Study on friction characteristics of micro-arc oxidation modification layer of titanium alloy surface in seawater environment

Lao Xingsheng*, Zhao Xufeng, Liu Yong, Dai Chunhui and Wang Wei

Science and Technology on Thermal Energy and Power Laboratory, Wuhan 2nd Ship Design and Research Institute, Hubei, 430205, P.R. China

Corresponding email: 460079620@qq.com

Abstract. In order to study the effect of surface microarc oxidation modification on the comprehensive properties of titanium alloys in seawater environment, the metallographic structure of titanium alloy Microarc oxidation modified surface layer and the basic physical parameters such as hardness, thickness and roughness were measured, and the PTFE, filled with 15% glass fiber +5% were filled with 25% fiberglass. The PTFE of graphite and the PTFE filled with 60% tin bronze were tested for friction by friction pair materials, and the wear amount and roughness of titanium alloy and Microarc oxidation modified surface layer were tested in simulated sea water as 3.5% NaCl solution, and the results showed that the surface modification of titanium alloy by Microarc oxidation could significantly improve its hardness. The surface roughness can reach 3.2μm, and the friction coefficient of different matching pairs is small, while the surface wear of microarc oxidation modification is less than that of substrate wear.

1. Introduction

Titanium and titanium alloy as an excellent ship material, with the following characteristics[1-2]: (1) small density, light weight, in its high specific strength at the same time, with good toughness and anti-brittle fracture strength; (2) titanium in neutral and oxidizing atmosphere and many harsh environments, with much higher corrosion resistance than other commonly used metals. In the long-term high temperature, high humidity and seawater splash of the ocean atmosphere can have a good corrosion resistance; (3) at the same time, it also has low magnetic, good sound transmittance and impact vibration, heat and low temperature resistance, good processing performance and other excellent comprehensive performance. When titanium alloy parts used in the marine environment for a long time, its surface can grow marine organisms, the use of low surface energy coating for surface modification can improve the difficulty of biological adhesion and reduce adhesion strength, when the surface of the modified layer and fluid there is a certain relative speed, the sea organisms attached to its surface will automatically fall off. Using micro-arc oxidation technology, nano-anti-fouling coating was prepared on the surface of titanium alloy, the coating has amorphous and 20-50nm nanocrystalline TiO2and Cu2O, the coating layer foundation bonding strength reaches 50MPa, the coating insulation and wear resistance is good, the anti-fouling performance is improved obviously, at the same time, Surface modification can also improve the surface hardness and wear resistance of titanium alloy materials and increase their application range. Many studies are focused in micro-arc oxidation process[3-5], in this paper, the basic properties and friction properties of Ti-6Al-4V ELI substrate and surface microarc oxidation modified
materials are compared and studied, which provides a strong basis for the selection of friction sub-
materials in seawater environment.

2. Micro-arc oxidation surface modification

2.1. Surface morphology and metallographic tissue

The surface Microarc oxidation modification morphology and analysis results of Ti-6Al-4V ELI for 
substrates are shown in Fig. 1. As can be seen from the morphological photographs of Fig.1 (a), the 
surface layer modified by Microarc oxidation technology is more flat, with many micropores of different 
sizes (2~5μm) distributed irregularly in the middle position of the membrane or at the edge of the raised 
ceramic particles, and the holes are not connected to form a network-shaped structure with microporous 
inlays. Some spherical protuberances appear in individual places. The microporous is a discharge 
channel formed by the high voltage breakdown of the ceramic membrane during the preparation of the 
coating, while the coarse spherical protuberance is a ceramic particle formed by the splash of the ceramic 
coating caused by a strong burst of arc, and the energy spectra of Fig. 1 (a’) show that Ti and O are the 
main components of the coating, while Si and P, V is the element contained in the substrate.

![Fig. 1 photo and energy spectrum of SEM morphology on modified layer surface](image)

Fig. 2 shows the cross-sectional metallographic microscopic photographs of three samples with 
different surface techniques after modification. As can be seen from Fig. 2, the coating and matrix are 
combined with the micro-region metallurgy, which is beneficial to improve the bonding force of the 
membrane Foundation, the inner layer of the coating is more dense, the outermost grain is slightly 
thicker, the tissue is loose, corresponding to the multi-empty form of the oxide coating surface. The 
chemical composition of the coating depends on the substrate material and the electrolyte composition. 
Ti and Al are the elements contained in the substrate, and Si and P are the elements contained in the 
electrolyte.
2.2. Surface physical performance parameters

The surface roughness of the sample was determined by roughness on the test block. Table 1 shows the surface roughness values of the samples modified by three surface techniques. The roughness of Microarc oxide film is 3.2μm. Using the Vickers Hardness meter (Wilson-wolpert Tukon® 2100B, United States) to test the microscopic Vickers hardness of the sample, with loading weight 200g and loading time 15s. Test on the cross section and the hardness test results are shown in Table 1. Compared with the Ti-6Al-4V ELI matrix without modified treatment, the microhardness of the sample was improved obviously after the surface technique modification treatment was used.

The thickness of the surface layer was measured by metallographic microscope (OM) or scanning electron microscope (SEM) by intercepting samples, mosaic samples, grinding and polishing, cleaning and etching, and the thickness of the Microarc oxide film layer was not obvious.

Table 1 Surface roughness value of coating (seepage) layer

| Serial | Item                  | Roughness, Ra/μm | Hardness (HV₀₂) | Thickness, δ/μm |
|--------|-----------------------|------------------|-----------------|-----------------|
| 1      | Ti-6Al-4V (substrate) | 0.51             | 315             | /               |
| 2      | Microarc oxide Film (TiO₂) | 2.28             | ~550            | 13±2            |

3. Friction Test

3.1. Friction pairs

In this experiment, the pin-disk contact method, titanium alloy and its surface treatment specimen were used as the disc model, and the reinforced PTFE with the pair as pin. Friction specimen basic material is TC4 titanium alloy, the surface after polishing, roughness is less than or equal to 0.9μm, there are three types of friction materials, respectively, filled with 25% glass fiber PTFE (referred to as 25% fiberglass), filled with 15% fiberglass +5% graphite PTFE (referred to as 15% fiberglass +5% graphite), and PTFE filled with 60% Tin Bronze (abbreviated as 60% Tin bronze).

Enhanced PTFE with pin-type specimen, the size of the matching machine is shown in Fig.3, where the contacting end with the plate sample is a pin with diameter of 2mm and height of 3mm.

Fig. 3 Enhanced type of PTFE matching pin sample size
3.2. Test scheme
Using the aqueous solution of 3.5% NaCl to simulate the seawater environment, the wear resistance of friction pair is evaluated by HT-1000 friction and wear tester, and the pin-disk contact mode is used in the experiment, the disk is fixed and the pin is rotated, as shown in Fig.4. Wear test trajectory (pin sliding track on disk) Radius: 4mm; Pin speed: 336 r/min; Contact load: 2000g (20N); wear travel time: 60min. And repeat three times to take the average.

![Fig.4 Schematic diagram of friction experiment](image)

4. Test results

4.1. Coefficient of friction
Table 2 shows the friction coefficient of the substrate surface and different reinforced PTFE composites as grinding material, and Fig.5 is the change of friction coefficient in the process of grinding. It can be seen that the friction coefficient between three kinds of reinforced PTFE composites and the substrate surface is close, the friction coefficient is the smallest when the substrate and 15% fiberglass +5% graphite are the same, but the friction coefficient between the substrate and 60% Tin Bronze is the largest, but not more than 0.12.

| Substrate                | Roughness (Ra/μm) | Pin length change(mm) | Average friction coefficient (total integral averaging) | Average friction coefficient (20~50min) at stable stage |
|--------------------------|-------------------|-----------------------|---------------------------------------------------------|-----------------------------------------------------|
|                          | Single specimen   | Average               | Single specimen                                        | Single specimen                                      | Average                                           |
| Grinding materials :     | 4#                | 0.126                 | 0.938                                                   | 0.106                                              | 0.098                                            |
| 15% fiberglass +5%       | 5#                | 0.110                 | 1.251                                                   | 0.109                                              | 0.116                                            |
| graphite                 | 9#                | 0.112                 | 1.105                                                   | 0.110                                              | 0.116                                            |
|                          | Average           | 1.098                 |                                                         |                                                     | 0.103                                            |
| Grinding materials :     | 1#                | 0.134                 | 1.140                                                   | 0.116                                              | 0.110                                            |
| 25% fiberglass            | 5#                | 0.122                 | 0.861                                                   | 0.097                                              | 0.088                                            |
|                          | 6#                | 0.129                 | 1.181                                                   | 0.125                                              | 0.126                                            |
|                          | Average           | 1.061                 |                                                         |                                                     | 0.108                                            |
| Grinding materials :     | 7#                | 0.115                 | 1.407                                                   | 0.122                                              | 0.119                                            |
| 60% Tin Bronze           | 8#                | 0.202                 | 1.055                                                   | 0.115                                              | 0.116                                            |
|                          | 10#               | 0.113                 | 1.357                                                   | 0.119                                              | 0.116                                            |
|                          | Average           | 1.273                 |                                                         |                                                     | 0.117                                            |
Fig. 5 Friction coefficient of substrates and different PTFE in the process of grinding

Table 3 shows the friction coefficient between the surface micro-arc oxidation specimen and the different reinforced PTFE composites, and Fig. 6 is the change of friction coefficient in the process of grinding. It can be seen that the micro-arc oxidation surface and 15% glass fiber +5% graphite composites, 25% fiberglass composites and 60% Tin bronze composites on the friction coefficient of the time is relatively close, are in the 0.1~0.12.

Table 3 Experimental data of micro-arc oxidation surface and different PTFE composites on friction

| Micro-arc oxidation specimen | Roughness (Ra/μm) | Pin length change(mm) | Average friction coefficient (total integral averaging) | Average friction coefficient (20~50min) at stable stage |
|-----------------------------|-------------------|-----------------------|--------------------------------------------------------|------------------------------------------------------|
|                             |                   |                       | Single specimen                                        | Single specimen                                       |
|                             |                   |                       | Average                                              | Average                                             |
| Grinding materials :        | 1# 0.512          | 2.156                 | 0.109                                                | 0.113                                                |
| 15% fiberglass +5% graphite  | 3# 0.649          | 2.057                 | 0.114                                                | 0.113                                                |
|                             | 10# 0.560         | 2.220                 | 0.117                                                | 0.117                                                |
|                             |                   |                       |                                                        |                                                     |
| Grinding materials :        | 2# 0.460          | 1.610                 | 0.118                                                | 0.112                                                |
| 25% fiberglass               | 8# 0.572          | 1.787                 | 0.123                                                | 0.112                                                |
|                             | 15# 0.521         | 1.380                 | 0.096                                                | 0.107                                                |
|                             |                   |                       |                                                        |                                                     |
| Grinding materials :        | 7# 0.590          | 1.795                 | 0.123                                                | 0.120                                                |
| 60% Tin Bronze              | 12# 0.627         | 1.709                 | 0.109                                                | 0.120                                                |
|                             | 13# 0.630         | 2.898                 | 0.127                                                | 0.117                                                |
4.2. Wear amount
Because the substrate surface has not been treated with any treatment, the hardness is small (315 HV0.2), therefore, the surface wear is more serious, scratches are more obvious, and filling 60% tin bronze PTFE than filling 25% glass fiber and filling 15% fiberglass +5% graphite wear is serious.

The sample measurement results show that the maximum roughness of the surface of 15% fiberglass +5% Graphite is about the maximum roughness of the surface of 5.5μm, 25% glass fiber is slightly larger, about 8.0μm, while the maximum roughness of 60% tin bronze surface is the largest, reaching the 15.0μm. After micro-arc oxidation of the substrate surface, the hardness increased to 560 HV0.2, the surface wear is relatively slight. And PTFE filled with 25% fiberglass, PTFE filled with 15% fiberglass +5% graphite and PTFE wear filled with 60% tin bronze were slightly worn.

The maximum roughness of the surface of 15% fiberglass +5% Graphite is about the maximum roughness of the surface of the 3.5μm, 25% glass fiber, which is about 6.0μm, while the maximum roughness of the surface of 60% tin bronze is about 5.5μm.

5. Conclusions
Based on the measurement of the physical parameters of the micro-arc oxidation modification layer on the surface of titanium alloy and the results of friction test in seawater environment, it can be concluded that: 1) The roughness of the Microarc oxide film is 3.2μm. The surface layer hardness is increased from 315HV0.2 to ~550HV0.2, but the thickness increase is only 13μm; 2) When the micro-arc oxidation surface and 15% fiberglass +5% graphite composites, 25% fiberglass composites and 60% Tin bronze composites are accompanied by pairs, the friction coefficient is about 0.1; 3) Also with 15% fiberglass +5% graphite composites, 25% fiberglass composites and 60% tin bronze composites with pairs, the wear of micro-arc oxidation surface treatment samples are lower than the wear amount of substrates. When grinding with the substrate, the wear amount is the largest when the PTFE is filled with 60% tin bronze, and the surface roughness reaches 15.0μm. Compared with the micro-arc oxidation surface treatment specimen, the maximum roughness of the surface of 25% fiberglass is larger, which is about 6.0μm.

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