International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

Short Communication

Electrochemical Corrosion Behavior of TA2 Titanium Alloy Welded Joint in Cl⁻ Containing Solutions

Sheji Luo^{1,*}, Pai Yan¹, Ming Liu^{2,*}, Yuna Xue¹, Wenwen Song¹

¹ School of Material Science of Engineering Xi'an Shiyou University, Xi'an 710065, PR China ² School of Material Science of Engineering Xi'an Jiaotong University, Xi'an 710049, PR China *E-mail: <u>sjluo@xsyu.edu.cn</u>, <u>liuming0313@xjtu.edu.cn</u>

Received: 6 May 2021 / Accepted: 17 June 2021 / Published: 10 August 2021

The electrochemical corrosion behavior of TA2 base metal and welded joint in Cl⁻ containing (3.5%NaCl, 5.0%NaCl, 7.5%NaCl) solutions was studied by electrochemical test method. The results show that with the increase of Cl⁻ concentration, the open circuit potential (OCP) of TA2 base metal and welded joint shifts negatively, the polarization resistance decreases gradually, and the corrosion current density increases. Compared with the base metal, the microstructure of the welded joint is different, which changes their corrosion resistance. It shows that the OCP of the welded joint shifts negatively, the polarization current density is smaller, which indicates that the corrosion resistance of the welded joint is better.

Keywords: TA2; welded joint; Microstructure; Polarization curve; EIS

1. INTRODUCTION

Titanium and its alloys have the advantages of low density, high strength, low hardness, high temperature resistance, as well as good mechanical properties and corrosion resistance, so they are widely used in the fields of aerospace, petroleum exploration and chemical industry, etc [1-8]. At the same time, because of their good welding performance, they have been widely used in various types of welding. However, research has shown that in the process of welding, the welding joint will experience a series of complex thermal cycling effect, thus leading to form different parts of microstructure, the hardness and chemical composition will be changed greatly, and corrosion failure may be easily induced. Thus, the corrosion resistance of the material can be seriously affected [9-15]. As a typical representative Titanium alloy, TA2 has a close-packed hexagonal structure, which belongs to the typical *a*- titanium alloy and is one of the most commonly used titanium alloy in industry [16-18]. In air and aqueous solutions, TA2 is easy to react with oxygen, forming a dense passive film on the surface, which hinders

the occurrence of corrosion [19-21]. At present, most studies about TA2 focus mainly on the influence of passive film corrosion resistance. The formed passive film on the surface of TA2 makes it has good corrosion resistance under strong oxidation, neutral or natural conditions [22,23]. He studied the polarization curve of titanium alloy in the mixed environment of NaCl, NaNO₃ and found that pitting corrosion could be observed in the solution containing NaCl [24]. However, there are few studies on the influence of Cl⁻ concentration change on the corrosion performance of titanium welt joint.

Therefore, the electrochemical corrosion behavior of TA2 base metal and welded joint in Cl⁻ containing (3.5%NaCl, 5.0%NaCl, and 7.5%NaCl) solutions was analyzed by using optical microscopic analysis and electrochemical test. The effect of Cl⁻ concentration on corrosion behavior of TA2 base metal and welded joint was summarized. The research results could have important theoretical significance and engineering application value for prolonging the service life and improving the safety and application of TA2 welded joint.

2. MATERIALS AND EXPERIMENTAL

The test material used in this test was TA2 base metal and its welded joint, and the chemical composition of TA2 is listed in Table 1. A TA2 plate with the thickness of 5 mm was used as the base material for welding samples. The welding wire was chosen to be the Gr.1 with the same chemical composition as the base metal. The welding process parameters were as follows: welding current was 100-130 A, welding voltage was 8.5-11.5 V, and welding speed was 50 mm/min. In the welding and the cooling processes, the welding joint was protected by Ar and the speed was 12-16 L/min.

Table 1. The chemical composition of TA2 (wt %).

 Fe	С	N	Н	0	Ti
0.019	0.019	0.015	0.0017	0.13	-

The samples were taken from TA2 base metal, heat effect zone and welded joint for optical microscopic analysis, with the size of $10 \text{mm} \times 10 \text{mm} \times 5 \text{mm}$. The stains on the surface of the samples were cleaned with ethanol, and the samples were sealed with epoxy resin to leave the observation surface. The samples were polished step by step with $120\#\sim1500\#$ sandpaper until no scratches could be found. The corrosion solution for optical microscopic analysis was HF, HNO₃ and H₂O with the ratio of 2.5:7.5:40, and the corrosion time was 10 s. Then the solution was cleaned with alcohol, dried, and observed by a HAL100 metallographic microscope.

Electrochemical samples were taken from TA2 base metal and welded joint (with weld seam as the center), and the size of the samples was 10mm×10mm×5mm. Copper wires were welded on the back of the samples, sealed with epoxy resin, and the working surface was 1cm². The working surface was polished step by step with 240#~1500# sandpaper, and cleaned with deionized water and alcohol. The corrosive medium was NaCl solution with mass fraction of 3.5wt.%, 5.0wt.% and 7.5wt.%, which was prepared by analytical pure NaCl and deionized water.

The open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and polarization curve of the samples were measured by PARSTAT-2273 electrochemical workstation. The traditional three-electrode system was used in the experiment, with platinum plate as the auxiliary electrode, Ag/AgCl electrode as the reference electrode and test samples as the working electrode.

The test time of OCP was 3600 s. EIS was tested with a wide frequency range of 5mHz-100kHz, and sinusoidal waves with a signal amplitude of 10mV were adopted. Zsimpwin software was used to analyze and fit the EIS data. The scanning rate of the polarization curve was 0.5mV/s. In the process of electrochemical potential controlled polarization testing, the relationship between electrode polarization potential and polarization current density satisfies the Butler-Volmer equation [25]:

$$I = I_{\rm corr} \{ \exp[\frac{2.303(E - E_{\rm corr})}{b_{\rm a}}] \} - \exp[\frac{-2.303(E_{\rm corr} - E)}{b_{\rm c}}]$$
(1)

where, I is the net current density in the case of polarization; E is the polarization potential; I_{corr} is the self-current density; E_{corr} is self-corrosion potential; b_a is the anode Tafel constant and b_c is the cathode Tafel constant.

Within the scope of the weak polarization potential region, $\eta = |E - E_{corr}| < 50$ mV. Eq. (1) can be used to analyze the polarization curve measured in the test, and the values of b_a , b_c and i_{corr} can be obtained [26-28].

3. RESULTS AND DISCUSSION

3.1 Microstructure

Fig. 1 shows the microstructure of base metal, heat-affected zone and weld of TA2 welding joint. As can be seen that the microstructure of the base metal is α grain with small and uniform grain size, as shown in Fig. 1(a). The microstructure of the heat-affected zone is serrated α grains with different directions, and the grain size becomes larger, as shown in Fig. 1(b). The microstructure of the weld is larger serrated α grains and a small amount of martensite could be observed, as shown in Fig. 1(c). The change of grain shape is due to the high heat input in the welding process, the temperature of the weld exceeds the phase transition point (882°C), and the $\alpha \rightarrow \beta$ phase transition occurs. During the cooling process, β -Ti phase changes from β -Ti to α -Ti phase, which results in the microstructure of irregular zigzag α grains, but the grains of the heat-affected zone are slightly smaller than those of the weld zone due to the more serious thermal impact [29].



Figure 1. Microstructure of TA2 base metal and welded joint. (a) base metal, (b) heat affected zone, (c) weld seam.

3.2 Electrochemical results analysis

3.2.1 OCP

Fig. 2 shows the 3600 s OCP of TA2 base metal and welded joint at different concentrations of NaCl. As can be seen from Fig. 2, in different concentrations of Cl⁻ solution, the OCPs of both base metal and welded joint increase with time, and gradually become stable after 2800s of immersion.

Fig. 3 shows the relationship between the OCP and the concentration of NaCl solution after immersed for 3600 s. As can be seen from Fig. 3, when the concentration of NaCl solution is in the range of $3.5\% \sim 7.5\%$, both OCPs of the base metal and the welded joint shift negatively. According to the thermodynamic law, the more negative of the OCP is, the worse the thermodynamic stability of the material is [30].



Figure 2. OCPs of TA2 base metal and welded joint at different concentrations of NaCl (a) base metal, (b) welded joint.



Figure 3. Open-circuit potentials of TA2 base metal and welded joint at different concentrations of Cl⁻.

Therefore, with the increase of Cl^{-} concentration, the thermodynamic stability of the base metal and the weld become worse. When the concentration of Cl^{-} is the same, the OCP of the base metal is more negative than that of the welded joint, so the thermodynamic stability of the base metal is even worse.

3.2.2 Polarization curve

Fig. 4 shows the polarization curves of TA2 base metal and welded joint in different concentrations of Cl⁻ containing solution. As can be seen from the Fig. 4, when the anode polarization potential is increased to 300 mV, the base metal and the welded joint are both in the passivation zone in different concentrations of Cl⁻ containing solution, the corrosion current density is almost unchanged, and there is a wide and stable dimensional blunt zone.



Figure 4. Polarization curves of TA2 base metal and welded joint in different concentrations of NaCl solutions. (a) base metal, (b) welded joints.

When the anode potential increases to 1500 mV, the current density gradually decreases, indicating that the stability of the passive film is destroyed, and pitting corrosion can be detected. Base metal and welded joint are very similar, the polarization curves of different concentrations all show passivation phenomenon, because the Ti and its alloys are easy to form a protective oxide film (TiO₂) on their surface in air and aqueous solution, so as to improve the corrosion resistance of the matrix, that is why they have good corrosion resistance.

Sample	$C_{\text{NaCl}}(\%)$	$b_a(mV/dec)$	$b_{\rm c}({\rm mV/dec})$	$I_{\rm corr}(\mu A \cdot {\rm cm}^2)$	$I_{\text{pass}}(\mu A \cdot \text{cm}^2)$
	3.5	88	-62	0.86	4.3
Base metal	5.0	207	-87	1.11	3.1
	7.5	276	-88	2.52	4.8
Waldadiaint	3.5	87	-62	0.54	4.4
welded joint	5.0	103	-96	0.82	4.4
	7.5	147	-104	1.17	4.3

Table 2. The fitting results of polarization curves of base metal and weld joint in different concentrations of NaCl solution.

Table 2 shows the electrochemical parameters of base metal and welded joint in different concentrations of Cl⁻ containing solution fitted by Eq. 1. Fig. 5 shows the comparison of the self-corrosion current density between the TA2 base metal and the welded joint. It can be seen that the self-corrosion current density of base material and welded joint increases with the increase of Cl⁻ concentration.



Figure 5. Self-corrosion current densities of TA2 base metal and welded joint in different concentrations of NaCl solution.

The corrosion resistance of welding joint is decreased with the increase of concentration of Cl⁻, because in the process of metal passivation, the Cl⁻ can accumulated on the surface of the defect and the number of local activation points increase, and the dissolution rate of material is accelerated. The greater the concentration of Cl⁻, the more adsorbed Cl⁻ on the substrate surface could be seen, the more serious corrosion could be [31]. In the same concentration NaCl solution, the self-corrosion current density of the welded joint is larger than that of the base metal, that is, the corrosion resistance of the base metal is better, because the size and shape of the metal grains will be changed due to the welding heat input, which affects the stability of the passive film on the metal surface and leads to the change of the corrosion resistance.

3.2.3 EIS

Figs. 6 and 7 show the EIS of TA2 base metal and welded joint respectively. As shown in Fig. 6(a) and 7(a), the Nyquist plots all show a high-frequency capacitive arc, and the radius of the capacitive arc reflects the size of the charge transfer resistance. The larger the radius of the capacitive arc is, the larger the charge transfer resistance is, and the better the corrosion resistance of the material will be. Therefore, in different concentrations of NaCl solution, the capacitive arc radius of the base metal and the welded joint decreases with the increase of NaCl concentration, that is, the corrosion resistance of the material becomes worse and worse with the increase of Cl⁻ concentration. According to the Bode diagram, the weld and base metal have the maximum phase Angle at around the frequency of 10 Hz, and the maximum phase Angle lag at the frequency of 100 kHz. In EIS, the corrosion resistance of materials is generally evaluated by comparing the charge transfer resistance R_{ct} and the maximum phase Angle [32]. As can be seen from the Figs. (6b) and (7b), the maximum phase Angle in three NaCl solutions

with different concentrations do not change greatly, so the corrosion resistance here was compared through the polarization resistance.



Figure 6. Electrochemical impedance spectra of TA2 base metal in different concentrations of NaCl containing solutions, (a) Nyquist plot, (b) Bode plot.



Figure 7. EIS of TA2 welded joint in different concentrations of NaCl containing solutions, (a) Nyquist plot, (b) Bode plot.



Figure 8. Equivalent circuit diagram R(QR) of EIS.

According to Figs. 6 and 7, the equivalent circuits of TA2 base metal and welded joint in different concentrations of NaCl containing solutions could be obtained, as shown in Fig. 8. R_s is the solution resistance which is from the reference electrode to the working electrode. Q_{dl} is the constant phase element of double-layer capacitance. R_t is the charge transfer resistance. The polarization resistance is equal to charge transfer resistance here, i.e. $R_p=R_t$ [30]. The greater the R_p value is, the better the corrosion resistance of the material will be. According to Faraday's second law, the corrosion current density is inversely proportional to the polarization resistance, that is, the larger R_p^{-1} is, the faster the corrosion rate would be, which is consistent with the previous result of the polarization curves. Based on the equivalent circuit diagram, Zsimpwin software was used to fit the EIS data, and the fitting results is listed in Table 3. Fig. 9 shows the polarization resistance of TA2 base metal and welded joint. As can be seen from the Fig. 9, the polarization resistance of both base metal and welded joint decreases with the increase the concentration of NaCl solution, that is, the corrosion resistance decreases. In the same concentration of NaCl solution, the polarization resistance of the base metal is greater than that of the welded joint, indicating that the corrosion resistance of the welded joint is worse than that of the base metal.

Table 3. EIS fitting parameters of TA2 base metal and welded joint.

Sample	$C_{\rm NaCl}(\%)$	$R_{\rm s}(\Omega \cdot {\rm cm}^2)$	$Q_{\rm dl}(\rm F \cdot \rm cm^{-2} \cdot \rm S^{n-1})$	n	$R_{\rm p}(\Omega \cdot {\rm cm}^2)$
Base metal	3.5	3	0.000087	0.76	467600
	5.0	8	0.000039	0.66	370400
	7.5	17	0.000047	0.65	258800
Welded	3.5	3	0.000053	0.72	1508000
joints	5.0	7	0.000019	0.84	607100
	7.5	16	0.000076	0.85	454600



Figure 9. Polarization resistance of TA2 base metal and welded joint at different concentrations of NaCl.

4. CONCLUSION

In this paper, the microstructure and electrochemical corrosion behavior of TA2 base metal and welded joint were studied by optical microscopic analysis and electrochemical test. The detail results are:

(1) The microstructure of TA2 base metal is α grain with small grain size. Due to the influence of welding heat input, the microstructure of heat-affected zone becomes larger serrated α grain, and the grain size becomes larger. The microstructure of welding seam is larger serrated α grain and a small amount of martensite.

(2) The stable passivation zones could be observed in both TA2 base metal and welded joint; with the increase of Cl⁻ concentration, the OCP of TA2 base metal and the welded joint shifts negatively, the polarization resistance gradually decreases, and the corrosion current density increases, indicating that the corrosion resistance of TA2 base metal and the welded joint becomes worse with the increase of Cl⁻ concentration.

(3) Compared with the base metal, the microstructure of the welded joint is changed, which changes the corrosion resistance of the welded joint. It shows that the OCP negative shifting degree of the welded joint is smaller, the polarization resistance is larger, and the corrosion current density is smaller, indicating that the corrosion resistance of the welded joint is relatively better.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial supports from the Shaanxi National Science Foundation (No. 2021JM-412, 2020JQ-773) and the Innovation Team Funding by Xi'an Shiyou University (No. 2019QNKYCXTD12).

References

- 1. J. Alipal, M Pu'ad N. A. S., N. H. M. Nayan., N. Sahari, H. Z. Abdullah, M. I. Idris and T. C. Lee., *Mater. Today: Proc.*, 42 (2021) 270.
- 2. N. A. Nochovnaya, P. V. Panin, E. B. Alekseev and K. A. Bokovts, *Met. Sci. Heat. Treat.*, 58 (2017) 520.
- 3. K. Hiroyasu, T. Yoshimasa, I. Hideyuki, K. Tatsushi and Y. Takayuki, *J. Prosthodont. Res.*, 63 (2019) 266.
- 4. S. Huanga, L.S. Swee, L Geoffde, W. Robert and Y.Y. Wai, *J. Mech. Behav. Biomed. Mater.*, 108 (2020) 103775.
- 5. R.K. Kumar, P. SampathKumaran, S. Seetharamu, S.K. Anand, T. Pramod and G.J. Naveen, *Proced. Struct. Integ.*, 14 (2019) 134.
- 6. W Liu, C Blawert, M. L. Zheludkevich, Y. Lin, M. Talha, Y. Shi and L. Chen, J. Alloys. Compd., 789 (2019) 996.
- K. Navneet, S. Prassan, W. Jwalant, P. Anjali and S. Julius, P. Franci, *Procedia. CIRP.*, 98 (2021) 175.
- 8. M. Liu, J. Li, D. Li and L. Zheng, Anti-Corros. Method., 68 (2021) 9.
- 9. W. Chuaiphan, L. Srijaroenpramong, J. Mater. Res. Technol, 9 (2020) 5174.
- 10. S.V. Pratap, P.S. Kumar and K. Basil, Intermetallics, 133 (2021) 107122.
- 11. S. Cui, Y. Shi and C. Zhang, Trans. Nonferrous. Met. Soc. China., 31 (2021) 416.

- 12. S. Bocchi, M. Cabrini, G. a D'Urso, C. Giardini, S. Lorenzi and T. Pastore, J. Manuf. Process., 35 (2018) 1.
- 13. J. Zhao, M. Liu, B. Tan. and Y. Zhang, Int. J. Electrochem. Sci., 16 (2021) 21024.
- 14. L. Li, S. Wang, W. Huang and Y. Jin. J. Manuf. Process., 50 (2020) 295.
- 15. S. Sinhmar and D. K. Dwivedi, J. Mater. Sci. Eng. A, 684 (2017) 413.
- 16. Y. Yang, C. Lin, X. Zhao and Y. Zhang, J. Chin. Soc. Corros. Prot., 37(2017) 540.
- 17. S. Chen, S. Luo, H. Yu, H. Geng, G. Xu, R. Li and Y. Tian, J. Manuf. Process., 58 (2020) 1221.
- 18. X. Cheng, X. Li, C. Dong and K. Xiao, Mater. Corros., 62 (2011) 1106.
- 19. S. Liu, B. Wang and P. Zhang, *Materials*, 9 (2016) 874.
- 20. T. L. Carmen, M. Daniel, S. Carmen, F. Mircea, B. Liviu, H. Luminiţa, C.f Ciprian, F. M. Luis, R. R. Raquel, S. Juan J and R. M. Souto, *Mater. Chem. Phys.*, 240 (2019) 122229.
- 21. Z. Jin, H. Ge, W. Lin, Y. Zong, S. Liu and J. Shi, Appl. Surf. Sci., 322 (2014) 47.
- 22. M Kovalev, A Shakhmatov and A Alhimenko, Mater. Today.: Proc., 30 (2020) 501.
- 23. Q. Guo, D. Xu, W. Yang, Y. Guo, Z. Yang, J. Li and P. Gao, *Surf. Coat. Technol.*, 386 (2019) 125454.
- 24. X. Yang, C. Du, H. Wan, Z. Liu and X. Li. Appl. Surf. Sci., 458 (2018) 198.
- 25. M. Liu, Y. Hao, L. Zheng, L. Niu and D. Miao, J. Mater. Eng. Perform., 28 (2019) 7527.
- 26. M Liu, S Luo, H Zhang and H Chen, Int. J. Electrochem. Sci, 14 (2019) 4838.
- 27. M. Liu, X. Cheng, X. Li and T. Lu, J. Electroanal. Chem., 803 (2017) 40.
- 28. R. Wang, S. Luo, M. Liu and Y. Xue, Corros. Sci., 85 (2014) 270.
- 29. X. Jiang, Y. Han, S. Chen, Y. Bai, T. Yuan and X. Wang, J. Mater. Sci. Technol., 36 (2020) 1628.
- 30. M. Liu, X. Cheng, X. Li, Z. Jin and H. Liu, Constr. Build. Mater., 93 (2015) 884.
- 31. P. Hu, R. Song, X. Li, J. Deng, Z. Chen, Q. Li, K. Wang, W. Cao, D. Liu and H. Yu, J. Alloys. Compd., 708 (2017) 367.
- 32. M Liu, X Cheng, X Li, C Zhou and H Tan, Constr. Build. Mater., 130 (2017) 193.

© 2021 The Authors. Published by ESG (<u>www.electrochemsci.org</u>). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).