Journal of the Technical University of Gabrovo
https://mc04.manuscriptcentral.com/jtug

STUDY ON THE INFLUENCE OF THE TECHNOLOGICAL PARAMETERS OVER THE CORROSION BEHAVIOR AND SURFACE CHARACTERIZATION OF Ti-6Al-4V AND Ti-6Al-7Nb ALLOYS AFTER PLASMA GAS NITRIDING

Hristo Skulev, Deyan Veselinov*
Institute of Metal Science, Equipment and Technologies with Hydro- and Aerodynamics Centre "Acad. A. Balevski", Bulgarian Academy of Sciences, Bulgaria

ARTICLE INFO

Article history:
Received 7 October 2021
Accepted 1 December 2021

Keywords:
titanium alloys, plasma gas nitriding, corrosion, microstructure, phase transformation

ABSTRACT

Titanium and titanium alloys are very attractive materials because of their superior combination of properties that enable their application in many industries. One of their biggest advantage is their excellent corrosion resistance. Two commercial titanium alloys Ti-6Al-4V and Ti-6Al-7Nb have been plasma gas nitrided with 20 kW power in a chamber with pure nitrogen atmosphere for 10 min to improve their surface properties. Their corrosion behavior before and after surface treatment has been studied using a weight loss method. Different media including 4.9M HCl, 0.5M NaCl, and 1.8M H_2SO_4 have been used at different temperatures (20 ºC, 40 ºC, and 80 ºC), for various periods of time to study the influence of the medium and temperature on the corrosion behavior of these materials. The phase modifications and the microstructure of the nitrided layers have been analyzed using X-ray diffraction and optical microscopy.

INTRODUCTION

One of the biggest advantages of titanium alloys is their good corrosion resistance. Much research has been carried out to assess the corrosive behavior of titanium and titanium alloys in different environments before and after different types of thermo-chemical surface treatments, which can either improve or worsen their corrosion resistance properties. The data in the literature [1-6] is quite diverse and inconsistent in this area and that is why a study of the corrosion resistance of two commercial titanium alloys Ti-6Al-4V (TAV) and Ti-6Al-7Nb (TAN) was conducted. The aim of this paper is to quantify the effect of the corrosive medium and test temperature on the corrosion behavior of TAV and TAN before and after thermo-chemical surface treatment by means of plasma gas nitriding. The phase transformations and microstructure of these alloys were also analyzed.

EXPERIMENTAL

Two commercial titanium alloys have been chosen for these tests, Ti-6Al-4V and Ti-6Al-7Nb. Their brief characteristics and chemical compositions are listed in Table 1.

Samples with dimensions of about 20x10x4 mm have been used before and after surface plasma gas nitriding at 20 kW for 10 min. The treatment was performed in a chamber filled with pure N_2 (99.998%) using a flow rate of 100 ml/min. The specimens were surface heated with indirect plasma torch, using 20 kW power for 10 min.

* Corresponding author. E-mail: dveselinov@ims.bas.bg

Table 1 *Characteristics and chemical composition of studied titanium alloys*

Alloy	β transus, ºC	*Chemical composition, wt. %*
Ti-6Al-4V	999±15	Al 5.5-6.7; Mo<0.01; V 4.2-4.5; C<0.08; Fe<0.25
Ti-6Al- 7Nb	1010±15	Al 6.2-6.5; Mo<0.005; Nb 7.2-7.4; Fe<0.12; C<0.004; Ta<0,6

The phase constitution on the surface of the samples after plasma gas nitriding and before the corrosion tests was determined using X-ray diffraction (XRD). The measurements were made at room temperature with a Philips diffractometer using Cu Kα1+α2 radiation from an angle of 30 to 75 deg (2θ), with a step size of 0.017 deg (2θ).

After plasma gas nitriding, all the samples were cut in the middle and the obtained cross sections were ground and polished. In order to study the microstructure of the surface layers after plasma gas nitriding, the cross sections were etched and studied by means of optical microscopy. The corrosion tests described below were carried out on uncut samples so all sides of the corrosion samples were nitrided.

Corrosion tests were performed using the weight loss method. The resistance to the general corrosion was calculated based on the total corrosion losses for different periods of time [7]. One salt solution 0.5M NaCl (2.8 wt.%)

and two reducing acid solutions, 4.9M HCl (12.3 wt.%) and 1.8M H_2SO_4 (14.7 wt.%), were used for the corrosion tests at three different temperatures of 20 ºC (except for the NaCl solution), 40 ºC, and 80 ºC and for different periods of time. All the solutions were prepared using distilled water. At various intervals the samples were taken out of the vessels, washed with distilled water, dried and weighed on an electronic scale. The weight loss values presented in the figures in the Results and discussion section are average values calculated from two samples for each condition.

RESULTS AND DISCUSSION

Phase transformations and microstructure

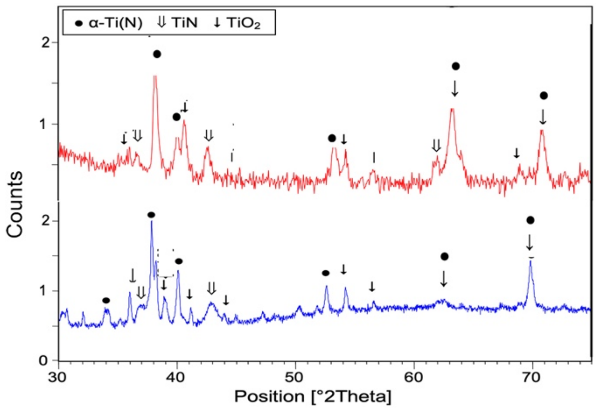

Fig. 1. X-ray diffraction patterns for TAV (blue) and TAN (red) after plasma gas nitriding at 20 kW for 10 min

The microstructure of the cross-sections of TAV and TAN plasma gas nitrided at 20kW for 10 min is shown in Fig. 2. The microstructure is homogenous for both samples, which is probably due to the fact that this surface temperature in below the β-transus temperature for these alloys. Considering that there are phase transformations taking place during plasma gas nitriding process one can expect that the newly formed surface layers would affect the corrosion properties.

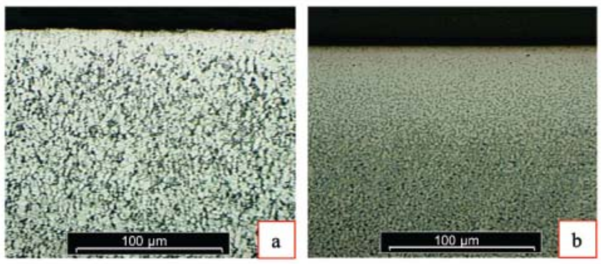

Fig. 2. Microstructure of (a) TAV and (b) TAN after plasma gas nitriding at 20 kW for 10 min

Influence of the alloy composition and surface gas nitriding

The two alloys chosen for the tests have different chemical composition and it is expected that they would have different corrosion behavior in various media. TAV consists of approximately 6% Al and 4% V. The other alloy consists of 7% Nb and 6% Al. Normally, the additions of Nb and V improve the corrosion resistance of titanium alloys and the Al worsens it.

0.5M NaCl - The corrosion behavior of TAV and TAN in 0.5M NaCl at 40°C and 80°C is illustrated in Fig. 3. It can be seen that in 40°C solution TAN samples show better corrosion resistance compared to TAV. At the higher tested temperature – 80°C the relative corrosion resistance between the two alloys is the opposite and the weight loss increases under each condition except for TAN, plasma gas nitrided at 20 kW for 10 min. Gas nitriding worsens the corrosion resistance of TAV at both medium temperatures but improves the corrosion resistance of TAN. Despite the above differences the corrosion resistance of these alloys in 0.5M NaCl at both solution temperatures may be concluded as excellent, with or without the nitriding, considering that the average weight loss values never reach 0.0005 g/cm^2 after 1500 hours of corrosion test. The level of the weight loss in this salt solution is insignificant in comparison to the weight loss in the other two acidic media.

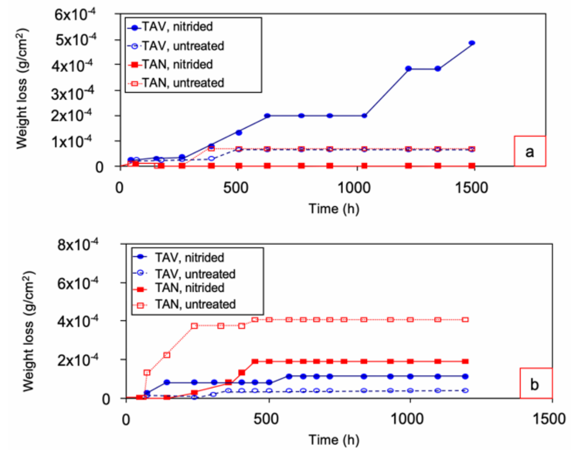

Fig. 3. Weight loss vs. time for TAV and TAN for samples untreated and plasma gas nitrided at 20 kW for 10 min after holding them in 0.5M NaCl at (a) 40ºC and (b) 80ºC

These results are partly in contradiction to the results given in ref. [7], where the authors reported that plasma nitriding significantly increased the corrosion resistance.

4.9M HCl - The weight loss values vs. time of TAV and TAN in 4.9M HCl at 40 and 80°C are graphically given in Fig. 4. The weight loss increases for all samples with the time prolongation and the increase of the temperature, except that there is no significant influence of the temperature on the corrosion behavior of the untreated samples of TAN alloy. The nitrided samples of TAN show in general better performance than the nitrided samples of TAV. The weight loss values of the untreated samples are similar for the two alloys at 20 and 40ºC. At 80ºC TAN shows a better performance in 4.9M HCl in comparison to TAV. These results are in contradiction with the results obtained for Ti-6Al-4V in ref. [8]. The results from this study have shown that plasma gas nitriding worsens the corrosion resistance of these alloys, especially of TAV. The reducing acid solution is very aggressive and breaks the oxide film and the nitrided compound layers, which leads to a significant increase of the weight loss values.

1.8M H_2SO_4 - The corrosion performance of TAV and TAN in 1.8M H_2SO_4 at 40 and 80°C is given in Fig. 5. Surface gas nitriding worsens the corrosion resistance of TAV in 1.8M H_2SO_4 at 20 and 80°C solutions. At solution temperature of 40°C the results of the untreated and nitrided samples are quite similar.

Surface plasma gas nitriding worsens the corrosion resistance of TAN in 1.8M H_2SO_4 at room temperature. After holding the samples of the same alloy at higher medium temperatures of 40 and 80°C, the nitrided samples showed better corrosion resistance than the untreated samples. The weight loss of the nitrided samples of TAN increases with the time prolongation and with the increase of the temperature from 40 to 80°C. In 40 and 80°C 1.8M H_2SO_4 solution surface plasma gas nitriding significantly improves the corrosion resistance of TAN and worsens it for TAV at 80°C. The nitrided samples of TAN show better performance than the samples of TAV and the opposite tendency can be seen for the untreated samples.

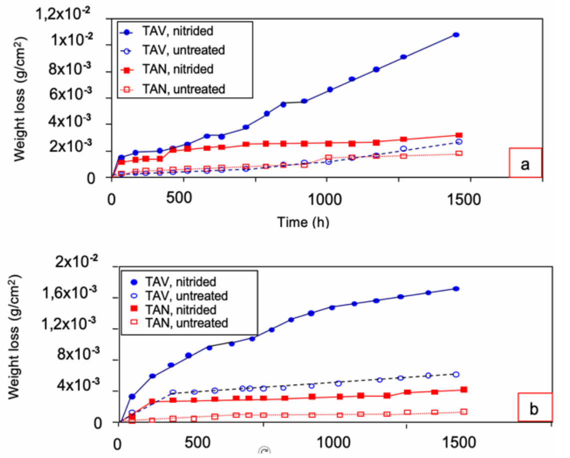

Fig. 4. Weight loss vs. time for TAV and TAN for samples untreated and plasma gas nitrided at 20kW for 10 min after holding them in 4.9M HCl at (a) 40ºC and (b) 80ºC

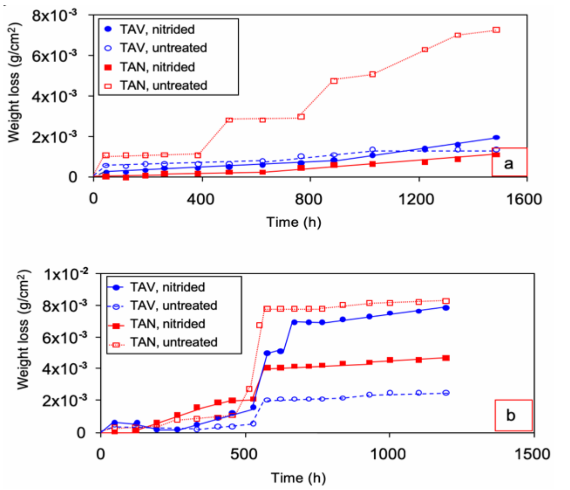

Fig. 5. Weight loss vs. time for TAV and TAN for samples untreated and plasma gas nitrided at 20kW for 10min after holding them in 1.8M H_2SO_4 at (a) 40ºC and (b) 80ºC

Influence of the corrosive medium

The corrosive medium is an important parameter influencing the corrosion behavior of the materials. Titanium alloys are highly resistant to salt solutions and very sensitive to reducing acids. At room temperature TAV alloy has better corrosion resistance in sulfuric acid solution than in hydrochloric acid solution. At 40°C the alloy shows a very good corrosion resistance in 0.5M NaCl. The corrosion resistance worsens in 1.8M H_2SO_4 and in the case of nitrided TAV the weight loss dramatically increases in 4.9M HCl. Similar tendency can be seen at the higher solution temperature of 80ºC. TAN is very resistant to 0.5M NaCl at 40 and 80ºC. The overall corrosion response is different from the one that can be seen for the nitrided TAV alloy.

Influence of the medium temperature

The corrosion resistance of titanium alloys in reducing acid media, such as hydrochloric and sulfuric acids, is very sensitive to the temperature and the acid concentration. When the temperature and/or the concentration of reducing acid solutions exceed certain values, the protective oxide film of titanium may break down, which would result in severe general corrosion.

In 4.9M HCl solution the weight loss values are quite similar at 20 and 40ºC and they increase with the increase of the temperature to 80ºC. The same tendency can be seen in 1.8M H_2SO_4 solution. The sudden jumps in the weight loss values in both reducing acid solutions at 80ºC are probably due to breaking of the surface oxide and nitride layers. As described in ref. [8] the failure of the compound layer is probably due to its local dissolution that leads to the penetration of the solution and then the fast corrosion of the inner titanium matrix that leads to cracking and removal of the fragile compound layer.

The corrosion rate in mm/yr of TAV and TAN was calculated after 1196 hours of exposure in the three different solutions at different temperatures. For both alloys the corrosion rate increases with the increase of the temperature which is in agreement with the data published in the literature. For most of the cases the corrosion rate after 1196 hours of testing is below 0.13 mm/yr, which is the maximum corrosion rate accepted by designers. The only exception is nitrided TAV in 4.9M HCl at 80ºC, for which the corrosion rate is 0.26 mm/yr. The cases for which we have corrosion rate below 0.04 mm/yr can be considered as being under fully passive conditions.

CONCLUSIONS

Corrosion tests of TAV and TAN in one salt solution 0.5M NaCl and two reducing acid solutions 4.9M HCl and 1.8M H2SO4 at solution temperatures of 20, 40 and 80°C up to 1500 hours have been performed in order to study the influence of the nitriding process on the corrosion behavior of titanium alloys. The study of the untreated and plasma gas nitrided TAV and TAN alloys leads to the following conclusions:

1) The surface phase composition of both alloys after surface plasma gas nitriding at 20kW for 10min is a mixture of α-Ti(N), TiN and TiO_2, though the three phases may be layered.

2) The weight loss tests in 0.5M NaCl show that plasma gas nitriding does not have a significant influence on the corrosion resistance properties of TAV and TAN. This treatment worsens the corrosion resistance of these alloys in 4.9M HCl at 20, 40 and 80ºC and of TAV in 1.8M H_2SO_4 at 20 and 80ºC. The results from the corrosion tests in 1.8M H_2SO_4 at 40 and 80ºC show that plasma gas nitriding improves the corrosion resistance of TAN.

3) The results from the weight loss tests show that TAN has better corrosion resistance in comparison with TAV in most of the cases in the corrosive medium used at different temperatures. The weight loss values increase in most cases with the increase of the solution temperatures from 20 to 80ºC and the time prolongation.

4) For most of the cases the corrosion rate of TAV and TAN after 1196 hours of testing in all corrosive medium used in the experiments is below 0.13 mm/yr. For nitrided TAV in 4.9M HCl at 80ºC the corrosion rate is 0.26 mm/yr.

ACKNOWLEDGEMENT

This work was supported by the Program M-ERA NET project №8315 AntiPathCoat № FNI-916/16.06.2020 on the topic "New generation of copper coatings with improved antimicrobial resistance to pathogens" and contract FNI №KP-06-DO02/1 from 08.07.2021.

REFERENCES

[1] Molaei M., Nouri M., Babaei K., Fattah-Alhosseini A., Improving surface features of PEO coatings on titanium and titanium alloys with zirconia particles: A review, Surfaces and Interfaces, 22 (2021) DOI:10.1016/j.surfin.2020.100888.

[2] Jáquez-Muñoz M.J., Gaona-Tiburcio C., Cabral-Miramontes J., Nieves-Mendoza D., Maldonado-Bandala E., Olguín-Coca J., López-Léon L.D., Flores-De los Rios J.P., Almeraya-Calderón F., Electrochemical Noise Analysis of the Corrosion of Titanium Alloys in NaCl and H2SO4 Solutions, Metals 11 (1) (2021) 105, DOI: 10.3390/met11010105

[3] Afzali P., Reza G., Reza H., On the Corrosion Behaviour of Low Modulus Titanium Alloys for Medical Implant Applications: A Review, Oskouei, 2019, Metals 9 (8) (2019) 878, DOI: 10.3390/met9080878

[4] Sugisawa H., Kitaura H., Ueda K., Kimura K., Ishida M., Ochi Y., Kishikawa A., Ogawa S., Takano-Yamamoto T. Corrosion resistance and mechanical properties of titanium nitride plating on orthodontic wires. Dent Mater J. 37(2) (2018) 286-292

[5] Lai F.D., Wu T.I., Wu J.K., Surface modification of Ti-6Al-4V alloy by salt cyaniding and nitriding, Surface modification of Ti-6Al-4V alloy by salt cyaniding and nitriding, 58 (1993)

[6] De Assis S.L., Wolynec S., Costa I., Corrosion characterization of titanium alloys by electrochemical techniques, Electrochimica Acta, 51 (8–9) (2006) 1815-1819, ISSN 0013-4686, DOI:10.1016/j.electacta.2005.02.121

[7] Pohrelyuk I.M., Tkachuk O.V., Proskurnyak R.V., Corrosion Behaviour of Ti-6Al-4V Alloy with Nitride Coatings in Simulated Body Fluids at 36oC and 40oC, International Scholarly Research Notices, 2013, Article ID 241830, 2013. DOI: 10.1155/2013/241830

[8] Galvanetto E., Galliano F.P., Fossati A., Borgioli F., Corrosion resistance properties of plasma nitrided Ti-6Al-4V alloy in hydrochloric acid solutions, Corrosion Science, 44 (7) (2002) 1593-1606