

Effect of pulsed plasma nitriding temperature on microstructure properties of AISI 304 stainless steel

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(Recibido: 29 de junio de 2006; Aceptado: 30 de agosto de 2007)

This study reports the surface modification of AISI 304 stainless steel by applying nitrogen ion implantation by low energy plasma at different temperatures (380°C, 400°C, 440°C). The temperature of the samples was adjusted by varying the implantation pulse width while keeping the voltage constant at 1.5 kV. Microstructure and phase characterization were carried out by scanning electronic microscopy (SEM) and X-ray diffractometry (XRD) respectively. The surface hardness was determined by Knoop measurements, and the results show that the treatment increases up to two times the substrate hardness value. Additionally, it was found a direct dependence between the substrate temperature and the nitrided layer thickness. X-ray diffraction patterns indicate the shift of the peaks of the treated samples to lower angles than those of the untreated samples, which is a clear signature of expanded austenite.

Keywords: Surface Treatments; Surface Hardening, Nitriding

1. Introduction

In a PIII (Plasma Immersion Ion Implantation) process [1] nitrogen atoms can be driven into the surface of steels or other iron based alloys kept at temperatures in the range 400-650°C [2] in order to enhance properties such as hardness and tolerance to both corrosion and wear. Thus, this treatment has been straightforwardly applied to tools and machinery parts [3-4].

When comparing traditional nitriding processes (*e.g.* gas or salt based) low energy PIII results very economically attractive due to the introduction of nitrogen by diffusion with lower energy and gas consumption and allowing a substantial reduction of the treatment temperature and/or the processing time [5]. Austenitic stainless steels, in particular, can be implanted at less than 450 °C so to prevent the precipitation of chrome nitrides which promotes the depletion of chrome and whereby the loss of corrosion resistance in this kind of steels [6].

Ionic nitriding of austenitic steels enables to obtain a meta-stable superficial phase, called expanded austenite, whose depths lie in the order of 1-10 µm and where nitrogen remains in a solid solution. In accordance with several authors, this phenomenon enhances both superficial hardness and wear resistance without compromising the corrosion tolerance [7-10].

This report presents some results from the pulsed PIII processing of austenitic AISI 304 stainless steel samples at

temperatures between 380 and 440 °C at 5×10^{-1} Torr gas pressures during 3 h periods.

2. Experimental details

Commercial AISI 304 stainless steel samples (carbon 0.04%, sulphur 0.025%, manganese 1.45%, phosphor 0.03, silicon 0.44%, chrome 18.21, nickel 8.02%, molybdenum 0.35%, copper 0.45%) were sectioned in 1 mm thick discs with 4.7 mm diameter, which were polished with silicon carbide sandpapers in a sequence 120 – 240 – 320 – 400 – 600 and then mirror finished using a velvet cloth embedded with an emulsion of 6 µm, 3 µm and 0.5 µm diamond and 0.05 µm alumina particles.

Once a base pressure of 1×10^{-3} Torr was achieved in a previously described cylindrical vessel [11], a nitrogen plasma was produced by means of a low pressure DC glow discharge at a working pressure of 5×10^{-1} Torr. Such conditions provide an ion plasma density up to 10^{10} cm^{-3} [12].

The ion nitriding process was conducted by biasing the samples with a pulsed potential of -1.5 kV (1.6 kHz), which pulse width was adjusted between 100 and 600 µs in order to gain control of the substrate temperature (to be maintained either at 380 °C, 400 °C or 440 °C) as a consequence of the ion bombardment. During the process duration (3 h), the temperature of the sample was monitored by means of a Novus N1100 temperature

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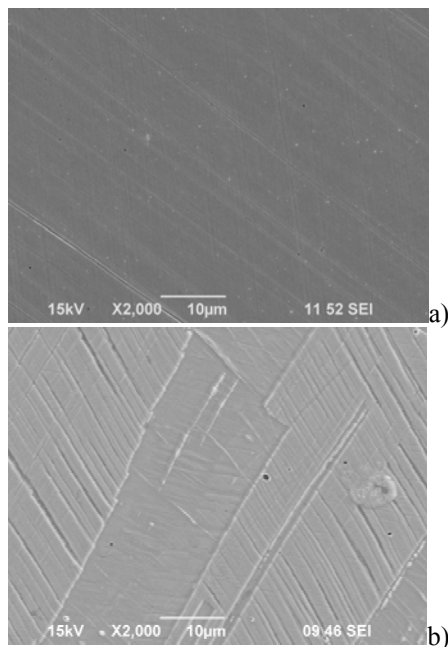


Figure 1. Superficial micrograph of a sample before (a) and after (b) its nitriding at 440°C

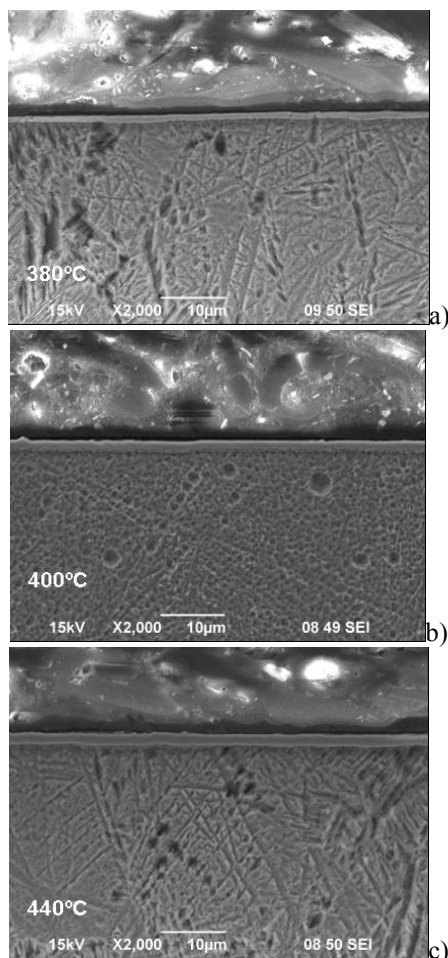


Figure 2. Cross sectional metallographies of the samples treated at: a) 380 °C, b) 400°C and c) 440°C

controller module using a K type thermocouple mechanically attached to the substrate.

The samples were characterized by means of X-ray diffraction (XRD), metallography and Knoop microhardness. The XRD spectra were obtained from the $K\alpha$ radiation of copper within a 2θ range from 20° to 80° at a 0.02° steps per second. The nitrided layer depth was determined through *image-pro plus* image processor while a Knoop indenter established the superficial microhardness under 100 g loads at 10 s intervals.

3. Results and discussion

Some processing effects became visible to the naked eye such as the loss of the mirror finishing of the samples which can be attributed to sputtering activity, namely, ion bombardment erosion induced by the sample bias. Figure 1 shows one sample surface before and after being treated at 440°C. It is clear the micro structural exposure created by the sputtering alone, that is, in the absence of any chemical attack, on the grain boundaries. Similar conditions are observed in the samples treated at 380°C and 400 °C.

With a view to exhibiting the presence of a modified superficial layer on the samples, these were cross sectioned and chemically prepared for metallographic observation. Figure 2 exemplifies the images obtained from three representative samples treated at the three temperatures. The superficial layer, a proof of the nitrogen admission, is apparent in all the cases yielding average depths of 1.40µm, 2.20µm and 3.04µm in the samples treated at 380°C, 400°C and 440°C, respectively.

Figure 3 presents the XRD spectra taken from the three representative samples and a referential untreated one. In 3(a) the reflections at $2\theta=44^\circ$, $2\theta=51^\circ$ and $2\theta=75^\circ$, characteristic of AISI 304 stainless steel, are clearly visible. Then, in Figures 3 (b), 3 (c) and 3 (d), new important reflections located to the left of the (111) and (200) peaks of the initial austenitic phase γ (44° y 51°), reveal the γ_N [13] expanded austenite phase layer depth. The reflections at lower angles correspond to a nitrided layer having an fcc structure similar to that of the untreated substrate, only with an expanded lattice [5]. Likewise an increase in the γ_N reflection intensities as a function of the sample temperature can be observed.

The average Knoop hardness values as well as the indenter penetration depth, calculated from the indentation diagonal length, of each of the three treated samples and the untreated referential one are summarised in Table 1. A rhomboidal Knoop indenter was employed with 100 g loads applied during 10 s periods. The test outcome points to the γ_N expanded phase as responsible for the improvement in superficial hardness by a factor of 1.6 in the case of the sample processed at 380 °C and of 2.0 in those of the ones at 400 and 440 °C

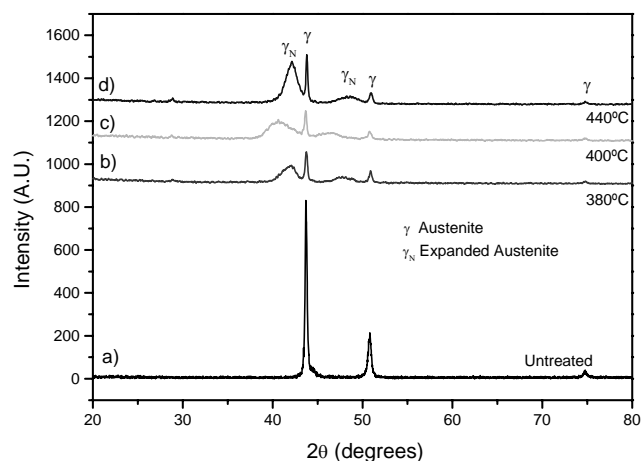


Figure 3. X ray diffraction patterns from: a) Untreated substrate b) 380. °C sample, c) 400°C sample and d) 440°C sample.

4. Conclusions

After a PIII ionic nitriding treatment of AISI 304 stainless steel samples at 380 °C, 400 °C and 440°C, modified superficial regions are created in which γ_N expanded austenite is prevalent down to 1.40 μ m, 2.20 μ m and 3.04 μ m depths respectively. Furthermore, it is found that the modified layer depth is directly proportional to the substrate temperature. X ray diffraction patterns reveal, in all three cases, the presence of the γ_N crystalline phase in the form of reflections at lower angles that those corresponding to the (100) and (200) peaks of the γ phase.

Table 1. Knoop microhardness.

Sample	Hardness [HK]	Indentation depth [μ m]
Untreated	362	2.06
380°C	569	1.64
400°C	724	1.45
440°C	756	1.42

Finally, the microhardness of the treated samples was increased up to twice as that of the untreated substrate in the samples processed at 400 °C and 440°C.

References

- [1] J. R. Conrad, J. L. Radtke, R. A. Dodd, F. J. Worzala, N. C. Tran, *J. Appl. Phys.* **62**, 4591 (1987).
- [2] G.F. Gomez and M. Ueda, *J. of Appl. Phys.* **94**, 1 (2003).
- [3] M. A. Bejar, C. González. *Rev. Mat.* **8**, 115 (2003).
- [4] D. Peix, M.A. Guitar, S.P. Bruhl, N. Mingolo, V. Vanzulli; A. Cabo, E. Forlerer. *Rev. Materia* **10**, 205 (2005).
- [5] W. Liang, *Appl. Surf. Sci.* **211**, 308 (2003).
- [6] L. Wang, X. Xu, Z. Yu, *Surf. and Coat. Technol.* **124**, 93 (2000).
- [7] A. Sakar, Ch. Leroy, H. Michel, *Mat. Sci. Eng. A* **140**, 702 (1991).
- [8] S. P. Hannula, P. Nenonen, J. P. Hirvonen, *Thin Sol. Films* **181**, 343 (1989).
- [9] M. J. Baldwin, M. P. Fewell, S. C. Haydon, S. Kumar, *Surf. and Coat. Technol.* **98**, 1187 (1998).
- [10] S. P. Bruhl, R. Charadia, N. Mingolo, *Rev. Mat.*, **10**, 1181 (2005).
- [11] R. López-Callejas, R. Valencia-Alvarado, O. Godoy-Cabrera, J. L. Tapia-Fabela, *Rev. of Sci. Instrum.* **73**, 4227 (2000).
- [12] E. E. Granda-Gutiérrez, R. López-Callejas, R. Peña-Eguiluz, J. S. Benítez-Read, J. O. Pacheco-Sotelo, R. Valencia A., A. Mercado-Cabrera and S. R. Barocio, *Surf. and Coat. Technol.* **201**, 5454 (2007).
- [13] M. Ueda, G. F. Gomes, *Braz. J. of Phys.* **34**, 1632 (2004).