The Effect of Gas Nitriding Process on the Corrosion Behavior of TiO_2 Coating Formed by Plasma Electrolytic Oxidation

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1. Introduction

Titanium has excellent corrosion resistance in acidic, alkaline, and organic environments. Different methods have been proposed for titanium coating, referred to as plasma spraying, anodic oxidation, sol-gel, and vapor deposition. Plasma electrolytic oxidation (PEO) is a relatively new method; Coatings applied by PEO have a two-layer structure consisting of an insulation layer and a porous layer. Coatings applied with this method have good adhesion to the substrate, which increases its performance. In general, the PEO is based on the anodic polarization in an aqueous electrolyte under plasma discharge conditions on an anode surface. Today, nitriding is used as an essential process in the industry. Nitriding was first used in industrially in 1920. Surface nitriding increases wear resistance, fatigue strength, surface hardness, and corrosion resistance. If the nitriding temperature exceeds 600℃, the rate of nitrogen incorporation into the titanium oxide increases, and the oxygen content of the system decreases to the point where the non-stoichiometric TiO_xN_y becomes a stoichiometric and stable TiN.

This study aimed to investigate the effect of the gas nitriding process on the corrosion behavior of titanium oxide coating formed by plasma electrolytic oxidation.

2- Materials and methods

The test samples in this study were selected from a grade 2 mm commercially pure titanium sheet with dimensions of 13×13 mm. The coating process was carried out in the first stage by PEO in electrolytes containing 0.2 M sodium carbonate with 5 g/l sodium hydroxide to form titanium oxide. Supplementary coating operation in the second stage was performed by gas nitriding in a tube furnace with N_2 gas (99.99%) flow at a temperature of 1000 °C and a nitrogen pressure of 1.5 bar for 6 hours.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns after PEO and gas nitriding processes in comparison with each other and the substrate metal. The X-ray diffraction pattern of the TiO_2 sample is related to the sample coated by the PEO, which contains rutile crystalline titanium oxide with a tetragonal structure. The XRD pattern of the TiN sample is related to the formation of a nitride layer in the flow of nitrogen gas on the surface of the titanium at high temperatures causing nitrogen to be adsorbed on the surface and diffused into the titanium; It consists of a composite layer on the metal surface consisting mainly of titanium nitrides with a cubic structure such as TiN and Ti_2N, followed by a diffusion zone consisting of a solid solution in the Ti-HCP α phase. In the TiO2-N, in addition to the mentioned phases δ-TiN, ε-Ti_2N, the phase of $TiO_{0.34}N_{0.74}$ with monoclinic structure along with rutile TiO_2 is also observed. The presence of $TiO_{0.34}N_{0.74}$ phase is due to the presence of nitrogen in the structure of TiO_2, which causes the amount of oxygen in the titanium oxide to decrease, increasing the penetration and formation of the mentioned phase and formation a non-stoichiometric composition.

Figure 2 shows a scanning electron microscope image of the surface of samples coated by PEO and gas nitriding. TiO_2 structure (2-a) consists of grains of different sizes and micro-cavities on these grains (pancake structure). The TiN (2-b) sample shows a dense appearance where the nitrified layer is entirely formed on the surface. The TiO_2-N morphology (2-c) is similar to the TiO_2 structure except that spherical particles have formed next to the existing cavities called cauliflower structure.

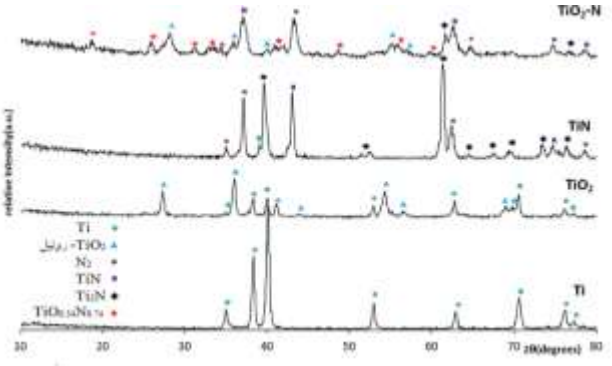

Figure 1. XRD pattern of uncoated and coated

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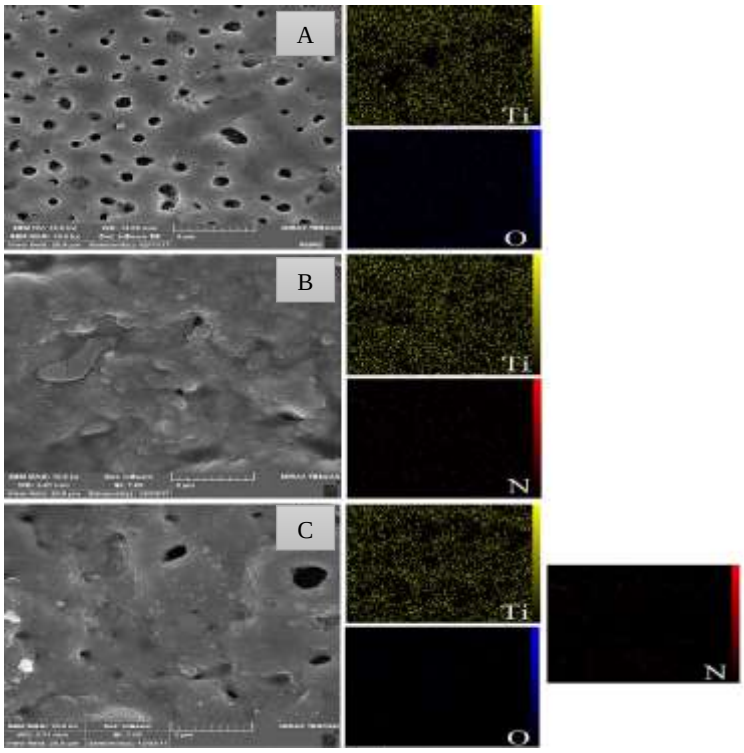

Figure 2. SEM images: (a) TiO2 coated by PEO method, (b) TiN coated by gas nitriding, and (c) TiO2 coated nitrified (duplex) samples by PEO method and gas nitriding

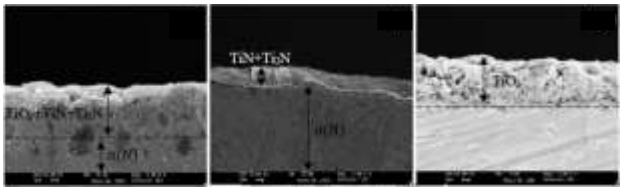

Figure 3. Cross-sectional images of coated specimens: (a) TiO_2, (b) TiN and (c) TiO_2-N

Figure 3 shows the cross-sectional images of the coated samples TiO_2, TiN, and TiO_2-N. As can be seen, after gas nitriding of TiO_2 coating, PEO, the filling of pores and cross-section porosity are observable, which indicates the penetration of nitrogen in the titanium oxide coating.

According to the corrosion results, the coated samples show a higher corrosion resistance compared to non-coated samples. Besides, both dense inner and outer porous coatings have much lower capacitance, indicating higher corrosion resistance of PEO and duplex coated specimens. In general, for TiO_2 and TiO_2-N samples, it can be said that due to the corrosive solution's easy penetration into the cavities of the outer layer, this layer has not shown much effect in electrochemical impedance spectroscopy. Therefore, this layer has no role in corrosion resistance. It, therefore, makes sense to accept the inner layer of the coating as a barrier against corrosion attacks. This layer creates a physical barrier against the corrosive solution and increases the corrosion resistance.

4- Conclusion

During the gas nitriding process on the surface of titanium and titanium oxide, nitrogen diffused into the surface of the samples and caused the formation of TiN, TiO_2-N, and TiO0.34N0.74 phases. The morphology of the TiN and TiO_2-N samples showed that the structure of the TiN sample has a dense appearance with holes in the surface, while the structure of the TiO_2-N sample is similar to the TiO_2 sample, except that the existing cavities are spherical. The corrosion behavior of TiO_2, TiN, and TiO_2-N coated samples showed that the highest corrosion resistance is related to the TiO_2 sample due to the coating's insulation as a result of less probable electron transfer and electrical charge exchange.