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RESEARCH PAPER

INCREASING HARDNESS AND CORROSION RESISTANCE OF COMMERCIALLY PURE TITANIUM BY USING PLASMA NITROCARBURIZING PROCESS

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ABSTRACT

Titanium tends to form nitrides and carbides. The plasma nitrocarburizing technique can generate these nitride and carbide compounds on the material's surface. The objective of this research is to use a plasma nitrocarburizing process to increase the hardness and corrosion resistance of commercially pure titanium. The generation of a thin layer with an average thickness of 1.88 µm was discovered using a Scanning Electron Microscope. The X-Ray Diffraction technique identifies this thin layer made of TiN and TiC compounds. The untreated commercially pure titanium hardness was 105.75 VHN, and the plasma nitrocarburized commercially pure titanium hardness was 312.68 VHN, according to the Vickers micro tester. After plasma nitrocarburizing, the corrosion rate of untreated commercially pure titanium decreased from 0.0061 mmpy to 0.00077 mmpy. The plasma nitrocarburizing process resulted in a 196 percent increase in hardness and an 87 percent reduction in corrosion rate.

Keywords: corrosion; hardness; plasma nitrocarburizing; Tafel; titanium

INTRODUCTION

Hardness and corrosion resistance are material properties that are heavily influenced by surface quality and modifications [1]. Plasma nitriding and nitrocarburizing are examples of thermochemical processes that can be used to modify the material's surface without generating significant size changes [2-5].
Plasma Nitrocarburizing is a surface hardening procedure that involves depositing nitrogen and carbon ions on the material's surface to create a hard nitride and carbide phase. The plasma nitrocarburizing process is carried out at low pressure and with a potential difference to strip the nitrogen and carbon atoms from the gas atoms, resulting in a glow discharge [6].
There are two processes involved in plasma nitrocarburizing: nitrogen and carbon decomposition and ionization. A dissociation event occurs during the decomposition of nitrogen and carbon, in which gas molecules are separated into their constituent atoms due to collisions between free electrons and gas particles. The generated nitrogen and carbon ions subsequently enter the specimen's surface to form a thin layer. Meanwhile, in the ionization process, Nitrogen and carbon ions formed due to the potential difference will move towards the cathode and collide with the specimen on the cathode, the collision causes the atoms on the surface of the specimen to be released and subsequently reacted with nitrogen ions to form nitrides and carbon ions to form carbides. Some of the nitrogen and carbon atoms will diffuse to a deeper place and form a solid solution. The process of deposition of nitrogen and carbon atoms into the surface of the specimen depends on the temperature of the specimen. The process of nitrogen atoms being deposited on a specimen's surface is based on the temperature of the specimen. The atoms in the specimen will vibrate as the temperature rises, causing wider distances between them and allowing carbon atoms to enter deeper between atomic gaps or occupy existing vacancies.
A schematic of the plasma nitrocarburizing equipment is shown in **Fig. 1**. The main components of the equipment are nitrocarburizing tube, vacuum system, heating system, high voltage system, and gas flow system [7].

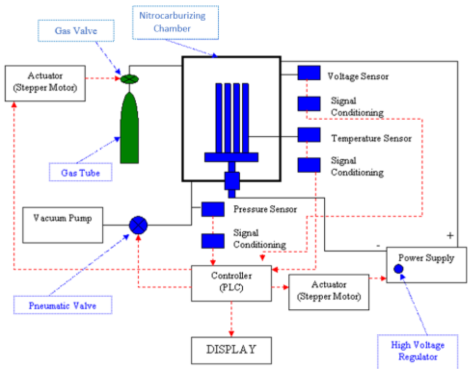

Fig. 1 Plasma nitrocarburizing equipment schematic

The nitrocarburizing chamber serves as a vessel for the nitrocarburizing process, which contains plasma nitrogen and carbon that spreads to the surface of the material. A mixture of gases such as N_2 and CH_4 can be used in the gas stream. Vacuum system using a vacuum pump maintained at a pressure of 10^{-3} mbar. A good vacuum will ensure a cleaner result considering contamination by residual oxygen, for example, can give a mixture of nitride, carbide, and oxide layers on a hardened surface layer. The heating system and temperature control maintain the temperature in the nitrocarburizing chamber by means of a temperature control device at a temperature of 350-590 °C provided by the heating system. The High Voltage System generates the required nitrogen plasma and carbon plasma with high DC voltage (0.5-100 kV) or by using AC radiofrequency. The gas flow system is designed to allow the use of mixed gases at a rated flow rate. For this design, the control and measurement of gas flow from the gas cylinder to the nitrocarburizing chamber is used by using a flowmeter and needle valve. The direction and output of gas in the nitrocarburizing chamber are designed with a variable connection so that the pipe height can be adjusted.

Plasma nitrocarburizing is a popular method for improving steel hardness, wear resistance, and corrosion resistance. Because titanium tends to develop nitrides and carbides, plasma nitrocarburizing can improve the hardness and corrosion resistance of the material. Thermally and mechanically, these newly generated phases are extremely stable [8-11].

Titanium is the 9^{th} most prevalent element in the Earth's crust, but because it binds with other elements, it is rarely encountered in its pure form. Titanium is a metal element that makes up 0.63 percent of the mass of the earth's crust in nature. Ilmenite, rutile, perovskite, anatase, brookite, sphene, and leucoxene are mineral forms of titanium that are widely distributed and generally present. Ilmenite and rutile are the most frequent minerals in nature. These two titanium minerals can be treated further for industrial applications [12-19].

Titanium possesses amazing properties such as a high strength-to-weight ratio, exceptional corrosion resistance, and excellent biocompatibility. Titanium, on the other hand, has weak tribological characteristics, particularly in sliding circumstances. As a result, when titanium is employed as a component that will come into contact with other parts, such as in hip joint replacement, the hardness value must be increased [20]

The titanium nitride and titanium carbide compounds combine to form a thin layer with high strength and hardness. The presence of ionic bonds accounts for the high strength and hardness of the material. In comparison to other primary and secondary bonds, ionic bonds are the strongest between primary atoms [21-22].

Several researchers including Sun et al. and Alphonsa et al. has performed plasma nitrocarburizing to modify the structure and increase its hardness and corrosion resistance. They researched steel and titanium.

Sun et al. [23] used a combination of deformation-led low-temperature plasma nitrocarburizing and deformation to improve Ti6Al4V's low hardness and poor surface wear resistance. To modify Ti6Al4V alloy, a composite process of solid solution + cold rolling and low-temperature plasma nitrocarburizing simultaneous aging is proposed. The experiment results show that when deformation rises, the degree of microstructure refinement increases, and the thickness of the nitrocarburized layer increases. The surface of the nitrocarburized specimen is composed of titanium nitrides and carbide. The overall hardness and wear resistance of Ti6Al4V is greatly increased after modification, and the specimen's cross-sectional hardness is continually improved.

Alphonsa et al. [24] used the plasma nitrocarburizing technique to increase the hardness and corrosion resistance of 2205 duplex stainless steel. The plasma nitrocarburizing technique was carried out for 4 hours at 350, 400, 450, and 500 ºC. The maximum corrosion resistance is seen in specimens treated with plasma nitrocarburizing at 400 °C, as well as a considerable increase in surface hardness. Specimens treated with this technique demonstrate poor corrosion resistance at higher temperatures.

Corrosion resistance and hardness are key material properties [25, 26]. Titanium, on the other hand, is notorious for forming nitrides and carbides. As a result, the objective of this research was to see how the plasma nitrocarburizing technique affected the hardness and corrosion resistance of commercially pure titanium.

MATERIAL AND METHODS

Commercially pure titanium (CP titanium) was used in this investigation, with chemical element concentration of N = 0.04 percent, C = 0.05 percent, H = 0.003 percent, Fe = 0.13 percent, O = 0.11 percent, Al = 0.49 percent, and S = 0.03 percent. The material was polished and etched to get microstructure images using a solution of 2 ml Hydrofluoric Acid (HF), 6 ml Nitric Acid (HNO_3), and 92 ml water (H_2O). After that, the CP titanium phase composition was determined using a Rax Vision RCM 3000 optical microscope. Plasma nitrocarburizing was performed on CP titanium at 450 ºC for 4 hours. At the temperature of 450 °C, the voltage is set higher at 745 volts, with the current 357 mA. The flow rates of N_2 and CH_4 gases into the plasma tube are controlled in a 1:1 ratio. The chamber's pressure was also set at 1.6 mbar.

The thickness of the layer generated on the CP titanium surface following the plasma nitrocarburizing process was measured using metallographic testing with a scanning electron microscope (SEM). The use of SEM test equipment in combination with Energy Dispersive X-Ray Spectroscopy (EDS) offered the added benefit of determining the chemical element content of the CP titanium surface layer following the plasma nitrocarburizing process. The SEM-EDS used was the QUANTA 650. X-Ray Diffraction (XRD) testing was carried out using the X'Pert PRO PANalytical Diffractometers machine to determine the compound or phase bonds formed on CP titanium after the plasma nitrocarburizing process.

The hardness of the CP titanium was determined using hardness testing equipment. The Micro-Vickers Hardness testing method was employed, and the Vickers Matsuzawa MMT-X7 Micro Hardness Tester was used. The loading in this test was carried out for 10 seconds and was given a load of 10 gf. This test was carried out at 5 points on each test specimen, both on untreated CP titanium and plasma nitrocarburized CP titanium.

The corrosion rate of untreated CP titanium and plasma nitrocarburized CP titanium was determined using potentiostat corrosion test equipment. Corrosion testing with a DC potentiostat tester employing an electrochemical approach and a potentiostat technology.

RESULTS AND DISCUSSION

Metallography Test

Figure 1 shows the result of phase observations using an optical microscope on the CP titanium microstructure. The presence of an α-Ti phase can be seen in the figure. Because the α-Ti is the only phase present, titanium is classified as an α-alloy.

The presence of a thin layer with an average thickness of 1.88 μm was observed using SEM on plasma nitrocarburized CP titanium (**Fig. 2**). Ionic bonds between nitrogen ions and titanium ions, as well as carbon ions and titanium ions, generate the TiN and TiC layers [27]. According to the EDS test results, this thin layer contains Ti (42.1 wt%), N (12.9 wt%), and C (12.3%). The presence of Ti, N, and C elements indicates the presence of TiN and TiC compounds (**Fig. 3**). This is confirmed by X-Ray Diffraction testing of the composition.

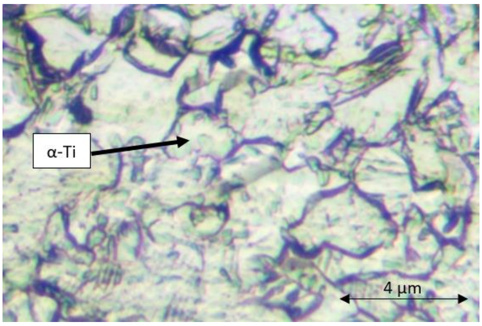

Fig. 1 CP titanium's microstructure

The results of composition testing with X-Ray Diffraction (**Fig. 4**) on untreated CP titanium showed that only titanium (Ti) was present in the material, while plasma nitrocarburized CP titanium showed the presence of titanium (Ti) at a 2θ value of 35.04°, 38.36°, 40.14°, 53.00°, 62.98°, 70.66°, 74.21°, 76.26°, 77.42°, and 86.84°, Titanium Nitride (TiN) at a 2θ value of 74.21°, and Titanium Carbide (TiC) at 2θ value of 38.36°.

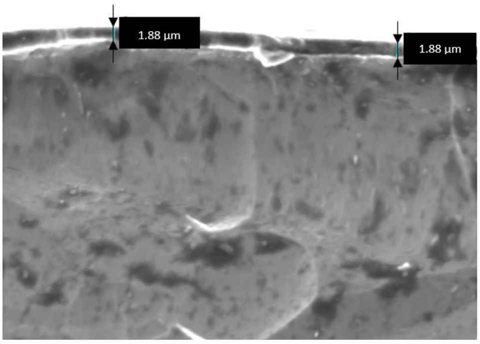

Fig. 2 The thickness of a thin layer on the CP titanium's surface

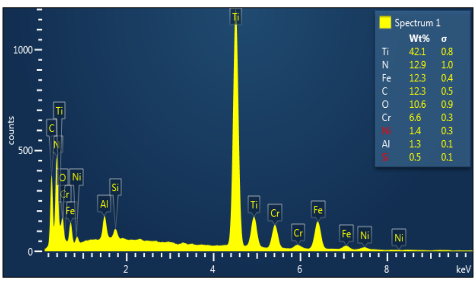

Fig. 3 The Energy Dispersive X-Ray Spectroscopy test result

Hardness Test

Figure 5 shows the results of hardness tests on untreated and plasma nitrocarburized CP titanium. Hardness test on untreated CP titanium resulted in a hardness value of 105.75 VHN. Meanwhile, the results of the hardness test on nitrocarburized plasma showed a hardness value of 312.68 VHN. The results show an increase in hardness by 196%. This increase occurred due to the diffusion of nitrogen atoms and carbon atoms to form TiN and TiC compounds [28, 29]. As has been shown by the results of X-Ray Diffraction.

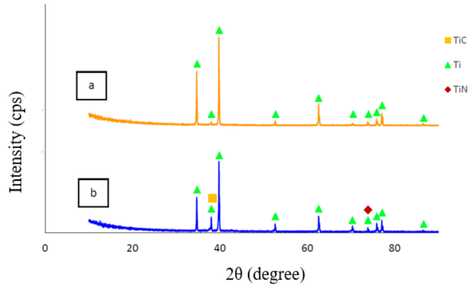

Fig. 4 X-Ray Diffraction test results of (a) untreated CP titanium (b) plasma nitrocarburized CP titanium

Corrosion Test

The processing of the test results in the form of a polarization curve in this study was carried out by the Tafel analysis method. This method is done by extrapolating straight lines on the cathodic and anodic regions so that they meet at one point. This point represents corrosion potential (E_{corr}) and corrosion current density (I_{corr}), so from this data, the corrosion rate can be known. The Tafel analysis method used in the test results is carried out with the help of Corrosion Test software, where the speed of reading from one point to another (scan rate) is set at 5mV/second to the corrosion potential or the number of electrons in the corrosion current. The counter electrode used is graphite, the reference electrode used is saturated calomel and commercially pure titanium as the working electrode.

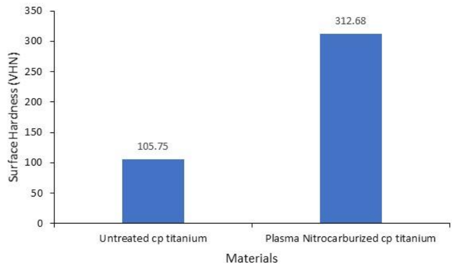

Fig. 5 Hardness test results on untreated and plasma nitrocarburized CP titanium

Corrosion testing was carried out to determine the effect of the plasma nitrocarburizing process on the surface corrosion rate of untreated CP titanium and plasma nitrocarburized CP titanium under aeration conditions. This condition is a common environmental condition that occurs when titanium is exposed to a marine environment. For seawater environmental conditions, the concentration of NaCl used is 3.5%.

This Tafel polarization curve shows an oxidation reaction and a reduction reaction at the working electrode (commercially pure titanium), where the oxidation reaction occurs when electrons are released, while the reduction reaction is a reaction that captures electrons. Corrosion potential can be measured by Tafel extrapolation from the polarization curve, where the size of I_{corr} indicates a lot or at least the dissolved metal ions in the electrolyte solution (NaCl), which means that the metal undergoes an oxidation reaction, and electrons are released so that the positive metal ions will dissolve in the electrolyte solution. If the measured I_{corr} is large enough, this means that the ions dissolved in the solution are also quite large, and vice versa. This has an impact on the metal surface will be damaged or eroded so that it will accelerate the corrosion rate.

Figure 6 shows the corrosion current for untreated CP titanium and Fig. 7 shows the corrosion current for plasma nitrocarburized CP titanium. Where the corrosion current in untreated CP titanium shows a higher value when compared to the corrosion current in nitrocarburized CP titanium plasma. The corrosion current for untreated CP titanium was 3.5903E-1 A/cm^2 while the corrosion current for plasma nitrocarburized CP titanium was 4.4085E-2 A/cm^2.

Changes in corrosion behavior on the surface of nitrocarburized CP titanium plasma are influenced by TiC and TiN compounds as a thin layer on the surface of the specimen to protect and hold the underlying titanium ions so that the titanium ion release process is inhibited. In this case, corrosion is hindered by the formation of a protective layer that inhibits the continuity of the reaction, resulting in a loss of reaction reactivity in CP titanium metal due to the presence of layers of TiC and TiN compounds [30].

Figure 8 provides information on corrosion rates. The corrosion rate is reduced from 0.0061 mmpy to 0.00077 mmpy after plasma nitrocarburizing. The rate of corrosion has been reduced by 87 percent. Passivation, caused by the presence of a thin coating of TiN and TiC, reduces the rate of corrosion.

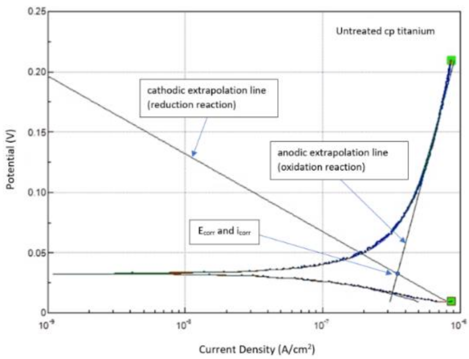

Fig. 6 The corrosion current of untreated CP titanium

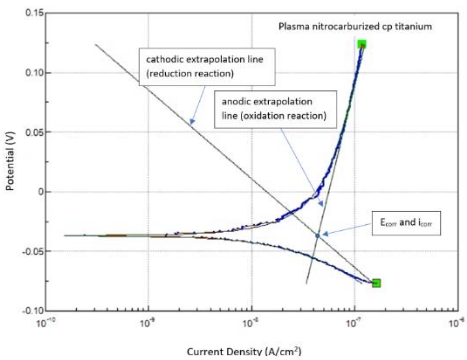

Fig. 7 The corrosion current of plasma nitrocarburized CP titanium

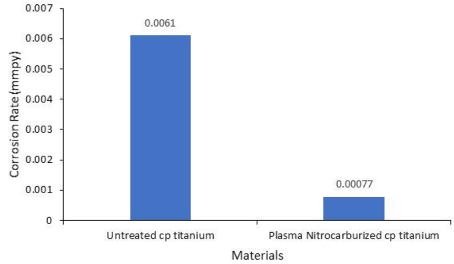

Fig. 8 The corrosion rate of untreated and plasma nitrocarburized CP titanium

CONCLUSION

From the results of the nitrocarburizing plasma process that has been carried out on CP titanium, it can be concluded that:

1. Plasma nitrocarburizing process on the surface of CP titanium can increase the surface hardness of CP titanium by 196%.
2. Plasma nitrocarburizing process on the surface of CP titanium can reduce the corrosion rate by 87%. This means increased corrosion resistance of titanium.

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