

THE INFLUENCE OF HYDROGEN ON PLASMA OXIDATION OF NITRIDED FERROUS ALLOYS¹

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Abstract

The effect of hydrogen on plasma post-oxidation, following plasma nitriding of a ferrous alloy was investigated. The increase of the hydrogen concentration in the plasma reduces progressively the hematite/magnetite concentration ratio in the outermost oxide layer down to zero at 25% H₂ concentration. Atomic hydrogen originated from scission of hydrogen molecules in the plasma leads to reduction of Fe(III) in hematite into Fe(II) in magnetite by controlling the gas mixture reduction potential.

Keywords: Plasma post-oxidation; Hydrogen; Magnetite.

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1 INTRODUCTION

Hydrogen is a versatile chemical agent which is widely used in plasma surface engineering. For example, the addition of hydrogen in plasma nitriding increases the nitrogen ionization.^[1] Moreover, hydrogen is added for cleaning purposes due to its chemical reduction properties. Thus, atomic hydrogen ions are reactive species leading to control the surface oxide content in ferrous alloys under plasma treatments. Indeed, hydrogen increases the reduction potential of the gas mixture in the plasma, decreasing the oxygen content in ion nitriding of austenitic stainless steels.^[2,3]

Plasma nitriding followed by post-oxidation is a good candidate as replacement for chromium electroplating and salt and gas oxidation techniques, due to environmental-friendly aspects and technical quality reasons. The combination of a hard and wear resistant underneath nitrided layer and a corrosion resistant and low friction outermost oxide layer provides a high performance mechanical system for hydraulic and automotive applications.^[4] It is well known that the hematite phase (α -Fe₂O₃) is porous and brittle,^[4] while the magnetite phase (Fe₃O₄) is compact and homogenous, two important technical characteristics for corrosion resistance and low friction coefficient.^[5] Hence, the formation of a hematite free oxide layer is the aim of any plasma post-oxidation process. However, although many studies have been devoted to characterize this sequential route or duplex process, plasma post-oxidation is not fully understood in terms of controlling the formation of different types of iron oxide phases and morphologies in the oxide layer.^[6] As a matter of fact, there are a large number of plasma post-oxidation atmospheres such as O₂, H₂O, and CO₂ with or without H₂ or Ar addition, most of them being unable to achieve a hematite free oxide layer.^[7-9] In this way, a careful choice of the plasma composition for post-oxidation process is indispensable to obtain only the magnetite phase in the oxide layer.

The aim of this paper is to investigate the effect of hydrogen on AISI 1045 plain steel plasma post-oxidation after plasma nitriding, focusing in the outermost layer, formed by different oxide phases.

2 EXPERIMENTAL

Samples from the same AISI 1045 plain steel source (C: 0.45, Si: 0.22 P: 0.03, S: 0.03, Mn: 0.18, Cu: 0.02, Cr: 0.02, Ni: 0.01, Mo: 0.002, A: 0.03, V: 0.001, Fe: balance in wt.%), (10 mm diameter), were used for the study. The substrates were mirror polished using standard metallographic techniques. Nitriding was performed in a laboratory-scale chamber. The chamber base pressure was < 2.8 Pa ($P_{O_2} < 5.6 \times 10^{-1}$ Pa). The chamber was pressurized with the feeding gases using mass flow controllers where a Pirani gauge was used to monitor de pressure. The gas total pressure was kept at 92 Pa and the gas mixture was fixed at 90% N₂ -10% H₂ during the nitriding process. The substrate temperature during nitriding was maintained at 550 +/- 2 °C during 5 hours. A pulsed DC power supply was used at a mean voltage of 720 V and current of 0.2 A. The frequency and duty cycle were set at 10 kHz and 40%, respectively. Following nitriding, post-oxidation was performed in the same chamber, without open it to air. The total gas pressure was kept at 112 Pa, the gas mixture was a fixed N₂/O₂ ratio of 7, and the H₂ proportion was varied from 0 to 25%. The post-oxidation temperature was maintained at 510 +/- 2 °C during 45 minutes. The pulsed DC power was used at a mean voltage of 850 V and current

0.5 A. The frequency and duty cycle were set at 10 kHz and 40%, respectively. The crystalline structures of plasma modified layers were determined by X-ray diffraction (XRD) in both geometries, Bragg-Brentano, inspecting the whole modified layer and glancing angle, at incidence angle of 2° , inspecting only the outermost layer. In both geometries, the samples were rotated during analysis in order to reduce texture effects. A Shimadzu XRD-6000 diffractometer with $\text{Cu K}\alpha$ ($U = 40$ kV and $I = 30$ mA) radiation was used. The Rietveld method^[10] was also applied for analysis and quantification of crystalline phases in the modified layer by using the FULLPROF software.^[11] Cross-section micrographs of nitrided and oxidized layers were recorded using a Shimadzu SSX-550 scanning electron microscope. The chemical bonds in the plasma modified surfaces were characterized by X-ray photoelectron spectroscopy (XPS). These measurements were performed in an Omicron SPHERA station using $\text{Mg-K}\alpha$ radiation (1253.6 eV) at a take-off angle of 60° with an energy resolution of 0.9 eV.

3 RESULTS AND DISCUSSION

The XRD patterns in Bragg-Brentano geometry are shown in Fig. 1 for samples obtained by plasma post-oxidation at different H_2 concentrations after plasma nitriding. For comparison purposes, the diffractogram of the nitrided samples without post-oxidation is also included at the bottom.

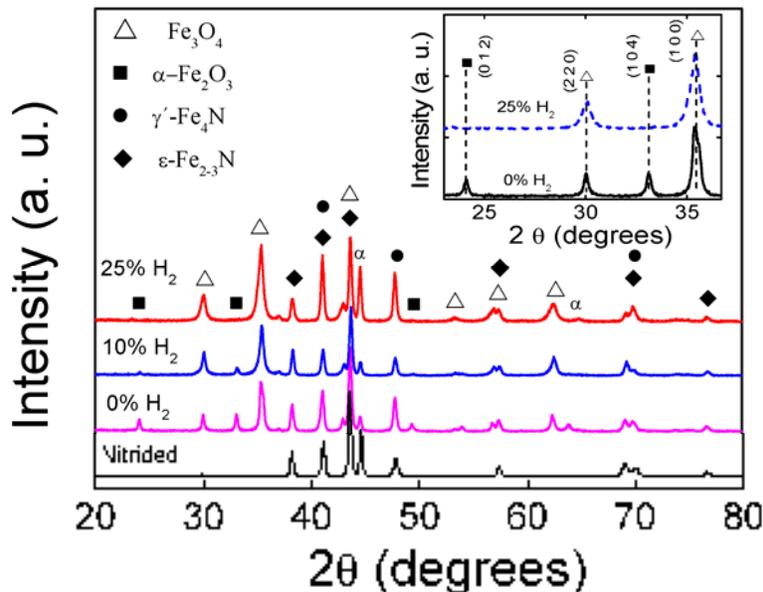


Figure 1. Bragg-Brentano X-ray diffractograms from samples obtained by plasma post-oxidation at different H_2 concentrations after plasma nitriding. For comparison purposes, the diffractogram of the nitrided samples without post-oxidation is also included at the bottom. The inset shows the range between $2\theta = 22$ to 38 degrees for two samples treated at 0% and 25% H_2 .

The diffraction patterns can be assigned to a mixture of iron nitrides such as $\gamma\text{-Fe}_4\text{N}$ and $\epsilon\text{-Fe}_{2-3}\text{N}$, iron oxides such as $\alpha\text{-Fe}_2\text{O}_3$ (hematite) and Fe_3O_4 (magnetite), as well as the original $\alpha\text{-Fe}$ (ferrite). Moreover, one can see that for increasing hydrogen concentrations, the intensity of the peaks located at 24.2 and 33.2 degrees, assigned here to hematite, decreases with respect to those assigned to

magnetite, from a significant contribution at 0% H₂ to almost vanishing completely at 25 % H₂. For the sake of clearness, the inset in Fig. 1 shows the range between 2θ = 22 to 38 degrees where the characteristic peaks for hematite and magnetite are stressed.^[12] Furthermore, GAXRD (not shown) confirms that the outermost layer (approximately 800 - 900 nm) is formed only by the iron oxides mentioned above. Fig. 2 shows the intensity ratio I_{104}/I_{100} as a function of the hydrogen concentration where the planes (104) and (100) are assigned to hematite and magnetite pure phases, respectively. The dashed line is only to guide the eyes. This intensity ratio decreases to almost 0 at 25 % hydrogen content. Hence, the oxide layer obtained in such condition is constituted only by the magnetite phase. In addition, photos of samples post-oxidized at 0% H₂ and 25% H₂ are presented as an inset in Fig. 2. One notices the different visual aspects between both extreme conditions, where a non-homogenous dark blue tone is observed on the surface of the sample post-oxidized at 0% H₂ in contrast with a homogenous black tone on the surface of sample treated at 25% H₂ (hematite free). Scanning electron microscopy confirms that the thickness of both nitrided and oxide layers (not shown) remain the same as the hydrogen concentration varies.

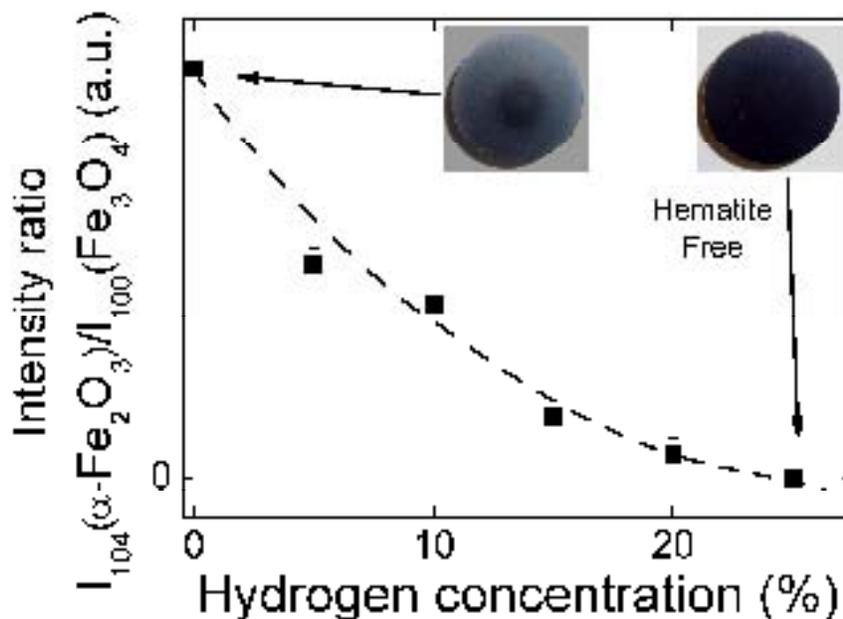


Figure 2. XRD I_{104}/I_{100} intensity ratio, assigned to hematite and magnetite pure phases, respectively, as a function of hydrogen concentration. The dashed line is only to guide the eyes. Also, the sample surface characteristics are shown after plasma post-oxidation treatments at 0% and 25% H₂.

Using the Rietveld method^[10] to analyze the XRD patterns obtained in Bragg-Brentano geometry, one can confirm the presence of 5 phases, as indicated above, in the modified layer. Moreover, one can quantify the hematite and magnetite contents as follows: 30 ± 1 wt. % (magnetite) and 15 ± 2 wt. % (hematite) at 0% H₂ and 56 ± 1 wt. % (magnetite) and 0 wt. % (hematite) at 25% H₂. The intensity ratios of the most important diffraction peaks for nitrides and oxides obtained in this work are very similar to standard XRD data of JCPDS file numbers 33-0664 (α -Fe₂O₃), 11-0614 (Fe₃O₄), 1-1236 (ϵ -Fe_{2.3}N), and 6-627b (γ -Fe₄N). The latter are obtained by powder diffraction technique with random distribution of grains assuring no

preferential orientation or no texture. Therefore, we can say that the present XRD results do not have significant texture contribution.

Fig. 3a and 3b show the Fe2p_{3/2} and O1s photoelectron regions, respectively, at two characteristic hydrogen concentrations. The Fe2p_{3/2} photoelectron regions (Fig. 3a) indicate the presence of Fe(II) and Fe(III) bonds in iron oxides and Fe(OH)₃ (iron hydroxide) contributions in the oxide layer. It is clearly seen that the main peak does not change either in position or intensity for different H₂ concentrations in the plasma. However, the Fe(III) satellite peak at a binding energy of 717 eV that corresponds to hematite,^[13] decreases drastically when the hydrogen concentration in the plasma changes from 0 to 20 % H₂. According to these authors, no evidences of such satellite appear when pure magnetite is analyzed. Moreover, Fig. 3b shows a shift of the components of the O1s photoelectron regions to higher binding energies for increasing hydrogen concentrations. This corroborates the previous results, since O binding energies are higher for magnetite than for hematite.^[14,15] XPS provides information of 7 to 10 nm below the sample surface, whereas it would be desirable to have information on far more deeper regions of the sample. However, this complementary technique entirely corroborates the present XRD results, which inspect much deeper layers. Therefore, one can be confident that the formed compounds at deeper regions are essentially the same as those near the surface. Furthermore, *in-situ* removal of significantly thick layers in order to analyze deeper regions is difficult to accomplish.

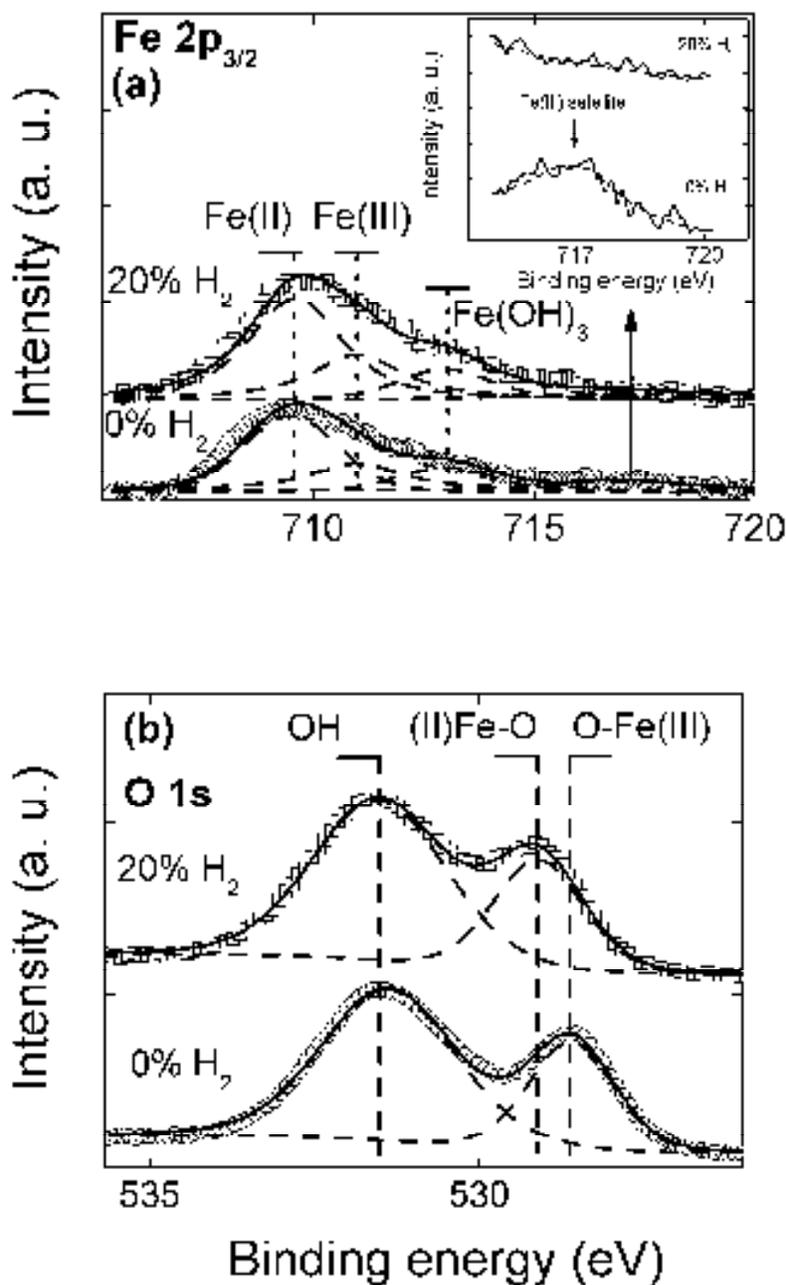


Figure 3a and 3b show the Fe2p_{3/2} and O1s photoelectron regions, respectively, at two characteristic hydrogen concentrations. The inset in Fig. 3a shows the Fe(III) satellite peak at a binding energy of 717 eV that corresponds to hematite.

Thus, the addition of hydrogen reduces Fe(III) ions in the oxide layer, transforming the hematite phase into magnetite phase. In the absence of a plasma, when only hydrogen molecules are present, the reduction of Fe(III) in hematite to Fe(II) in magnetite is not spontaneous. Indeed, we estimated the Gibbs free energy in this case as being $\Delta G = + 227 \text{ kJ.mol}^{-1}$ at 500°C.^[16,17] On the other hand, scission of hydrogen molecules into atomic hydrogen in the plasma does have sufficiently negative Gibbs free energy to reduce Fe(III) into Fe(II). In this last case, our estimation gave $\Delta G = - 158 \text{ kJ.mol}^{-1}$ at 500°C (spontaneous process).^[16] The change

of Gibbs free energy for reduction from hematite to magnetite at 500°C was estimated for two different routes, namely $3 \alpha\text{-Fe}_2\text{O}_3 + \text{H}_2 \rightarrow 2 \text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$ and $3 \alpha\text{-Fe}_2\text{O}_3 + 2\text{H} \rightarrow 2 \text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$. ΔG of formation for H and H_2O were taken from Ref.16 and 17. The values of ΔG of formation for $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 at 500°C were calculated using $\Delta G = \Delta H - T.\Delta S$. ΔH , where ΔH and ΔS of formation and C_p at 25°C (Ti) were taken from Ref. 16.

Thus, the presence of atomic hydrogen is mandatory in order to eliminate the hematite phase in plasma post-oxidation processes by achieving a sufficient gas mixture reduction potential. This easy control of such a duplex process that yields the formation of a hematite free oxide layer on nitrided surfaces could open new possibilities for establishing an environmental-friendly plasma process instead of toxic and less controlled techniques like chromium electroplating and gas oxidation, respectively, in surface engineering of ferrous alloys.

4 CONCLUSIONS

In conclusion, atomic hydrogen can act as a chemical agent in order to produce a hematite free iron oxide layer in pulsed plasma post-oxidation following plasma nitriding of ferrous alloys. The gas mixture reduction potential must be controlled and the presence of atomic hydrogen is mandatory to render spontaneous the reduction of Fe(III) in hematite to Fe(II) in magnetite. This versatile and environmental-friendly process could open new possibilities for replacing chromium electroplating and gas oxidation treatments.

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