Int. J. Electrochem. Sci., 17 **(2022)** Article Number: 221175, doi: 10.20964/2022.11.75

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Nitride Layer on TC4 Alloy Prepared by Ultrasonic Surface Rolling and Plasma Nitriding and Its Effect on Corrosion Resistance in LiBr Solution

Wenming Tian[1,2,*], *Fangfang Chen*[1], *Yang Lei*[3], *Fasong Cheng*[4], *Yanxia Li*[1], *Tao Fan*[1]

[1] School of Materials Engineering, North China Institute of Aerospace Engineering, No.133 Aimindong Road, Langfang Hebei Province 065000, China.
[2] Hebei Key Laboratory of Trans-Media Aerial Underwater Vehicle, North China Institute of Aerospace Engineering, No.133 Aimindong Road, Langfang 065000, China
[3]AVIC Harbin Aircraft Industry Group Co., Ltd., Harbin 150066, China
[4]AECC Guizhou Liyang Aviation Power CO.,LTD. Guiyang Guizhou 550014, China
[*]E-mail: tianwenming.dhr@163.com

Received: 8 August 2022 / *Accepted:* 20 September 2022 / *Published:* 20 October 2022

Titanium-nitride layer on TC4 alloy was prepared by ultrasonic surface rolling process (USRP) and plasma nitriding (PN) to promote corrosion resistance of alloy in 90 °C LiBr solution. The microstructure and electrochemical properties of PN treated titanium alloy were investigated by scanning electron microscopy (SEM), open circuit potential (OCP) test, potentiodynamic polarization, and electrochemical impedance spectrum (EIS). The results showed that the thickness of PN layer was 6.5 μm to 750 °C PN treatment, and its value was 10 μm to USRP+650 °C PN multiple treatment. The USRP could dramatically promote the thickening of PN layer even at a lower temperature. The PN layer significantly increased the OCP value, and decreased the corrosion current density of titanium in 90 °C LiBr solution. A thicker PN layer showed a higher film ohmic resistance and a bigger charge transfer resistance in electrolyte. The PN layer prepared by USRP+650 °C PN multiple process had the biggest thickness and exhibited the best corrosion resistance.

Keywords: Titanium alloy; Electrochemical corrosion; Ultrasonic surface rolling; Plasma nitriding; Potentiodynamic polarization

1. INTRODUCTION

LiBr absorption heat-exchanging (refrigeration) system has been developed to replace the chlorofluorocarbon refrigeration system in recent years because of its high efficiency, relatively low cost and environmental-friendly feature [1-2]. However, ferrous alloys such as carbon steel, stainless steel and nonferrous alloys such as cooper alloys and aluminum alloys all suffer from severe corrosion in the high concentration (55wt.%) LiBr aqueous solution which is used as service fluid in LiBr absorption heat-exchanging system [3-6]. Titanium and its alloy show good corrosion resistance in high concentration LiBr aqueous solution, and thus are incrementally used as heat-transfer tubes in LiBr absorption refrigeration system. While, the good corrosion resistance of titanium alloy usually attributes to its superficial oxide film which shows a low hardness and wear-resistance. Localized corrosion such as pitting and cavitation corrosion will occur on titanium alloy tubes when the oxide film being worn and broken in high pressure and flowing LiBr solution [7-9].

Some kinds of surface modifications are usually performed in order to increase the surface hardness and corrosion resistance of titanium alloy. Micro-arc oxidation coating for instance, can prepare an oxide film with thickness of dozens of microns on titanium surface to increase hardness and corrosion resistance simultaneously [10-13]. While, the micro-arc oxidation film has a very low thermal conductivity and too thick to transfer heat, it is not suitable to heat-transfer tubes in LiBr absorption heat-exchanging system. Plasma nitriding is a relatively new technique developed in recent decades to harden titanium alloys. Nitride layer on titanium alloys usually shows a high hardness value ($\geqslant$1000HV) and dramatically reduces the occurrence of wear and localized corrosion on titanium surface [14-16]. Furthermore, the titanium-nitride film has a higher thermal conductivity and a smaller thickness than the micro-arc oxidation film, therefore, it is suitable to be used on heat-exchange tubes in LiBr heat-exchanging system. however, the traditional plasma nitriding of titanium is usually performed at a relatively high temperature ($\geqslant$750 ^{o}C) and with a long processing time ($\geqslant$12 h). The above processing feature will coarsen the microstructure of alloys such as grain growth and second phases coarsening, and thus deteriorate the mechanical properties of titanium alloys. The LiBr heat-exchanging system usually operates at a high fluid pressure, and the degraded mechanical properties of titanium usually increases the fracture risk of tubes [17-19].

In this work, the ultrasonic surface rolling process (USRP) was used to accelerate the nitriding speed in order to minimize the disadvantage of high temperature plasma nitriding [20-23]. The USRP was used to crush the titanium surface and increase the crystal defects such as vacancy and grain boundary which would provide many diffusion paths to nitrogen atoms. And then low temperature ($\leqslant$ 650 ^{o}C) PN was adopted to prepare the final nitriding layer. The microstructure and electrochemical corrosion properties of USRP-PN layer were also systematically characterized by electrochemical testing method and scanning electron microscopy (SEM).

2. EXPERIMENTAL

2.1. Specimen preparation

The untreated alloy used in this work was commercial TC4 titanium alloy with annealing treatment. The USRP treatment was carried out by Huayun CNC machine center. The ultrasonic plunger chip was a WC-Co cemented-carbide ball with 10 mm diameter. The vibration frequency and amplitude of the ultrasonic plunger chip were 30 kHz and 8 μm, respectively. The pre-pressure of USRP treatment was 0.5 MPa, and the horizontal moving speed of plunger chip was 5 mm/s. Treated titanium alloy and ultrasonic plunger chip were refrigerated by lubricating oil during USRP processing.

The PN treatment was performed by LDM2 plasma nitriding furnace in ammonia atmosphere under 200 Pa atmospheric pressure. The heating rate was 30 ºC/min. Two PN temperatures namely 750 ºC and 650 ºC were adopted in this work. The hold time of above two temperatures was 12 h. The PN temperature to USRP treated alloy was 650 ºC, and was 750 ºC to untreated alloy. Therefore, three kinds of TC4 alloys treated by different processes were used to estimate their corrosion resistance in LiBr solution, namely, Untreated, 750 ºC PN, and USRP+650 ºC PN. All of the TC4 alloy samples were ground by emery paper and polished by 250 nm diamond suspension before USRP and PN treatment.

2.2. Morphological measurement

The microstructure of surface and cross-section as well as the corrosion morphology of titanium alloys treated by different processes were observed by S-3400N scanning electron microscopy (SEM). SEM observation was performed with 20 kV electron accelerating voltage and in secondary electron imaging (SEI) mode.

2.3. Electrochemical measurement

The deoxidized 55wt.% LiBr aqueous solution was used as the testing electrolyte. The testing temperature of LiBr solution was set as 90 ºC in order to simulate the actual working conditions of LiBr heat-exchanger system. Electrochemical tests were performed by CS350H electrochemical workstation. A three-electrode system was adopted in electrochemical measurements in this work. A saturated calomel electrode (SCE) was used as the reference electrode, and all the potential mentioned in this work were all referred to SCE. The auxiliary electrode was a platinum sheet with a working area of 8 cm^2. The working electrode of three kinds of TC4 alloys had an area of 1 cm^2 and cleaned by deionized water and alcohol in turn.

Open circuit potential (OCP) measurement recorded the potential-time curve during 1 h immersion period. Potentiodynamic polarization test was started at 200 mV below to the OCP and scanned upwards to 1200 mV above to OCP, or ceased until the anodic current density reached 0.1 mA/cm^2 with a potential scan rate of 0.5 mV/s. Electrochemical impedance spectrum (EIS) test was carried out at OCP under a 10 mV AC excitation voltage with the frequency range of 0.01 Hz to 100 kHz. The corrosion morphologies of different treated titanium alloys were obtained after 168 h immersion test in 90 ºC LiBr solution.

3. RESULTS AND DISCUSSION

3.1. Morphology of PN treated titanium

The surface morphology of TC4 alloy with different treatments are shown in Figure 1. Both of USRP and PN treatments can obviously increase the surface roughness of TC4 alloy. TiN, Ti_2N, Ti_3N, and Ti-N solid solution will be formed during PN process and cause volume increase of TC4 alloy, and thus increase the alloy surface roughness [17-23]. These multifarious titanium nitrides constitute the off-white particles on PN treated TC4 surface. The USRP treated sample shows stripe-like appearance which is severe plastic deformation zone and attributed to high-energy ultrasonic peening [20-23]. The 750 ºC and 650 ºC PN treated samples exhibit the similar surface morphology, while 650 ºC PN samples still appears some residual stripe-like feature generated during USRP process. The titanium nitrides particles formed on 750 ºC PN sample also show a bigger size compared to those formed on 650 ºC PN sample, since a higher temperature promotes the generation and coarsening of titanium nitrides.

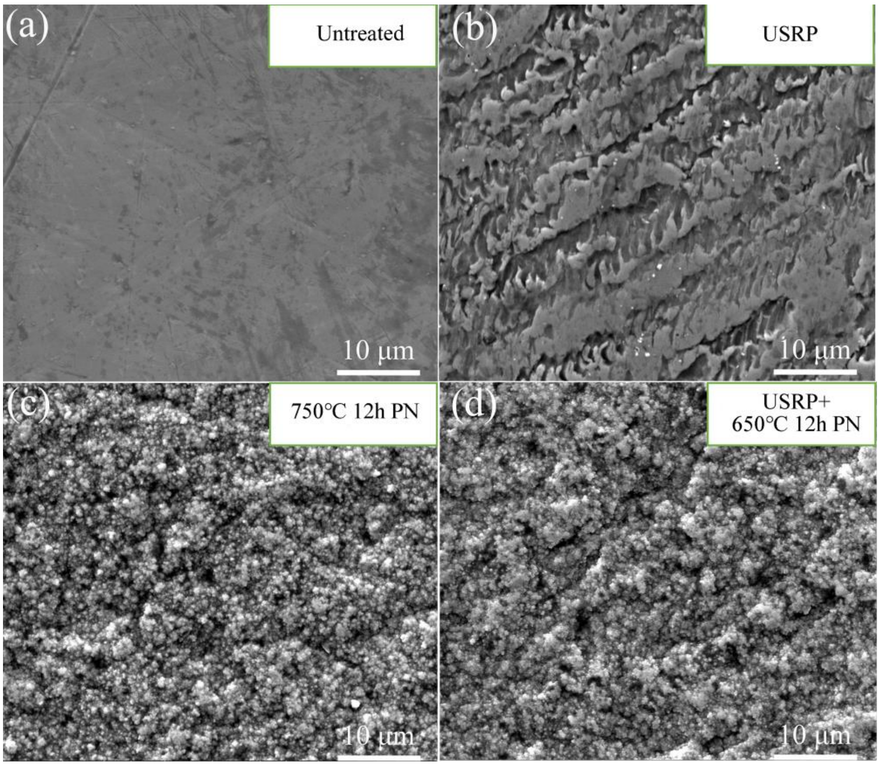

Figure 1. Surface morphology of TC4 titanium alloy with different treatments observed by SEM at 20 kV, (a)untreated one, (b)USRP treated one, (c)750 ºC 12 h PN treated one, and (d) USRP+650 ºC 12 h PN treated one.

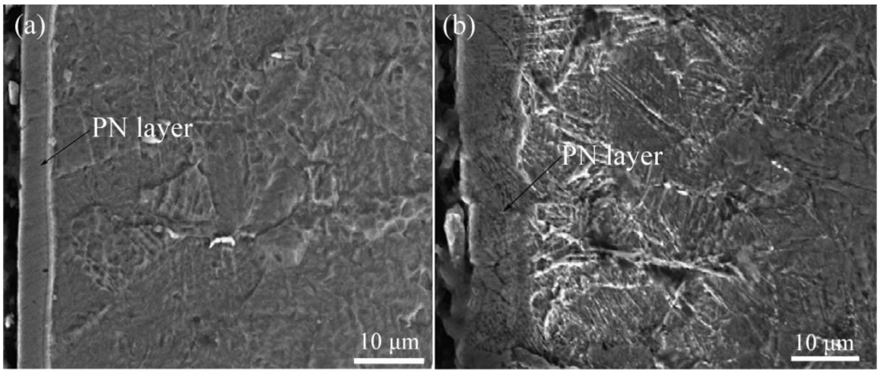

Figure 2. Cross-section morphology of TC4 titanium alloy with different treatments observed by SEM at 20 kV, (a) 750 ºC 12 h PN treated one, and (b) USRP+650 ºC 12 h PN treated one.

Figure 2 shows the cross-section of 750 ºC PN treated and USRP+650 ºC PN treated TC4 alloys. The titanium nitride layers are easily distinguished in SEM pictures. The final thickness of PN layer is about 6.5 μm to 750 ºC PN treatment, while its value is about 10 μm to USRP+650 ºC PN treatment. The USRP+650 ºC PN sample formed a thicker PN layer under a lower temperature with the same PN processing time compared to the 750 °C PN one, which indicates that USRP process dramatically accelerates the diffusion of nitrogen atoms into the titanium lattice and promotes the formation of a thicker PN layer. The severe deformation layer created by USRP usually has a thickness of dozens to hundreds of microns and contains more lattice defects such as grain boundary, vacancy and dislocation as much as 10^4 to 10^6 times to untreated TC4 alloy. Such lattice defects provide many effective diffusion path to nitrogen atoms to diffuse into titanium lattice. And the titanium atoms in such defects usually have higher Gibbs free energy and react with nitrogen atoms more easily than the metal atoms in general titanium lattice [20-23]. Therefore, the USRP treated TC4 could form a thicker PN layer at a lower temperature (650 °C). While, the normal TC4 just generate a thinner PN layer at a higher temperature (750 °C) without USRP. The severe deformation surface prepared by USRP usually shows a lower corrosion resistance in an active-corrosive medium and a higher corrosion resistance in a passive medium. While, a thicker PN layer theoretically has a better corrosion resistance in both active-corrosive and passive media. The USRP+650 °C PN treated TC4 alloy should exhibit the best corrosion resistance in this study, which would be verified by electrochemical testing in next section.

3.2. OCP and potentiodynamic polarization test

The OCP test results of different treated TC4 alloys during 1 h immersion period in 90 °C LiBr solution are shown in Figure 3. Untreated TC4 exhibits a relatively stable OCP value of -0.3V. The 750 °C PN and USRP+650 °C PN treated TC4 alloys have the similar OCP range of 0.2 to 0.4 V which is obviously higher than that of untreated TC4. The OCP value of PN treated sample slowly declines with the prolonged immersion period, which could be attributed to the Br^- ions inserting into PN layer and hydration of titanium nitrides in 90 °C LiBr solution. In addition, USRP+650 °C PN treated sample has a more noble OCP compared to the 750 °C PN treated one due to its thicker PN layer. On the whole, the PN layer formed by PN process remarkably increased the OCP value of TC4 alloy.

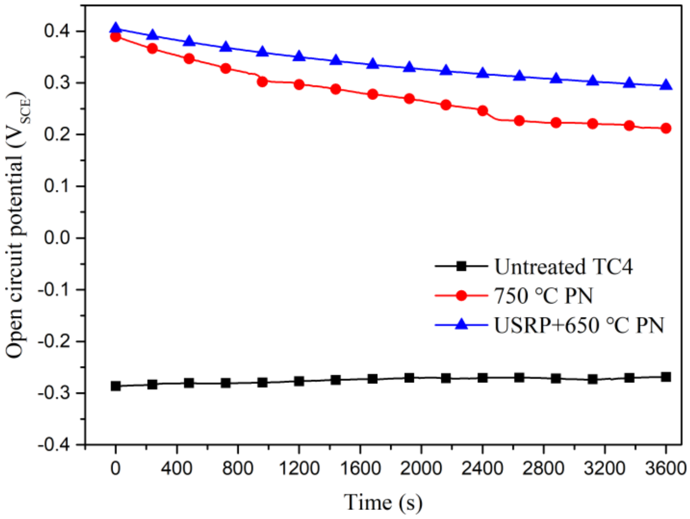

Figure 3. OCP test results of TC4 titanium alloy with different treatments in 90 °C LiBr solution during 1 h immersion.

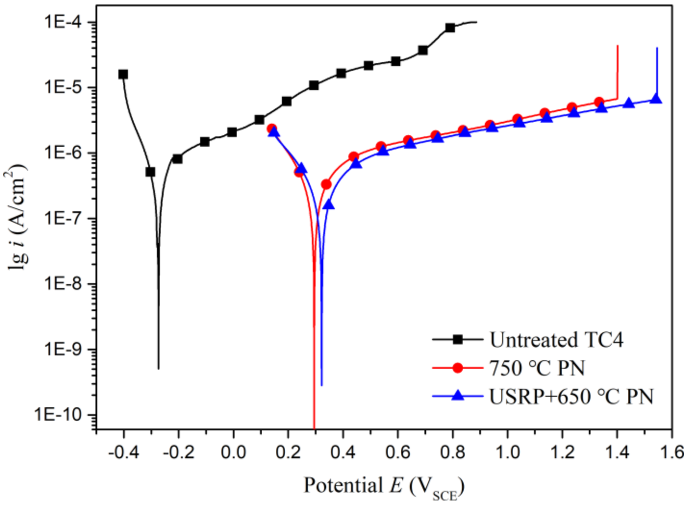

Figure 4. Potentiodynamic polarization curves of TC4 titanium alloy with different treatments in 90 ^{o}C LiBr solution after 30 min OCP stabilization.

Figure 4 shows the typical potentiodynamic polarization curves of untreated, 750 ^{o}C PN and USRP+650 ^{o}C PN treated TC4 alloys. The untreated sample exhibits obvious active-dissolution behavior in 90 ^{o}C LiBr solution, because its native oxide film is very thin and not stable enough to insulate metal matrix from high temperature corrosive medium. While, the 750 ^{o}C PN and USRP+650 ^{o}C PN treated samples show typical passive behavior in high temperature medium because of the protective PN layer which can effectively inhibit metal dissolution. The passive current density of 750 ^{o}C PN and USRP+650 ^{o}C PN treated samples increase tinily with the up-scanning potential. This indicates that the PN layer is a semiconducting film. When the overpotential exceeded 80 to 100 millivolts relative to the corrosion potential E_{corr} at both anodic and cathodic branch, the log current density and polarization potential exhibited typical linear relationship, i.e., Tafel behavior [24-25]. Therefore, the Tafel extrapolation was used to analyze the potentiodynamic polarization curves. And the fitting results are shown in Table 1. The E_{corr} of untreated TC4 is about -0.217 V, while, its value increases by more than 0.5 V when PN layer forming on titanium surface. Besides, the E_{corr} is little higher, and the passive current density is smaller of USRP+650 ^{o}C PN treated sample than those of 750 ^{o}C PN treated sample, because of the thicker PN layer formed on USRP+650 ^{o}C PN treated sample. The USRP+650 ^{o}C PN treated sample also has a wider passive potential range compared to the 750 ^{o}C PN treated one, due to its thicker PN layer. The cathodic Tafel slope b_c increases significantly as the PN layer formed on alloys which can attribute to the restricted hydrogen reduction. The LiBr solution was deoxidized and under high temperature of 90 ^{o}C, thus the hydrogen reduction was the main cathodic reaction in this study. While, the PN layer effectively retarded the hydrogen reduction because of its semi-conducting properties. The anodic Tafel slope b_a also increases significantly with the formation of PN layer which provides a physical barrier to prevent the contact between titanium matrix and corrosive medium. A bigger b_a and b_c usually mean a bigger resistance of anodic and cathodic electrochemical reaction, which means that the PN treatment can effectively decrease the corrosion susceptibility of TC4 in 90 ^{o}C LiBr solution. The corrosion rate reduces by 3 to 4 times after PN treatment. In addition, the PN layer prepared by USRP+650 ^{o}C PN shows a better corrosion resistance than that formed during 750 ^{o}C PN treatment, indicating that USRP not only accelerates the growth of PN layer, but also increases its corrosion resistance.

Table 1. Tafel extrapolation results of potentiodynamic polarization curves to different treated TC4 titanium alloys in 90 °C LiBr solution after 30 min OCP stabilization.

Alloy	E_{corr} (V_{SCE})	b_a (V/dec)	b_c (V/dec)	i_{corr} ($\mu A/cm^2$)
Untreated	-0.217 ± 0.020	0.315±0.037	0.097±0.019	0.86± 0.13
750 °C PN	0.275 ± 0.026	0.546 ±0.053	0.171± 0.026	0.28 ± 0.05
USRP+650 °C PN	0.292± 0.032	0.620± 0.067	0.203 ± 0.029	0.23 ± 0.08

3.3. Electrochemical impedance spectrum measurement

The EIS was also used to evaluate the corrosion resistance of TC4 alloy with and without PN treatment. Figure 5 shows the Nyquist and Bode plots of EIS measurements. All the Nyquist plots of untreated and treated TC4 alloys show two depressed capacitive arcs at high and low frequency ranges, indicating that all the samples encounter the similar electrochemical reaction mechanism, i.e., hydrogen reduction and titanium dissolution under protective film [17-19]. The high frequency capacitive arc usually associates with the semi-conducting film on TC4 alloy such as air-formed oxide film and PN layer. While, the low frequency capacitive arc associates charge transfer process at or under the weak points of superficial films. The dramatically increased ｜Z｜ module value and radius of Nyquist loop indicate that PN layer can effectively decrease the electrochemical reactivity of TC4 alloy in 90 °C LiBr solution.

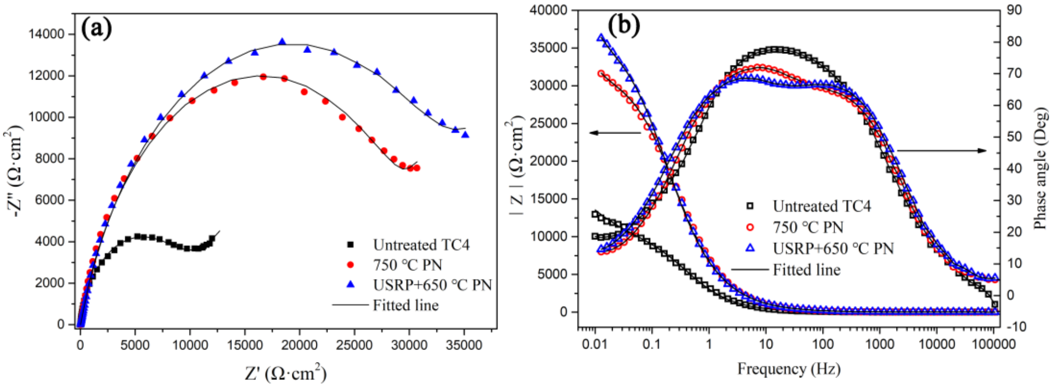

Figure 5. EIS measurement results of TC4 titanium alloy with different treatments in 90 °C LiBr solution after 30 min OCP stabilization, (a)Nyquist plots, and (b)Bode plots.

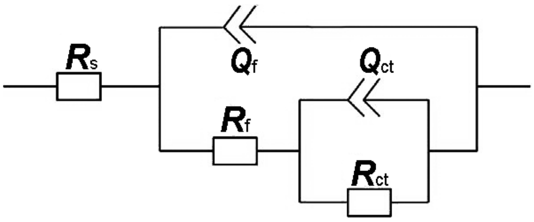

Figure 6. Equivalent circuit used to fit EIS spectra of different treated TC4 titanium alloys.

Table 2. Fitted values of solution resistance R_s, film resistance R_f, and charge transfer resistance R_{ct} of EIS measurements to different treated TC4 titanium alloys using equivalent circuit.

Alloy	**R_s (Ωcm^2)**	**R_f (Ωcm^2)**	**R_{ct}(Ωcm^2)**
Untreated	14.38 ± 2.06	9336±676	12904±1463
750 °C PN	14.83 ± 1.99	34268±2378	24183 ± 2076
USRP+650 °C PN	13.58 ± 2.36	39796±2695	25238 ± 1998

The equivalent circuit shown in Figure 6 was applied to fit the EIS spectra because of its small fitting error ($\chi^2 \leqslant 1 \times 10^{-3}$). R_s is the solution resistance, Q_f associates with the oxide film or PN layer capacitance at high frequency, R_f is oxide film or PN layer resistance, Q_{ct} associates with interfacial capacitance of active corroded surface under protective layer, R_{ct} is the charge transfer resistance of metal dissolution [24,26]. The fitted values of R_f and R_{ct} which directly associate with the corrosion resistance of titanium are listed in Table 2.

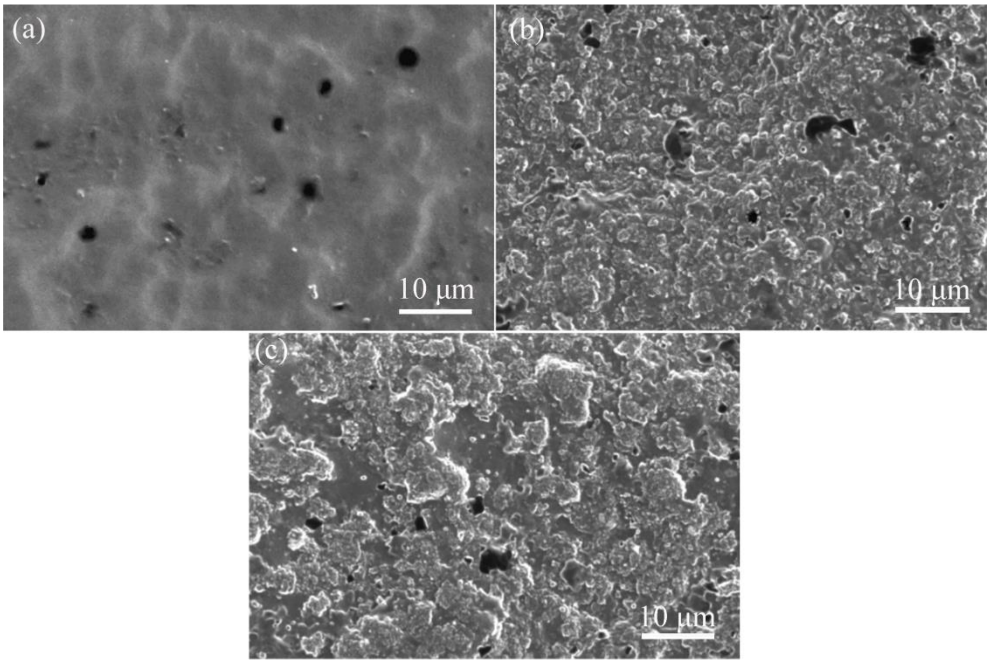

Figure 7. Surface corrosion morphology of TC4 titanium alloy with different treatments after 128 h immersion in 90 °C LiBr solution, (a)untreated one, (b)750 °C 12 h PN treated one, and (c) USRP+650 °C 12 h PN treated one.

The average film resistance is about 9336 Ω to untreated TC4 alloy, while, its value exceeds 34000 Ω to PN treated alloy. The film resistance increases by about 4 times due to the formation of pyknotic and thick PN layer which can retard the metal dissolution and ions diffusion. The USRP+650 °C PN treated sample has the biggest R_f, it means that USRP+PN process can provide a better anti-corrosion PN layer than the single PN process. The PN layer not only increase the R_f value, but also effectively increases the R_{ct} value, which indicates that the PN layer also slows down the charge transfer process and thus decrease the corrosion rate. Based on the above data, it is reasonable to deduce that PN process is an effective anti-corrosion technique to titanium alloy in high temperature LiBr solution, and USRP+PN process is better than single PN treatment.

The corrosion morphology of all samples after 128 h immersion in 90 °C LiBr solution are shown in Figure 7. Some localized corrosion such as pitting has been occurred on untreated TC4 alloy. Some little titanium nitride particles also dissolved after 128 h high temperature immersion. Therefore, the surface roughness of 750°C PN and USRP+650 °C PN treated TC4 alloys obviously decreased after immersion testing. However, there is still no obvious corrosion occurred on PN treated TC4 alloys. The PN layer is an effectively protective film for TC4 alloy in high temperature LiBr solution.

4. CONCLUSION

(1) PN could prepare titanium-nitride layer on titanium alloy to increase corrosion resistance of TC4 in 90 °C LiBr solution. The TC4 without USRP treatment formed a 6.5 μm thick PN layer at 750 °C temperature with 12 h processing period. The USRP treated TC4 formed a 10 μm thick PN layer at 650 °C temperature with 12 h processing period. It indicated that USRP could effectively accelerate the growth of PN layer on TC4 titanium alloy.

(2) The OCP and corrosion current density of TC4 alloy without PN layer were -0.3 V and 0.86 μA/cm^2, respectively. The OCP increased to 0.2 to 0.4 V, and corrosion current density decreased to about 0.23 to 0.28 μA/cm^2 for PN treated TC4. PN treatment also increased the film ohmic resistance and charge transfer resistance of titanium, and could effectively increase corrosion resistance of TC4 alloy in 90 °C LiBr solution.

(3) The corrosion current density decreased, and the film ohmic resistance as well as charge transfer resistance increased with the increasing thickness of PN layer. The USRP+650 °C PN treated TC4 had the thickest PN layer and the best corrosion resistance.

ACKNOWLEDGEMENT
This research is sponsored by the Research Projects of North China Institute of Aerospace Engineering ZD202201, Youth Fund of the Hebei Natural Science Fund project under Grant No. E2019409052, and the Education Department Science Research project of Hebei under Grant No. QN2019104.

References

1. Z. Jin, S. Li, R. Zhou, M. Xu, W. Jiang, and K. Du, *Int. J. Refrig.,* 131 (2021) 826.
2. S.Y. Misyura, *Int. Commun. Heat Mass.*, 117 (2020) 104727.
3. A.E. El Melleigy, A.A. El Warraky, Sh.E. Abd El hamid, and El-Sayed M. Sherif, *Int. J. Electrochem. Sci.,* 15 (2020) 2243.
4. A.E. El Melleigy, A.A. El Warraky, Sh.E. Abd El hamid, and El-Sayed M. Sherif, *Int. J. Electrochem. Sci.,* 15 (2020) 2281.
5. E. Blasco-Tamarit, D.M. García-García, and J. García Antón, *Corros. Sci.,* 53 (2011) 784.

6. A.K. Larios-Galvez, R. Guardian-Tapia, R. Lopez-Sesenes, and J.G. Gonzalez-Rodriguez, *Int. J. Electrochem. Sci.,* 17 (2022) 220131.
7. E. Blasco-Tamarit, A. Igual-Muñoz, J. García Antón , and D.M. García-García, *Corros. Sci.,* 51 (2009) 1095.
8. M.J. Muñoz-Portero, J. García-Antón, J.L. Guiñón, and R. Leiva-García, *Corros. Sci.,* 53 (2011) 1440.
9. R.M. Fernández-Domene, E. Blasco-Tamarit, D.M. García-García, and J. García-Antón, *Electrochim. Acta*, 58 (2011) 264.
10. X. Chen, D. Liao, D. Zhang, X. Jiang, P. Zhao, and R. Xu, *Int. J. Electrochem. Sci.,* 15 (2020) 710.
11. S. Luo, P. Yan, M. Liu, Y. Xue, and W. Song, *Int. J. Electrochem. Sci.,* 16 (2021) 21096.
12. V. Romanovski, Y.S. Hedberg, A. Paspelau, V. Frantskevich, J.J. Noël, and E. Romanovskaia, *Eng. Fail. Anal.,* 129 (2021) 105722.
13. R.M. Fernández-Domene, E. Blasco-Tamarit, D.M. García-García, and J. García Antón, *J. Electrochem. Soc.*, 161 (2014) C25.
14. D. She, W. Yue, J. Kang, F. Huang, C. Wang, and J. Shen, *Tribol. T.,* 61 (2018) 612.
15. İ. Hacısalihoğlu, G. Kaya, T.O. Ergüder, E. Mandev, E. Manay, and F. Yıldız, *Surf. Interfaces,* 22 (2021) 100893.
16. J. Morgiel, Ł. Maj, K. Szymkiewicz, M. Pomorska, P. Ozga, D. Toboła, M. Tarnowski, and T. Wierzchoń, *Appl. Surf. Sci.,* 574 (2022) 151639.
17. T. Deng, Z. Zhu, X.Li, T. Ma, and Q.Wang, *J. Mater. Process. Tech.*, 282 (2020) 116669.
18. M.A. Deyab, *Desalination*, 439 (2018) 73.
19. Y. Gong, F. Ma, Y. Xue, C. Jiao, and Z. Yang, *Eng. Fail. Anal.,* 101 (2019) 172.
20. L. Ge, N. Tian, Z. Lu, and C. You, *Appl. Surf. Sci.,* 286 (2013) 412.
21. Q. Yao, J. Sun, G. Zhang, W. Tong, and H. Zhang, *Vacuum*, 142 (2017) 45.
22. Y. Lin, J. Lu, L. Wang, T. Xu, and Q. Xue, *Acta Mater.*, 54 (2006) 5599.
23. K. Ren, W. Yue, and H. Zhang, *Surf. Coat. Tech.,* 349 (2018) 602.
24. W. Tian, Z. Li, H. Kang, F. Cheng, F. Chen and G. Pang, *Materials*, 13 (2020) 3236.
25. W. Tian, F. Chen, Z. Li, G. Pang and Y. Meng, *Corros. Sci.*, 173 (2020) 108775.
26. W. Tian, F. Chen, F. Cheng, Z. Li, and G. Pang, *Int. J. Electrochem. Sci.,* 15 (2020) 9120.