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Studies of nitrogen implantation in an iron alloy using photoemission electron spectroscopy, sputtered neutral mass spectrometry, and elastic recoil detection analysis, reveal an enhancement of nitrogen diffusion when deuterium replaces hydrogen in the gas. Compared to hydrogen, deuterium reduces NO_x species on the surface (geometric barrier), increasing the nitrogen activity at the surface and consequently nitrogen diffusion into the solid solution. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2737956]

Nitrogen implantation in metal alloys is an established technique for surface modification to improve mechanical and chemical properties of the material such as hardness, corrosion, and wear resistance, as well as, biocompatibility.[1] However, recent advances have shown that events at the surface mechanism play an important role in determining nitrogen content in depth.[2] In plasma nitriding, the oxygen concentration on the surface is a critical parameter for nitrogen retention.[3] Moreover, hydrogen acts as a chemical agent, etching oxygen from the surface and augmenting the nitrogen content on surface.[4,5] On the other hand, previous work demonstrated that deuterium is more efficient in removing oxygen than hydrogen, thus increasing the material hardness in depth.[6] From the Fick's laws, the nitrogen atoms can go further into bulk material by increasing the process time, temperature, and concentration gradient.[7] In this context and taking into account the limitations for process time and temperature entailed in plasma nitriding of austenitic stainless steels, the control of the nitrogen activity on the surface, i.e., the nitrogen available for diffusion, is an important key for enhancing nitrogen bulk penetration. Therefore, a better understanding of the role of oxygen, nitrogen, hydrogen, and deuterium is fundamental in plasma nitriding processes.

Briefly, the surface mechanism is an interaction of oxygen absorption from the atmosphere with nitrogen-deuterium (hydrogen) implantation from the ion beam to metal atoms on surface. An oxygen-free atmosphere yields, on the surface during plasma nitriding, a mixture of nitrogen in solid solution (metallic nitrides) and bound to surface active sites.

Oxygen acts as a potential barrier for nitrogen implantation and its absorption can be modeled by a Langmuir isothermal law.[8,9] The presence of oxygen can limit the available nitrogen on the surface for diffusion into bulk material because of both energetic and geometric effects. Thermodynamically, metal-oxygen bonds are more stable than metal-nitrogen bonds, promoting the formation of metallic oxides instead of metallic nitrides when oxygen is adsorbed. On the other hand, and at relative higher oxygen partial pressures, the oxygen can cover many of the surface active sites so as to reduce the number of paths of entry for nitrogen.[8] This deleterious oxygen effect can be diminished by using a chemical removal agent such as hydrogen or deuterium.[4] The hydrogen and deuterium atoms arriving at the surface react with oxygen, with metal atoms acting as catalytic centers, to produce species like HO and H_2O which are easily desorbed form the surface to the atmosphere (chemical etching).[10] Although the etching effect occurs at the surface, the bulk properties depend strongly on the surface mechanism because oxygen removal leaves open active sites for nitrogen incorporation and diffusion into the interior. Moreover, the driving force for nitrogen diffusion is the nitrogen chemical potential that depends on nitrogen activity.[11] Thus, one strategy to improve the nitrogen diffusion into bulk material is to increase the nitrogen activity on the surface.

Mirror polished, rectangular samples, 20×10 mm and 1 mm thick were prepared from one commercial lot of AISI 316 stainless steel (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 diameter direct current Kaufman ion source attached to an ultrahigh vacuum chamber for XPS analysis. Details of

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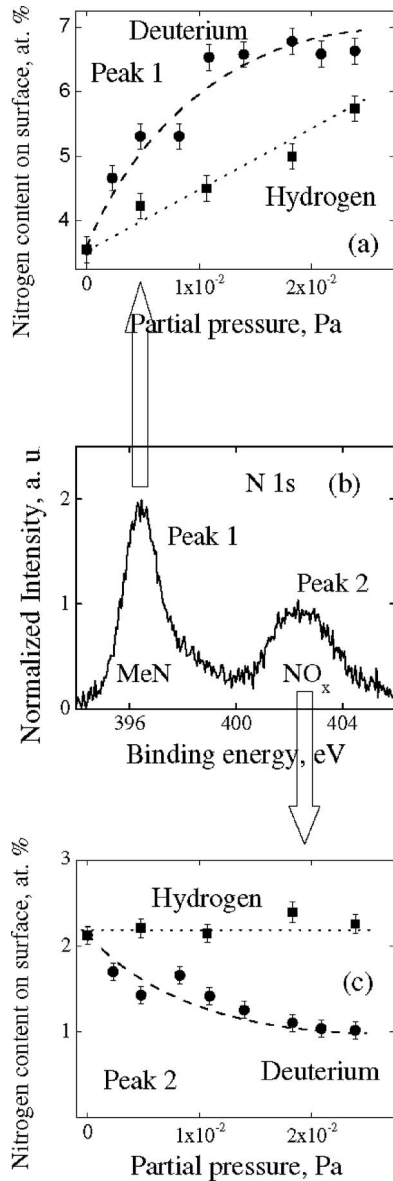
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FIG. 1. (a), (b), and (c) Typical N 1*s* core-level photoemission spectrum (b). Nitrogen content evolution, on surface, as a function of the deuterium (hydrogen) partial pressure for MeN$_x$ (a) and NO$_x$ (c) contributions. The lines are guides for the eyes.

FIG. 2. Deuterium surface density as a function of its partial pressure being fed through the ion gun. The line is a guide for the eyes.

the apparatus are found elsewhere.[12] The sample temperature was maintained at (380 ± 10) °C during the implantation time of 30 min. This implantation time ensures a steady state at the sample surface.[13] The background chamber pressure was $<10^{-4}$ Pa $(P_{O2}<2\times10^{-5}$ Pa). Nitrogen is fed into the ion source directly at a constant flow rate, resulting in a chamber partial pressure of 10^{-2} Pa. The deuterium and hydrogen partial pressures in the vacuum chamber varied from 2.3×10^{-3} to 2.4×10^{-2} Pa. The oxygen partial pressure in the chamber was controlled and fixed at 3.2×10^{-3} Pa. To maintain a fixed total chamber pressure (1.2 Pa), helium was added to the chamber as needed. These experimental conditions guarantee a N_2^+ and D_2^+ (or H_2^+) [and N^+ and D^+ (or H^+)] ions mean-free-path, i.e., constant energy, for all implantation experiments.[14] It is stressed that the oxygen and helium gases were introduced in the chamber through an independent inlet not through the ion source. The current density and
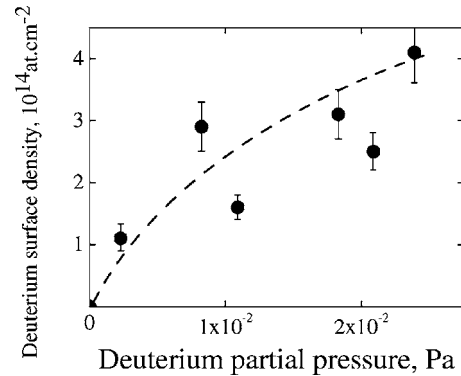
particle energy of the ion beam were fixed at 0.28 mA/cm^2 and $\sim$50 eV, respectively. Finally, the samples were transferred to the attached ultrahigh vacuum chamber for the XPS analysis. The XPS spectra were obtained by using the 1486.6 eV photons from an Al target ($K\alpha$ line) and a VG-CLAMP-2 electron analyzer. The total apparatus resolution was $\sim$0.85 eV (linewidth plus analyzer). The relative atomic composition at the sample surfaces was determined by integrating the core level peaks, properly weighted by the photoemission cross section. The composition (Ni, Cr, Fe, Mo, C, and N) of the nitrided layers was determined by SNMS analysis. A thermionic filament, in addition to a secondary ion mass spectrometry laboratory (VG. Instrument), constitutes the SNMS apparatus. A $5-8$ keV Ar$^+$ beam produces 250 or 500 μm square craters, depending on the scanning speed of the beam. The depth of each sputter crater is measured with a high precision profilometer in order to calibrate the depth scale over the whole profile. A quantitative nitrogen concentration determination is obtained using a γ'-Fe$_4$N reference sample. Deuterium was detected by ERDA using an incident 7 MeV ^{12}C beam. Deuterium surface density was determined by comparing the number of detected deuterium recoils arising from samples and a reference D-implanted Si wafer. Measurements of hydrogen surface density were also performed by ERDA, however, atmospheric water contamination introduced a considerable error.

Figures 1(a)–1(c) show the evolution of two different nitrogen contributions on the surface as a function of deuterium and hydrogen partial pressure by XPS. In Fig. 1(b), the N 1*s* core-level photoemission spectrum shows two contributions, P1 and P2, related to nitrogen involved in metallic solid solution (MeN) and oxynitride compounds (NO$_x$), respectively.[15,16] Figure 1(a) indicates that the number of nitrogen atoms involved in metallic bonds are enhanced by the presence of deuterium and hydrogen. On the other hand, Fig. 1(c) shows that nitrogen content involved in oxynitride compounds can be lowered by deuterium but not hydrogen. For the sake of clarity, Fig. 2 shows the evolution of deuterium density on the surface as a function of its partial pressure in the ion gun. It is clearly seen that the deuterium density on the surface augments with the deuterium partial pressure that feeds the Kaufman ion source.

Figure 3 shows the nitrogen content profile as a function of sample depth for a given deuterium (hydrogen) partial
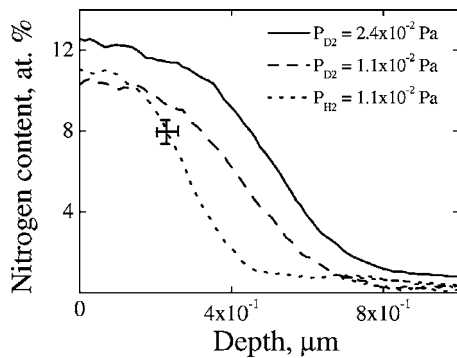
FIG. 3. Nitrogen depth concentration profile at different deuterium (hydrogen) chamber partial pressures. The gases are incoming into the chamber through the ion gun. The cross represents the experimental error.
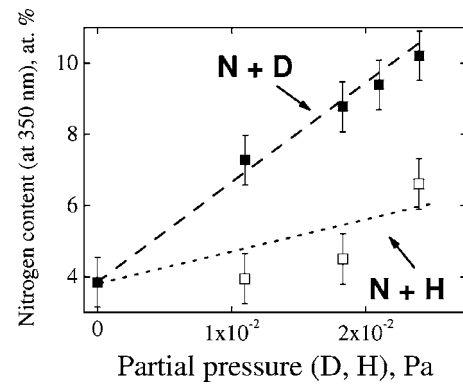

FIG. 4. Nitrogen content at a constant sample depth (350 nm) as a function of the deuterium (hydrogen) partial pressure. The lines are guides for the eyes.

pressure. Here, it is important to remark that the nitrogen concentration on the surface is the same in both cases, although deuterium increases the nitrogen profile more than does hydrogen. Figure 4 shows the nitrogen content as a function of the deuterium (hydrogen) partial pressure at a constant depth (350 nm). In this example, the use of deuterium instead of hydrogen augments up to ∼65% the nitrogen content at that depth.

According to these results, we explain the nitrogen diffusion enhancement into bulk material in terms of the surface mechanism proposed at the end of the introduction. The measurements were taken after ion implantation, however, the rapid cooling by helium freezes the species on the surface, consequently, we can detect the surface compounds in the last seconds of the implantation process. From Figs. 1(a) and 1(c), the nitrogen contributions to metal and oxynitride species are increased and reduced, respectively, in the case of the use of deuterium. In a previous work, it was concluded that the residence time of deuterium at the material surface is higher than that of hydrogen, which speeds up the water formation, considerably enhancing the oxygen removal.[6] The efficiency of deuterium in etching oxygen is higher than that of hydrogen creating more surface active sites for nitrogen. In fact, the oxygen from oxynitride compounds can only be etched by deuterium: see P2 in Figs. 1(b) and 1(c). From an atomistic point of view, we suggest that the increment of P1 intensity is due to the removal of oxygen from metallic oxides, promoting the incorporation of nitrogen in solid solution (metallic nitrides). On the other hand, the oxynitride compounds, the group of molecules constituted by NO, N_2O_3, and N_2O (NO_x), are weakly adsorbed on the surface and we suggest that they are the geometric barrier opposing nitrogen incorporation. The adsorbed oxygen atoms on the surface interact with nitrogen forming the oxynitride compounds and avoiding nitrogen incorporation into solid solution. Physically, the nitrogen activity on the surface is diminished due to the formation of this geometric barrier (oxynitride compounds). The presence of deuterium instead of hydrogen can increase the nitrogen activity by etching oxygen from these oxynitride compounds. Therefore, the enhancement of nitrogen diffusion is associated with a reduction of the NO_x concentration.

In conclusion, the use of deuterium instead of hydrogen in thermochemical nitriding significantly enhances nitrogen diffusion in ferrous alloys due to an enhancement of nitrogen activity on surface. The surface mechanism and the bulk properties are closely correlated. The presence of deuterium reduces the geometric barrier constituted by oxynitride compounds (like NO, N_2O_3, and N_2O) adsorbed on the surface. This reduction allows more efficient nitrogen incorporation into solid solution, enhancing the nitrogen activity on the surface. The nitrogen activity controls the nitrogen flux into the bulk material at constant time and temperature. At the same relative nitrogen concentration on the surface, the use of deuterium instead of hydrogen increases the nitrogen available for diffusion into the solid.

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