrogen starts and sustains the nitriding process.

The surface hardening of the samples is accomplished due to the formation of both, “diffusion zone” and “compounds layer”. The nitriding reaction takes place at the surface as well as in the subsurface by the diffusion of nitrogen atoms from the surface towards the core. The diffusion zone consists of very fine nitride particles and the nitrogen contents decreases towards the core, this particles result from the combination of diffused nitrogen with some

alloying elements. “Compounds layer”, also called “white layer” because it is not etched by alcoholic nitric acid reagent [7], consists of a thin iron nitrided layer constituted of γ - Fe_4N / ϵ - $Fe_{2,3}N$ intermetallic compounds. This layer is some microns depth, has a high hardness value, and increase wear and corrosion resistance; in contrast, the diffusion zone is softer and without pronounced interface, promotes the hardening of the inner metal substrate and increase the fatigue resistance of the material [8, 9].

In this study is analyzed the effect on mechanical and microstructural properties of low alloy AISI 4340 steel samples as a result of the duty cycle variation in a pulsed plasma nitriding process. Several analyses for the nitrided region are presented, including surface and transversal hardness test, analysis by Scanning Electron Microscopy (SEM) and crystalline phase analysis by X Ray Diffraction (XRD).

2. Experimental details

Samples of AISI 4340 steel were used in all the experiments, being 40 x 40 x 5 mm the dimensions of each specimen. The samples surface was ground using different grades of SiC emery paper (120, 240, 320, 400, 600) and then polished with a 6 μ m diamond suspension. AISI 4340 steel has the following nominal composition (wt. %): 0.38 C, 0.017 S, 0.63 Mn, 0.008 P, 0.19 Si, 0.80 Si, 1.64 Ni, 0.20 Mo, 0.137 Cu and Fe balance.

The samples were processed in the nitriding system exhibited in figure 1. It consists of a vacuum chamber containing a central cathode which is negatively biased respect to the wall chamber. The temperature of the sample was controlled by an auxiliary heating system and was measured by means of a K-Type thermocouple

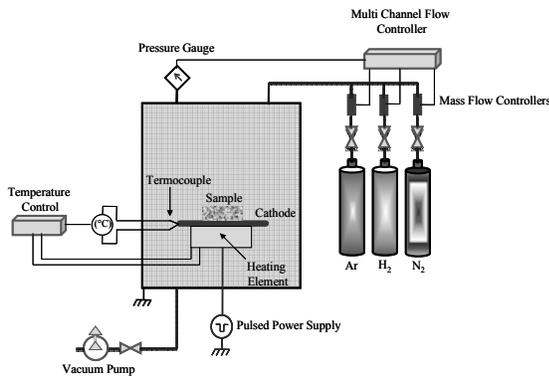


Figure 1. Schematic diagram of the plasma nitriding system.

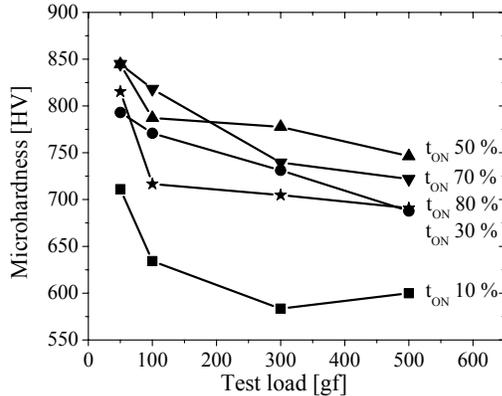


Figure 2. Surface microhardness for treated samples, as a function of the applied load.

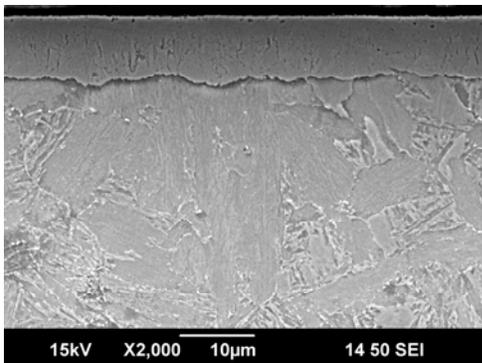


Figure 3. Micrograph of the sample (cross section view) treated at t_{ON} = 10 %.

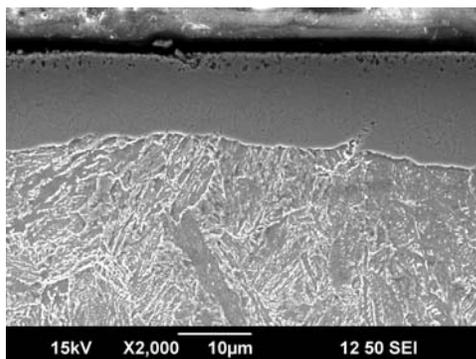


Figure 4. Micrograph of the sample (cross section view) treated at t_{ON} = 30 %.

attached directly to the work piece and sealed with a ceramic to avoid plasma arcs.

In order to clean the surface prior the nitriding process, the samples were subject to a sputtering stage during 0.5 hour using a 50% Ar – 50 % H₂ plasma, at 1.3 Torr and a -500 V potential applied as a 1000 Hz pulse train whose duty cycle was fixed at 50 % (500 µs).

The nitriding process was conducted in a 50% N₂ - 50% H₂ reactive atmosphere, at constant pressure of 1.3 Torr. The samples were biased by means of a pulsed potential of -800 V, providing a current 400 mA. The pulse train frequency was held constant at 1000 Hz, and the duty cycle was adjusted between 10 – 80 % (100 – 800 µs respectively) with the purpose of appreciate the effect of pulse width. Meanwhile, sample temperature was held constant at 540 °C.

After 4 hours of nitriding, the samples were slowly cooled to room temperature in an inert argon atmosphere. The samples were cross sectioned and then ground and polished, as well as chemically etched for analysis.

With an aim to identify the existing phases in the surface layers, samples were characterized through X-Ray diffraction analysis (Cu K α radiation) in a 2 θ range from 30 to 120°. Also, Scanning Electron Microscopy (SEM) was used for evaluate the thickness of the nitrided layer.

Surface hardness measurements were performed to each sample by means of several test loads (100, 200, 300, 400, 600 gf, Vickers indenter), for evaluating the whole surface hardness effect. Moreover, a transversal hardness test using a 50 gf load (Vickers) in order to verify the nitrogen diffusion depth was done.

3. Results and discussion

3.1. Microhardness

Once the surface of the samples was modified using the nitriding process described before, the microhardness of the samples surface was characterized using several test loads. The measurements for all the treated samples are shown in figure 2, revealing that the hardness is substantially improved in comparison with the untreated reference sample (270 HV at 50 gf load).

In addition, the treatment with pulse width of t_{ON} = 50 % and t_{ON} = 70 % demonstrated an increase of about three times in hardness (50 gf load). For the selected values of t_{ON}, the variation in hardness as a function of load suggests a synergy effect of the white layer, the diffusion zone and the substrate hardness.

The diffusion zone depth was measured by a transversal analysis using a 50 gf Vickers indenter. The maximum Nitrogen diffusion depth is considered when the measured hardness value is 10 % greater than the substrate hardness [10]. In this sense a diffusion depth of 350 µm from the surface was measured for all the treated samples. The later has explanation in the thermal nature of the nitrogen-diffusion mechanisms; so, if the nitriding process is

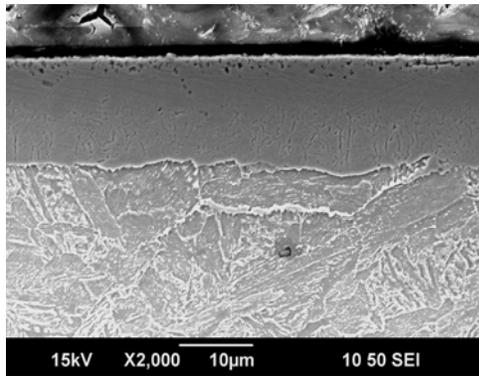


Figure 5. Micrograph of the sample (cross section view) treated at $t_{ON} = 50\%$.

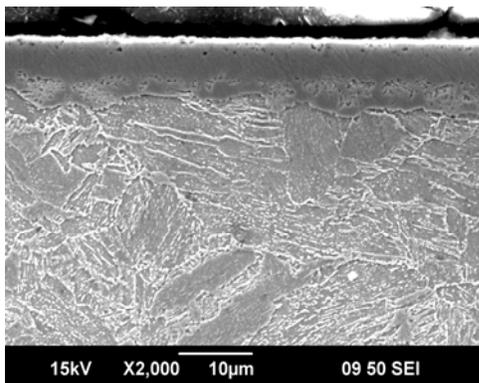


Figure 6. Micrograph of the sample (cross section view) treated at $t_{ON} = 70\%$.

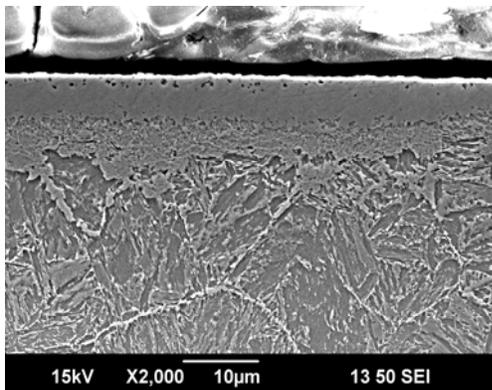


Figure 7. Micrographs of the samples (cross section view) treated at $t_{ON} = 80\%$.

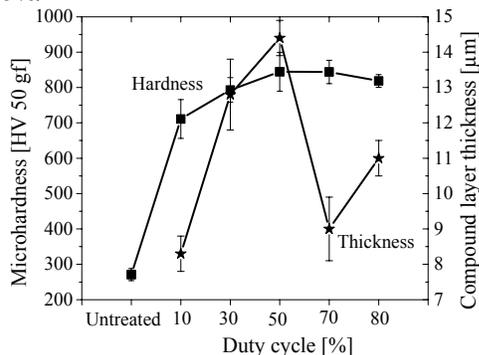


Figure 8. Layer thickness and maximum microhardness value as a function of the pulse width.

achieved at the same temperature, it produces similar diffusion zones in all of the cases, despite of the difference in the superficial hardness, which mainly depends of the compound zone properties.

From figure 2 can be observed that, although the applied load is relatively high, hardness of all the treated samples is always greater than the hardness of the untreated reference sample. This behavior is because the indenter penetrate only about 5 – 10 µm inside the sample, while the diffusion zone is up to 350 µm depth. Even at high loads, when the indenter goes deeper, the effect of the diffusion zone hardness is remarkable.

3.2. Metallographic study to the modified zone

With the purpose of evaluate the modified superficial layer, the samples were cross sectioned, polished and prepared by chemical etch (nital) for the observation with SEM using a 2000 X magnification. Some of the obtained micrographs are shown in figures 3 to 7.

Samples processed at $t_{ON} = 10\%$ (figure 3), $t_{ON} = 30\%$ (figure 4) and $t_{ON} = 50\%$ (figure 5), exhibit the modified layer (compound zone), whose depth is directly proportional to the duty cycle. Below the layer, the typical microstructure of the diffusion zone is evident.

In contrast, samples treated at $t_{ON} = 70\%$ (figure 6) and $t_{ON} = 80\%$ (figure 7) present two regions in the white layer: the upper region shows a homogeneous aspect while the lower one put on view a faded or “fuzzy” layer. In both cases, the upper layer is 5 – 6 µm depth; however, as an evidence of the modified layer evolution as consequence of the increase of the pulse width, the sample treated at $t_{ON} = 80\%$ (figure 7) shows indication of a deeper “fuzzy” region.

In order to link the thickness of the modified layer and the effect in the white layer previously discussed, the figure 8 presents the evolution of the layer depth as a function of the applied pulse width. Also, figure 8 shows the maximum attained hardness value. The error bars are the mean absolute deviation of six measurements in random regions of the sample.

For pulse widths in the interval of $10\% \leq t_{ON} \leq 50\%$, the white layer depth increases directly with t_{ON} , achieving up to 14.5 µm. Furthermore, the maximum hardness value of the samples reports similar results, reaching up to 850 HV (50 gf) when $t_{ON} = 50\%$. However, for $t_{ON} = 70\%$ and $t_{ON} = 80\%$ a reduced layer thickness is noticeable, as well as a slight decrease in hardness.

The behavior described in the precedent paragraphs is attributed to a nitrogen-saturation in the compound layer when t_{ON} is approximately 50%. This saturation does not allow the diffusion of new nitrogen ions into the crystalline lattice, thus causing the production of a thinner compound zone, although the pulse width is increased over 50%.

Even if the upper region saturates, nitrogen diffuses deeper in the substrate because of thermal and concentration gradients, leading to the development of a

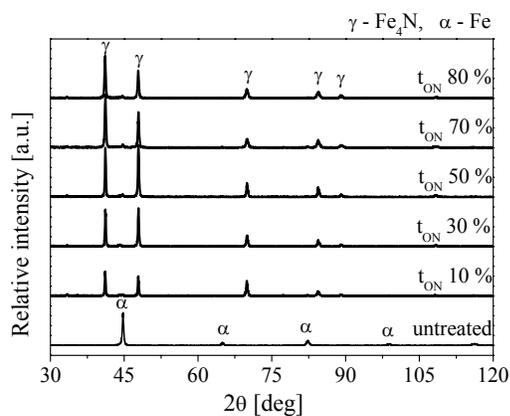


Figure 9. XRD patterns for different conditions in the pulse width.

second faded (fuzzy) layer. Both, the thinner compound zone and the second faded layer, are responsible of the reduction in the microhardness value for $t_{ON} = 70\%$ and $t_{ON} = 80\%$.

All the nitrided samples evaluated here exhibit both, the diffusion zone (about $350\ \mu\text{m}$ thick) and the compound layer ($7.5 - 14.5\ \mu\text{m}$). Although the compound layer has a relatively high hardness, the internal stresses make it brittle; in this sense, the width of this layer is often minimized in order to preserve the sliding wear and fatigue resistance in specific applications [11].

In contrast, the white layer provides the material with good physical characteristics against wearing and rolling friction [12], 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 [13]. The thickness of this layer should therefore be determined according to the use of the material and can be inferred from the results that the duty cycle can be considered as a compound layer control method.

3.3 X-ray diffraction

In the nitrided samples, the mechanical properties greatly depend of the iron–nitride phase, whose formation mechanism seems to be a function of the sample temperature [10, 14]. Hence, in order to identify the existing phases in the modified zone, XRD analyses were performed in all treated samples, as well as a reference untreated sample and the results are exhibited in figure 9. A $\gamma - \text{Fe}_4\text{N}$ compound layer was identified for each treated sample at the typical diffraction angles, as it is observed in the respective diffraction patterns.

In accordance with other authors, single phase $\gamma - \text{Fe}_4\text{N}$ layers, as those studied here, demonstrate better tribological properties in comparison with two-phase layers made of Fe_3N (ϵ -phase) - Fe_4N (γ -phase) [14]. In this sense, the achievement of a single-phase layer is a remarkable result which was possible thanks to the control of the sample temperature during the process time ($540\ ^\circ\text{C}$)

and a constant pulse frequency, preventing the formation of other iron–nitride phases. The null effect of the duty cycle on the obtained phases is noticeable.

Conclusions

After analyzing the effect of duty cycle on the surface properties in samples of AISI 4340 steel processed by plasma nitriding, it is concluded:

1. Pulsed plasma nitriding process increases the surface hardness of AISI 4340 steel. By using a 50 % duty cycle, a maximum surface hardness of 850 HV (50 gf load) was obtained, being up to three times harder than untreated AISI 4340 steel reference sample.
2. Duty cycle has null effect on phase composition for all evaluated samples. It is clear that phase composition is essentially a function of treatment temperature, for a given gas mixture and working pressure. In all cases, $\gamma (\text{Fe}_4\text{N})$ mono-phase compound layers were obtained.
3. Compound layer thickness increases for duty cycles from 10 % to 50 % (around 8 to $14\ \mu\text{m}$) but it decreases for duty cycles 70 and 80 %. Additionally, as function of compound layer thickness, surface hardness increases for duty cycles from 10 % to 50 % and decreases for duty cycles 70 and 80 %.

It is evident that the variation in the pulse width has a negligible effect on the obtained phases. Thanks to this phenomenon, the pulse width is proposed as an alternative control technique over the white layer thickness and, presumably, over the nitrogen-saturation in the lattice of the compound zone, while the preferred phase can be obtained by controlling the temperature of the sample, once the N_2/H_2 ratio and the treatment pressure has been optimized.

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