



Article Microstructure and Properties of MAO-Cu/Cu-(HEA)N Composite Coatings on Titanium Alloy

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Abstract: In this paper, MAO-Cu/Cu-(HEA)N composite coatings on TC4 titanium alloy were prepared by combining micro arc oxidation (MAO) with magnetron sputtering (MS) to enhance the wear resistance and antibacterial ability of the substrate in simulated seawater. The number of micropores on the surface of the composite coatings decreased with increasing CuSO₄ concentration in the electrolyte, causing the surfaces to be flat and smooth. XPS and EDS analyses revealed that the MAO-Cu/Cu-(HEA)N composite coatings predominately contained TiO₂, Cu₂O, and (HEA)N. Moreover, the addition of CuSO₄ increased the growth rate of the MAO coatings. Comparatively, the MAO-Cu/Cu-(HEA)N composite coating with 5 g/L CuSO₄ showed superior wear resistance, reduced friction coefficient (approximately 0.2), and shallow and narrow grinding cracks were observed compared to the other coatings. Antibacterial experiments showed that the MAO-Cu/Cu-(HEA)N composite coating bacterial killing effects than the TC4 substrate, which is of great significance to the antifouling abilities of titanium alloys in marine applications.

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). **Keywords:** TC4 titanium alloy; micro arc oxidation; magnetron sputtering; HEA film; microstructure and properties

1. Introduction

Titanium alloys are widely used in the marine and biomedical field owing to their light weights, high specific strengths, and many other advantages [1–6]. Titanium alloys are extensively used as biomedical materials in various artificial joints, bone fixings, dental implants, heart stents, etc., [5–8]. The use of titanium alloys in the marine industry can effectively reduce the weight of equipment, thus improving their payloads, which ultimately improves their reliability and reduces their maintenance costs. They are therefore ideal materials for marine equipment. However, titanium alloys face extremely harsh service conditions in marine environments, such as abrasion resulting from the erosion and collision of seawater and stones, corrosion of other alloy parts after connection, and adhesion and fouling of marine bacteria and microorganisms. Although titanium alloys exhibit excellent corrosion resistance when used as marine materials, they have poor wear resistance compared with stainless steel and other alloys [6,9,10]. In addition, the loss of titanium alloys from biological fouling is also a problem requiring urgent solutions. Micro arc oxidation (MAO) is a promising surface engineering technology which is used for the surface modification of various metals [11–17]. Some studies have shown that metallurgically bonded MAO layers on titanium alloy substrates can effectively improve the corrosion resistance, wear resistance, and hardness of the alloy [18–20]. It has also been reported that the addition of various soluble chemicals into the electrolyte used for the fabrication of MAO coatings can modify the structure of the coatings, which in turn affects the performance of titanium substrates [9,21-23]. The addition of particles into the electrolyte can also affect the discharge channel in the MAO process, change the structures and surface

morphologies of the films, and affect the protective performances of titanium alloys [24]. However, the porous oxide coating formed on the surface of titanium alloys provides more possibilities for the adhesion of bacteria and microorganisms due to its usually large surface area. The addition of antibacterial elements into the coating is one of the methods adopted to improve the antibacterial properties of the alloy [25]. Noting that Cu is a common antibacterial element [26–28], V. Stranak et al. [29] found that the Ti-Cu films prepared by the dual-HiPIMS technique had good antibacterial ability against Staphylococcus epidermidis and *Staphylococcus aureus*. Zhang et al. [30] found that Cu exists in the form of Cu₂O and CuO for MAO coating doped with Cu. The addition of Cu significantly improved the antifouling performance of the studied metal substrate. Despite having excellent antibacterial properties, Cu has relatively poor corrosion and wear resistance [31,32]. Therefore, using a single Cu film as a protective coating for titanium alloy in marine environments will pose some protective limitations. Recently, high-entropy alloy nitride ((HEA)N) films have gained popularity due to their high hardness, improved oxidation and corrosion resistance, and high temperature stability [33,34], and a comprehensive literature survey proves that there is scant information existing for the addition of Cu to (HEA)N films.

In this paper, the morphology and structure of MAO coatings were adjusted by adding different concentrations of $CuSO_4$ in a phosphate system, followed by the deposition of Cu and high-entropy alloy nitrides (Cu-(HEA)N) film by magnetron sputtering. Cu and (HEA)N films were deposited on the surface of the MAO layer to provide a feasible approach for fabricating anti-wear and antibacterial composite coatings. The MAO-Cu/Cu-(HEA)N composite coating prepared by this method is expected to improve the wider application of titanium alloys in the marine field.

2. Experimental

2.1. Preparation of MAO-Cu/Cu-(HEA)N Composite Coatings

TC4 titanium alloy (Baoji Titanium Industry Co., Ltd, Xi'an, China) circular disk samples with dimension of ϕ 20 mm × 4 mm were used as the substrate material in the experiments. The chemical composition of TC4 is displayed in Table 1. The TC4 substrates were polished by SiC sandpaper from 200# to 2000#, ultrasonically cleaned with alcohol for 10 min to remove surface stains, and dried by a blower. The MAO equipment was independently developed by Xi'an University of technology, with TC4 substrates as anode and stainless-steel barrel as cathode. In the micro-arc oxidation process, DC pulsed constant current mode is used. The basic electrolyte contained sodium hexametaphosphate ((NaP₂O₅)₆, 20 g/L), potassium hydroxide (KOH, 4 g/L), sodium tungstate (Na₂WO₄·2H₂O, 3 g/L) and potassium fluoride (KF·2H₂O, 3 g/L). Varying concentrations of CuSO₄ solution (5, 10, and 15 g/L) were added to the base electrolyte with a MAO process of 10 min at constant voltage of 450 V, frequency of 800 Hz, and a duty cycle of 3%.

Table 1. The composition of the simulated seawater solution.

Composition	NaCl	MgCl ₂	Na_2SO_4	CaCl ₂	KC1	NaHCO ₃	KBr	HBO ₃	SrCl	NaF
g/L	24.53	11.11	4.09	1.16	0.685	0.201	0.101	0.027	0.028	0.003

The MAO coatings with different CuSO₄ concentrations were ultrasonically cleaned with alcohol for 10 min to remove the electrolyte on the surface of the coatings. Copper alloy target and AlSiTiCrNbV high entropy alloy target prepared by an arc melting furnace were cut into 50 mm \times 2 mm disc. Cu-(HEA)N films with thickness of 1 µm were deposited on the surface of the MAO coatings by a double target magnetron sputtering deposition system. Pretreatment of the substrate cavities was carried out before deposition. The surface impurities on the sleeve of the fixed target were removed by a sandblasting machine (Taseken Trading Co., Shanghai, China) and the substrates were ultrasonically cleaned with acetone and alcohol at room temperature for 10 min. All the substrates were wiped clean with dry non-woven cloths, and residual surface impurities or oxides were removed by setting a negative bias of 400 V for 20 min before deposition. During the deposition, the powers of the copper alloy target and AlSiTiCrNbV high entropy alloy target were 20 W and 200 W, respectively. The negative bias voltage was 200 V and deposition time was 120 min. The preparation process of the MAO-Cu/Cu-(HEA)N composite coatings are shown in Figure 1.



magnetron sputtering treatment: Cu Power 16 W, HEA Power 200 W, negative bias voltage 200 V, 120 min

Figure 1. Preparation process of MAO-Cu/Cu-(HEA)N composite coatings.

2.2. Coating Characterization

The surface morphologies and elemental compositions of the coatings were analyzed by VEGA3-SBH scanning electron microscope (Taseken Trading Co., Shanghai, China) and energy dispersive spectrometer with a working voltage of 10 KV and a working distance of 3 mm (Taseken Trading Co., Shanghai, China). The composition and chemical states of coatings were analyzed by XPS (Shimadzu-Kratos Co., Hadano, Japan). The thicknesses of the MAO coatings were measured with a coating thickness gauge, and the average thickness after fifteen random measurements at different points was taken as the final thickness value. The friction coefficients of the coatings in simulated seawater were obtained using a HT-1000 high temperature friction and wear tester (Zhongke Kaihua Technology Development Co., Lanzhou, China). The chemical composition of the simulated seawater is shown in Table 1. A GCr15 bearing steel ball with a diameter of 6 mm was used as the wear material, and the wear time in the wear resistance test was set at 20 min. The Staphylococcus aureus (S. aureus) used for antimicrobial testing was cultured in LB medium and added into the coatings with simulated seawater by a pipette gun, and then cultured for 3 days at room temperature. The optical density of the bacterial solution was measured by a microplate reader, and bacterial adhesion was observed and measured based on the drying of the coating. Then, the bacteria liquid was coated on the surface of solid medium for 24 h, and colony growth was observed.

3. Results and Discussion

3.1. Analysis of Surface Morphology and Composition

The surface morphologies and compositions of the MAO-Cu/Cu-(HEA)N composite coatings with different concentrations of $CuSO_4$ are shown in Figure 2 and Table 2. It can be seen that the four composite coatings exhibited typical crater-like morphologies with uniform pore distributions. The pores on the surface of the MAO coatings were not completely covered by the Cu-(HEA)N films, maintaining the typical feature of microarc oxidation coatings [35–37]. Figure 2 shows that the nanoscale representation of the deposited Cu-(HEA)N films on micron-scale MAO layers had no obvious effect on the

surface morphology of the MAO coating. The composite coating prepared from the base solution had a considerable number of protrusions and pores in various sizes, as observed in Figure 2a. However, with the addition of CuSuO₄ into electrolyte, the number of pores and protrusions on the coating surface decreased, as shown in Figure 2b. It is noteworthy that small amounts of CuSO₄ increased the conductivity of the solution, thereby promoting the growth of the MAO coating. The conductivity of the solution and its reaction rate were continuously enhanced with increasing CuSO₄ concentration. More melt was produced at high temperatures and high pressures during the micro arc oxidation [31], which solidified and accumulated on the surface of the TC4 substrate after expulsion through the discharge channel. Therefore, the increase in concentration to 10 g/L and 15 g/L CuSO₄ did not reduce the number of micropores and protrusions on the surface of the composite coatings, as displayed in Figure 2c,d. Table 2 shows that the composition of the MAO-Cu/Cu-(HEA)N composite coatings with different CuSO₄ concentrations exhibited a certain trend. The coatings were mainly composed of nitrides formed by the reaction of the elements in the (HEA)N target with N₂ and oxides of Cu and Ti. It was observed that the Cu content in the coatings increased with increasing CuSO₄ concentration in the electrolyte.



Figure 2. The surface morphologies of MAO-Cu/Cu-(HEA)N composite coatings with different CuSO₄ concentrations: (**a**) 0 g/L; (**b**) 5 g/L; (**c**) 10 g/L; and (**d**) 15 g/L.

Samples	Ν	0	Al	Si	Ti	Cr	Nb	V	Cu
0 g/L	24.0	24.0	4.5	2.8	10.1	3.7	4.1	4.1	21.6
5 g/L	24.5	24.5	4.3	2.7	10.3	3.6	4.2	4.1	20.6
10 g/L	21.7	21.7	4.5	3.0	11.8	3.8	4.6	4.6	22.7
$15 \mathrm{g/L}$	22.9	22.9	2.3	1.5	12.6	3.8	4.6	3.4	25.0

Table 2. The composition of MAO-Cu/Cu-(HEA)N composite coatings with different $CuSO_4$ concentrations.

3.2. XPS Analysis

The surface characteristics of the MAO-Cu/Cu-(HEA)N samples were analyzed by XPS and displayed in Figure 3. The XPS fit was carried out using advantage software (version 5), and the peak of C1s was used to calibrate the peak of each element. The results show that the MAO-Cu/Cu-(HEA)N composite coatings surfaces were mainly composed of Ti, Cu, and O elements. The binding energy of Ti 2p was located at 458.17 eV and 464.48 eV, and assigned to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ of Ti⁴⁺, as shown in Figure 3a, indicating that O element mainly existed in the MAO-Cu/Cu-(HEA)N composite coatings in the form of TiN and TiO₂. The Cu 2p two main peaks were observed at 932.71 eV and 952.78 eV, and assigned to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of Cu⁺, but no obvious peaks were detected

around 944.0–941.5 eV according to Figure 3b, signifying that the Cu⁺ of Cu₂O rather than the Cu²⁺ of CuO was the existing form of Cu in the MAO-Cu/Cu-(HEA)N composite coating [38–40]. The peak value of the O 1s peak was detected at 530.45 eV and 532.09 eV in Figure 3c, confirming the existence of TiO₂ and Cu₂O [41,42]. In the micro-arc oxidation process, the arc discharge generates instantaneous high temperature and high pressure. CuSO₄ decomposes at high temperatures to produce CuO, which in turn decomposes to produce Cu₂O.



Figure 3. XPS spectra analysis (black line) and XPS fitting (purple line) on the surface of the MAO-Cu/Cu-(HEA)N composite coating: (a) Ti 2p (red line is Ti-N, blue line is Ti-O and green line is base line), (b) Cu 2p (red line is Cu-O, green line is Cu-N and blue line is base line), (c) O 1s (red line is Ti-O, red line is Cu-O and green line is base line).

3.3. Thickness

The thicknesses of the MAO coatings are shown in Figure 4. It can be seen from the figure that the thickness values of the four coatings were between 20 and 30 μ m. It is possible that the Cu²⁺ in CuSO₄ solution was responsible for the enhancement of the conductivity of the electrolyte and the increase in current which significantly increased the generation and dissolution rate of the surface melt, which improved the growth rate of the MAO coating increased by more than 40% with the addition of 5 g/L CuSO₄ solution. However, the effect of the MAO treatment was limited at higher CuSO₄ concentrations because electric breakdown was more difficult in the thicker coatings [43]. Hence, the thickness of the composite coating did not necessarily increase at CuSO₄ concentrations above 5 g/L.



Figure 4. The thickness of MAO coatings with different CuSO₄ concentrations.

3.4. Wear Resistance

Friction coefficient is an important parameter employed to evaluate the wear resistances of materials [44–46]. Figure 5 depicts the friction coefficient (CoF) vs. sliding time for the TC4 material and the four MAO-Cu/Cu-(HEA)N composite coatings at an applied load of 2 N in simulated seawater. The friction coefficient of the TC4 material fluctuated significantly in simulated seawater with values ranging from 0.3 to 0.8. The TC4 material had a relatively low hardness and high viscosity [37]. With continuous friction of the grinding ball and the TC4 surface, the material viscosity and wear contact surface increased together with the increasing frictional force. Therefore, TC4 material had large friction coefficient and obvious fluctuations. The friction coefficient curve of the composite coating with the base solution exhibited a heavy fluctuation, and the friction coefficient gradually increased with increasing wear time. Specifically, the friction coefficient of the MAO-Cu/Cu-(HEA)N composite coating with 5 g/L CuSO_4 was about 0.21 with the extension of wear time, and the friction coefficient curve was relatively stable. However, the friction coefficient of the MAO-Cu/Cu-(HEA)N composite coatings with 10 g/L and 15 g/L CuSO₄ increased to 0.3 and 0.4, respectively. The addition of CuSO₄ to the electrolyte reduced the number of micropores in the MAO layers, making the coatings flat and smooth [47–49], and the Cu-(HEA)N films covered parts of the tiny pores in the MAO layers. The low friction of the Cu element in the MAO layers decreased the friction coefficient, thereby improving the wear resistance. In addition, the simulated seawater stored in the MAO layers formed a liquid film during wear, which further decreased the friction coefficient. The weightlessness percentages of the four composite coatings calculated after wear are shown in Table 3. As can be seen from the table, the weightlessness percentages of the four composite coatings were lower than that of the TC4 material. The lowest weightlessness percent of the MAO-Cu/Cu-(HEA)N composite coating was recorded for the coating with 5 g/LCuSO₄, indicating that it had the best wear resistance of the four coatings. Overall, the MAO-Cu/Cu-(HEA)N composite coatings improved the wear damage usually associated with TC4 materials.



Figure 5. Friction coefficient curves of TC4 and MAO-Cu/Cu-(HEA)N composite coatings with different CuSO₄ concentrations.

Table 3. Percent of weight loss of TC4 and MAO-Cu/Cu-(HEA)N composite coatings with different CuSO₄ concentrations.

Samples	Percent of Weightloss (%)
TC4	1.310 ± 0.004
0 g/L	0.016 ± 0.001
5 g/L	0.011 ± 0.001
10 g/L	0.016 ± 0.001
15 g/L	0.014 ± 0.001

The surface morphologies by SEM examination and EDS micrographs of the wear scars are shown in Figure 6. Additionally, the widths of the wear scars were marked in the SEM micrographs. After wear, the surface of the TC4 material had the widest wear mark width of $551.45 \,\mu\text{m}$ with obvious furrow morphology, indicating a typical abrasive wear characteristic (Figure 6a) [43]. The rough surface of the GCr15 grinding ball played a vital role in ploughing the surface of the TC4 alloy, leaving ploughing grooves on the worn surface. Compared to the TC4 material, the wear marks on the surface of the MAO-Cu/Cu-(HEA)N composite coatings were shallow without obvious grooves, as displayed in Figure 6b-e. The four MAO-Cu/Cu-(HEA)N composite coatings had narrow wear scar widths, which first increased and then decreased with increasing CuSO₄ concentrations. The composite coating with 5 g/L CuSO₄ exhibited the least wear mark width and friction coefficient. The surface of the composite coating without the addition of CuSO₄ has more micropores and larger bumps, with a large degree of wear on the grinding balls. The introduction of CuSO₄ improves the structure of the coating, the number of micropores is reduced and the surface of the coating is smooth, so the wear on the grinding balls and the coating is slight. The TiO₂ layer of microporous sodium storage seawater formed a liquid film to reduce the degree of wear on the grinding ball and the coating. As can be seen from the EDS diagram, Fe element did not only exist at the wear mark locations, but also on the whole surface of the TC4 material, as shown in Figure 6a. Obviously, the Fe element was largely characterized on the wear marks of the composite coatings. This was due to compaction of the wear debris produced by repeated friction and wear on the grinding balls in the numerous micropores on the surface of the composite coatings (Figure 6b-e). The GCr15 grinding ball only wore out the surface of the four composite coatings but did not damage the TC4 substrate, indicating that the four composite coatings played effective roles in protecting the TC4 substrate.



Figure 6. The surface SEM and EDS of TC4 and MAO-Cu/Cu-(HEA)N composite coatings with different CuSO₄ concentrations: (a) TC4; (b) 0 g/L; (c) 5 g/L; (d) 10 g/L; and (e) 15 g/L.

3.5. Antibacterial Ability

Figure 7 shows the macrophotographs of *Staphylococcus aureus* (*S. aureus*) colonies cultured on TC4 and MAO-Cu/Cu-(HEA)N composite coatings with different CuSO₄ concentrations attached to the surface of LB solid medium. The bacteria cultured on the surface of TC4 survived well on the surface of LB solid medium and they proliferated and grew in large numbers, as shown in Figure 7a. With increasing CuSO₄ concentrations, the MAO-Cu/Cu-(HEA)N composite coatings demonstrated excellent antibacterial abilities. For the coating containing 5 g/L CuSO₄, only few *S. aureus* existed on the surface of the solid medium after culture, indicating that the increasing CuSO₄ concentration was beneficial to the improvement of the antibacterial properties of the MAO-Cu/Cu-(HEA)N composite coatings (Figure 7b). It was reported that the presence of Cu₂O nanoparticles will completely inactivate bacterial growth through the release of Cu ions which generates reactive oxygen species [50]. In this study, the inactivation of *S. aureus* on the surface of the solid medium is also attributed to the presence of Cu ions in the MAO-Cu/Cu-(HEA)N composite coatings.



Figure 7. The macrophotographs of *Staphylococcus aureus* colonies cultured by TC4 and MAO-Cu/Cu-(HEA)N composite coatings with different CuSO₄ concentrations attached to the surface of LB solid medium: (a)TC4; (b) 0 g/L; (c) 5 g/L; (d) 10 g/L; and (e) 15 g/L.

Figure 8 shows the optical density of *S. aureus* increment in the simulated seawater. Optical density reflects the antibacterial ability of samples to *S. aureus* [51], and a low optical density represents poor livability of *S. aureus* and an excellent antibacterial ability. Comparing the optical density of the *S. aureus*-cultured TC4 with those of the different composite coatings, it was observed that the optical density decreased significantly with increasing CuSO₄ concentration. The optical densities of the four *S. aureus*-cultured composite coatings were lower than that of the *S. aureus*-cultured TC4. As Cu content in MAO-Cu/Cu-(HEA)N composite coatings increased, the precipitation of Cu ions increased, and the sterilization performance of the MAO-Cu/Cu-(HEA)N composite coating were also enhanced. The optical density of the composite coating containing 5 g/L CuSO₄ was 0.19, and this presented the most favorable condition for bacterial deactivation of all the composite coatings.



Figure 8. Optical density of *S. aureus* cultured by TC4 and MAO-Cu/Cu-(HEA)N composite coatings with different CuSO₄ concentrations.

Figure 9 represents the microcosmic surface adhesion of *S. aureus* on TC4 and the MAO-Cu/Cu-(HEA)N composite coatings. A large number of *S. aureus* were attached to the surface of the TC4 sample, and the TC4 provided favorable living conditions for the growth and reproduction of the *S. aureus*, as depicted in Figure 9a. The adhesion rates of the *S. aureus*-cultured composite coatings containing different concentrations of CuSO₄ in basic electrolyte were comparatively lower than that of the *S. aureus*-cultured TC4. Some of the *S. aureus* agglomerated to form a grape-like structure which adhered to the surface of the MAO-Cu/Cu-(HEA)N composite coatings, as shown in Figure 9c. In addition, there were almost no agglomerations of *S. aureus* on the surface of the MAO-Cu/Cu-(HEA)N composite coatings on the surface of the MAO-Cu/Cu-(HEA)N composite coatings.



Figure 9. The microcosmic adhesion of *S. aureus* on TC4 and MAO-Cu/Cu-(HEA)N composite coatings surface with different CuSO₄ concentrations attached: (**a**) TC4; (**b**) 0 g/L; (**c**) 5 g/L; (**d**) 10 g/L; and (**e**) 15 g/L.

Cu₂O has been proven to have good antibacterial effects [50,52–56]. Studies have shown that reactive oxygen species (OH, H₂O₂ and O₂⁻) produced by Cu₂O may interact with bacterial cell membranes and promote bacterial permeation [57]. Disturbance of bacterial cell membranes by Cu₂O can cause a number of functional disorders that impede the growth of bacteria and may eventually lead to the growth of bacterial species and possibly eventually their death [57,58]. The small size (nanoscale) of Cu₂O makes it easy for Cu₂O to penetrate the cell membrane compared to the pore size (microns) of bacteria [59]. The XPS result displayed in Figure 4 shows that after the MAO process and sputtering, TiO₂ and Cu₂O were the main components on the surface of the coatings. Based on the above observation, it is reasonable to conclude that Cu₂O was generated after the addition of CuSO₄ to the electrolyte, and it played an important role in the antibacterial behavior of the coatings. As shown in Figure 10a, there was no Cu₂O in the pores on the MAO layer without CuSO₄ addition. Here, the antibacterial effect was mainly dependent on the Cu₂O on the surface of the Cu-(HEA)N films. This means that the incompletely killed bacteria continued to grow and reproduce in the pores. The increasing concentration of CuSO₄ changed the structure and Cu₂O content of the MAO-Cu/Cu-(HEA)N composite coatings. From Figure 10b, the Cu₂O in the pores of the MAO layer interacted with the active bacteria on the surface of the MAO-Cu/Cu-(HEA)N film and continued to kill them, hence bacterial inactivation continued in the pores [60]. Moreover, the rough structure of the coatings increased their surface areas or contact interface areas, thereby improving their antibacterial performances.



Figure 10. Mechanism of the effect of CuSO₄ on the antibacterial ability of MAO-Cu/Cu-(HEA)N composite coating: (**a**) without CuSO₄; and (**b**) with CuSO₄.

4. Conclusions

MAO-Cu/Cu-(HEA)N composite coatings were successfully prepared on titanium alloy by MAO and MS. With the addition of CuSO₄ to the electrolyte, the surface of the composite coating became flat and smooth with the existence of dense and uniform pores. Cu mainly existed as Cu₂O in the composite coatings, and the introduction of CuSO₄ promoted both the growth rates and thicknesses of the coatings. The wear resistance and antibacterial property of the composite coating was improved in simulated seawater with increments in CuSO₄ concentration. The friction coefficient of the composite coating with 5 g/L CuSO₄ was reduced to about 0.2, and the wear marks were shallow and narrow. Compared with the TC4 material, the optical density of the composite coatings decreased to 0.19, and the adhesion of *S. aureus* on the surface of the composite coatings were significantly weakened. MAO-Cu/Cu-(HEA)N composite coatings are important for surface modification of titanium alloys, but the wear and antimicrobial mechanisms of the composite coatings need to be investigated in more depth. In addition, the composite coatings research will focus on corrosion and erosion resistance in the marine environment.

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