

A comprehensive nitriding study by low energy ion beam implantation on stainless steel

C.A. Figueroa, D. Wisnivesky¹, P. Hammer, R.G. Lacerda, R. Droppa Jr., F.C. Marques, F. Alvarez*

Instituto de Física 'Gleb Wataghin', Unicamp, 13083-970, Campinas, SP, Brazil

Abstract

In this paper we report nitriding studies of stainless steel 316 using a broad ion beam source. Experiments performed by changing the ion energy (0.2–1.5 KeV), ion current density (1.4–5.7 mA/cm²) and implantation times (1 and 8 h) at a temperature around 380°C are reported. The microstructure and morphology are studied by glancing angle X-ray diffraction and scanning electron microscopy. For constant ion energy, higher nitrogen ion flux increases the hardness. At higher ion energies the sputtering process prevents the formation of a thick-nitrated layer, even for longer implantation times. The results are examined in the light of recent studies on physical models for ion implantation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: (Nitrogen) N²⁺ ion implantation; Hardening; Nano-indentation

1. Introduction

Plasma nitriding is an established method for surface hardening of metals, improving wear, friction and corrosion resistance [1]. In particular, the processes using ion beam implantation, at high and low energy, have proved to increase the wear resistance of stainless steel, a relatively soft metal, maintaining its relatively good corrosion resistance properties [2]. Nowadays, there are many plasma technologies in use but there is not a full understanding of the physical phenomena involved in the non-equilibrium process of ion implantation, nitrogen diffusion and structural changes induced in the material. In contrast to gaseous nitriding, ion beam implantation (IBI) presents excellent parameter control. This characteristic is very important for systematic studies that can be extrapolated, at least qualitatively, to other plasma technologies. Only recently, however, some reports were made on IBI, which consider several different conditions of energy, intensity and implantation time at relatively low energy [3–7]. Another factor

generally neglected is related with the sputtering, an unavoidable sub-product of the implantation processes. As is well known, ion energies above 100 eV produce significant surface erosion by physical and/or chemical sputtering. This process increases, among other things, with ion energy and current density. These are important control parameters in view of the fact that a bad system variable optimization could jeopardize the hardening by partial material losses of the nitrogen-rich layer.

In this paper we address the influence of the IBI parameters, time treatment and sputtering effects on the properties of SS 316. In situ electron photoemission spectroscopy (XPS), hardness measurement (nano-indentation), scanning electron microscopy (SEM) and glancing angle X-ray diffraction, were used to characterize the samples.

2. Experimental

Rectangular samples of 20×10 mm and 2 mm thick, from the same source of AISI 316 stainless steel, were used for all the studies. One face of each studied sample was mirror polished using standard metallurgical techniques. The nitriding experiments were performed in an ion beam apparatus with a 3-cm diameter DC Kaufman ion source [8]. The implantation chamber is directly

* Corresponding author. Tel.: +55-19-3788-5372; fax: +55-19-3788-5376.

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

¹ Also at the LNLs, CNPq.

Table 1
The process parameters at 380°C

Sample	U , KeV	I , mA/cm ²	Implantation time, h
STN 1	1.0	1.9	1
STN 2	0.2	1.4	1
STN 3	0.6	1.5	1
STN 4	0.2	2.7	1
STN 5	0.8	2.7	8
STN 6	0.2	2.7	8
STN 7	0.2	2.7	1
STN 8	1.5	2.7	1
STN 9	1.5	5.65	1
STN 10	1.2	2.7	8
STN 11	1.5	1.5	1
STN 12	1.0	5.65	1
STN 13	0.6	5.65	1
STN 14	1.0	2.7	1

attached to the ultra high vacuum (UHV) chamber for XPS analysis. More detailed descriptions of the implantation system are found elsewhere [9]. Nitrogen gas was introduced in the Kaufman ion source and the ions flux impacted the surface samples perpendicularly. The set of studied samples was implanted at 380°C with ions in the energy (current density) range of 0.2 KeV (1.4 mA/cm²) to 1.5 KeV (5.7 mA/cm²) nitrogen ion beam. The substrate holder was temperature controlled by a thermocouple touching the substrate and using a proportional feedback heater. The current density was estimated dividing the nominal beam current of the Kaufman ion source by the beam area. Two implantation times of 1 and 8 h were selected for the studies. The main implantation conditions of the studied samples are displayed in Table 1. The base pressure of the chamber was $<10^{-4}$ Pa. Immediately after the implantation, the samples were transferred to the UHV chamber (pressure $<10^{-7}$ Pa) for photoelectron spectroscopy measurements (XPS). After the implantation experiment, the in-depth nitrogen concentration was obtained by sputtering with argon ions the implanted layer and XPS measurements. The phases near to the surface layers were identified using glancing angle X-ray diffraction (GAXD). The radiation used was Cu K $_{\alpha}$ ($\lambda = 1.54$ nm, $U = 50$ KeV and $I = 100$ mA) at incident angle of 2°. The hardness was obtained using a Berkovich diamond tip (NanoTest-100) at depths varying between 50 and 1800 nm and the results analyzed using the Oliver and Pharr method [10]. The indentation experiments were performed perpendicularly to the nitrated surface and the tip load controlled the penetration depth. The piling-up effects were not considered. The step produced by sputtering a suitable shaded region of the sample was measured using a standard profilometer. The sputtering rates were obtained dividing the step size by the implantation time. The cross-section of the nitrated layers were revealed by attacking the samples at room temperature

with NITAL 1.5% and observed by scanning electron microscopy (SEM/JEOL JMS-5900LV).

3. Results

The relationship between nitrogen and hardness is an important subject of research. The incorporation of nitrogen increases, in general, the hardness of the material. However, depending on the formed structure, the relationship between those two quantities is not straightforward. Moreover, as shown below, good nano-indentation depth resolution is essential to gain physical insight into the understanding of the relationship between hardness and nitrogen content. To analyze this correlation, the hardness (nitrogen concentration) vs. depth was studied in a sample (STN5) implanted at 0.8 KeV (Fig. 1). Fig. 2a,b shows the hardness vs. depth for a 1 h-implanted sample at two different ion energies and variable ion current density. Fig. 3a,b shows the hardness profile in samples implanted at constant ion current density and variable ion energy. Fig. 4 shows the structural dependency of the superficial layer on the ion density current obtained by GAXD. Fig. 5 shows the diffusion zone obtained by SEM (sample STN12). Fig. 6 represents the hardness vs. depth profile for fixed ion current density at several ion energies and two implantation times. Surprisingly, the experiments of an 8-h ion implantation do not show a hardness profile fundamentally different from samples subjected to a 1-h implantation in similar experimental conditions. Finally, Fig. 7 shows the sputtering rate vs. ion energy with ion density current as parameter.

4. Discussion

The proportionality between nitrogen concentration and hardness in stainless steel is an expected result

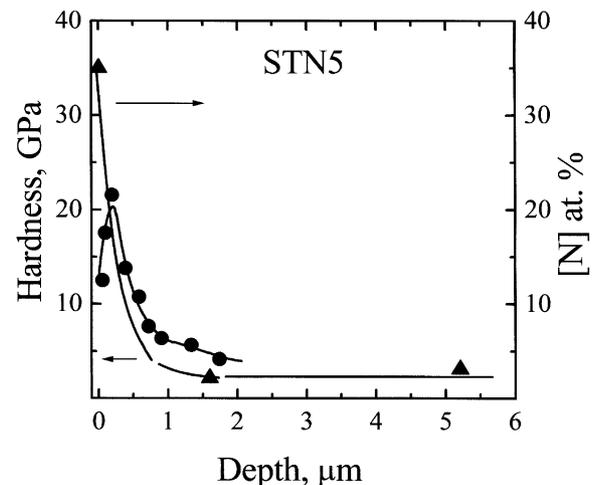


Fig. 1. Nitrogen concentration and hardness profiles vs. depth (STN5).

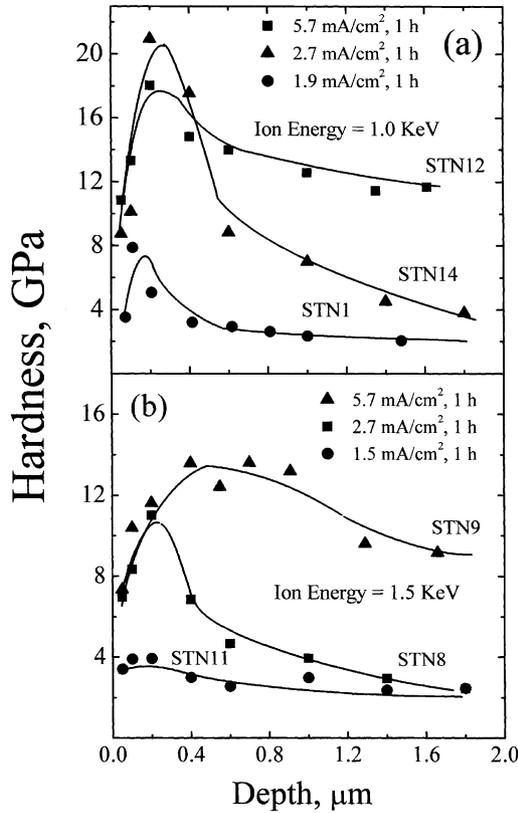


Fig. 2. Hardness profiles of 1-h implanted samples: (a) at three different ion current densities and constant energy (1.0 KeV); and (b) at three different ion current densities and constant energy (1.5 KeV).

already reported in the literature (see Fig. 1) [11]. Since nitrogen forms metal nitrides, increasing amounts of nitrogen will increase, in principle, the hardness of the material [12]. It is important to note, however, that the formation of different types of nitrides makes establishing a universal nitrogen content–hardness relationship difficult. This is probably the cause of the few reports showing this proportionality unambiguously.

Fig. 2a,b shows the dependence of the hardness on both ion energy and current density. These plots indicate that current density seems to determine the hardness above a $\sim 0.4\text{-}\mu\text{m}$ depth, i.e. the diffusion region of the nitrated layer. However, above $\sim 0.4\text{-}\mu\text{m}$ depth, the ion energy does not have a profound influence on the shape of the curve (see Fig. 3a,b). As already proposed, this is due to the fact that a minimum ion energy threshold is necessary to overcome a surface barrier [3]. After the formation of an underneath nitrogen-rich layer, diffusion is the main driving force moving the nitrogen into the bulk [13,14]. Therefore, regarding the hardening properties, current density is far more important than the energy of the ions. Nevertheless, since the sputtering yield strongly depends on ion energy, the influence of nitrogen erosion deserves special attention. We shall come back to this point below. Finally, the depth of the

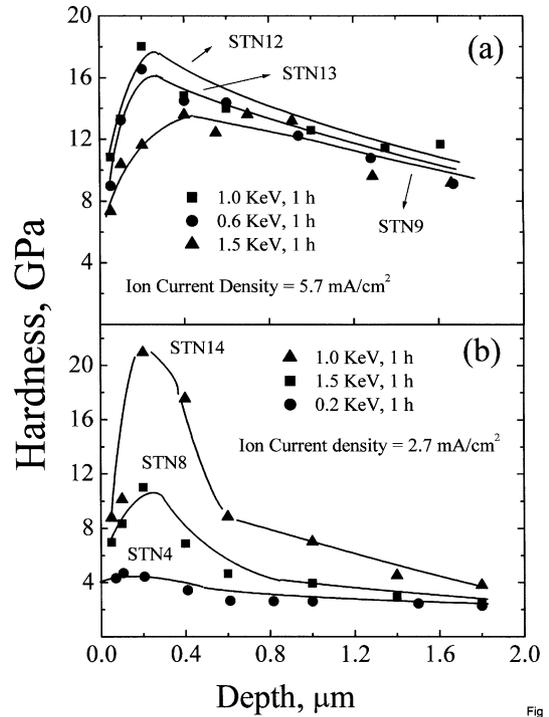


Fig. 3. Hardness profiles of 1-h implanted samples: (a) at three different ion energy conditions and constant density of current (5.7 mA/cm^2); and (b) at three different ion energy conditions and constant density of current (2.7 mA/cm^2).

maximum hardness of the profile curves depends on the ion energy, a result compatible with the ion implantation processes (Figs. 2, 3 and 6). Indeed, a numerical simulation shows that the maximum of the implanted nitrogen profile depends on ion energy. As is expected, this maximum shifts to deeper depth on increasing ion energy [16]. This explains why below $\sim 0.4\text{ }\mu\text{m}$ a sample implanted with 1 KeV is harder than a sample

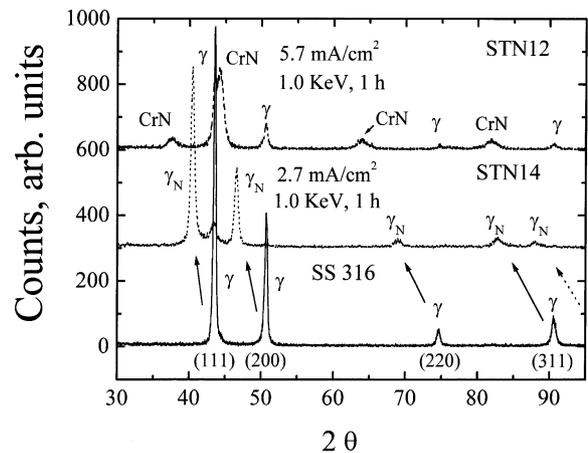


Fig. 4. X-Ray diffraction patterns at different ion current density and same ion energy. The original pattern for a blank substrate is displayed.

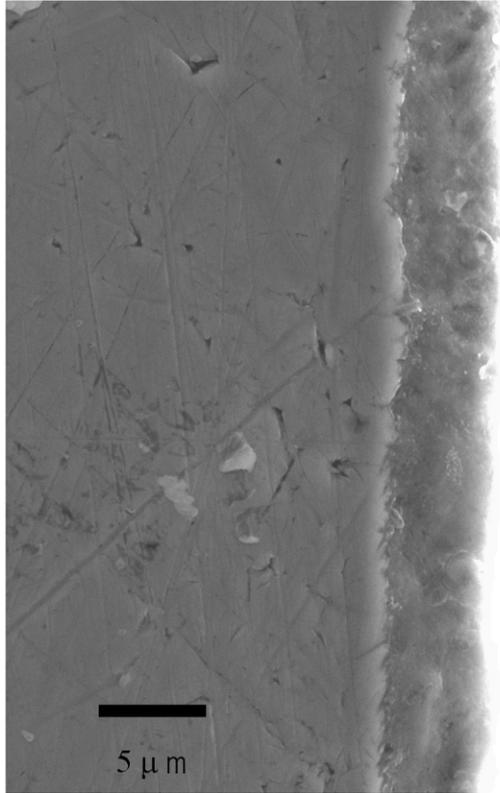


Fig. 5. Cross section of sample STN12 obtained by SEM. The microstructure was revealed by attacking the material at room temperature with NITAL 1.5%.

implanted with 1.5 KeV (Fig. 3a). Moreover, for high ion energy implantation, strong ion erosion makes it difficult to fully understand the hardness profile below $\sim 0.4 \mu\text{m}$, a nitrated region out of the scope of this paper.

It is well known that the hardness introduced by nitrogen depends on the steel composition and especially on Cr contents [15]. Fig. 4 shows that the diffraction curve of the sample implanted at low ion current density (2.7 mA/cm^2 , STN14) presents peaks of the austenite γ_{N} , a fingerprint of the nitrogen expanded fcc lattice. Moreover, as indicated by the shifting of the peaks associated with γ -phase, low current density expands the network *without visible* nitride precipitations (Fig. 4). The macroscopic expansion of the grain boundaries and the high internal stress increases the material hardness. However, high ion current density promotes a phase separation by the formation of CrN precipitates, an efficient material hardening. Also, due to the high ion density current, a richer nitrogen layer is formed that probably enhances the diffusion process. Fig. 5 displays the cross section of the sample STN12 obtained by SEM, showing a nitrided layer of $\sim 5 \mu\text{m}$.

So far we have discussed 1-h implantation results. Now we shall discuss the effects of longer implantation

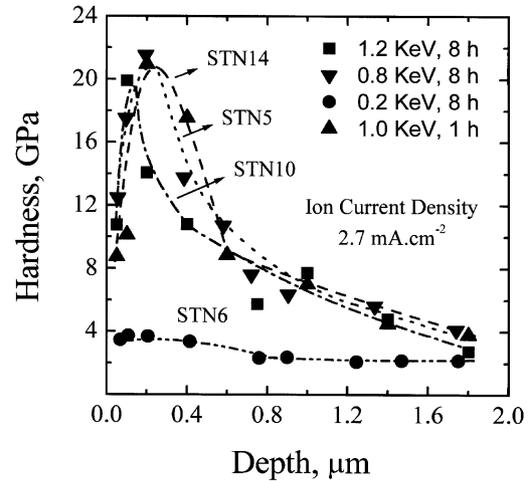


Fig. 6. Hardness profiles at different deposition conditions.

times (8 h) with 2.7 mA/cm^2 current density at several ion energies (Fig. 6). For comparison purposes the curve obtained for sample STN14 from Fig. 2a was added. The ion nitriding processes can be envisaged as occurring in three-steps: (1) ion implantation; (2) diffusion into the material bulk; and (3) material erosion by physical and/or chemical sputtering. The sputtering rates of the studied samples are displayed in Table 2. Fig. 7 shows that the sputtering rate increases by a factor of four when doubling the current from 2.7 mA/cm^2 to 5.7 mA/cm^2 .

The similarity of the diffusion region of the curves obtained in samples implanted at approximately 1 KeV and different deposition times is remarkable (Fig. 6). This similarity suggests that the diffusion rate is comparable to the sputtering rate and that longer implanta-

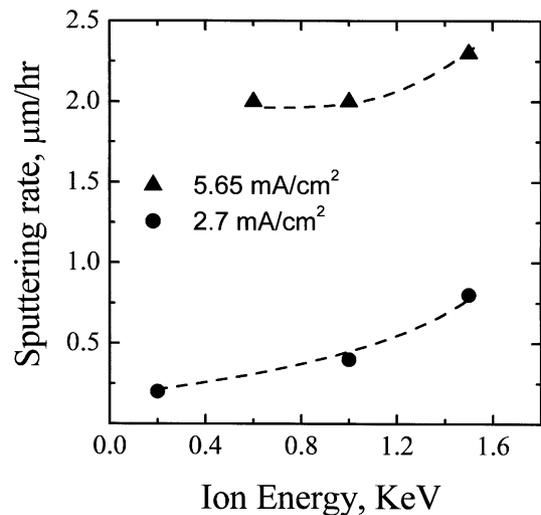


Fig. 7. Sputtering rate vs. ion energy with ion current density as parameter.

Table 2
Sputter removal

Sample	Absolute sputter, μm	Sputtering rate, $\mu\text{m/h}$
STN 1	0,6	0,6
STN 2	0,2	0,2
STN 3	0,4	0,4
STN 4	0,2	0,2
STN 5	7	0,9
STN 6	1,4	0,2
STN 7	0,2	0,2
STN 8	0,8	0,8
STN 9	2,3	2,3
STN 10	7	0,9
STN 11	0,6	0,6
STN 12	2	2
STN 13	2	2
STN 14	0,4	0,4

tion times do not enlarge the nitrated layer. As shown by Parascandola et al. [14,15], a nitrogen-rich layer must be formed underneath the surface to saturate *traps* that prevent further diffusion of nitrogen. Therefore, a low diffusion rate as compared to the sputtering rate is probably associated with (relative) low ion current density (2.7 mA/cm^2), i.e. an insufficient dose of nitrogen to saturate traps. Indeed, the result for sample STN9 (5.65 mA/cm^2) shown in Fig. 2b supports this assumption. Also, the X-ray diffraction data show that the raising of CrN_x precipitates is noticeable when higher current densities are used (Fig. 4).

5. Conclusions

We report the influence of the ion current density in nitrogen implantation in SS316 performed a low ion energy (0.2–1.5 KeV) and low temperature (480°C). The hardness depth profile was studied as a function of ion energy, current density and implantation time. High ion current density is the main factor which is fundamental in allowing nitrides species to diffuse efficiently into the bulk material and in forming of a harder structure by promoting nitrides (CrN_x) precipitates. For fixed current density, higher ion energy does not improve the hardness of the nitrated layer. Moreover, the deleterious

influence of high ion energy on the material erosion by physical and/or chemical sputtering is established. Indeed, due to the sputtering effects, longer implantation times do not necessarily lead to a thicker hard layer. Therefore, a careful combination of ion energy, current density and implantation time must be exercised for optimum results.

Acknowledgements

The authors are indebted to C.T.M. Ribeiro for helping us with X-ray measurements. This work was partially sponsored by FAPESP, grant 97/2069-0. CAF, RGL and PH are Fapesp fellows. FA, FCM, DRJr and DW are CNPq fellow.

References

- [1] A.H. Deutchman, R.J. Partyka, C. Lewis, Conference Proceedings of the ASM, Ohio, 1989, p. 29.
- [2] C. Blawert, A. Weisheit, B.L. Mordike, F.M. Knoop, Surf. Coatings Technol. 85 (1996) 15.
- [3] R. Wei, Surf. Coatings Technol. 83 (1996) 216.
- [4] R. Wei, J.J. Vajo, J.N. Matossian, P.J. Wilbur, J.A. Davis, D.L. Williamson, G.A. Collins, Surf. Coatings Technol. 83 (1996) 235.
- [5] S. Leigh, M. Samandi, G.A. Collins, K.T. Short, P. Martin, L. Wielunsky, Surf. Coatings Technol. 85 (1996) 37.
- [6] P.J. Wilbur, J.A. Davis, R. Wei, J.J. Vajo, D.L. Williamson, Surf. Coatings Technol. 83 (1996) 250.
- [7] S.J. Bull, A.M. Jones, A.R. McCabe, Surf. Coatings Technol. 83 (1996) 257.
- [8] H.R. Kaufman, J. Vac. Sci. Technol. 15 (1978) 272.
- [9] P. Hammer, N.M. Victoria, F. Alvarez, J. Vac. Sci. Technol. A 16 (1998) 2491.
- [10] W.C. Oliver, G.M. Pharr, J. Mater. Res. 7 (1992) 1564.
- [11] M. Berg, C.V. Budtz-Jørgensen, H. Reitz, K.O. Schweitz, J. Chevallier, P. Kringhøj, J. Böttiger, Surf. Coatings Technol. 124 (2000) 25.
- [12] O. Öztürk, D.L. Williamson, J. Appl. Phys. 77 (8) (1995) 3839.
- [13] W. Möller, S. Parascandola, O. Kruse, R. Günzel, E. Richter, Surf. Coatings Technol. 116–119 (1999) 1.
- [14] V.A. Kukareko, A.V. Byeli, Surf. Coatings Technol. 127 (2000) 174.
- [15] S. Parascandola, W. Möller, Appl. Phys. Lett. 76 (16) (2000) 2194.
- [16] J.P.B. Biersack, G.L. Haggmark, The simulation used the TRIM software, Nucl. Instrum. Methods 174 (1980) 257.