

Influence of Alkali Heat Treatment of Titanium Alloys on the Preparation of HA Coating

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Abstract

The HA coating was prepared by immersing TC4 alloy in different concentrations of NaOH solution at 60°C for 24 h and heat treating at 600°C, combined with sol-gel method. The effects of alkali concentration on the surface of titanium alloy and the physical phase of HA coating were analysed by X-ray diffractometer, the effects of alkali concentration on the surface morphology of titanium alloy and the morphology of HA coating were analysed by scanning electron microscope, the effects of alkali concentration on the hydrophilicity of HA coating were analysed by contact angle measuring instrument, and the effects of alkali concentration on the corrosion resistance of HA coating were analysed by electrochemical workstation. The results of the surface: alkali heat treatment can generate Na₂Ti₅O₁₁ phase on the surface of TC4 and the surface has micro-nano porous structure, when the concentration of alkali solution is 7.5 mol /L, the HA coating has the least cracks on the surface and the highest degree of integrity, and at the same time, improves its hydrophilicity (the wetting angle is 32 °) and corrosion resistance (the corrosion current is 1.870×10^{-7} A/cm²).

Keywords

Alkali Heat Treatment; Surface Modification; Naoh Solution; HA Coating; Hydrophilicity; Corrosion Resistance.

1. Introduction

Titanium and its alloys are often used as implant materials due to their better corrosion resistance[1], and biocompatibility[2]. However, as a biologically inert material, titanium alloys cannot form a strong bond with bone tissue and tend to become loose after long-term use, thus losing implant effectiveness[3]. In order to improve the biological properties of titanium implants and to achieve a strong bond with bone tissue, hydroxyapatite (HA), a major inorganic component of natural bone tissue, is often deposited on the titanium surface [4-6]. The methods currently used to produce HA coatings on titanium surfaces include sol-gel, pulse deposition, magnetron sputtering and plasma spraying[7,8]. The sol-gel method involves turning the coating substance into a sol so that it covers the titanium surface evenly. The gel method is to make the coating material into a sol so that it is uniformly covered on the surface of the substrate due to the rapid volatilisation of the solvent and the subsequent polycondensation reaction and gelation[9-12]., and then after drying and heat treatment, the coating can be obtained. With simple process, low forming temperature, easy to control the composition and microstructure, low cost and so on. However, the disadvantage of this method is that the gel shrinks drastically during the drying process, resulting in a large number of cracks, unsatisfactory bonding strength between the coating and the substrate, and a thick coating that is easy to peel off[13]. Therefore, improving the interfacial bond strength between the HA coating and the Ti substrate is a key factor in ensuring the success of clinical implantation[14]. A strong correlation was found between the average roughness of the substrate surface and the adhesion strength of the

coating. Compared to smooth surfaces, HA coatings on highly roughened substrate surfaces exhibited high bond strengths, mainly due to the fact that roughened surfaces induce mechanical interlocking between the substrate and the coating[15]. Therefore, appropriate pretreatment of the substrate, such as chemical etching[16], sand blasting and laser gas nitriding[17], can improve the bond strength between the coating and the substrate. In addition, the design of a porous structure at the interface between the coating and the substrate, its larger specific surface area and roughness, is conducive to inducing HA to grow into the pores and form a higher bond strength. This paper investigates the alkali pretreatment of TC4 alloy specimens to improve the structural properties of the titanium alloy surface in preparation for the subsequent preparation of HA coatings by the sol-gel method and to improve the bond strength between the alloy and the substrate. The effects of varying the alkali concentration on the surface morphology and physical phase of the titanium alloy and on the morphology, physical phase, wettability and corrosion resistance of the HA coating was studied in order to obtain the optimum alkali concentration for alkali pretreatment.

2. Materials and Methods

2.1 Preparation of Samples

The thickness of 3 mm TC4 alloy plate cut into 10mm × 10mm specimens will be cut substrate cleaning and drying, with metallographic sandpaper (400~1500#) from small to large a grinding and polishing, remove the surface of the oxide film and contaminants. Substrates were ultrasonically cleaned in acetone, anhydrous ethanol and deionised water for 30 minutes each, then dried and set aside. The TC4 substrate was placed in a solution of different NaOH concentrations, respectively, 2.5 mol/L, 5 mol/L, 7.5 mol/L, 10 mol/L, placed in a water bath at 60 °C under the condition of reaction for 24 h, cleaning and drying for heat treatment, selecting the heating temperature of 600 °C temperature, the rate of temperature increase are 5 °C / min, holding 1 h after cooling with the furnace.

The HA sol was prepared according to $n(\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}) : n(\text{P}_2\text{O}_5) = 10 : 3$. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and P_2O_5 were weighed, placed in a beaker and mixed with an appropriate amount of anhydrous ethanol. The $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution was stirred in a constant temperature water bath at 60 °C for 1 h, then the P_2O_5 solution was slowly added and stirred for 2 h. The solution was filtered, the pH was adjusted to 8.0 and it was aged for 24 h. The HA sol was prepared by mixing the pre-treated and alkaline heat-treated HA sols. The pre-treated and alkaline heat-treated TC4 substrate was introduced into the prepared sol at a rate of 1 mm/s, immersed for 2 min, then removed at a rate of 3 mm/s, dried at 60 °C for 2 h and heat-treated at 550 °C for 2 h. The HA coating was obtained.

2.2 Surface Characterization

Diffraction (referred to as XRD, D8 ADVANCE) was used for the phase analysis of the surface of the samples. The scanning angle 2θ range was set as 20–60°, and the speed was set to 5°/min. The surface morphology of the samples was characterized by scanning electron microscopy (SEM, Quanta FEG 450). At room temperature, 3.5 mL of simulated body liquid was dropped onto the sample surface, and the surface wettability was evaluated using the hanging drop method of the contact angle analyzer (Dataphysics, OCA20, Germany). The contact angle was calculated by a five-point fitting method. Three different positions were randomly selected for each sample to obtain average values with standard deviations.

2.3 Electrochemical Testing

The corrosion resistance of the coating was measured by an electrochemical workstation through the potential polarization method. All corrosion tests were conducted by soaking the samples in simulated body fluid (SBF) in advance. The conductor was connected to the sample with a conductive adhesive. The sample had a working area of 1.5 cm². In electrochemical work, the sample was used as the working electrode, the saturated calomel electrode (SCE) was used as the reference electrode, and the platinum electrode was used as the auxiliary electrode. Corrosion resistance was characterized by measuring the Tafel curve of the tested sample. The self-corrosion current density derived from the

Tafel curve was used to evaluate the corrosion resistance of the sample. All tests were repeated at least three times.

3. Results and Discussion

Fig1.shows the XRD spectra of TC4 substrate after 2.5, 5, 7.5, 10 mol/L NaOH solution at a constant temperature of 60 °C immersed in 24h and 600 °C heat treatment, it can be seen that the concentration of NaOH solution 2.5mol/L XRD diffraction spectrum and the untreated specimen is almost the same, which may be the titanium sheet in contact with the air after polishing, the rapid formation of a layer of dense oxidation on the surface, this layer of oxide film has good chemical stability, strong corrosion resistance, so when the lower concentration of NaOH solution does not react with the titanium or its oxides, may be obtained at this time the gel layer is still very thin, corrosion resistance is strong. This may be due to the fact that the titanium sheet contacted with air after polishing, quickly formed a dense oxide film on the surface, which has good chemical stability and strong corrosion resistance, so when the concentration of NaOH solution is low and can not react with the titanium or its oxides, the gel layer obtained at this time may still be very thin, the diffraction peaks are not obvious. When the NaOH solution concentration of 5 mol / L, in addition to the matrix TC4 peaks, but also the appearance of sodium titanate ($\text{Na}_2\text{Ti}_5\text{O}_{11}$). This is due to the fact that NaOH solution immersion of titanium alloy sheet will form a sodium titanate gel layer on the surface, and the gel layer can be transformed into porous sodium titanate ($\text{Na}_2\text{Ti}_5\text{O}_{11}$) after 600 °C heat treatment. Comparison of different concentrations of alkali immersion XRD spectra can be concluded. The peaks of ($\text{Na}_2\text{Ti}_5\text{O}_{11}$) produced by 2.5 mol/L NaOH immersion are not obvious, and the width of the peaks is not large and sparse. With the increase of alkali concentration, the peak of ($\text{Na}_2\text{Ti}_5\text{O}_{11}$) is more obvious, indicating that at the same immersion temperature and time, the larger the alkali concentration, the easier it is to form the ($\text{Na}_2\text{Ti}_5\text{O}_{11}$) phase on the surface of titanium alloy.

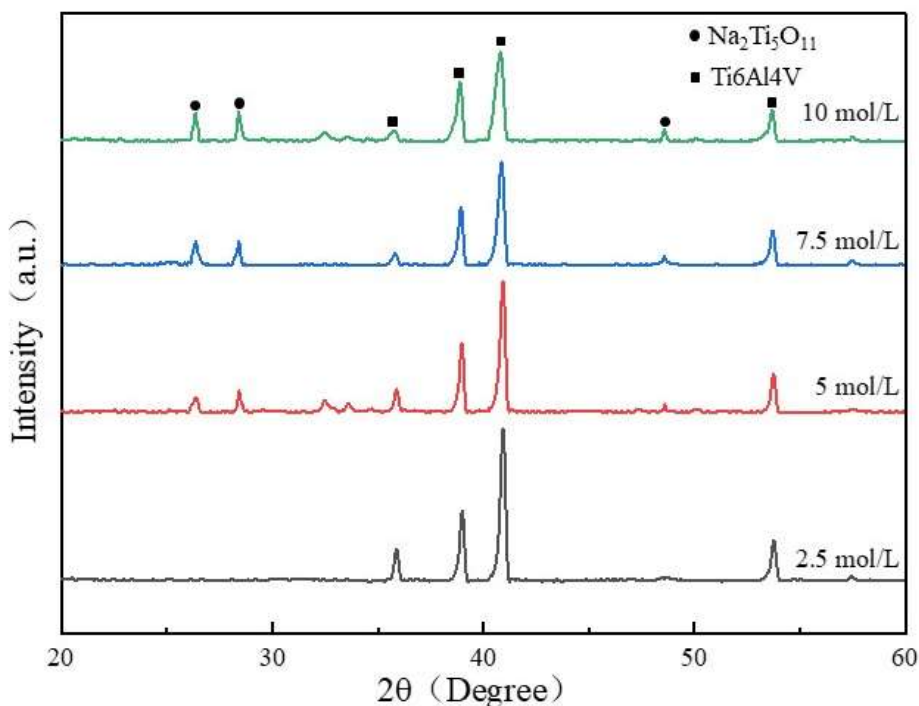


Fig. 1 XRD pattern of TC4 alloy after heat treatment with different concentrations of NaOH solution at 60°C for 24 h and after heat treatment at 600°C for 1 h

Fig.2 shows SEM images of the surface topography of a titanium alloy after immersion in NaOH solution at a constant temperature of 60 °C for 24 h.after heat treatment at 600°C for 1 h .From Fig.2,

it can be seen that the alkali heat-treated titanium sheets successfully formed a network structure. When the concentration of NaOH solution is 2.5 mol/L, the surface of titanium sheet is corroded by NaOH solution to form a larger mesh structure; concentration of 5 mol/L when the mesh size becomes more and more uniform, dense, but when the concentration reaches 7.5 mol/L, the mesh mouth began to close, the pore size decreased, and the concentration of 10 mol/L, the surface cracks. Cracks on the surface of titanium alloy may be due to stress, NaOH reacts with titanium to form sodium titanate gel, as the reaction progresses, more and more sodium titanate gel is deposited on the surface of titanium alloy, resulting in smaller mesh on the surface, and when the amount of sodium titanate gel deposition reaches a certain thickness, the water in the subsequent drying process can not escape, resulting in cracks.

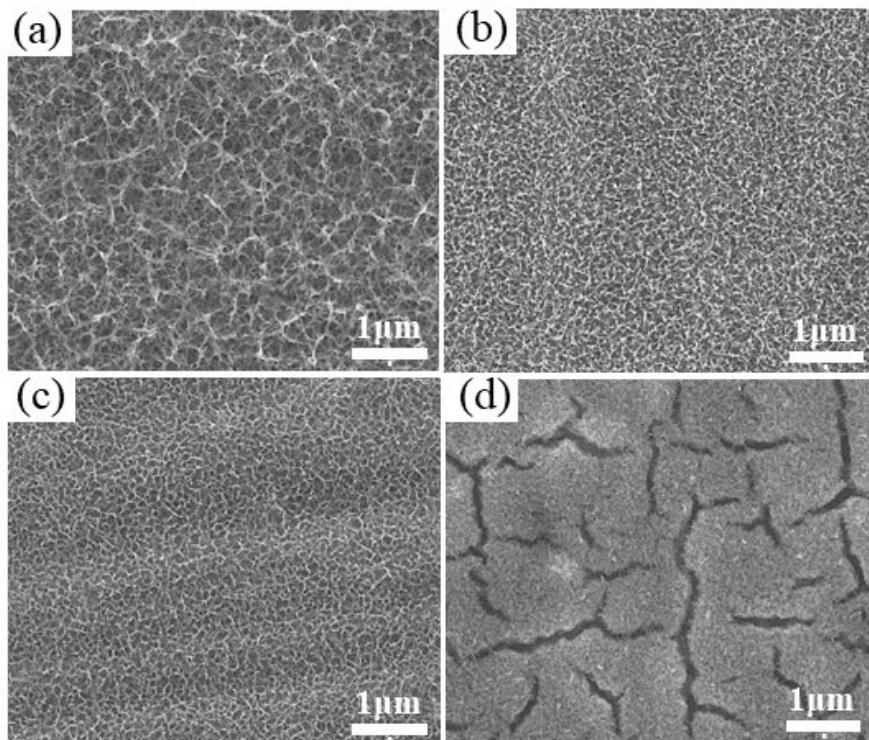


Fig. 2 SEM images of TC4 alloy after heat treatment with (a) 2.5 mol/L, (b) 5 mol/L, (c) 7.5 mol/L and (d) 10 mol/L NaOH solution in a water bath at 60°C for 24 h and after heat treatment at 600°C for 1 h

Fig.3 shows the XRD patterns of HA coatings on TC4 substrate after alkali heat treatment with different concentrations of NaOH solution using the sol-gel method of immersion coating, it can be seen that HA coatings can be successfully prepared on the surface of titanium alloys by using a combination of alkali heat treatment and sol-gel method, followed by a holding time of 2 h at 550 °C for the treatment. In addition to the physical HA phase, there is also a $\text{Na}_2\text{Ti}_5\text{O}_{11}$ phase, in which the $\text{Na}_2\text{Ti}_5\text{O}_{11}$ phase acts as an intermediate transition layer. According to the XRD diffraction pattern, the HA peaks were distributed at $2\theta = 26.3, 32.2, 32.5$ and 40.08° positions. When the concentration of the NaOH solution was 7.5 mol/L, the diffraction peaks were the sharpest. According to Scherrer's theory, the sharpening of the characteristic peaks of the crystalline phase in the XRD spectra implies that the crystallinity of HA is increased, and it is concluded that the obtained HA coatings have high crystallinity.

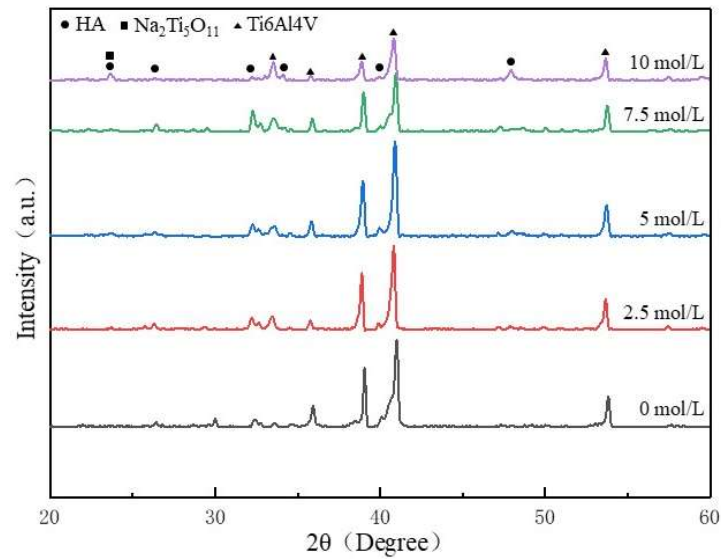


Fig. 3 XRD patterns of dip coated HA coatings of TC4 alloy after alkaline heat treatment with different concentrations of NaOH solution.

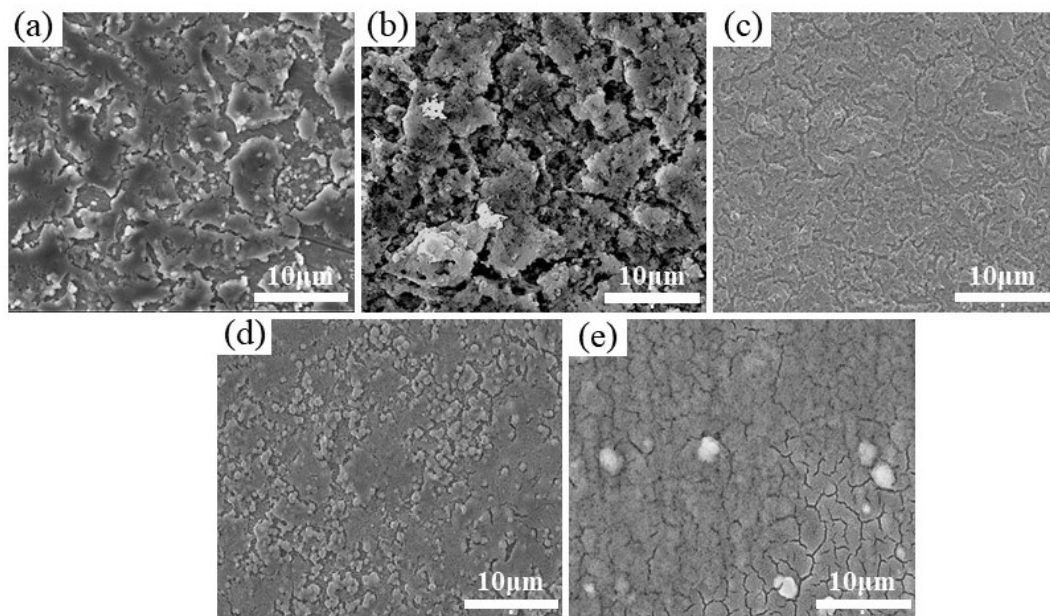


Fig.4 SEM images of dip-coated HA coatings of TC4 alloy after alkaline heat treatment with (a) 0 mol/L, (a) 2.5 mol/L, (b) 5 mol/L, (c) 7.5 mol/L and (d) 10 mol/L NaOH solutions.

Fig. 4 shows the SEM images of TC4 alloy after alkaline heat treatment with (a) 0 mol/L, (b) 2.5 mol/L, (c) 5 mol/L, (d) 7.5 mol/L and (e) 10 mol/L NaOH solution for dip coating of HA coatings using the sol-gel method. One of the most critical parameters affecting the adhesion and hardness of coatings is the micro- and nanocracking on the coating surface. Pure HA coatings have severe microcracks that do not cover the surface of the substrate, and the low bond strength and nanohardness of HA coatings are due to the inhomogeneity of this coating and the severe cracks, the cause of which can be attributed to the inherent brittleness of HA. Therefore, pure HA coatings cannot be used on human tissue because a large part of the substrate surface is exposed to human body fluids. When the concentration of NaOH solution was 2.5 mol/L, the sol-gel dip-coated HA coating still had many cracks, and when the concentration of NaOH solution was increased to 7.5 mol/L, the coating had the least number of cracks and the best surface integrity, and the dip-coated HA coating of the titanium

substrate treated with 10 mol/L NaOH solution was not homogeneous and did not completely cover the surface, and when the concentration of NaOH solution was increased to 7, As the reaction progresses, more and more sodium titanate gel is deposited on the surface of the titanium alloy, and when the amount of deposited sodium titanate gel reaches a certain thickness, water cannot escape during the subsequent drying process, and thus cracks are formed, resulting in the subsequent decrease in the bond strength between the HA coating and the substrate.

As shown in Fig.5, the contact angle of untreated titanium alloy dip-coated with HA coating is 51 °, and the alkali heat treatment angle is significantly reduced, HA coating -OH and PO₄³⁻ are hydrophilic groups, which can form hydrogen bond with water, inducing the expansion of water on the surface of the material to increase the surface energy and improve the wettability. The size of the contact angle is related to the surface integrity of the HA coating, as shown in the SEM images, the HA coating is the most complete after treatment with 7.5 mol/L NaOH solution, and the contact angle of the HA coating is the smallest after treatment with 10 mol/L NaOH, which may be due to the incomplete dip coating of the HA coating, and the porous structure of the surface generated by alkali heat treatment leads to the increase in surface tension of the contact between the water and titanium flake, and thus the contact angle becomes smaller.

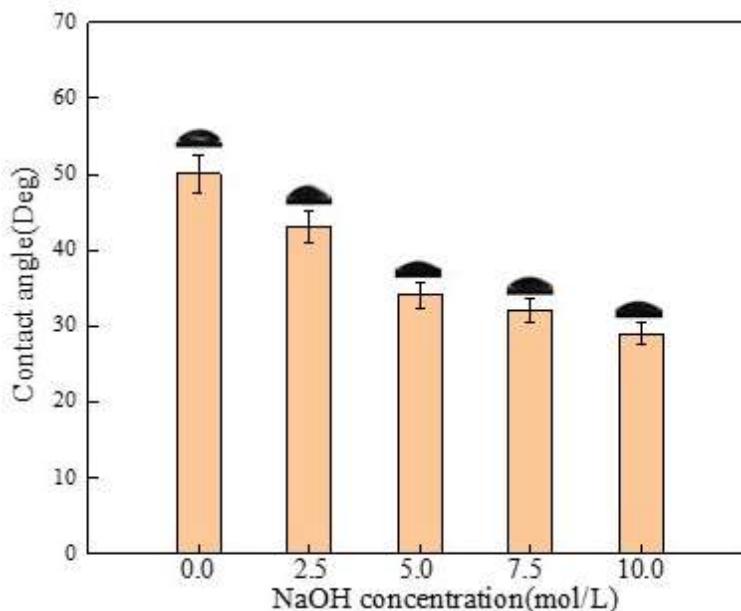


Fig. 5 Hydrophilicity of dip deposited HA coatings on TC4 alloys after alkaline heat treatment with (a) 0 mol/L, (a) 2.5 mol/L, (b) 5 mol/L, (c) 7.5 mol/L and (d) 10 mol/L NaOH solution.

Fig. 6 shows the polarisation curves of different samples, and the parameters obtained by fitting according to Tafel's linear extrapolation method are shown in Table. As shown in Fig.6 and Table.1, the corrosion current for (*i*_{corr}) of TC4 substrate is 1.024×10^{-5} A/cm², indicating negligible corrosion resistance. The corrosion current density of dip-coated HA on TC4 substrate after mechanical treatment only is 4.910×10^{-6} A/cm², which improved the corrosion resistance of the titanium alloy. However, this current density was still high due to the presence of severe cracks in the pure HA coating, and most of the substrate surface was exposed to the SBF solution. The corrosion resistance of the HA coating was improved by dip-coating the TC4 substrate with HA using the sol-gel method after alkali heat treatment. The nano-micropore mesh structure generated by the alkali heat treatment reduces the cracks in the HA coating and eliminates gaps in the interface. The corrosion current density ($1,870 \times 10^{-7}$ A/cm²) at a NaOH solution concentration of 7.5 mol/L indicated that the coating had the least porosity and cracks and the best corrosion resistance. The SEM images also showed that the coating had the best integrity and the least cracks. When the concentration of NaOH solution was

increased to 10 mol/L, the corrosion current density increased, but it was smaller than the corrosion current of the substrate.alkaline heat treatment can form a dense oxide film or oxide layer, and this film can effectively prevent the erosion of titanium alloys by external media, thus improving the corrosion resistance of titanium alloys.

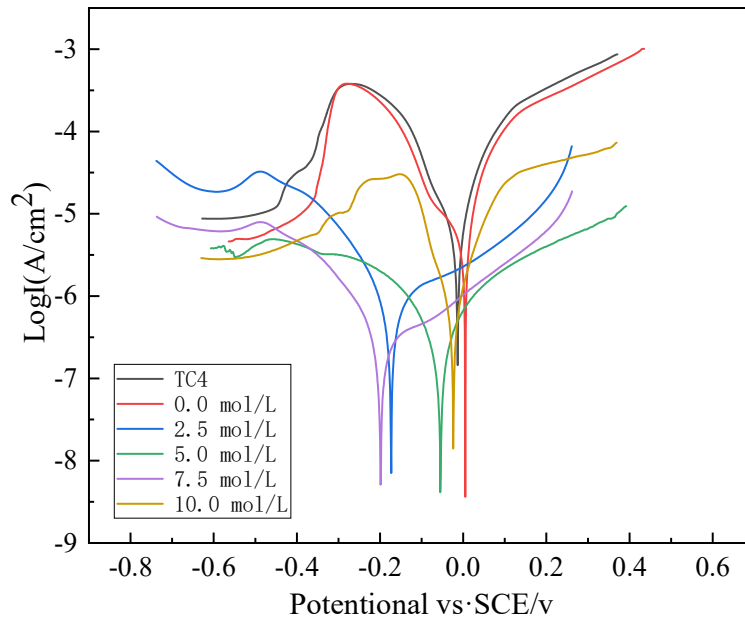


Fig. 6 Polarisation curves of different samples

Table 1. Corrosion potentials and corrosion current densities of different specimens obtained by Tafel curve fitting

Sample	I _{corr} (A/cm ²)	E _{corr} (V)	EOCP(V)
TC4	1.024×10 ⁻⁵	-0.0127	-0.1294
0.0 mol/L	4.910×10 ⁻⁶	0.0037	-0.0650
2.5 mol/L	5.324×10 ⁻⁷	-0.1628	-0.2390
5.0 mol/L	2.300×10 ⁻⁷	-0.0534	-0.1080
7.5 mol/L	1.870×10 ⁻⁷	-0.1940	-0.2380
10.0 mol/L	6.619×10 ⁻⁶	-0.0223	-0.1310

4. Conclusion

In this paper, the Influence of alkali heat treatment of titanium alloys with different concentrations of NaOH solution on the preparation of HA coatings by the sol-gel method was investigated. SEM images showed that the dip-coating of HA coatings on the surfaces of titanium alloys with 7.5 mol/L NaOH solution was more effective, which could reduce the microcracks in the HA coatings, make the HA coatings more intact and increase the bonding strength of the coatings. Surface wettability and electrochemical experiments showed that the hydrophilicity and corrosion resistance of the coatings were significantly improved by alkaline heat treatment with 7.5 mol/L NaOH solution.

References

- [1] Zeng, X.; Han, T.; Guo, Y.; Wang, F. Molecular Dynamics Modeling of Crack Propagation in Titanium Alloys by Using an Experiment-Based Monte Carlo Model. *Engineering Fracture Mechanics* 2018, 120–133.

- [2] Gao, C.; Li, C.; Wang, C.; Qin, Y.; Wang, Z.; Yang, F.; Liu, H.; Chang, F.; Wang, J. Advances in the Induction of Osteogenesis by Zinc Surface Modification Based on Titanium Alloy Substrates for Medical Implants. *Journal of Alloys and Compounds* 2017, 1072–1084.
- [3] Zhang, M.; Wang, Y.; Jia, W.; Ma, D.; Huang, X.; Yu, S.; Wu, Y. Ta₂O₅-Doped TiO₂ Nanotubes on Ti6Al4V Alloy with Improved Cytocompatibility to Endothelial Cells. *Vacuum* 2022, 110713.
- [4] Wang, X.; Li, B.; Zhou, L.; Ma, J.; Zhang, X.; Li, H.; Liang, C.; Liu, S.; Wang, H. Influence of Surface Structures on Biocompatibility of TiO₂/HA Coatings Prepared by MAO. *Materials Chemistry and Physics* 2018, 215, 339–345.
- [5] Hu, Y.; Chen, J.; Fan, T.; Zhang, Y.; Zhao, Y.; Shi, X.; Zhang, Q. Biomimetic Mineralized Hierarchical Hybrid Scaffolds Based on in Situ Synthesis of Nano-Hydroxyapatite/Chitosan/Chondroitin Sulfate/Hyaluronic Acid for Bone Tissue Engineering. *Colloids and Surfaces B: Biointerfaces* 2017, 157, 93–100.
- [6] Ahmadi, R.; Asadpourchallou, N.; Kaleji, B. K. In Vitro Study: Evaluation of Mechanical Behavior, Corrosion Resistance, Antibacterial Properties and Biocompatibility of HAp/TiO₂/Ag Coating on Ti6Al4V/TiO₂ Substrate. *Surfaces and Interfaces* 2021, 101072.
- [7] Jemat, A.; Ghazali, M. J.; Razali, M.; Otsuka, Y. Surface Modifications and Their Effects on Titanium Dental Implants. *BioMed Research International* 2015, 1–11.
- [8] Surmeneva, M. A.; Chudinova, E. A.; Grubova, I. Yu.; Korneva, O. S.; Shulepov, I. A.; Teresov, A. D.; Koval, N. N.; Mayer, J.; Oehr, C.; Surmenev, R. A. Effect of Pulsed Electron Beam Treatment on the Physico-Mechanical Properties of Hydroxyapatite-Coated Titanium. *Ceramics International* 2016, 42 (1), 1470–1475.
- [9] Sidane, D.; Chicot, D.; Yala, S.; Ziani, S.; Khireddine, H.; Iost, A.; Decoopman, X. Study of the Mechanical Behavior and Corrosion Resistance of Hydroxyapatite Sol–Gel Thin Coatings on 316 L Stainless Steel Pre-Coated with Titania Film. *Thin Solid Films* 2015, 71–80.
- [10] Sidane, D.; Khireddine, H.; Yala, S.; Ziani, S.; Bir, F.; Chicot, D. Morphological and Mechanical Properties of Hydroxyapatite Bilayer Coatings Deposited on 316L SS by Sol–Gel Method. *Metallurgical and Materials Transactions B* 2015, 46 (5), 2340–2347.
- [11] WEN, C.; XU, W.; HU, W.; HODGSON, P. Hydroxyapatite/Titania Sol–Gel Coatings on Titanium–Zirconium Alloy for Biomedical Applications☆. *Acta Biomaterialia* 2007, 3 (3), 403–410.
- [12] Liu, D.-M.; Yang, Q.; Troczynski, T. Sol–Gel Hydroxyapatite Coatings on Stainless Steel Substrates. *Biomaterials* 2002, 23 (3), 691–698.
- [13] Choi, A. H.; Ben-Nissan, B. Sol-Gel Production of Bioactive Nanocoatings for Medical Applications. Part II: Current Research and Development. *Nanomedicine* 2007, 2 (1), 51–61.
- [14] Ahmadi, R.; Afshar, A. In Vitro Study: Bond Strength, Electrochemical and Biocompatibility Evaluations of TiO₂/Al₂O₃ Reinforced Hydroxyapatite Sol–Gel Coatings on 316L SS. *Surface and Coatings Technology* 2021, 405, 126594.
- [15] Guipont, V.; Jeandin, M.; Bansard, S.; Khor, K. A.; Nivard, M.; Berthe, L.; Cuq-Lelandais, J.; Boustie, M. Bond Strength Determination of Hydroxyapatite Coatings on Ti-6Al-4V Substrates Using the LASER Shock Adhesion Test (LASAT). *Journal of Biomedical Materials Research Part A* 2010, 95A (4), 1096–1104.
- [16] LI H, SIMA C, DAI J, et al. Delving into the Devils of Bird’s-eye-view Perception: A Review, Evaluation, and Recipe[J].
- [17] Zavgorodny, A. V.; Borrero-López, O.; Hoffman, M.; LeGeros, R. Z.; Rohanizadeh, R. Mechanical Stability of Two-Step Chemically Deposited Hydroxyapatite Coating on Ti Substrate: Effects of Various Surface Pretreatments. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 2011, 99B (1), 58–69.