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In-line nitrogen PIII/ion nitriding processing of metallic materials

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Abstract

Hybrid surface modification involving plasma immersion ion implantation (PIII) and ion nitriding has been attempted. DC cathode nitrogen glow discharges with 600–1000 V, 50–300 mA were typically obtained using the sample support as the cathode and the vacuum chamber as the anode. In this mode, sample temperatures of 500–600 °C can be reached easily while PIII at 10 kV, 50 μs and 400 Hz alone can provide about 300 °C heating. Combining these two highly conformal treatments and achieving high temperature, high efficiency three dimensional ion implantation is our objective. X-ray diffractions (XRD and high resolution XRD in the glancing mode) showed effects of ion nitriding in the AISI 304 stainless steel samples surface which indicate very thick nitrided layer, especially when operating the glow discharge in the low pressure but with high temperature nitriding mode. Auger electron spectroscopy and microhardness measurements confirmed nitriding in the sample surface. The hybrid treatment (PIII/ion nitriding) is expected to improve further these surfaces.

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Keywords: Plasma nitriding; Plasma immersion ion implantation; X-ray diffraction; AES

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1. Introduction

Plasma immersion ion implantation (PIII) is an advanced surface modification technique that allows three dimensional ion implantation of industrially relevant components with complex shape, in a cost effective manner [1]. Hybrid processes involving PIII and other traditional techniques of deposition, electroplating, etc. have been used quite often recently to achieve higher performance surfaces than ones obtained by pure PIII processing [2]. Using a modest experimental system (in terms of volume and pulse power available), we are studying a hybrid process using nitrogen PIII with ion nitriding.

Ion nitriding of metal components, in particular those made of steel, has been used quite extensively in the contemporary industries. It is a mature technology which is used in the metal

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industries to increase the surface hardness and wear resistance of metal component surface. In the conventional ion nitriding of steels temperatures over 500 °C are required to reach satisfactory results [3]. The components under treatment are used as cathodes of the discharges that can be run at the DC or pulsed mode (typically with 700–1500 V). Although a completely closed theoretical model in the atomistic level has not yet been developed for the ion nitriding process, it is widely accepted that the nitrogen ions present near the cathode are thermally diffused into the surfaces resulting in a deep (10–20 μm typically) nitrided layer [4].

On the other hand, PIII processing is a more recently developed technique for the surface modification of a broader range of materials [5] and is based primarily on the ion implantation process. Samples or components to be processed are immersed in a plasma and high voltage pulses (typically >10 kV) are applied to them until ion doses over 10^{17} cm^{-2} are achieved. Improvements in hardness, wear and corrosion resistance in various types of materials have been obtained by this technique also.

A hybrid process combining the high temperature attained by the glow discharge ion nitriding and possibilities of high energy ion injection through the native (or formed during the treatment) oxide layer provided by PIII is being attempted. High temperature (400–800 °C) PIII of Al, steels and Ti6Al4V are being pursued in the first phase. A low pressure glow discharge ion nitriding alternated with a high pressure cycle consists in another interesting duplex treatment under study. It is similar to the high temperature DC PIII studied before [6]. Results from in-line configuration of these hybrid treatments will be discussed focusing on the stainless steel samples.

2. Experimental

The experimental set-up used for the hybrid treatments is shown in Fig. 1. As described elsewhere [7], a 30-l stainless steel chamber is used for this in-line experiment. In the present set-up two feedthroughs are used to power the glow discharges and the high voltage pulses. Both the primary DC power supply for high pressure glow discharge nitriding and the high voltage pulser for PIII are connected to feed 1. Furthermore, the high voltage bias during the low pressure glow discharge is also applied through this feed. On the other hand, for the low pressure glow we use a low power DC voltage supply into the feed 2.

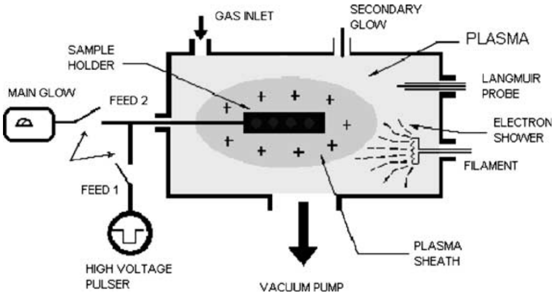

Fig. 1. Schematics of the plasma immersion ion implantation (PIII) and nitriding experiments, at Laboratório Associado de Plasma, LAP-INPE/Brazil.

For the measurements of X-ray diffraction (XRD) of nitrided and nitrogen implanted 304 stainless steel samples, a Philips 3410 diffractometer in the Seeman–Bohlin 2θ mode and a high resolution Philips X'Pert MRD X-ray diffractometer in the Bragg–Brentano geometry glancing incidence (GXRD) mode were used. As will be discussed in the next section, different phases as γ_N, that corresponds to the austenite with nitrogen in solid solution and α, a martensitic iron form, were detected in the SS 304 samples treated with low and high pressure ion nitriding and PIII/nitriding processing.

The samples were analyzed by Auger electron spectroscopy (AES) using the FISONS Instruments Surface Science, model MICROLAB 310-F.

For the measurement of the treatment temperature we used the RAYTEK infrared pyrometer, sensitive in the 200–2000 °C range. Calibrations of the pyrometer were carried out with thermocouple sensor in the lower end of the range.

3. Results and discussions

In the first part of the experiment exploring the hybrid treatment concept, we performed high pressure ion nitriding of SS 304 samples by glow discharge with nitrogen (N_2) gas only. In this way, with discharges running the main power supply at 500–700 V, with 200–300 mA and under working pressures of 4×10^{-1} mbar, resulting in sample temperatures of 400–500 °C, we induced α-phase in the surfaces, as indicated by XRD analysis. The corresponding XRD result is shown in Fig. 2, dotted line.

Using the same operating conditions but with feeding gas mixtures of 50% N_2 and 50% H_2, γ_N phase was obtained, as indicated by glancing incidence XRD measurements shown in Fig. 3. As the glancing incidence XRD probes a thin layer, only diffraction peaks of the γ_N appear, shifted from the ordinary γ peaks of the austenitic structure of the bulk SS 304. AES was used for elemental profile measurements and confirmed good nitriding in this sample, as shown in Fig. 4(a). Nitrogen diffused up to 650 nm while residual oxygen and carbon were also up-taken to shallower depths.

Low pressure ($p = 8 \times 10^{-4}$ mbar) nitriding using both nitrogen and nitrogen/hydrogen plasma mixtures was successful when combined with high temperature (350–500 °C) obtained by the high pressure cathodic glow and −700 V bias on the substrate holder. We believe that the effective acceleration of the nitrogen ions in the low pressure regime allows a deeper penetration of the ions into the sample in contrast to the case of high pressure glow nitriding where despite a similar voltage applied to the samples, the final acceleration voltage of the ions is much reduced due to the shorter mean free path [5]. In the case of low pressure ion nitriding, the plasma was produced by the secondary power supply running at 900 V, 80 mA. The best nitriding results were attained by applying the high and low pressure nitriding in sequence, alternately (15 min each) for a total of 150 min.

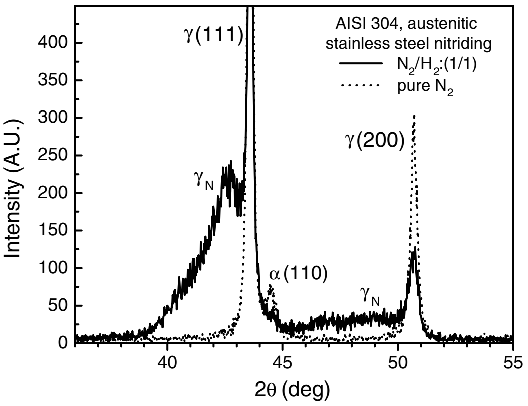

Fig. 2. XRD patterns of SS 304 nitrided in pure N_2 and in a mixture of (N_2/H_2):(1/1). Pure N_2 nitriding was run at 500–700 V, 200–300 mA, 4×10^{-1} mbar and induced the α-phase in the surface. The samples nitrided with the mixture of (N_2/H_2):(1/1) and alternating high and low pressure nitridings, showed a very broad and intense γ_N peak, that can be seen to the left of γ(1 1 1).

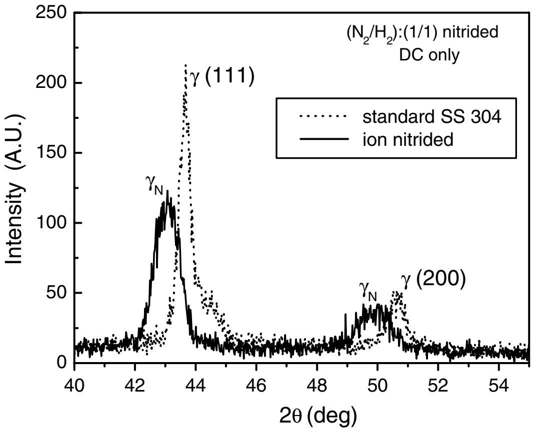

Fig. 3. XRD patterns of γ_N phase obtained, as indicated, by glancing incidence XRD measurements. The diffraction peaks seen in the figure are the γ_N peaks shifted from the ordinary γ peaks from the austenitic stainless steel structure of the bulk.

Again, in Fig. 2, solid line, a very broad and intense γ_N peak can be seen near 43.5°, in the vicinity of the γ(1 1 1), which resulted from the hybrid treatment described above when a 1 to 1 mixture of H_2 and N_2 was used. Vickers hardness with 25 gf load indicated an increase of about 2.7 times compared to the standard SS 304 sample. AES data also confirmed strong nitriding, as shown in Fig. 4(b), where for the sake of clarity, only N, C and O are depicted.

Preliminary tests on nitriding/PIII hybrid treatment have also been carried out. PIII processing with 10 kV, 50 μs, 200 Hz parameters was tried in the temperature range of 330–410 °C

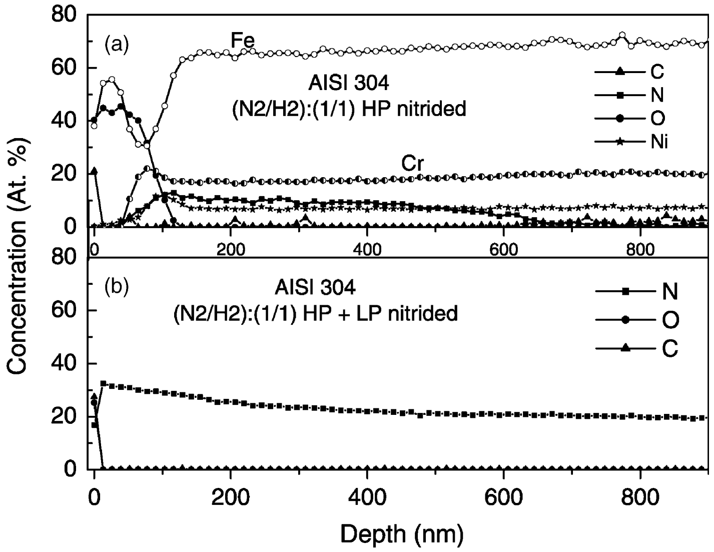

Fig. 4. AES profiles of SS 304, plasma of (N_2/H_2):(1/1) mixture nitrided (a) bias 500–700 V, current 200–300 mA, pressure 4×10^{-1} mbar and temperature around 500 °C and (b) alternating high pressure (HP) cycle with a low pressure (LP) cycle, temperature range of 300–500 °C.

achieved by both glow discharge ion nitriding and the high voltage pulsing of the SS 304 samples. It was confirmed that high temperature regimes can be explored and we hope faster nitrogen diffusion in metals can be achieved by this hybrid treatment.

PIII treatment alone with 10 kV, 50 μs, 400 Hz condition allowed maximum sample temperatures of about 300 °C. However, it is necessary to pulse the samples for more than 30 min under that pulser condition to reach these temperatures. Therefore an additional heating source as the ion nitriding glow is necessary to access the high temperature PIII mode when using a power limited pulser (<1 kW) as in our case.

A major difficulty arising in our experiment exploring the hybrid PIII/nitriding processing was the buildup of carbon and oxygen containing film, which makes it difficult to implant nitrogen ions into the samples for sufficiently long time treatments. We conjecture that this film deposition on

Table 1
SS 304 surface Vickers hardness measurements with 25 gf load, for different nitriding and nitriding/PIII processing

Treatment	$HV_{0.025}$ (enhancement over standard SS 304 hardness)
Sequential plasma nitriding, $N_2/H_2 = 1:1$ gas mix, 15 min HP, T: 450 °C, alternating with 15 min LP, T: 330 °C, total treatment time of 150 min	542.1 (2.7×)
Plasma nitriding, pure nitrogen, 800 V bias, HP, 2 h at 330 °C	348.3 (1.7×)
Sequential nitriding, pure N_2, small intervals (5 min) HP, T: 450 °C, followed by longer nitriding times (15 min) LP, T: 330 °C, 150 min total nitriding time	326.8 (1.6×)
Sequential nitriding, $N_2/H_2 = 80:20$ gas mix, small intervals (5 min) HP, T: 450 °C, followed by longer nitriding times (15 min) LP, T: 330 °C, 150 min total nitriding time	360.5 (1.8×)
75 min pure N_2, plasma nitriding, HP, −600 V bias, followed by 75 min pure N_2 PIII, at 10 kV pulses, 8×10^{-4} mbar	346.9 (1.7×)
75 min, $N_2/H_2 = 50:50$ plasma nitriding HP, −600 V bias, followed by 75 min $N_2/H_2 = 50:50$ PIII, at 10 kV pulses, 8×10^{-4} mbar	318.7 (1.6×)

HP: high pressure, 3–4×10^{-1} mbar, LP: low pressure, 8×10^{-4} mbar.

the sample surface is due to the hydrocarbon containing oil vapour (and residual oxygen) from the diffusion pump which contaminates the process chamber when high pressure ion nitriding is performed. This could be avoided by using an oil free vacuum system which can operate continuously under working pressures around 5×10^{-1} mbar. The above results are summarized in Table 1 where we show the treatment conditions and the corresponding Vickers hardness obtained with 25 gf load. All of the treatments produced surfaces significantly harder than the standard SS 304 surface.

4. Conclusion

Austenitic steel samples were nitrided combining glow discharge ion nitriding and PIII. The sequential treatments, combining high pressure and high temperature stage followed by lower pressure and temperature nitriding with pure nitrogen or with a mixture of nitrogen and hydrogen and treatments combining ion nitriding with PIII, showed good results.

The best results were obtained from the sequential nitriding, under plasma of the (N_2/H_2):(1/1) gas mixture condition, in two steps: the first, ion nitriding at high pressure, when the sample reaches high temperature, followed by a low pressure glow ion nitriding with negative bias. A thick layer was created with surface hardness of 2.7 times the standard non-treated surface value. XRD showed the presence of γ_N, the expanded austenite, a form of austenite with solid solution of nitrogen with enhanced hardness. Auger measurements showed >600 nm penetration of nitrogen and the real nitrided layer will be measured by glow discharge optical spectroscopy technique soon.

Other nitriding sequences showed 1.6–1.8 times enhancements in surface hardness. In some cases, the presence of α-phase, the martensitic iron, ensures some enhancement in the surface hardness, as the martensite is harder than the austenite.

On the other hand, ion nitriding combined with PIII showed only hardness enhancements in the order of 1.6–1.7 times the standard hardness.

Thus, we were able to produce thick layers of nitrides and expanded austenite by fast and reliable treatment, ensuring enhancements of 1.6–2.7 times in the surface hardness of austenitic stainless steel AISI 304. Further experiments with hybrid nitriding and PIII is underway.

Acknowledgements

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