

## Surface hardness-increasing of iron alloys by nitrogen-deuterium ion implanting

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### Abstract

*In situ* photoemission electron spectroscopy (XPS) is used to study the deuterium and hydrogen oxygen etching effect in nitrogen implanted iron alloys. The presence of deuterium considerably increases metallic nitrides and decreases nitrogen oxides formation, improving nitrogen diffusion in the material. A suitable deuterium-nitrogen mixture can increase the surface original steel hardness up to ~ 40 %. In similar conditions, hydrogen-nitrogen mixtures improve the hardness by ~ 10 %. On deuteration, the main change is the reduction of the zero-point energy of the hydrides bond. Due to this, the lower scission energy of hydrogen-metal bonds as compared with deuterium-metal bonds determines the favourable effect of deuterium on the nitriding process.

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Nitriding is a thermo-chemical diffusion process that increases steel hardness, corrosion resistance, and improves tribological properties. These benefits come from nitrogen interstitial compounds and fine nitrides precipitation at the boundary grains.<sup>1,2</sup> Gas and salt baths nitriding are old processes from the beginning of the XX century using aggressive elements.<sup>3,4</sup> Modern plasma nitriding combine nitrogen ions implantation and thermal diffusion.<sup>5</sup> In nitriding processes, residual oxygen forms compounds such as metallic oxides and metal-NO<sub>x</sub> complexes that compete with metallic nitride (FeN<sub>x</sub> and CrN<sub>x</sub>), the main precursors of nitrogen diffusion in metal alloys.<sup>6</sup> Incorporation of hydrogen to the process is a standard procedure to reduce residual oxygen, avoiding the formation of a barrier to nitrogen diffusion.

In this letter we report that deuterium can increase the surface original steel hardness up to ~ 40 %. In similar conditions, hydrogen

improves the hardness by ~ 10 %. The lower scission energy of hydrogen-metal bonds as compared with deuterium-metal bonds determines the oxygen etching process. These results should lead to a considerable increase in surface steel hardness in plasma nitriding processes and to a new manufacture path.

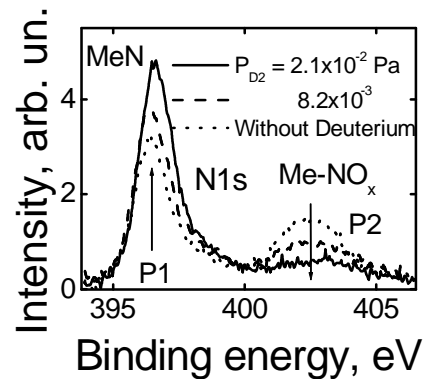


Figure 1. Intensity of the N1s core level photoemission spectra of three samples using different mixtures of N<sub>2</sub> and D<sub>2</sub>. MeN and MeNO<sub>x</sub> stand for nitrides and oxidized metal nitrides, respectively. The arrows indicate the evolution of the bands on increasing partial pressure of deuterium in the ion source chamber.

The studied material was AISI 316 stainless steel lot (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 steel was implanted at 680 K using a 3 cm-diameter DC Kaufman ion source fed with N<sub>2</sub>, D<sub>2</sub> (H<sub>2</sub>) gases in a system attached to an ultra high vacuum chamber for *in situ* XPS analysis. Details of the apparatus are found elsewhere.<sup>7</sup> The background chamber pressure was < 10<sup>-4</sup> Pa (P<sub>O<sub>2</sub></sub> < 2x10<sup>-5</sup> Pa). The working oxygen partial was controlled by an independent leakage. In order to maintain a fixed total chamber pressure (1.2 Pa), an appropriate helium flux was added into the chamber. These experimental conditions guarantee a constant ion mean-free-path.<sup>8,9</sup> The nominal current density and energy of the ion beam for all experiments were fixed at ~ 0.3 mA/cm<sup>2</sup> and ~50 eV, respectively. Immediately after nitrogen implantation, the chamber is flooded with helium to rapidly cool down the samples. Thereafter, the samples were transferred to the attached ultra high 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 is ~0.85 eV (line-width plus analyzer).<sup>6</sup> The hardness measurements were performed with a nano-indentation apparatus using a Berkovich diamond tip (*NanoTest-300*). The load-displacement curves were analyzed using the Oliver and Pharr method.<sup>10</sup>

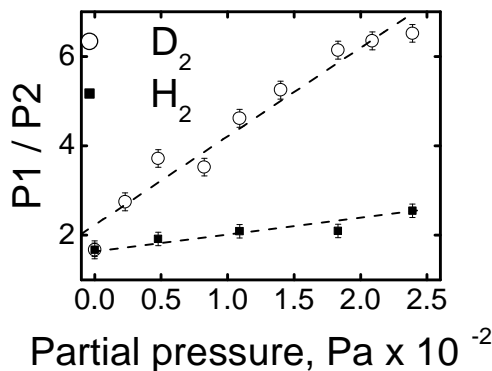


Figure 2. Ratio of the integrated areas (P1/P2) of the N1s core level photoemission spectra (from Figure 1) at variable partial pressures of deuterium (hydrogen) in the ion source chamber.

Figure 1 shows the N1s core electron level photoemission spectra of samples implanted using different mixtures of N<sub>2</sub> and D<sub>2</sub> in the ion beam. The peak 1 (P1) is related to the formation of metallic nitrides such as FeN<sub>x</sub> and CrN<sub>x</sub>. These components increase when a higher relative deuterium partial pressure is used, i.e., more deuterium ions present in the beam. On the other hand, the P2 band, related to Me (metal)-NO<sub>x</sub> complexes, diminishes as increases the number of deuterium ions present in the beam. The chemically absorbed oxygen atoms have a deleterious effect on nitrogen diffusion.<sup>9,11</sup> The presence of D<sub>2</sub> (H<sub>2</sub>), however, chemically etches the oxygen, thus increasing metallic nitrides (P1) on the surface.

Figure 2 shows the ratio of the integrated areas P1/P2 from the photoemission spectra of the N1s at different partial pressures of the nitrogen plus deuterium (hydrogen) ion beam. The key role of deuterium relies on the important reduction of absorbed oxygen (Figure 3). Indeed, the augment of the P1/P2 ratio reflects in the hardness, a bulk material property.

Figure 4 shows the nano-hardness at constant depth (280 nm) of implanted samples at constant chamber oxygen partial pressure and variable D (H) partial pressure in the ion source chamber. Here, the remarkable effect of deuterium is manifest. Nitrating experiments show a lineal correlation between hardness and nitrogen concentration (not shown). Therefore, the hardness curves are profiling nitrogen concentration (Figure 4, inset). The particular high hardness value at the material surface is a consequence of the increasing metallic nitrides formation (see Figure 2).

The oxygen etching mechanism occurs in three steps: D<sub>2</sub> (H<sub>2</sub>) dissociation forming D (H)-metal hydrides on surface, D<sub>2</sub>O (H<sub>2</sub>O) formation, and water de-sorption from surface. The catalytic effect of d-electrons of iron on D<sub>2</sub> (H<sub>2</sub>) dissociation determines the formation of hydrides, a fundamental step to water synthesis. Indeed, identical experiments performed with aluminum show no effect either with hydrogen or deuterium on nitrogen implantation. The lower scission energy of the hydrogen-metal bond than of the deuterium-metal bond limits the oxygen etching process. Indeed, in order to escape back to the vacuum chamber, hydrogen must surmount an energy barrier E(MeH) of the activated metal-hydrogen bond complex. On deuteration, the main change is the reduction of the zero-point energy of the energy barrier E(MeD) (due to the greater isotope mass), not affecting the barrier of the activated complex.<sup>12</sup> Therefore, the ratio of the de-

sorption scission constants rate  $R(\text{MeH} / \text{MeD}) = K_{\text{MeH}} / K_{\text{MeD}}$  is approximately given by the ratio of the Boltzman factors.<sup>12</sup>

$$R(\text{MeH} / \text{MeD}) = K_{\text{MeH}} / K_{\text{MeD}} \approx \exp[h(v_{\text{MeH}} - v_{\text{MeD}}) / (2kT)].$$

Where  $K_{\text{MeH}}$  ( $K_{\text{MeD}}$ ) is de-sorption scission constant of MeH (MeD) complex,  $h = 2\pi\hbar$  is the Planck constant,  $(\hbar/2)v_{\text{MeH, D}} = (\hbar/2)(k_f / \mu_{\text{MeH, D}})^{1/2}$  is the zero-point energy of the MeH (MeD) complex vibration energy,  $\mu_{\text{MeH(D)}}$  is the metal-hydrogen (deuterium) reduced mass,  $k_f$  is the force constant,  $k$  is the Boltzman constant, and  $T$  the absolute temperature. Substituting the mass ratio  $\mu_{\text{MeD}} / \mu_{\text{MeH}} \approx m_{\text{H}} / m_{\text{D}} = 2$ ,  $T = 680$  K for the working temperature, and considering that  $v_{\text{MeH}} \approx 1850 \text{ cm}^{-1}$ ,  $R \approx 2$ .<sup>13</sup> Here we have used the fact that the metal mass is much larger than the hydrogen (deuterium)  $m_{\text{H}}$  ( $m_{\text{D}}$ ) mass. This estimation predicts that in identical conditions, MeH splits about twice as fast as MeD cleaves. We remark that lowering the temperature increases the ratio  $R$ , i.e., the H scission will be still larger than D.

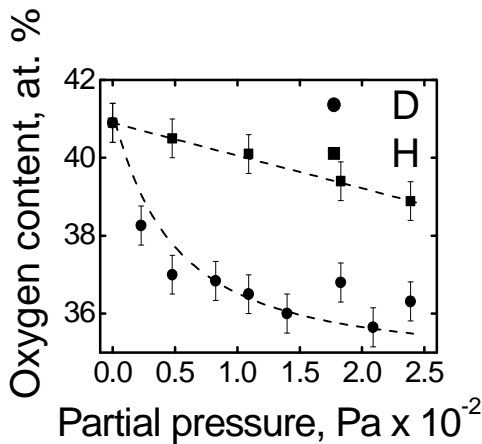


Figure 3. Atomic oxygen content on surface at variable partial pressures of deuterium (hydrogen) in the ion source chamber.

In addition, by the same arguments, the scission of H is easier than the scission of D from the water molecule. Indeed, considering a reaction only along the stretching O-H(D) coordinated in the water molecule, an oxygen-hydrogen mass ratio  $\mu_{\text{OD}} / \mu_{\text{OH}} \approx m_{\text{H}} / m_{\text{D}} = 2$ , and  $v_{\text{OH}} \approx 3652 \text{ cm}^{-1}$ ,  $R(\text{H}_2\text{O} / \text{D}_2\text{O}) \sim 7.5$ .<sup>14</sup> Therefore, the O-H rupture is  $\sim 7.5$  times faster than the O-D rupture. Therefore, it is easier to break up a  $\text{H}_2\text{O}$  than a heavy water molecule prior to desorbs, thus contributing to diminish the oxygen etching efficiency of  $\text{H}_2$  as compared with  $\text{D}_2$ .

In conclusion, the use of deuterium in the plasma nitriding process increases the formation of iron nitrides on surface and decreases metallic oxides. Diminishing the metallic oxides on the material surface improves nitrogen diffusion, i.e., hardness profile. The isotope produces a more efficient chemical etching of oxygen than hydrogen. This is due to the lower scission energy of hydrogen-metal than deuterium-metal bonds. New applications to metallic alloys where high temperatures are not recommended and stable metallic oxides formation seriously prevent efficient nitriding could benefit from the enhance deuterium etching of oxygen.

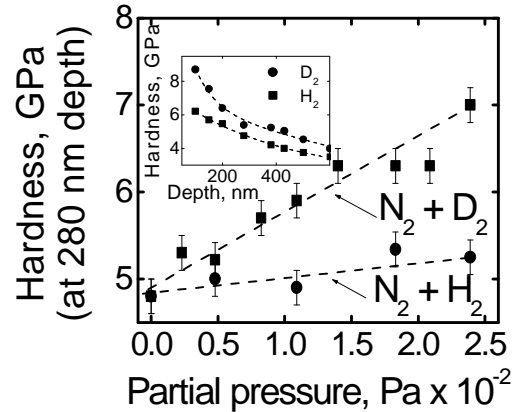


Figure 4. Hardness at constant depth of different samples implanted at variable partial pressures of deuterium (hydrogen) in the nitrogen ion source chamber. Inset: hardness vs. depth of typical curves at constant partial pressure of deuterium and hydrogen ( $1.1 \times 10^{-2}$  Pa).

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