Int. J. Electrochem. Sci., 13 (**2018**) 353 – 361, doi: 10.20964/2018.01.23

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Effect of *in situ* Ion NitrideTreatment on the Corrosion Behavior of Titanium

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Received: 26 August 2017 / *Accepted:* 23 October 2017 / *Online Published:* 1 December 2017

Ion nitriding was applied to titanium grade Ⅱ(TA2) to observe the impact it had on corrosion behavior of Titanium structures. X-ray diffraction, potentiodynamic polarization, electrochemical impedance spectroscopy and Mott-Schottky were used to study the microstructure, electrochemical corrosion properties and semiconducting behaviors of Titanium samples. Cubic TiN and tetragonal Ti_2N were formed using ion nitriding treatment. Compared with TA2, ion nitrided TA2 had better resistance to corrosion. The Mott-Schottky curves indicated that the surface layers of TA2 and ion nitride TA2 were not sensitive to the frequency response. TA2 showed n-type and p-type semiconducting behaviors over the potential range measured However, ion nitride TA2 showed only n-type semiconducting behavior.

Keywords: Ion nitriding; TA2; Corrosion resistance; Semiconducting behavior

1. INTRODUCTION

Titanium and titanium alloys have been widely used in the chemical industry, aerospace, artificial joints, odontology, pressure vessels, etc. because of their superior high specific strength, fatigue and corrosion resistance, and biocompatibility [1-5]. Although titanium and titanium alloys have considerable advantages compared to other metal and their alloys, surface modification is often used to improve the wear and corrosion resistance in some situations. Hence, a number of surface treatments have been developed to improve wear and corrosion resistance, including cold spray coatings, hot spray coatings, diffusion coatings, etc [6-8].

In recent years, TiN has been successfully used as coatings to protect against damage as a result of wear and improve the corrosion resistance of titanium alloys, due to its high hardness, conductivity, density and chemical stability. Specifically, a surface coating of TiN prevent corrosives penetrating the

structure and protecting it from corrosion. A considerable number of studies have been undertaking. TPN (triode plasma nitriding) [9], PVD (physical vapor deposition) [10, 11] and CVD (chemical vapor deposition) [12] were used to coat titanium and titanium alloys with TiN, showing excellent results in the prevention of corrosion. However, there are still some problems, such as low coat binding force and high cost, which need to be addressed.

The ion nitriding method is a traditional *in-situ* preparation process, which is widely used to enhance the resistance to wear of steels. The major advantage of the ion nitriding method is that the nitride coatings are formed *in-situ* with no obvious interface between the substrate and coating, which eliminates the existence of a coating binding force. In this work, we adopt the ion nitriding method to form TiN_X *in-situ* on industrially pure titanium grade Ⅱ(TA2), and study the electrochemical corrosion properties and semiconducting behaviors.

2. EXPERIMENTAL

2.1 Ion nitriding of TA2

Industrially pure titanium grade II (TA2) was used as the substrate. After sand- blasting and oil removal, it was cut into squares 2×2 cm. The ion nitriding process was carried out in a glow plasma vacuum furnace filled with H_2 and N_2 at a ratio of 3 to 10 and temperature 850℃ for 8 h, and then cooled inside the furnace to room temperature. Ion nitrided TA2 had a golden appearance (Fig. 1).

Figure 1. Photos of ion nitrided TA2 and untreated TA2.

2.2 Microstructure

D/max 2000PC X-ray diffraction equipped with Cu-Kα radiation and Ni filter was using to determine the X-ray diffraction character of treated TA2.

2.3 Electrochemical measurement

A three-electrode cell system was adopted to measure the electrochemical properties using EG&G PAR potentiostat/galvanostat (model 273). The ion nitrided TA2 plate and untreated TA2 plate were the working electrode and a platinum plate was the counter electrode. KCl saturated calomel electrode (SCE) was taken as a reference. 3.5% NaCl solution was used as the electrolyte. The polarization curves tested were between the potentials of -0.2-1.5 V (vs. SCE) at 0.5 mV/s. The EIS

measurement was taken in a open circuit (vs. SCE) with an ac sine signal amplitude of 5 mV, and frequency range of 0.01Hz to 100 kHz. A Mott-Schottky measurement was taken between -0.2-1.5 V (vs. SCE) with an ac signal amplitude of 5 mV and testing frequencies of 100 Hz and 1000 Hz.

3. RESULTS AND DISCUSSION

3.1 Composition and microstructure

The X-ray diffraction patterns of the TA2 and ion nitrided TA2 are shown in Fig. 2. The results indicate that only peaks characteristic of Ti can be observed for TA2, and TiN and Ti_2N peaks can be observed alongside the Ti peak. Furthermore, data from XRD indicated that the crystal structure of TiN is cubic and that for Ti_2N is tetragonal.

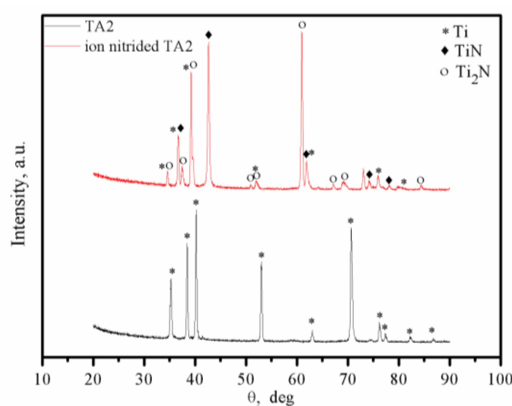


Figure 2. XRD patterns of untreated TA2 and ion nitrided TA2.

3.2 Potentiodynamic corrosion testing

The potentiodynamic polarization curves for TA2 and ion nitrided TA2 in 3.5% NaCl solution are shown in Fig. 3, and exhibit typical active to passive properties. No obvious over-passivation phenomenon can be observed within the range of potentials measured. Corrosion potential is usually used to measure the tendency of corrosion. The TA2 exhibits a corrosion potential of -0.063 V (vs. SCE) and the corrosion potential of ion nitrided TA2 is greater than that of TA2, -0.031 V (vs. SCE), which indicates that TA2 has higher susceptibility to corrosion than the ion nitride treated TA2. The corrosion current density can be used to assess the kinetics of the corrosion reaction and calculate the corrosion rate. The corrosion current density of ion nitride TA2 was 1.855×10^{-5} A/cm^2, which is significantly lower than that of untreated TA2 (1.417×10^{-4} A/cm^2). Ion nitriding reduces the tendency of TA2 to corrode and the corrosion rate. The reason for this is due to the presence of TiN_X coating covering the entire surface, which will then reduce the accessibility of the corrosive media to the substrate and causes a retardation in the electrochemical polarization process [13]. In NaCl solution, chloride ions are adsorbed onto the surface, not enabling oxygen into the passive film (TiO_2). The

cations migrate away to the electrolyte continuously, resulting in lower corrosion potentials of TA2. This results in ionic conduction and dissolution rates are greater compared to untreated TA2 which are absent of chloride ions. Hydrolysis of the dissolved metal ions results in an increase in hydrogen ion concentration [14, 15]. The corrosion rate increases with increasing chloride ion concentration resulting in severe corrosion. However, the existence of a TiN_X layer created by ion nitriding isolates the Ti substrate from electrolytes and chloride ions. Chloride ions lost the capacity to crow oxygen out from the passive film, which protects Ti from being corroded.

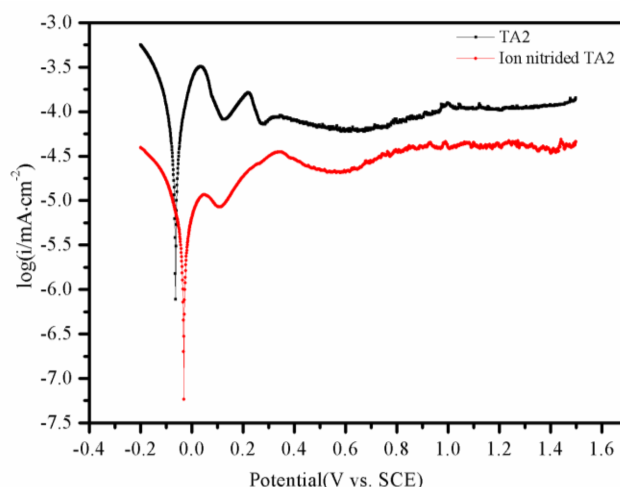


Figure 3. Polarization curves of untreated TA2 and ion nitrided TA2.

3.3 Electrochemical impedance spectroscopy

The EIS responses of TA2 and ion nitrided TA2 in 3.5% NaCl solution were carried out with an open-circuit potential, shown in Fig.4. The Bode and Nyquist plots indicate similar semicircular patterns at high frequency, but the patterns differ in the middle to low frequency ranges. The TA2 sample showed a typical capacitive response reflecting the inert characteristics of titanium.

The measured impedance data of TA2 can be simulated using an equivalent circuit model, shown in Fig. 5(a). In this equivalent model, Q is the constant phase element, Rt the charge transfer resistance or polarization resistance, and Rs represents the solution resistance. It can be used to calculate the formation and dissolution of the passive film reaches the dynamic balance. The capacity response at high frequency of the ion nitrided TA2 is similar to that of untreated TA2, indicating the electrochemical process is charger transferred controling [16]. A linear relationship exists at low frequencies of the ion nitrided TA2, indicating that the electrochemical process is mass transferred controlling [17]. Researchers [18] had reported this phenomenon where more and more chloride ions adheres to the surface as the electrochemical process proceeds. The impedance data of ion nitride TA2 can be measured by simulating with an equivalent circuit model, shown in Fig. 5(b), where Q is the constant phase element representing the capacitance behavior of the surface, Rt is the charge transfer resistance, Rs is represents the solution resistance, W is the Warburg resistance.

CPE (constant phase element) reflects the capacitance bahavior, which is a frequency dependent capacitance expressed in Eq. (1)

$$CPE = \left[Q(j\omega)^n\right]^{-1} \qquad \text{Eq. (1)}$$

Where Q is a frequency independent constant, ω is the angular frequency, n is power factor, n with a value of 0 corresponds to the CPE with a pure resistor, a value of 1 corresponds to the CPE with a pure capacitor and a value of 0.5 corresponds to Warburg impedance. The fitted EIS data for all the electrical parameters are listed in Table 1.

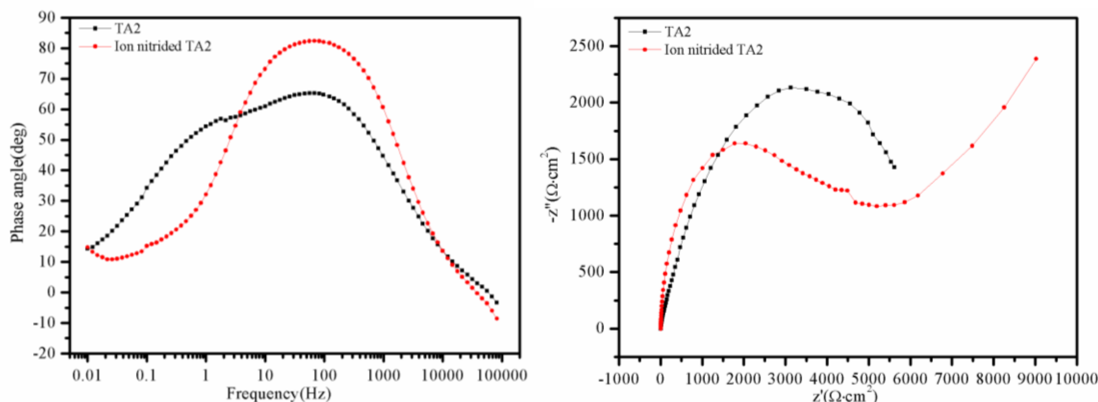


Figure 4. EIS patterns for untreated TA2 and ion nitrided TA2 of (a) Bode diagrams, (b) Nyquist diagrams.

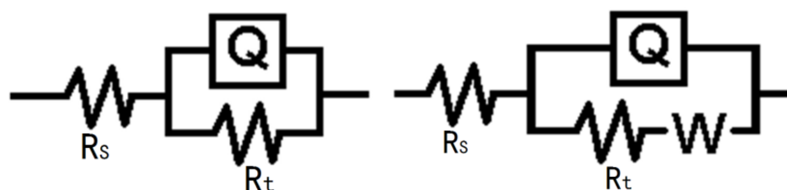


Figure 5. Equivalent circuit model for EIS of (a) untreated TA2, (b) ion nitrided TA2.

Table 1. Fitting EIS parameters of the samples.

	Rs/ ($\Omega \cdot cm^2$)	Q/ ($s^n \cdot \Omega^{-1} \cdot cm^{-2}$)	n	Rt/ ($\Omega \cdot cm^2$)	W/ ($s^{0.5} \cdot \Omega^{-1} \cdot cm^{-2}$)
Ion nitrided TA2	4.31	1.93 E-4	0.7354	6241	---
Untreated TA2	4.19	2.75 E-5	0.9486	3736	8.97 E-4

The charge transfer resistance was characterized using the capacitance loop to determine the corrosion resistance of the passive film and reflects the rate of the electrode reaction. Electrode processes on the surface of the specimen are primarily redox process of losing or gaining electrons. As can be seen in Table 1, the Rt value of untreated TA2 was 3736 Ω and that of ion nitrided TA2 was 6241 Ω. This indicates the ion nitriding process can increase the charge transfer of resistance. The stability of the passive film of ion nitriding TA2 is greater compared to untreated TA2, indicating the

TiN_X coating can effectively prevent TA2 from being corroded. The Q reflects the double layers of capacitance on the surface of the electrode, which is inversely proportional to roughness. The Q value of ion nitriding TA2 is 1.93×10^{-4} $s^n\cdot\Omega^{-1}\cdot cm^{-2}$, greater than that of untreated TA2 (2.75×10^{-5} $s^n\cdot\Omega^{-1}\cdot cm^{-2}$), indicating that the roughness of TA2 is greater than ion nitrided TA2. The possible reason for this phenomenon could be the high energy plasma bombarding during the ion nitriding process. Warburg impedance indicates there was a diffusion controlling step, which was generated by a gathering of a large number of chloride ions on the surface during the electrochemical process.

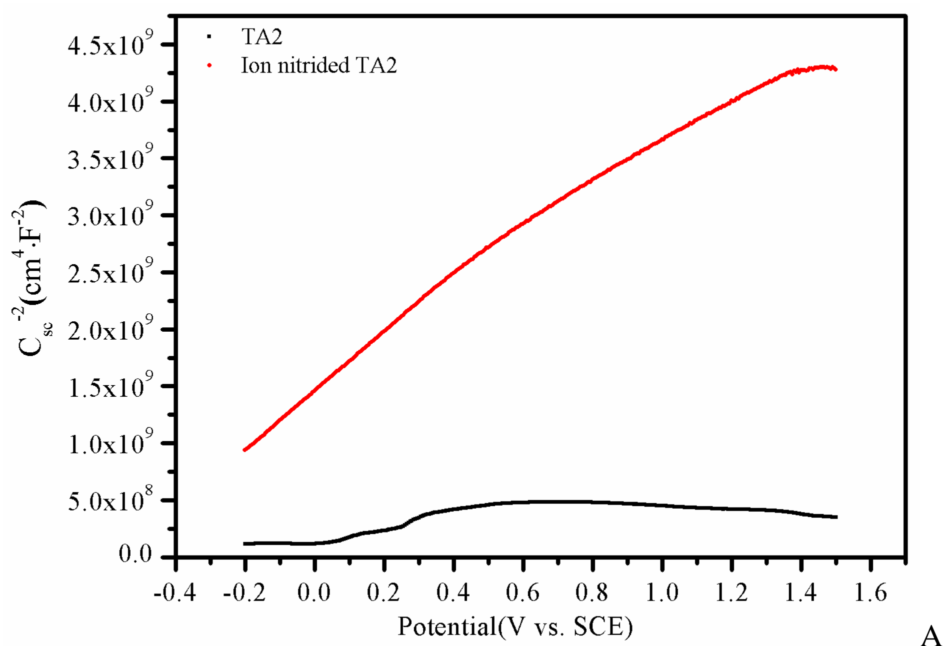
3.4 Mott-Schottky analysis

Mott-Schottky analysis was used to determine the semiconductor type and dopant density of coatings or passive films. Capacitance of the space charge region (C_{sc}) is based on the Mott-Schottky relationship of a semiconductor represented, by Eq. (2) and Eq. (3): n-type semiconductors can be calculated using Eq. (2) and p-type semiconductor can be calculated using Eq. (3).

$$\frac{1}{C_{sc}^2} = \frac{2}{\varepsilon\varepsilon_0 e N_D A^2}(E - E_{fb} - \frac{kT}{e}) \quad \text{Eq. (1)}$$

$$\frac{1}{C_{sc}^2} = \frac{2}{\varepsilon\varepsilon_0 e N_A A^2}(E - E_{fb} - \frac{kT}{e}) \quad \text{Eq. (2)}$$

Where C_{sc} is the space charge capacitance, N_D and N_A represents the donor and acceptor densities for n-type and p-type semiconductors, respectively, ε the relative electric permittivity, ε_0 the vacuum electric permittivity, e the elementary charge, A the surface area, k the Boltzmans constant, T the absolute temperature, E_{fb} the flat band potential and E is the applied potential [19]. E_{fb} can be calculated from the linear line in dC_{sc}/d_E plot with constant intercept [20]. It is possible to calculate the concentration of electron donors or acceptors in the space charge region, as well as estimate the flat band potential.



A

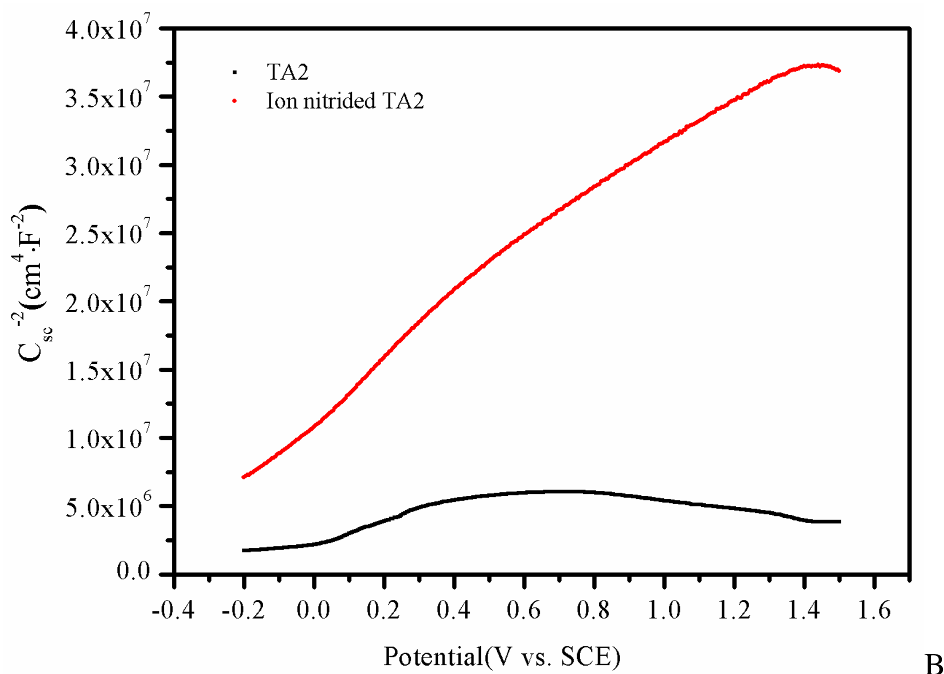


Figure 6. Mott-Schottky curves for untreated TA2 and ion nitrided TA2 of (a) 100 Hz, (b) 1000 Hz.

Fig. 6 shows Mott-Schottky plots of untreated TA2 and ion nitrided TA2 samples in 3.5% NaCl solution at a frequencies of 100Hz (Fig.6 (a)), and 1000 Hz (Fig.6(b)). The curves of untreated TA2 and ion nitride TA2 at 100 Hz are similar to those at 1000 Hz, suggesting that they are not sensitive to the frequency response. Moreover, TA2 exhibited duplex structure, according to their n-type and p-type semiconducting behaviors, and ion nitride TA2 only exhibited n-type semiconducting behavior.

Both curves of TA2 at 100 Hz and 1000 Hz exhibit similar behavior and consist of two distingguished regions, suggesting that more than one space charge region existed in the suface layer. The capacities of the space charge regions were connected in series [21]. The positive slope in the potential range of -0.2-0.6 V (vs. SCE) is tyoical of n-type semiconducting behavior, while the negative slope at the potential range of 0.6-1.5 V (vs. SCE) is typical of p-type behavior. At the potential range of -0.2-0.6 V (vs. SCE) the n-type semiconducting behavior is a result of the TiO_2 passive film properties. At the potential range of 0.6-1.5 V (vs. SCE), the p-type semiconducting behavior can be correlated to an increase in the conductivity of the passive film, a result of the generation of cation vacancies (electronic acceptor and p-type dopants) at the interface of the passive film and solution [19].

Similar to TA2, both curves of the ion nitrided TA2 at 100 Hz and 1000 Hz exhibit similar behavior, but consist of only one region. The positive slope indicates a n-type semiconducting behavior, which is related to the properties of the TiN surface layer. The Helmholtz layer at the dielectric-electrolyte contact, increased the area of the Helmholtz layer over the dielectric due to the high corrosion resistance of TiN [22].

4. CONCLUSIONS

Ion nitriding treatment was carried out on TA2 in this study. Cubic TiN and tetragonal Ti_2N were produced after ion nitriding of TA2. Potentiodynamic polarization indicated that TA2 was corroded more easily with a higher corrosion rate compared to ion nitrided TA2. Electrochemical impedance spectroscopy indicated that the formation and dissolution of the passive film achieved a dynamic balance with TA2. The electrochemical process of ion nitride TA2 was controlled by electrochemical polarization and concentration polarization. The Mott-Schottky plot indicated that the surface layers of TA2 and ion nitrided TA2 were not sensitive to the frequency response. Moreover, TA2 showed n-type semiconducting behavior at -0.2-0.6 V (vs. SCE) and p-type semiconducting behavior at 0.6-1.5 V (vs. SCE), which reflected the properties of the passive film and the process of dynamic balance. However, ion nitride TA2 showed n-type semiconducting behavior across the potential range measured, reflecting the properties of TiN_X film.

ACKNOWLEDGEMENTS
This work was supported by scientific research key project fund of The Education Department Henan Province of China under Grant (number 16A460008).

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