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# Parametric study of nitrided AISI 304 austenite stainless steel prepared by plasma immersion ion implantation

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**Abstract**

This paper investigates the characteristics of plasma immersion nitrogen-ion implanted AISI 304 austenite stainless steel against such processing parameters as bias voltage (5–20 kV), substrate temperature (300–500 °C), and implantation fluence ($1.4\times10^{18}$–$4.2\times10^{18}$ $cm^{-2}$). Characteristics of the as-implanted specimens under investigation included elemental depth profile, hardness depth profile, crystallographic structure, and corrosion behavior and were determined using glow discharge spectrometry (GDS), the Vickers hardness tester, X-ray diffractometry (XRD), and the potentiodynamic polarization test, respectively. The results show that nitrogen depth profiles strongly depend on these processing parameters and closely relate to the corresponding chromium depth profiles. The hardness depth profiles increase and widen as substrate temperature, bias voltage, and implantation fluence increase. In particular, an improvement in hardness is accompanied by a reduction in corrosion resistance when substrate temperature reaches 500 °C. The corrosion-resistance degrader, CrN, precipitates as substrate temperature exceeds 450 °C, a phenomenon which is clearly evident in the chromium depth profiles as well as the XRD results.


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## 1. Introduction

In recent years, surface modification of materials has attracted much interest in both academic research and industrial applications. Among currently available technologies, plasma immersion ion implantation (PIII or $PI^3$) [1] has gained the most attention primarily due to its exceptional capability of being processed at lower temperatures, an especially significant factor in treating widely-used materials such as austenitic stainless steels. PIII (i.e. immersing the specimen in plasma) is a hybrid technology that combines nitrogen ion implantation with plasma nitriding processes [2]. During the process of applying high-voltage (HV) pulses on-time, the specimen is negatively biased while nitrogen ions are driven from the plasma and implanted into the specimen. However, during the process of applying HV pulses off-time, additional nitrogen atoms are thermo-chemically absorbed into the specimen through a direct current (D.C.) self-bias [2].

In essence, austenitic stainless steels contain good mechanical properties and excellent corrosion resistance, making them well-suited for a wide range of fields and uses. However, their poor hardness properties greatly limit the extent of their usage. Hence, the feasibility of improving their hardness properties via surface modification treatments while at the same time retaining their intrinsic superior properties (e.g. corrosion resistance) is deemed beneficial. A thorough understanding of their properties in reaction to the processing parameters of surface modification treatments is therefore necessary and constitutes the main objective of this study. Furthermore, AISI 304 austenite stainless steel (hereafter abbreviated as AISI 304) is one of the most popular steels currently in use. Hence, this study aims to parametrically investigate the properties of nitrided AISI 304 against various processing parameters available in PIII technology.

## 2. Experimental details

AISI 304 specimens measuring 3 cm×2.5 cm in area and 1.5 mm in thickness were used in the present study. The

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constituents (wt.%) in the specimens included Cr (18.18), Ni (8.48), Mn (1.75), Si (0.5), Mo (0.36), C (0.051), N (0.005), S (0.005), P (0.028), and Fe (70.641) [3]. Prior to the PIII treatments, all of the specimens underwent a thorough process of polishing and cleaning. In addition, a 15 kV argon ion bombardment was employed to enhance surface cleanliness and to perform beam heating of the specimens until the desired substrate temperature ($T$) was reached. Substrate temperature was monitored using a thermocouple attached to the backside of the specimens. In this study, the reacting gases used in the PIII treatments were comprised of hydrogen and nitrogen molecules at an optimum molecule-number-ratio ($H_2$:$N_2$) of 4 to 1 in order to produce a thicker nitrided layer with greater nitrogen content and superior properties [4]. Notably, the role of hydrogen in the reacting gases is apt to reduce oxides [4] and to better enable more nitrogen atoms to diffuse further into the bulk. The working pressure was $10^{-3}$ Torr. The microwave plasma was formed by electron cyclotron resonance (ECR). In regards to the nitrogen constituent, the ion $N_2^+$ and active molecule $N_2^*$ were the main species in the plasma [5]. It is thus reasonable to assume that all of the implanted nitrogen ions were $N_2^+$. Also, Langmuir probe measurements of the plasma yielded an electron temperature of 3 eV and a plasma density of $10^{10}$ $cm^{-3}$. That is, the plasma contained $0.8\times10^{10}$ $H_2^+/cm^3$ and $0.2\times10^{10}$ $N_2^+/cm^3$. High-voltage (HV) pulses with a width ($t_p$) of 20 μs and a bias voltage ($V_b$) were used to negatively bias the specimens. The substrate temperature was kept constant by varying the repetition rate ($f$) of HV pulses. The processing parameters under investigation consisted of bias voltage (5–20 kV), substrate temperature (300–500 °C), and implantation fluence ($\Phi=1.4\times10^{18}$–$4.2\times10^{18}$ $cm^{-2}$). The unit of $cm^{-2}$ used for $\Phi$ hereafter stands for $N_2^+/cm^2$. Implantation fluence, including contributions from HV pulses on-time ($\Phi_{on}$) [6] as well as off-time ($\Phi_{off}$) [7], can be obtained using the following formulas:

$$\Phi_{on} = \frac{t}{qt_p}\int_0^{t_p} J_c(t)\mathrm{d}t, \tag{1}$$

where $t$ denotes implantation time, $q$ represents electric charge, and $J_c(t)$ denotes current density across the sheath edge;

$$J_c(t) = \frac{4}{9}\varepsilon_o\left(\frac{2q}{M}\right)^{1/2} V_b^{3/2}\left[\frac{1}{s(t)^2}+\frac{s_o^2}{s(t)^4}\right], \tag{2}$$

where $\varepsilon_o$ denotes the permittivity of free space, $M$ represents the effective mass of the plasma, $s(t)$ denotes the location of the sheath edge relative to the specimen, and $s_o$ represents the thickness of the initial matrix sheath;

$$\Phi_{off} = \frac{t}{q}(1-t_p f)J_s, \tag{3}$$

where $J_s$ denotes the stationary current density and is given by

$$J_s = 0.6 n_o v_B, \tag{4}$$

where $n_o$ denotes plasma density and $v_B$ represents Bohm velocity.

In the characteristic analysis, elemental depth profiles in the specimens were measured using glow discharge spectrometry (GDS) while hardness depth profiles were probed using a Vickers hardness tester with a load ranging from 10 to 500 g. Corrosion behavior in the specimens was analyzed through the potentiodynamic polarization test using 1 M $H_2SO_4$ solution at ambient temperature. A Gamry PC4/300 electrochemical analyzer was used in conducting the polarization analysis. The sweep rate was 1 mV/s. The potential was measured against a saturated calomel electrode (SCE). The crystallographic structures in the specimens were identified using X-ray diffractometry (XRD). The X-ray employed was the Kα line of copper atoms and the wavelength was 1.5405 Å.

## 3. Results and discussion

Fig. 1 displays $\Phi_{on}/\Phi_{off}$ versus repetition rate for various bias voltages. All of the other parameters are kept constant. As can be seen, $\Phi_{on}/\Phi_{off}$ increases as repetition rate and bias voltage increase, while $\Phi_{off}$ outweighs $\Phi_{on}$ at lower repetition rates. Also, $\Phi_{on}/\Phi_{off}$ increases as pulse width increases but is independent of implantation time. Furthermore, in this study, the repetition rates required to obtain substrate temperatures of 300, 400, and 500 °C with a bias voltage of 15 kV were 82, 120, and 210 Hz, respectively. The repetition rates required to obtain a substrate temperature of 400 °C with bias voltages of 5, 10, 15, and 20 kV were 1010, 320, 120, and 41 Hz, respectively. These results show that there is a greater repetition rate when the derived substrate temperature increases but bias voltage decreases.

Fig. 2 illustrates both the nitrogen and chromium depth profiles against bias voltage, substrate temperature, and implantation fluence. As can be seen, nitrogen depth profiles become broader and deeper as bias voltage increases. Also, the nitrogen depth profiles are far beyond the range of ion-implanted nitrogen. For example, the nitrogen depth profile for the 20 kV bias voltage is visible up to 6 μm which is much deeper than the projected range ($R_p$) and projected range straggling ($\Delta R_p$), which are of 13.5 and 7.1 nm, respectively, for the 10 keV $N^+$ ion implantation yielded from SRIM calculations [8]. In short, a much thicker nitrided layer can be obtained through the PIII treatments at elevated substrate temperatures. In particular, an

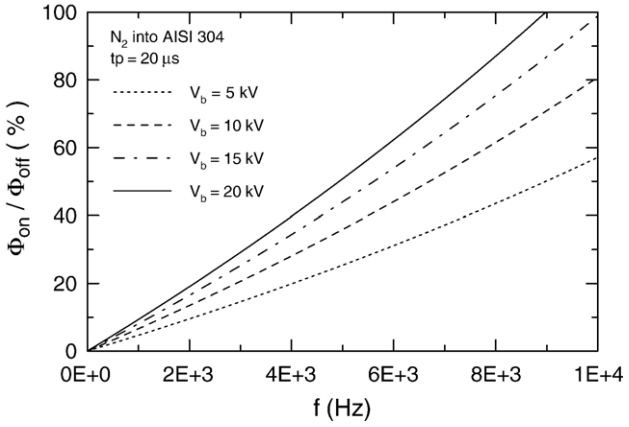


Fig. 1. $\Phi_{on}/\Phi_{off}$ as a function of repetition rate for various bias voltages.