New pathways in plasma nitriding of metal alloys

C.A. Figueroa, F. Alvarez*

Instituto de Física "Gleb Wataghin", Universidade Estadual de Campinas, Unicamp 13083-970, Campinas, São Paulo, Brazil

Abstract

In this paper, we report the effects of oxygen, hydrogen, and deuterium on nitrogen implanted stainless steel AISI 316. The samples were studied in situ by photoemission electron spectroscopy (XPS), nano-indentation (hardness), and scanning electron microscopy (SEM). At relative higher oxygen partial pressures, a surface potential barrier for nitrogen implantation is created by the oxygen absorption. The absorption process obeys a Langmuir isothermal law. The surface barrier is formed by the oxidation of metallic nitrides. The bulk properties such as nitrided layer thickness can be modeled by studying the surface properties. Hydrogen improves the nitrogen content on surface and, consequentially, the hardness in-depth. Surprising efficient oxygen elimination was detected using deuterium instead of hydrogen. This is due to the fact that deuterium improves the nitrogen chemical potential, augmenting the material hardness in depth up to 30% compared to the case when hydrogen is used. This phenomenon is interpreted by an increasing isotope residence time. These novel results suggest that new pathways can be opened in plasma nitriding processes using deuterium in industrial equipment for treatments of metal alloys with stable oxides on the surface.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Plasma nitriding; Deuterium effect; Oxygen effect

1. Introduction

Plasma nitriding is a well-established technique for surface modification of metal alloys, improving the mechanical and chemical properties of the materials [1]. Although many industrial applications of these technologies are used day-to-day, models and quantitative interpretations remain incomplete. It is well known that oxygen creates a potential barrier on surface to nitrogen diffusion. Parascandola et al. have shown that increasing the background oxygen partial pressure in the implantation chamber increases the surface oxygen retention [2,3]. This increment reduces the nitrogen content into bulk material by the formation of an oxidized surface potential barrier. Recently, advances in the understanding of the barrier composition and the surface limiting mechanism in plasma nitriding processes of the barriers have been reported [4–6]. Moreover, bulk properties were modeled as a function of the oxygen partial pressure [7].

In industrial processes, hydrogen is added to improve the process of nitrogen incorporation by chemically etching oxygen. These facts are fundamentally empirical and more experimental results and interpretations are necessary to explain the hydrogen effect. Finally, is important stressing the surface character of this phenomenon.

Paying particular attention to the well-established concepts of chemical potential and surface composition will guide attempts to improve nitriding processes [8,9]. Indeed, the nitrogen chemical potential is the driving force in the diffusion process, i.e., the concentration gradient determines the species diffusion into the bulk material [10]. Although these effects are abundantly discussed in the literature, a combination of both effects (oxygen and hydrogen) is not yet satisfactory and a comprehensive global understanding should be attempted taking into account the nitrogen chemical potential on the surface.

The aim of this paper is to study the effects of oxygen, hydrogen and deuterium in nitrogen implantation of ferrous

* Corresponding author.
E-mail address: alvarez@ifi.unicamp.br (F. Alvarez).

alloys focusing the study on the surface and its influence on the material bulk properties.

2. Experimental

Samples $20 \times 10 \times 1$ mm from the same AISI 316 stainless steel source (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) were used for the study. The substrata were mirror polished using standard metallographic techniques. The nitriding experiments were performed in an ion beam apparatus with a 3-cm diameter DC Kaufman ion source [11,12]. The background chamber pressure is $<10^{-4}$ Pa ($P_{O_2} < 2 \times 10^{-5}$ Pa). The feeding gases of the Kaufman ion source are trough mass flow-meter controllers and the ion impacts perpendicular to the surface samples. The chamber pressure is monitored using a *Varian* cold cathode gauge. The absolute pressure values are obtained using the appropriate gas correction factor provided by the manufacturer [13]. The sample temperature was maintained at $(380 +/- 5)$ °C during the implantation times of 60 and 30 min The oxygen partial pressure for the studies was varied from 10^{-3} to 10^{-2} Pa. The implanted zone composition was in-situ characterized by photoemission electron spectroscopy (XPS) [4]. The effect of hydrogen and deuterium on the ion implantation process was performed and a constant nitrogen ion mean free path obtained by a background helium pressure of 1.2 Pa. This total pressure guarantees a N_2^+ and H_2^+/D_2^+ (and N^+ and H^+/D^+) constant ions mean free path for all experiments. The hydrogen/deuterium partial pressure in the ion source was varied from 4.4×10^{-3} to 2.2×10^{-2} Pa. The oxygen partial pressure for the studies was fixed at 3.2×10^{-3} Pa. 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). Immediately after nitrogen implantation, the chamber is flooded with helium, rapidly cooling down the samples. Immediately, the samples are transferred to the attached ultra high vacuum chamber for XPS analysis, where all elements with atomic content >0.5 at.% were quantified. The XPS spectra were obtained using the 1486.6 eV photons from an Al target (Kα line) and a VG-CLAMP-2 electron analyzer. The total apparatus resolution was ~0.85 eV (line-width plus analyzer).

The hardness was obtained using a Berkovich diamond tip (NanoTest-300) at depths varying between 50 and 1800 nm and the results analyzed using the Oliver and Pharr method [14]. The indentation was perpendicular to the nitrated surface and the tip load controlled the penetration depth. Piling-up effects were not considered. The oxygen effect on the thickness of the nitrided layer was ex situ characterized by secondary electron microscopy (SEM) [7]. The cross-section of the nitrated layers was revealed by attacking the samples, at room temper-

ature, with Marble's solution. The thickness of the nitrated layer was directly measured from the SEM images (JEOL JMS-5900LV).

3. Results and discussion

3.1. Oxygen effect

Fig. 1 shows the evolution of the $Fe2p^{3/2}$ core level binding energy at the lowest and at the highest background oxygen partial pressure nitrogen implanted samples. The chemical shift of the spectra to higher binding energies indicates the formation of metallic oxides such as FeO_x and mixing compound (XM_2O_4, X, M: Fe and/or Cr), accompanied by the degradation of the more unstable metallic nitrides [15]. At higher oxygen partial pressures the evolution of the N1s core level binding energy presents two trends: (1) the reduction of the metallic nitrides; and (2) the formation of nitrogen oxides (NO_x). Finally, as shown elsewhere, the oxygen adsorption obeys a Langmuir isothermal law [4].

The modified layer thickness is a parameter characterizing a bulk property of the implanted samples. Fig. 2 shows the evolution of the nitrided layer thickness as a function of the oxygen partial pressure in the chamber.

A thinner nitrided layer indicates poor nitrogen diffusion due to the absorbed oxygen on the surface. By assuming a nitrided layer thickness inversely proportional to nitrides surface compound and an oxygen Langmuir isothermal absorption, a theoretical expression is obtained (solid line, Fig. 2) [7].

These results stem from the fact that oxygen adsorption degrades metallic nitride forming nitrogen oxides, diminishing the surface nitrogen concentration occupying "active
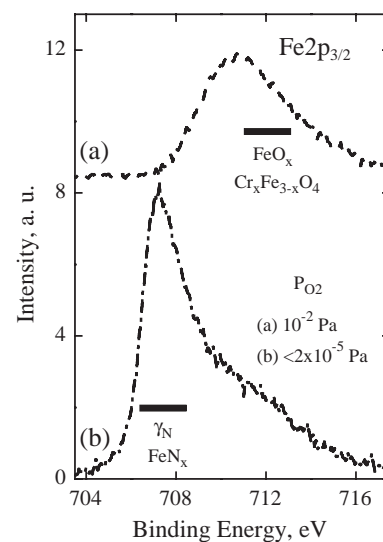

Fig. 1. Evolution of the $Fe2p^{3/2}$ core level binding energies at the lowest and highest oxygen partial pressure in the implantation.
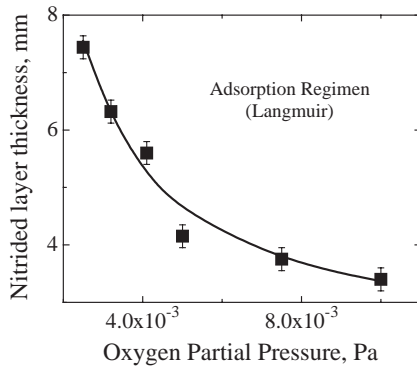
Fig. 2. Evolution of the nitrided layer thickness as a function of the background oxygen partial pressure and using a pure nitrogen ion beam.

Fig. 4. Evolution of the N1s core level binding energy (normalized) of samples prepared at three different gaseous mixtures (pure N_2, and $N_2:H_2$, $N_2:D_2$ mixtures).

sites". The overall result is a poor diffusion by lower nitrogen concentration at the surface, i.e., low nitrogen chemical potential at the gas–solid interface.

3.2. Hydrogen effect

Fig. 3 shows the surface nitrogen content and the hardness (fixed depth) as function of the hydrogen partial pressure added in the Kaufman ion gun at constant offer of nitrogen. We note that the surface oxygen content is reduced by the presence of hydrogen (not shown). These results show that the increment of nitrogen content at the surface improves the nitrogen diffusion, yielding a relatively harder material in depth [16].

3.3. Deuterium effect

The oxygen etching mechanism can be tested using deuterium, a heavier hydrogen isotope [17,18]. Fig. 4 shows the normalized evolution of the N1s core level binding energy in samples prepared at three different gaseous mixtures (pure N_2, and $N_2:H_2$, $N_2:D_2$ mixtures).

The augment (diminishing) of the P1 (P2) band is sizable when H_2 is added to N_2. However, the behavior of the spectra, when a mixture $N_2:D_2$ is used, is remarkable. The intensity of the P1 increases even more than in the hydrogen

case and the P2 shows a considerable intensity reduction. Therefore, compared to hydrogen, the deuterium produces more efficient oxygen removal form the surface. These effects increase the nitrogen concentration, i.e., the chemical potential on the surface and, consequently, increasing the nitrogen diffusion into bulk material. As it is expected, this phenomenon reflects in the material hardness sample profile. Fig. 5 shows the hardness at a constant depth as a function of the hydrogen and deuterium partial pressures in the ion gun. As observed in the plot, up to 30% hardness increasing can be obtained by employing deuterium instead of hydrogen.

These effects can be explained by the lower scission energy of the hydrogen-metal bond as compared to the deuterium-metal bond. 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) [10]. Therefore, as the *dissociation barrier* of the activated complex does not depend on the isotope mass, the MeD complex is more stable than the MeH complex [19]. Therefore, higher deuterium retention than hydrogen increases the probability of D_2O formation and a posterior de-sorption.

These interesting results could open new possibilities for practical applications such as pulsed plasma nitriding of high alloyed steel forming stable oxides on the surface (i.e.,
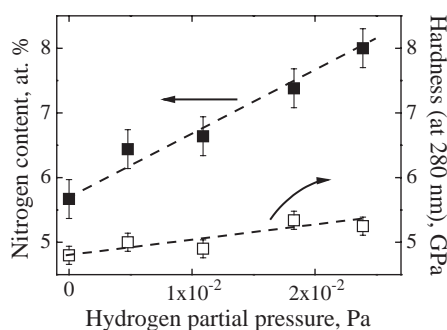

Fig. 3. Surface nitrogen content and hardness at a constant depth (280 nm) as function of the hydrogen partial pressure added in the Kaufman ion gun at constant offer of nitrogen.
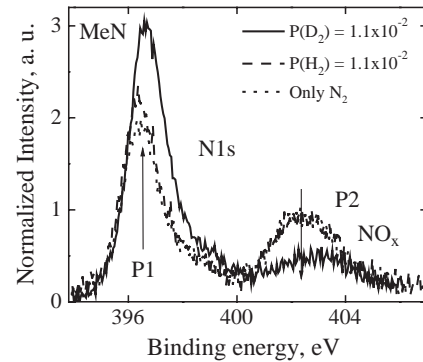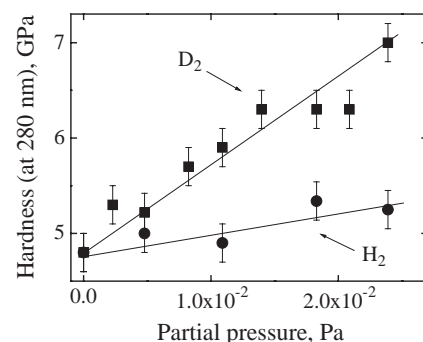

Fig. 5. Hardness at a constant depth as a function of the hydrogen and deuterium partial pressures.

stainless steels) and plasma treatment of other types of metal alloys.

4. Conclusions

New pathways could be opened in plasma nitriding processes taking into account the following facts: (1) the nitrogen chemical potential is a fundamental parameter correlating the surface and bulk properties, (2) the changes in the physical–chemical structure of the surface by oxygen adsorption and its relationship with bulk properties bring qualitative and quantitative new insights about the role of the oxygen effect on nitriding processes, (3) hydrogen improves the nitrogen content on surface and harder materials are obtained, and (4) deuterium produces a larger oxygen removal compared to hydrogen. Depending on the experimental conditions, up to 30% higher hardness increasing is obtained. This is due to the fact that the isotopic effect yields a higher deuterium residence time on the surface than hydrogen, improving the rate of the heavy water formation and de-sorption (i.e., oxygen removal). Metal alloys with stable oxides on the surface such as stainless steel could be probably treated in industrial equipment employing lower times.

Acknowledgements

References

[1] A.H. Deutchman, R.J. Partyka, C. Lewis, in: T. Spalvins, W.L. Kovacs (Eds.), Conference Proceedings of the ASM—2nd Int. Conf., Cincinnati, OH, USA, ASM International, Mat. Park, Ohio 44073, USA, 1989, p. 29.
[2] S. Parascandola, O. Kruse, W. Möller, Appl. Phys. Lett. 75 (1999) 1851.
[3] S. Parascandola, O. Kruse, E. Richter, W. Möller, J. Vac. Sci. Technol., B 17 (1999) 855.
[4] C.A. Figueroa, A.S. Ferlauto, F. Alvarez, J. Appl. Phys. 94 (2003) 5435.
[5] W. Moller, S. Parascandola, T. Telbizova, R. Gunzel, E. Ritcher, Surf. Coat. Technol. 136 (2001) 73.
[6] C.A. Figueroa, F. Alvarez, unpublished results.
[7] C.A. Figueroa, D. Wisnivesky, F. Alvarez, J. Appl. Phys. 92 (2002) 764.
[8] C.A. Figueroa, D. Wisnivesky, P. Hammer, R.G. Lacerda, R. Droppa Jr., F.C. Marques, F. Alvarez, Surf. Coat. Tech. 405 (2001) 146.
[9] C.A. Figueroa, E. Ochoa, F. Alvarez, J. Appl. Phys. 94 (2003) 2242.
[10] P.W. Atkins, Physical Chemistry, 492, Fourth Edition, Oxford University Press, Oxford, UK, 1990.
[11] H.R. Kaufman, J. Vac. Sci. Technol. 15 (1978) 272.
[12] P. Hammer, N.M. Victoria, F. Alvarez, J. Vac. Sci. Technol., A, Vac. Surf. Films 16 (1998) 2491.
[13] Multi-Gauge Controller, Manual 6999-08-091, revision U, December 1998, Varian Vacuum Tech., Lexinton, Mass., USA.
[14] W.C. Oliver, G.M. Pharr, J. Mater. Res. 7 (1992) 1564.
[15] M.W. Chase Jr., NIST–JANAF Thermochemical Tables, Fourth ed. Phys. J. Chem. Ref. Data, Monograph 9, Parts I and II, 1998.
[16] E. Ochoa, C.A. Figueroa, F. Alvarez, Surf. Coat. Technol. (to be published).
[17] Processo de Modificação de superfícies metálicas por plasma de nitrogênio e deutério, Fernando Alvarez e Carlos Alejandro Figueroa, Brazilian Patent, Instituto Nacional de Propriedade Industrial (INPI), 16-10-03, 10:27 hs, Protocolo #5.030.
[18] C.A. Figueroa, F. Alvarez, J. Appl. Phys. 96 (2004) 7742.
[19] I.N. Levine, Physical Chemistry, 824, Fourth Edition, McGraw-Hill, Inc., New York, USA, 1995.