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FORMATION OF TIO_2 NANOPOROUS LAYER ON THE SURFACE OF $TI_{13}NB_{13}ZR$ TITANIUM ALLOY TREATED BY ECAP-CONFORM AND ROTARY SWAGING

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ABSTRACT

This paper focuses on the formation of nanoporous layer on the surface of the third-generation biomedical $Ti_{13}Nb_{13}Zr$ titanium alloy widely used in the biomedical field. First of all, the alloy was subjected to equal channel angular pressing (ECAP) + Conform treatment (ECAP-Conform) and Rotary Swaging forging. Then the anodic oxidation method with 0.5 wt% HF electrolyte was used to prepare a uniformly arranged porous layer on the surface of the samples with the different microstructure from ECAP-Conform. The features of the formed porous layer were investigated. The effects of oxidation time and oxidation voltage on the porous morphology of the surface porous layer were investigated in detail. The optimal anodic oxidation parameters for the formation of surface porous layer were established. The hydrophobic properties of the samples were tested and the contact angles were calculated. Finally, the weightlessness of body fluid corrosion in Hanks´ solution was simulated.

KEYWORDS

Anodization; ECAP-Conform; Rotary Swaging; $Ti_{13}Nb_{13}Zr$ alloy; Hydrophobic property.

ФОРМИРОВАНИЕ НАНОПОРИСТОГО СЛОЯ TIO_2 НА ПОВЕРХНОСТИ ТИТАНОВОГО СПЛАВА $TI_{13}NB_{13}ZR$, ПОДВЕРГНУТОГО ОБРАБОТКЕ МЕТОДАМИ РКУП-КОНФОРМ И РОТАЦИОННОЙ КОВКИ

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АННОТАЦИЯ

Данная статья посвящена формированию нанопористого слоя на поверхности биомедицинского титанового сплава третьего поколения $Ti_{13}Nb_{13}Zr$, широко используемого в биомедицине. Сначала сплав подвергался обработке методами равноканального углового прессования (РКУП) по схеме «Конформ» (РКУП-Конформ) и ротационной ковки. Затем применялся метод анодного оксидирования с использованием электролита – 0,5вес.% раствора HF – для формирования однородного пористого слоя на поверхности образцов с различной микроструктурой, полученной методом РКУП-Конформ. Изучались особенности сформированного пористого слоя. Проводилось подробное исследование влияния времени оксидирования и напряжения оксидирования на пористую морфологию поверхностного пористого слоя. Были определены оптимальные параметры анодного оксидирования для формирования поверхностного пористого слоя. Исследовались гидрофобные свойства образцов, и проводились расчеты углов контакта. В конце путем погружения в раствор Хэнкса проводилось моделирование коррозии, протекающей в биологических жидкостях организма.

КЛЮЧЕВЫЕ СЛОВА

Анодирование; РКУП-Конформ; ротационное обжатие; сплав $Ti_{13}Nb_{13}Zr$; гидрофобное свойство.

Introduction

$Ti_{13}Nb_{13}Zr$ alloy is a representative of the third generation of biomedical titanium alloys [1, 2]. The alloys belonging to this generation utilize Nb, Zr, Mo and other internationally advocated vital group elements and replace the second generation of biomedical titanium alloys which contain harmful to the human body chemical elements. Moreover, the modulus of this new β-titanium alloy is closer to that of the human cortical bone and it has superior biocompatibility. So, it is worth studying as a material for human implants [3].

Equal channel angular pressing (ECAP) is widely used as a mature metal processing severe plastic deformation (SPD) technology. It results in the refinement of the microstructure up to submicron (less than 1 micrometer) and even nanometer (less than 100 nm) levels. The obtained ultrafine-grained (UFG) structure often contains nanograins, nanotwins, nanosegragations, nanoprecipitates and in this case the UFG materials are called nanostructured (NS) metals and alloys. The UFG and NS materials are characterized by enhanced multifunctional properties. So, they are very attractive for the different industrial applications. However, problems still exist when the ECAP is to be transferred to manufacture bulk nanostructured materials in the industrial level.

In order to overcome the inability to achieve continuous production of UFG and NS materials by SPD, in 1997, Dr. Green in the UK first pioneered continuous extrusion technology [4]. This technology is the combination of ECAP and continuous extrusion technology and is a new composite process called continuous equal channel pressing, or ECAP-Conform (ECAP-C), or ECAP-E (ECAP-extrusion). Raab et al. used this technique to obtain titanium ultrafine grained (UFG) materials [5,6]. At present, ECAP-Conform has been applied in titanium alloys. With the application of this technique, uninterrupted continuous production and cost reduction can be achieved [7].

Rotary Swaging refers to the high-frequency hammering of forgings while they move axially and rotate simultaneously. It is beneficial for the metal to undergo uniform deformation while improving plasticity. The forgings that have undergone rotary forging have both high dimensional accuracy and quality [8]. Therefore, this process can be widely applicable to different types of alloys. Compared to unprocessed titanium alloy, the deformed titanium alloy after ECAP Conform + Rotary Swaging multi-stage plastic deformation has a more significant grain refinement effect, significantly improved strength, fatigue limit, thermal stability temperature, and superplastic process performance [9]. So, the overall mechanical properties of the alloys can be significantly improved.

The deformation treated ingots of the biomedical titanium alloys are a subject for the following treatment aimed in the formation of the strong protective layer on their surface. A titanium dioxide nanotube array layer can be formed on the surface of titanium alloys. The porous surface layers are more advantageous because they are more biocompatible. However, there are currently only a few studies on the preparation of porous structures on the surface of deformed titanium alloys [10].

The aim of the present paper is to study the process of the formation and the features of the porous layer formed on the surface of the ingots of the third-generation biomedical titanium $Ti_{13}Nb_{13}Zr$ alloy subjected to combined cold SPD processing and test the surface hydrophobicity and corrosion weight loss.

1. Material and methods

1.1. Solid solution treatment, ECAP-Conform and RS procedures

The $Ti_{13}Nb_{13}Zr$ alloy rods were placed into the furnace, heated up to 750 °C at 10 °C/min, held for 40 minutes, and then immediately put into water for rapid cooling.

The titanium alloy rods were treated with ECAP-Conform after solid solution treatment. The channel angle of the ECAP-Conform deformation mold was 90°, and the extrusion speed was 16 mm/s. Before extrusion, lubricant was placed inside between the mold channel and the alloy surface. The lubricant was MoS_2 and engine oil with the ratio of 2:1. After the alloy was subjected to ECAP-Conform, its diameter reduced from 10 mm to 8 mm.

The feeding speed of the Rotary Swaging process was 16 mm/s. Before processing, the surfaces of the rods were polished and cleaned, the oxide layer was removed, and then the rods were placed in the machine to obtain a 5 mm diameter rod.

1.2. Sample preparations for anodization

The rods were cut by wire electrical discharge machining into round discs of thickness 1 mm. Discs surface was ground by a series of metallographic alumina sandpapers (180#, 500#, 1000#, 1200# and 1500#) in order to remove the layers influenced by Electrical Discharge Machining. Samples were then placed in the hypertrophic solution, subsequently dried by exfoliating water.

1.3. Anodization

$Ti_{13}Nb_{13}Zr$ alloy discs served as anode, while graphite rods acted as cathode. The graphite rod had a diameter of 5 mm, a length of 5 cm, and the part entering the electrolyte was about 3 cm. 0.5%wt HF water solution system was used for anodic oxidation assessment. The anodic oxidation was performed at a constant voltage of 15 V, 20 V, 25 V, and 30 V. The oxidation time was 20 min, 30 min, 40 min and 60 min. The solution temperature was kept at 35 °C. Before anodization, the mechanical stirring was conducted with 240 r/min for 15 min. In the process of the entire anodic oxidation, the smooth surface of the titanium disc was facing the graphite rod. The distance between the poles was 3 cm. The mechanical stirring was used to ensure that anodic oxidation was performed evenly to form titanium oxide nanopores. The mechanical stirring rate was 180 r/min when anodizing. The samples were taken out from the solution after the oxidation immediately, and cleaned with distilled water and dried in oven.

1.4. Characterization and testing

The field emission scanning electron microscope (FE-SEM, Hitachi Regulus 8100) was used to characterize the shape of nanopores in the surface layer of $Ti_{13}Nb_{13}Zr$ alloy. The acceleration voltage was 10 kV for SEM characterization.

The analysis and calculation of the pore size, pore thickness, and porosity were conducted using such software as Image Pro and Nano Measure. The five-point angle measuring method was applied to calculate the contact angle by dropping one drop of water on the surface layer of $Ti_{13}Nb_{13}Zr$ alloy. After treatment under the optimal anodizing process parameters, the samples were immersed into Hanks´ solution for 7 days and the weight loss of them was measured.

2. Results and discussion

The ultimate tensile strength (UTS), yield strength (YS), and elongation (EL) of $Ti_{13}Nb_{13}Zr$ alloy after the solid solution (ST), ECAP-Conform, and ECAP-Conform + RS processing are shown in Fig. 1 and Table 1. After the solid solution treatment, the alloy transforms into a fully metastable phase structure (Fig. 2), and the ultimate tensile strength reached 580.8 MPa. After ECAP-Conform, the tensile strength is increased by 52.3% compared to the solid solution state, reaching 884.7 MPa. RS treatment made the microstructure more uniform and the grains smaller (Fig. 2). Compared with the solid solution state, the tensile strength increased by 101.1%, reaching 1167.7 MPa, while the elongation decreased to 8.6%.

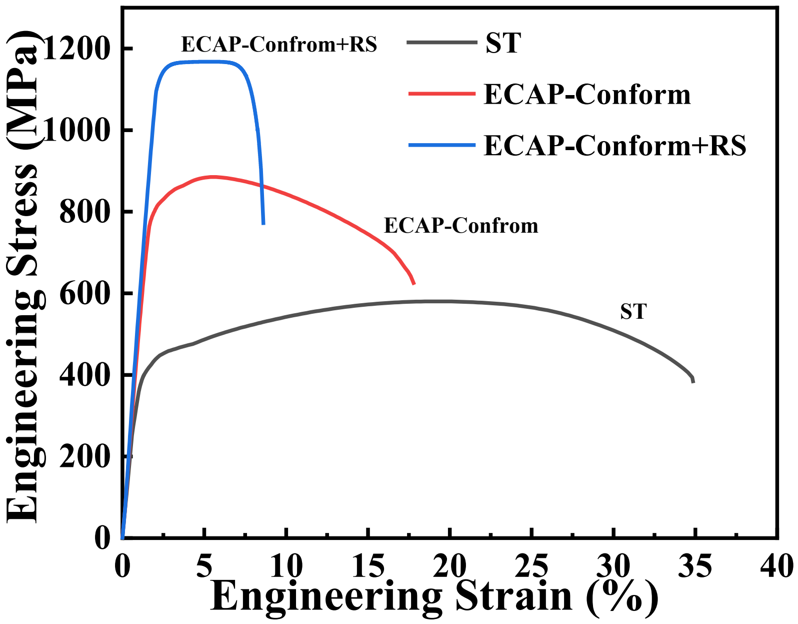

Fig. 1. Stress-strain curves for the different states after ST, ECAP-Conform, and ECAP-Conform + RS

Рис. 1. Кривые «напряжение – деформация» для различных состояний: после обработки на твердый раствор (ST), РКУП-Конформ (ECAP-Conform) и РКУП-Конформ + ротационной ковки (ECAP-Conform + RS)

Table 1. Yield strength (YS), ultimate tensile strength (YTS), and elongation to failure (EL) of the alloy after ST, ECAP-Conform, and ECAP-Conform + RS

Таблица 1. Предел текучести (YS), предел прочности на растяжение (YTS) и удлинение до разрушения (EL) сплава после обработки на твердый раствор (ST), РКУП-Конформ (ECAP-Conform) и РКУП-Конформ + ротационной ковки (ECAP-Conform + RS)

Sample	YS (MPa)	UTS (MPa)	EL (%)
ST	383.1 ± 17.3	580.8 ± 15	34.9±1.5
ECAP-Conform	770.1 ± 22.1	884.7 ± 14.7	17.8 ± 1.1
ECAP-Conform + RS	1082.7 ± 33.5	1167.7 ± 29.5	8.6 ± 0.3

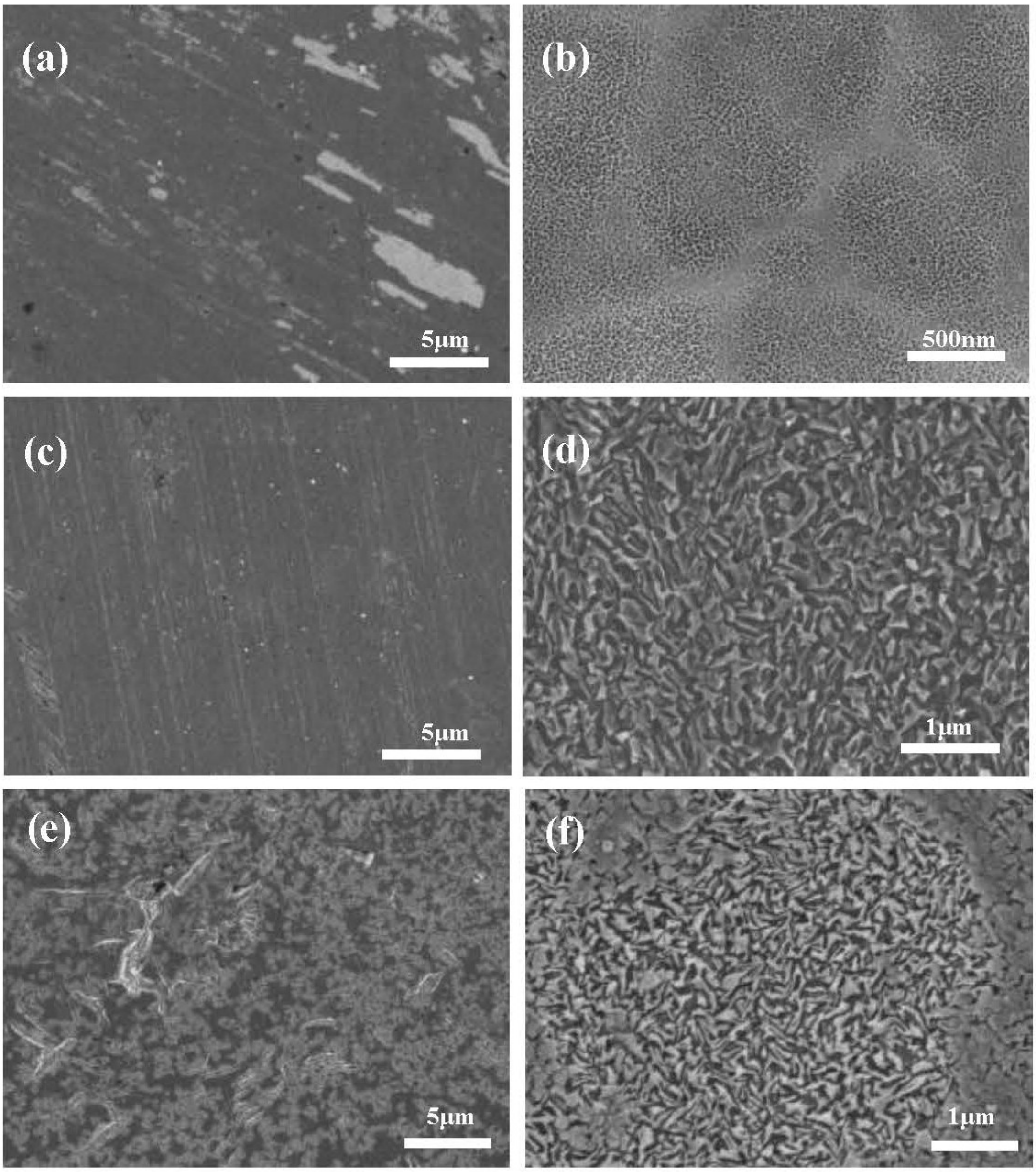

Fig. 2. The solid solution state (*a*); ECAP-Conform state (*c*); ECAP-Conform + RS state (*e*); the surface porous structures of the corresponding states after anodization (*b, d, f*)

Рис. 2. Состояние после обработки на твердый раствор (*a*); состояние после РКУП-Конформ (*c*); состояние после РКУП-Конформ + ротационной ковки (*e*); поверхностные пористые структуры соответствующих состояний после анодирования (*b, d, f*)

Fig. 2 (a) shows the surface morphology of the untreated solid solution titanium alloy. After anodizing, a nanoporous structure appears in the surface layer and then agglomerates, as shown in Fig. 2 (b). Fig. 2 (c) shows the titanium alloy treated with ECAP-Conform, and it can be seen that its growth exhibits a certain directionality. This is due to the crushing of grains caused by extrusion, which to some extent refines the structure and, simultaneously, makes the grain direction follow a specific extrusion direction. After anodizing treatment, there were no nanotube arrays on the surface of the titanium alloy treated with ECAP-Conform, but a uniformly distributed porous structure also appeared, with larger pore sizes. The surface pores were not regular circular pores, but slightly distorted and showed a certain degree of directionality as shown in Fig. 2 (d), which is related to the pressure treatment process. Fig. 2 (e) shows the surface of titanium alloy treated with ECAP-Conform + Rotary Swaging. The above two processing methods have played a role in fine grain strengthening, improving the strength and hardness of the titanium alloy, as well as improving the plasticity and toughness. The large amount of patterned structure on the surface is precipitated α-phase.

The titanium alloy processed by ECAP-Conform and RS was anodized. The porous structure formed on the surface was similar to that of solid solution treated titanium alloy.

Fig. 3 (a, b) shows that after anodizing with a voltage of 15 V and a time of 20 minutes, a uniform porous structure appears on the surface. However, due to the short anodizing time, there is still a titanium dioxide barrier layer on the surface that has not peeled off. Some crushed grains generated during the extrusion deformation treatment are scattered in the porous structure on the alloy surface.

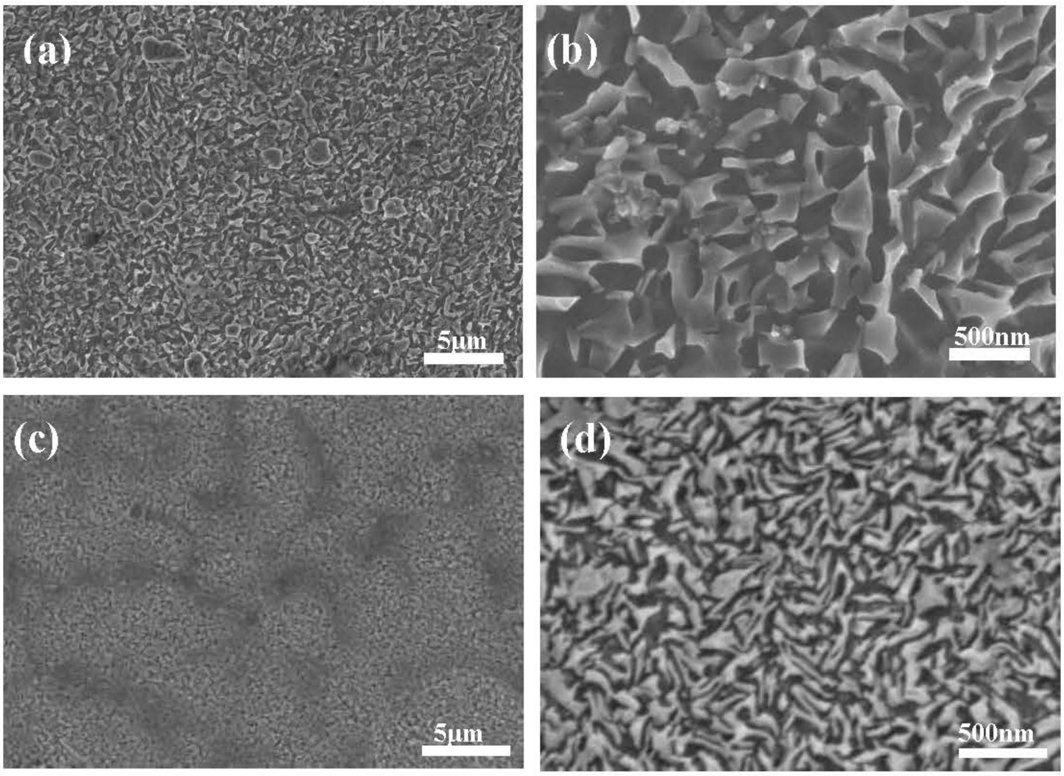

Fig. 3. Porous structure formed on the surface of ECAP-Conform (*a*, *b*) treated under 15 V, 20 min conditions and ECAP-Conform + RS (*c, d*) treated under 25 V, 40 min deformed titanium alloy

Рис. 3. Пористая структура, сформированная на поверхности титанового сплава после РКУП-Конформ (*a*, *b*), подвергнутого обработке при 15 В в течение 20 мин., и после РКУП-Конформ + ротационной ковки (*c, d*), подвергнутого обработке при 25 В в течение 40 мин

From Fig. 3 (c, d), it can be observed that under the parameter conditions of anodizing voltage of 25 V and anodizing time of 40 minutes, the pores distribution formed on the surface of titanium alloy is very uniform. This may be due to the incomplete formation of a barrier layer on the titanium surface under the conditions of this anodic oxidation parameter, forming a micro cell structure, which accelerates the dissolution of the filmless area.

As the anodizing time increases, such a porous layer is formed on the surface of titanium alloy, where the uniform pores are distorted due to the influence of ECAP-Conform and RS.

β titanium alloy has better corrosion resistance than α titanium alloy. So, β phase gradually generates oxides to cover the surface, which is shown in Fig. 3, as a nonporous dimpled structure. With the increase of anodizing voltage, the rate of increase in surface oxide film thickness is uneven, and the number of pits gradually increases, forming a continuous and undulating porous structure on the titanium alloy surface.

From Fig. 4, it can be seen that the critical conditions for the appearance of nanoporous layers on the surface of deformed titanium alloy treated with ECAP-Conform is the anodic oxidation voltage of 15 V and the anodic oxidation time of 20 minutes. In this case the porosity reaches a maximum value of 80% at 20 V, 20 min. When the anodizing voltage reaches 30 V, the porous size decreases under different anodizing time conditions and approaches the same value, indicating that there is a certain change in the surface structure of titanium alloy at 30 V. The pore size is significantly higher than that of unprocessed titanium alloy, possibly due to the ECAP-Conform process. The grains are crushed and recrystallized, resulting in a larger average pore size.

The optimal anodizing parameters for the deformed titanium alloy treated with ECAP-Conform + RS are 25 V, 40 min, and the porosity reaches 60%. After Rotary Swaging, the influence of ECAP-Conform on the material is greatly alleviated, and the grain refinement phenomenon occurs. The material forms a surface porous structure with an average pore size of less than 100 nm while increasing its strength and hardness.

The hydrophobic properties of titanium alloy treated by ECAP-Conform and anodization composite process did not show significant changes in comparison with initial sample. The hydrophobicity of titanium alloy treated by ECAP-Conform + RS and anodization composite process significantly increased, compared with ECAP-Conform + RS samples. The contact angle of the water drop on the surface of the sample after anodizing reached 120°, which corresponds to an increase of 30%. After ECAP-Conform + RS treatment, the surface microstructure of titanium alloy is closer to the surface of unprocessed titanium alloy, and the strength and hardness are significantly improved. The average pore size of the surface porous structure formed after anodization is lower than that of titanium alloy only treated with ECAP-Conform [11].

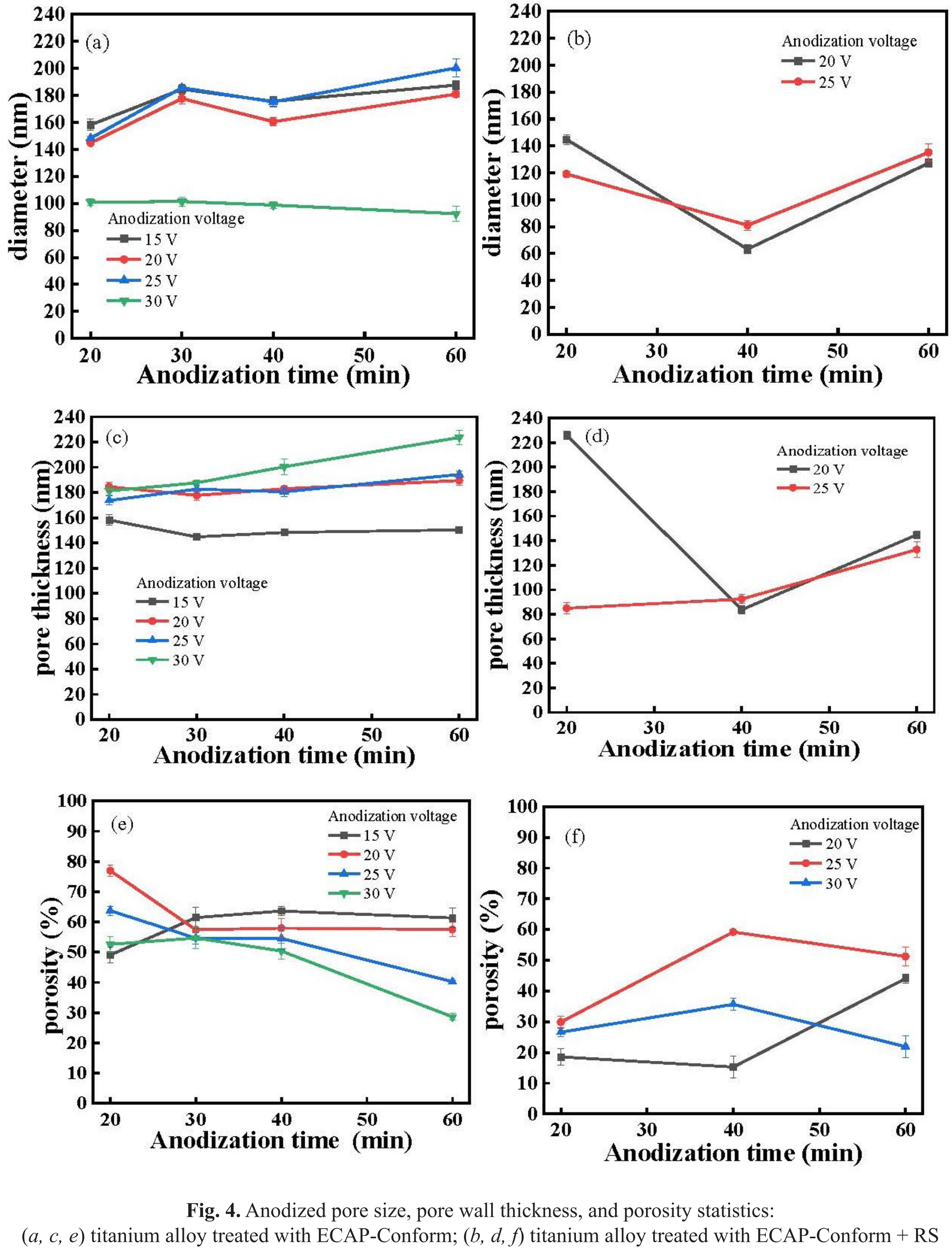

Fig. 4. Anodized pore size, pore wall thickness, and porosity statistics:
(*a, c, e*) titanium alloy treated with ECAP-Conform; (*b, d, f*) titanium alloy treated with ECAP-Conform + RS

Рис. 4. Размер пор, толщина стенок пор и пористость после анодирования: (*a, c, e*) в случае титанового сплава после РКУП-Конформ; (*b, d, f*) в случае титанового сплава после РКУП-Конформ + ротационной ковки

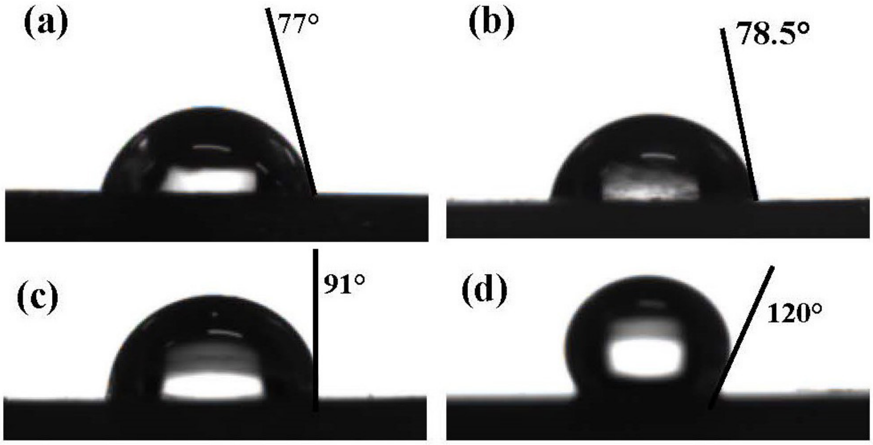

Fig. 5. The drop of water on the surface of titanium alloy treated with ECAP-Conform (*a, b*) and ECAP-Conform and RS (*b, d*): (*a, c*) not anodized; (*b*) anodized with parameters of 20 V and 20 min; (*d*) anodized with parameters of 25 V and 40 min

Рис. 5. Капля воды на поверхности титанового сплава после РКУП-Конформ (*a, b*) и после РКУП-Конформ с последующей ротационной ковкой (*b, d*): (*a, c*) без анодирования; (*b*) при анодировании с параметрами 20 В и 20 мин.; (*d*) при анодировании с параметрами 25 В и 40 мин

As shown in Fig. 6, the weight of the deformed titanium alloy samples increases with the increase of immersion time in Hanks' solution. The initial rate of increase is faster at 24 hours, then the growth rate gradually decreases, and gradually approaches a stable value after 120 hours. The titanium alloy with a porous surface structure did not lose mass in Hanks' solution. Cl^- ions are very sensitive to crevice corrosion and is usually preferentially are adsorbed by the oxide film on the surface of titanium alloys. Cl- ions combine with cations in the oxide film to form soluble chlorides, accelerating corrosion [12, 13]. Therefore, Cl^- are the main factor causing corrosion and quality loss. Hanks' solution is similar to the human body fluid environment, and the Ca^{2+}, SO_4^{2-}, and other ions in the solution may inhibit the corrosion effect of Cl^-. At the same time, molecules such as Na_2HPO_4 and KH_2PO_4 can be adsorbed by the metal surface, and the porous structure on the metal surface forms barrier, suppressing the crevice corrosion mechanism of Cl^- [14, 15].

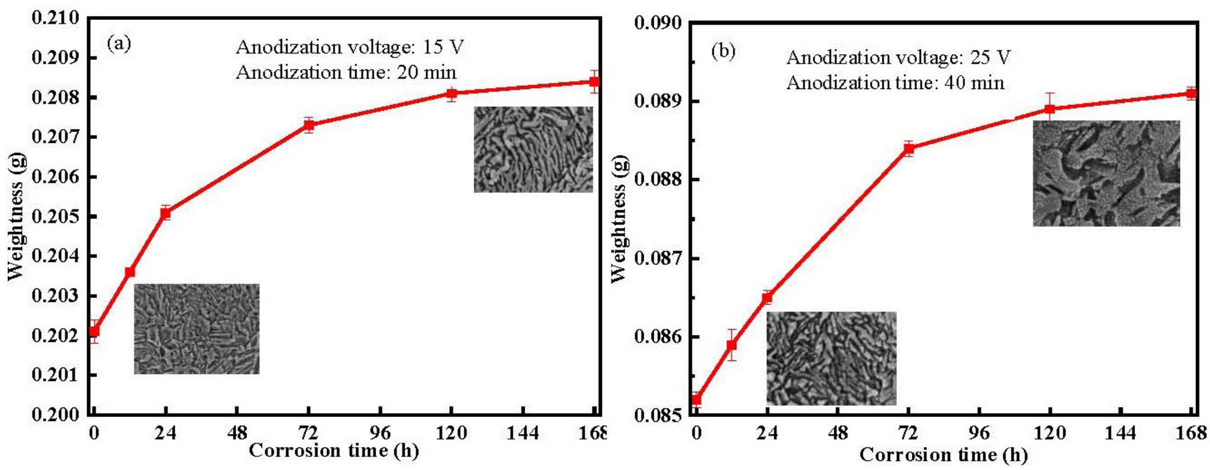

Fig. 6. Mass change after immersion in Hanks' equilibrium salt solution: (*a*) titanium alloy treated with ECAP-Conform, anodization parameters of 20 V and 20 min; (*b*) titanium alloy treated with ECAP-Conform + RS, anodization parameters of 25 V and 40 min

Рис. 6. Изменение массы после погружения в равновесный солевой раствор Хэнкса: (*a*) титановый сплав после РКУП-Конформ, параметры анодирования: 20 В и 20 мин.; (*b*) титановый сплав после РКУП-Конформ + ротационной ковки, параметры анодирования: 25 В и 40 мин

Conclusion

This study used the method of anodic oxidation to prepare nanoscale porous layer on the surface of the $Ti_{13}Nb_{13}Zr$ alloy subjected to ECAP-Conform and RS and explored the following rules:

1. The uniform nanoporous layer was formed on the surface of the ECAP-Conform + RS alloy due to anodization.

2. The optimal anodic oxidation parameters for the formation of uniform surface porous layer were established.

3. A homogeneous nanoporous layer reduces the wettability of the surface of a titanium alloy subjected to ECAP-Conform + RS. The titanium alloy with a porous surface structure did not lose mass in Hanks' solution.

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REFERENCES

1. Long M., Rack H. J. Titanium alloys in total joint replacement-a materials science perspective // Biomaterials. 1998. V. 19, Iss. 18. P. 1621–1639. DOI: 10.1016/s0142-9612(97)00146-4.

2. Ning C., Zhou Y. Development and research status of medical titanium alloy // Mater. Sci. Technol. 2002. V. 10, Iss. 1. P. 7–10. DOI: 10.3969/j.issn.1005-0299.2002.01.026.

3. Wu Y., Guo A. Development and research status of biomedical titanium alloys // Mater. Dev. Appl. 2010. V. 25, Iss. 2. P. 5–11. DOI: 10.3969/j.issn.1003-1545.2010.02.018.

4. Yang X., Zhao X., Fu W. Deformed microstructures and mechanical properties of CP-Ti processed by multi-pass ECAP at room temperature // Rare Met. Mater. Eng. 2009. V. 38, Iss. 6. P. 955–957. DOI: 10.1016/S1875-5372(10)60039-2.

5. Raab G. J., Valiev R. Z., Lowe T. C., Zhu Yu. T. Continuous processing of ultrafine grained Al by ECAP–Conform // Mater. Sci. Eng. A. 2004. V. 382, Iss. 1–2. P. 30–34. DOI: 10.1016/j.msea.2004.04.021.

6. Raab G. J., Gunderov D. V., Polyakov A. V., Semenova I. P. Evolution of microstructure, macrotexture and mechanical properties of commercially pure Ti during ECAP-conform processing and drawing // Mater. Sci. Eng., A. 2013. V. 562. P. 128–136. DOI: 10.1016/j.msea.2012.11.007.

7. Li H., Nong D., Hu Z. Study on the preparation of ultrafine grain materials using ECAP-Conform new technology // New. Technol. New Process. 2006. V. 8. P. 30–32. DOI: 10.3969/j.issn.1003-5311.2006.08.009.

8. Kuroda D., Niinomi M., Morinaga M., Kato Y., Yashiro T. Design and mechanical properties of new β type titanium alloys for implant materials // Mater. Sci. Eng. A. 1998. V. 243, Iss. 1–2. P. 244–249. DOI: 10.1016/S0921-5093(97)00808-3.

9. Fang X., Li M., Lin Y. Formation of ultra-fine grained titanium alloy by equal channel angular pressing // Mater. Rep. 2006. V. 20, Iss. 10. P. 107–110. DOI: 10.3321/j.issn:1005-023X.2006.10.027.

10. Jin H. The development and research status of medical titanium alloy // Chin. J. Rare Met. 2003. V. 27, Iss. 6. P. 794–798. DOI: 10.3969/j.issn.0258-7076.2003.06.029.

11. Liu X., Wang T., Tong W., Xu Q., Kong J. Fabrication of unmodified bionic copper surfaces with highly stable hydrophobicity and anti-icing properties via a transfer

with Zr-based metallic glasses // Adv. Mater. Interfaces. 2020. V. 8, Iss. 3. Article number 2001743. DOI: 10.1002/admi.202001743.

12. Zhang C., Liu C., Yang H. Study on electrochemical corrosion property of magnesium alloy AZ31 in Hanks' solutions // J. Wuhan Univ. Technol. 2014. V. 36, Iss. 2. P. 21–25. DOI: 10.3963/j.issn.1671-4431.2014.02.005.

13. Xiao S., Chao M., Liu J. Research on influence rule of technological parameter for new-style titanium alloy anodization // Trainer. 2011. V. 2. P. 35–39. DOI: CNKI:SUN:HDKO.0.2011-02-011.

14. Bai Y., Li S., Hao Y., Yang R. Electrochemical corrosion behavior of a new biomedical Ti-24Nb-4Zr-8Sn alloy in Hanks´ solution // Acta Metall. Sin. 2012. V. 48, Iss. 1. P. 76–84. DOI: 10.3724/SP.J.1037.2011.00530.

15. Yi X., Fan Z., Zhang J. Experimental study of preparation of TiO_2 porous films on the surface of TC4 titanium al1oy by anodic oxidation // J. Mater. Eng. 2010. V. 3, Iss. 38–41. DOI: 10.3969/j.issn.1001-4381.2010.03.010.