

Hydrogen etching mechanism in nitrogen implanted iron alloys studied with *in situ* photoemission electron spectroscopy (XPS)

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In situ photoemission electron spectroscopy (XPS) is used to elucidate the hydrogen etching mechanism in nitrogen implanted iron alloys. The samples were prepared by bombarding stainless steel with a broad nitrogen ion source in a high vacuum chamber. The photoemission spectra evolution on increasing hydrogen ion current is correlated with the nitrified surface properties. The presence of hydrogen is associated with oxygen removal, augmenting the surface nitrogen concentration. The total active sites at the surface are constant, i.e., oxygen competes with nitrogen sites on the surface. The absorbed oxygen is etched following a linear law on hydrogen ion flux. Simultaneously, the formation of metallic nitrides is enhanced. At the working temperature, the efficiency of the process is determined by a *characteristic time* that depends on hydrogen retention time, water formation and desorption time. © 2005 American Vacuum Society.

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The hydrogen etching mechanism is very important in thermochemical processes where surface oxygen determines bulk properties. Generally speaking, there is an abundant bibliography reporting that hydrogen eliminates oxygen on surface by chemical etching. However, the explanation of this effect relies on the general phenomenon of water formation from oxygen absorbed on Pt and Pd due to the presence of hydrogen.^{1,2} Indeed, the surface etching mechanisms in complex processes such as plasma nitriding metal alloys are not yet available. Indeed, in this type of process, the control of the surface compounds is necessary to tailor the diffusion layer. This is particularly important for nitrogen diffusion in metallic alloys like stainless steel where stringent exigencies such as corrosion resistance, hardness, strength, and low resistance coefficient are required.^{3,4} Among several nitriding methods, plasma is an important technology currently used to improve the alloy properties. This process consists first of nitrogen implantation and/or adsorption and afterward its bulk thermal diffusion. Indeed, an interplay involving plasma, neutral gaseous phases (including residual oxygen), nitrides surface formation, chemical etching, and physical sputtering, makes the problem particularly complex. The microscopic role at the material surface of hydrogen and oxygen on the nitrogen diffusion processes is especially important. For instance, it is well established that above a critical oxygen partial pressure with fixed ion beam energy, and current density, the chemisorptions of oxygen diminish the nitrogen diffusion into the bulk.^{5,6} Indeed, hydrogen is used as a chemical etching agent to prevent the deleterious effect of oxygen without a full understanding of the mechanisms involved. Therefore, a better understanding of how the hydrogen interacts with oxygen, nitrogen, and the metallic surface is mandatory for further improvement of nitrogen diffusion

in bulk. Finally, we stress the importance of performing the experiments *in situ*, i.e., in a very precisely controlled atmosphere to elucidate the role of hydrogen.

In this article, we report the influence of the hydrogen etching mechanism in a metallic alloy during the nitrogen implantation process by *in situ* photoemission electron spectroscopy (XPS) studies. In this specific study, nitrides and oxygen species formed underneath the material surface are the focus of interest. Considering this premise, XPS is a well-established technique proving exactly the structure and composition of the most-top surface atomic layers.⁷

Mirror polished, rectangular samples, 20 × 10 mm and 1 mm thick were prepared from the same commercial AISI 316 stainless steel lot (chemical composition in wt %, C: <0.08, Si: <0.5, P: 0.05, S: 0.03, Mn: 1.6, Mo: 2.1, Ni: 12.0, Cr: 17.0, Fe: balance). The implantation was performed in a high-vacuum chamber containing a 3-cm-diam dc Kaufman ion source attached to an ultrahigh vacuum chamber for XPS analysis. This type of gun allows a precise control of ion energy and current density. Details of the apparatus are described elsewhere.⁸ The sample temperature was maintained at (380 ± 10) °C during the implantation time of 30 min. This temperature was selected to avoid the CrN formation into the bulk, so corrosion resistance might be guaranteed.⁹ This implantation time ensures a compositional dynamic equilibrium during implantation at the sample surface.¹⁰ The background chamber pressure was <10⁻⁴ Pa (P_{O₂} < 2 × 10⁻⁵ Pa). Nitrogen enters directly into the ion source with a constant flow rate, resulting in a partial pressure of 10⁻² Pa. The hydrogen partial pressure in the ion source was varied from 4.4 × 10⁻³ to 2.2 × 10⁻² Pa. The nominal current of the Kaufman cell essentially did not change when hydrogen was added to the feeding gases of the gun. The oxygen partial pressure was fixed at 3.2 × 10⁻³ Pa. In order to maintain a fixed total chamber pressure (1.2 Pa), an appropriated helium flux was added into the chamber,

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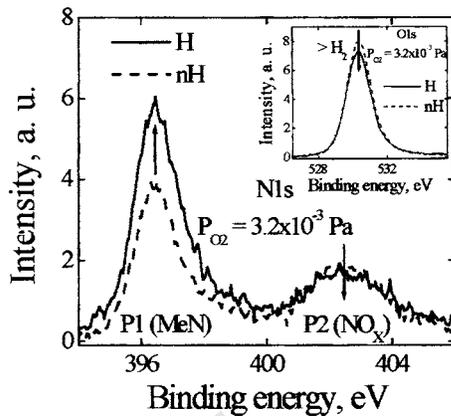


FIG. 1. N $1s$ core level photoemission spectra of two samples implanted using a beam containing N^+ and H^+ ions and only N^+ (nH). The inset shows the O $1s$ core level photoemission spectra in the same samples.

guaranteeing a N_2^+ and H_2^+ (and N^+ and H^+) ions mean-free path for all experiments.^{11,12} It is stressed that the oxygen and helium gases were introduced in the chamber through an independent inlet (i.e., not through the ion source). The current density and energy of the ion beam were fixed at 0.28 mA/cm^2 and $\sim 50 \text{ eV}$, respectively. The ion current at the sample surface was measured using a Faraday cup and the mean ion energy was calculated using a scattering model that depends on the mean-free path.^{9,13} For N_2^+ ions with this energy, numerical simulation shows that the thickness of the implanted nitrogen layer is $\sim 4\text{--}5 \text{ nm}$.¹⁴ Conveniently, this thickness is similar to the characteristic escape depth for photoemitted electrons with kinetic energy in the $200\text{--}1500 \text{ eV}$ energy range.⁵ Immediately after nitrogen implantation, the chamber is flooded with helium to rapidly cool down the samples. Finally, the samples are transferred to the attached ultrahigh vacuum chamber for the XPS analysis. The XPS spectra were obtained by using the 1486.6 eV photons from an Al target ($K\alpha$ line) and a VG-CLAMP-2 electron analyzer. The total apparatus resolution was $\sim 0.85 \text{ eV}$ (linewidth plus analyzer).⁶ The relative atomic composition at the sample surfaces was determined by integrating the core level peaks, properly weighted by the photoemission cross section.

Figure 1 shows the N $1s$ core electron level photoemission spectra of two implanted samples using a nitrogen beam containing (H) and without (nH) hydrogen ions. The peak 1 (P1) is related to the formation of metallic nitrides (FeN_x , CrN and $\gamma_N\text{-FeN}_4$) and clearly increases when a relatively higher hydrogen partial pressure is used, i.e., if more hydrogen ions are present in the beam. On the other hand, the P2 band, which is related to NO_x species, does not show appreciable changes on increasing the number of hydrogen ions present in the beam. In a previous work, it was demonstrated that oxygen is chemisorbed following a Langmuir isothermal law.^{4,7} One can think that the surface contains absorption active sites, with oxygen and nitrogen competing for them. Figure 1 strongly suggests that the presence of hydrogen ions in the beam leaves more free nitrogen atoms to form nitride

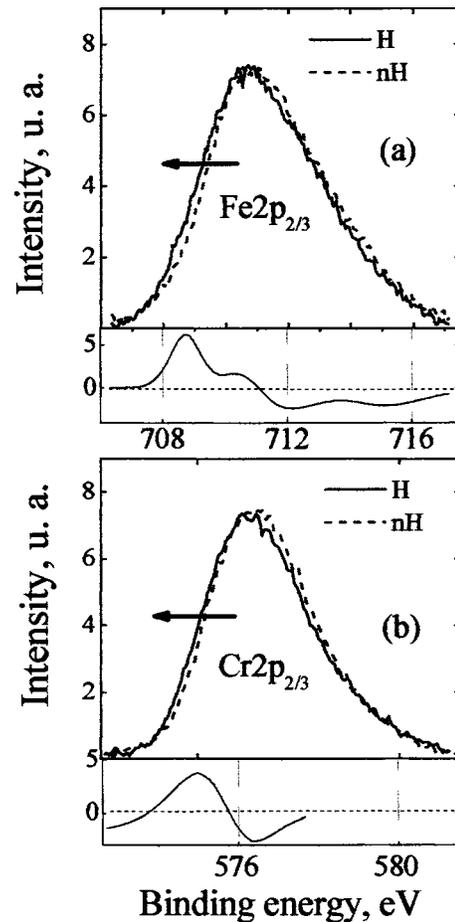


FIG. 2. Fe $2p_{2/3}$ (a) and Cr $2p_{2/3}$ (b) core electron level photoemission spectra using a beam containing N_2^+ and H_2^+ ions and only N_2^+ (nH). Lower panels: difference spectra.

compounds on the material surface (P1 band). Moreover, the inset shows that the total oxygen content decreases when hydrogen is used, confirming a chemical etching effect of hydrogen.

Figure 2 shows the photoemission spectra of the Fe $2p_{3/2}$ (a) and Cr $2p_{3/2}$ (b) core electron levels. These spectra correspond to the same sample studied in Fig. 1. When a beam containing N_2^+ and H_2^+ ions is used, the peaks shift to lower binding energies. This is seen in the lower panels of the figure where the spectra difference is shown. This shift (“chemical shift”) comes from an increment of the metallic nitrides and concomitantly, with a decreasing metallic oxides formation.¹⁵ The origin of the bandwidth stems from different compound contributions and is beyond the scope of this article.

It is enlightening to investigate the influence of increasing hydrogen in the ion gun on the nitrogen retention at the material surface. Figure 3 shows a quite impressive linear dependence of nitrogen content at the surface as a function of the hydrogen partial pressure in the ion source. Moreover, the inset shows that hydrogen also diminishes the oxygen content at the surface. Indeed, the total content of nonmetallic elements (N+O) at the material surface is constant. These

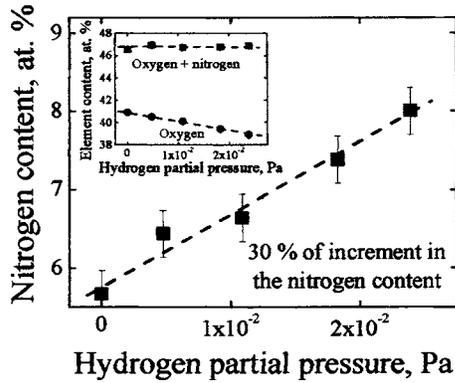
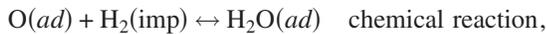
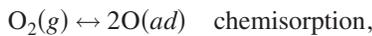


FIG. 3. Surface nitrogen content at different hydrogen partial pressures inside the ion source. The inset shows the oxygen content dependence and the total content of nonmetallic elements (N+O) as a function of hydrogen partial pressure inside the ion source.

apparent complementarities strongly suggest a constant total number of surface active sites, i.e., oxygen competes with nitrogen for active sites. Indeed, this implies that extra hydrogen is necessary to increase surface nitrogen concentration since metallic oxides are thermodynamically much more stable than metallic nitrides.¹⁶ An etching mechanism is suggested, assuming a process of absorption, water formation (thermodynamically speaking, water is a more stable reaction product than ammonia) and subsequent desorption. Therefore



where $\text{H}_2(\text{imp})$ stands for implanted H_2 molecules.

The formation of water and desorption causes the oxygen elimination, i.e., a chemical etching of the absorbed oxygen by hydrogen. In order to estimate the hydrogen flux, $\phi(\text{H}_2)$, let us assume that the total ion current density is proportional to the sum of the partial pressure of each gas feeding the gun. Therefore $\phi(\text{H}_2) = C\sigma_{\text{H}_2}P_{\text{H}_2}$, where C is a constant, and σ_{H_2} (P_{H_2}) represents the gas ionization cross sections (hydrogen partial pressure). In addition, x-ray experiments, that provide structural information up to 500 nm, show (not displayed) that N incorporates interstitially in the original γ phase (Fe-N centered face cubic) forming the γ_{N} phase. This corresponds to the γ phase with N occupying octahedron interstitial sites.¹⁷ The oxygen present in the chamber is chemically absorbed on this crystalline surface. Therefore, using the density of metallic atoms present at the surface (two metallic atoms per crystal face and per unit cell) and the metal $[\text{Me}/\text{O}]$ ratio concentration obtained from XPS, one can obtain the surface oxygen density, i.e., $[\text{O}]_{\phi}$ (No. atoms/cm²) at each hydrogen flux. Therefore, assuming that the difference between the oxygen surface density at zero hydrogen flux ($[\text{O}]_0$) and the actual surface density at ϕ hydrogen flux ($[\text{O}]_{\phi}$) is proportional to the hydrogen flux $\phi(\text{H}_2)$, the following phenomenological relationship follows:

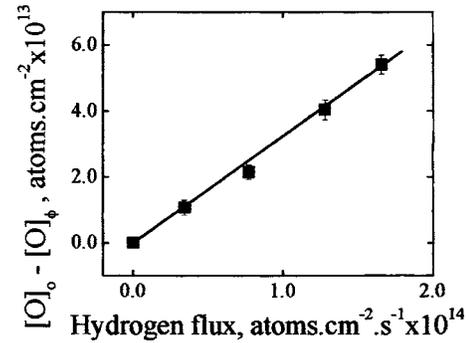


FIG. 4. Extracted oxygen from the surface at different hydrogen incident flux. The surface density is measured after interrupting hydrogen irradiation and freezing the diffusion by flooding the deposition chamber with helium. The solid line is a linear fitting using Eq. (1).

$$[\text{O}]_0 - [\text{O}]_{\phi} = \tau\phi(\text{H}_2). \quad (1)$$

Here, τ is a temperature dependent *characteristic time* of the surface process related to the hydrogen retention, water formation, and desorption. As shown in Fig. 4, the experimental data are very well fitted with Eq. (1). From the graph, $\tau = (0.32 \pm 0.01)\text{s}$ at 380 °C.

In conclusion, the use of hydrogen in the plasma nitriding process increases the metallic nitrides content on the surface, simultaneously reducing the absorbed oxygen content. The surface active sites for nitrogen and oxygen are constants, i.e., oxygen competes with nitrogen to fill up the surface sites. The oxygen etching process is proportional to the hydrogen flux. The proportionality constant is a reaction *characteristic time* depending on temperature, hydrogen retention, water formation, and desorption processes. For the experiments reported here, this time is $(0.32 \pm 0.01)\text{s}$ at 380 °C, indicating a rather slow process.

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- ¹A. B. Anton and D. C. Cadogan, J. Vac. Sci. Technol. A **9**, 1890 (1991).
- ²M. Johansson and L.-G. Ekedahl, Appl. Surf. Sci. **180**, 27 (2001).
- ³M. Hudis, J. Appl. Phys. **44**, 1489 (1973).
- ⁴A. Szasz, D. J. Fabian, A. Hendry, and Z. Szaszne-Csuh, J. Appl. Phys. **66**, 5598 (1989).
- ⁵S. Parascandola, O. Kruse, and W. Möller, Appl. Phys. Lett. **75**, 1851 (1999).
- ⁶C. A. Figueroa, D. Wisnivesky, and F. Alvarez, J. Appl. Phys. **92**, 764 (2002).
- ⁷In *Practical Surface Analysis*, 2nd ed., edited by D. Briggs and M. P. Seah (Wiley, New York, 1996). Vol. 1.
- ⁸P. Hammer, N. M. Victoria, and F. Alvarez, J. Vac. Sci. Technol. A **16**, 2941 (1998).
- ⁹M. Samandi, B. A. Shedden, D. I. Smith, G. A. Collins, R. Hutchins, and S. Tendys, Surf. Coat. Technol. **59**, 261 (1993).
- ¹⁰C. A. Figueroa, A. S. Ferlauto, and F. Alvarez, J. Appl. Phys. **94**, 5435 (2003).
- ¹¹The mean free path turns out to be important since the ultimate energy of nitrogen ions depends on this parameter. See R. Wei, Surf. Coat. Technol. **83**, 218 (1996).
- ¹²C. A. Figueroa, E. Ochoa, and F. Alvarez, J. Appl. Phys. **94**, 2242 (2003).
- ¹³H. Ch. Paulini and U. Littmark, Nucl. Instrum. Methods Phys. Res. B **58**, 260 (1991).

¹⁴J. P. B. Biersack and G. L. Haggmark, The simulation used the TRIM software, Nucl. Instrum. Methods **174**, 257 (1980).

¹⁵J. P. Riviere, M. Cahoreau, and P. Meheust, J. Appl. Phys. **91**, 6361 (2002).

¹⁶M. W. Chase, Jr., *NIST-JANAF Thermochemical Tables*, 4th ed., J. Phys. Chem. Ref. Data, Monograph 9, Parts I and II, 1998.

¹⁷M. P. Fewell, D. R. G. Mitchell, J. M. Priest, K. T. Short, and G. A. Collins, Surf. Coat. Technol. **131**, 300 (2000).

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