Microstructure and Wear Resistance of WS$_2$/W Composite Coating on TC4 Titanium Alloy Surface

Huang Junqi$^{1,a}$, Ma Jie$^{1,b,*}$, Wu Long$^1$, Wei Jianzhong$^1$, Li Hongyi$^1$

$^1$Faculty of Materials and Manufacturing, Beijing University of Technology, Beijing, 100124
$^a$e-mail: 2016654984@qq.com
$^*\text{corresponding author's e-mail: } b\text{email: majie@bjut.edu.cn}$

Abstract: In order to achieve the demand for improving the wear resistance of titanium alloy surfaces, a combination of magnetron sputtering (PVD), chemical vapor deposition (CVD) and thermal vulcanization methods is used to prepare highly wear-resistant WS$_2$/W Composite coating on the surface of TC4 titanium alloy. Scanning electron microscope (SEM), X-ray diffractometer (XRD) and X-ray energy dispersive spectrometer (EDS) were used to characterize the micro-morphology, microstructure and chemical composition of the composite coating. The micro-hardness and wear resistance of the composite coating were tested. The results show that the thickness of each layer of the WS$_2$/W composite coating prepared by the experiment is about 16μm and 60μm respectively, the coating structure is dense, and the interface between the layers is obvious. The average micro-hardness of WS$_2$ layer and W layer are 110.4HV and 740.1HV respectively. The surface friction factor of WS$_2$/W composite coating is 0.15, which is about 18% of the matrix (0.85). The wear rate is $1.184\times 10^{-6}\text{mm}^3\cdot\text{mm}^{-1}$, which is about 45% of the substrate $(1.628\times 10^{-6}\text{mm}^3\cdot\text{mm}^{-1})$, which has better wear resistance and anti-friction characteristics.

1. Introduction
Titanium alloy has the characteristics of low density, high specific strength, good corrosion resistance and biocompatibility, etc. It is widely used in aviation, ships, vehicles and medical fields$^{[1-5]}$. However, the surface friction coefficient of titanium alloy is large, adhesion or abrasive wear is easy to occur, and the friction performance is poor, which is very unfavorable for the titanium alloy motion pair structural parts in the high speed, high load and high wear working environment, and limits its wider application range$^{[6-8]}$. At present, the surface modification technologies used in titanium alloys mainly include ion implantation, laser cladding, thermal spraying, vapor deposition, thermal diffusion, etc.$^{[9-15]}$, among which the physical vapor deposition film is firmly bonded to the substrate, the chemical vapor deposition has good winding property, and the thermal diffusion processing efficiency is high, all of them are widely used. At first, this essay introduced the method of magnetron sputtering in the middle of the titanium alloy surface preparation combined with matrix solid transition layer, using the method of chemical vapor deposition rapid preparation tungsten coating deposition. Finally, using the method of hot vulcanization will tungsten coating in situ into high wear resisting sulfide coating, to improve the titanium alloy surface wear resistance, antifriction and lubrication performance provides a new method.

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2. Experiment

2.1 Preparation of composite coating
Matrix material TC4 titanium alloy, specifications of 15mm×15mm×2mm. The matrix was pretreated by ultrasonic, acid pickling and drying. And then the Cu transition layer was prepared by magnetron sputtering on the surface of titanium alloy. Cu was used as the target material, the sputtering power was 150W, the sputtering time was 7200S, and the sputtering temperature was 450℃. WF₆ and H₂ were used as reaction source gases in CVD. The ratio of WF₆ to H₂ gas was 2g/min and 1L/min. The process temperature was 450℃ and the process time was 4min. Finally, the sample was heated in a high-temperature furnace, and the tungsten coating is converted into sulfide coating by thermal vulcanization method. The reaction raw material was pure S powder, the process temperature was 900℃, the process time was 6h, and Ar was used as the protective gas.

2.2 Analytical test method
The surface morphology, elements and contents were observed by Zeiss-SUPRA55 scanning electron microscope and energy spectrum analysis system. The coating structure was determined by Shimadzu XRD-7000 X-ray diffractometer. The microhardness of the coating was measured by HVS-1000 Vickers microhardness tester. The friction and wear resistance of the coating was studied by CFT-1 friction and wear tester in the form of cyclic wear. The bearing steel ball with a diameter of 6mm was used as the friction pair. The loading load was 5 N, the loading time was 30min, the friction rate was 500 r/min, and the ambient temperature was 25℃.

3. Results and Discussion

3.1 Analysis of microstructure and composition of composite coating
Because the titanium substrate oxidized easily in the air or oxygen medium, forming titanium oxide film, and the reaction products in the process of CVD tungsten deposit HF erodes the titanium substrate, directly caused the titanium substrate surface CVD tungsten coating binding force only 41.3 N. That is not conducive to further modification and membrane layer on the surface of the titanium alloy conversion process. As a result, this essay in the process of preparing coating first by magnetron sputtering method in the preparation of Cu transition layer on titanium alloy surface. The oxide layer on the surface of titanium alloy is firstly removed by ion bombardment pretreatment before sputtering, and the Cu transition layer can also protect the substrate from the corrosion of HF produced during CVD deposition. Figure 1(a) shows the cross section structure of Cu/W composite coating prepared on the surface of titanium alloy by magnetron sputtering Cu transition layer. Then, using chemical vapor deposition of tungsten on it. It can be seen from the figure that the CVD tungsten coating has a columnar crystalline structure, compact structure and no crack. The Cu transition layer is about 2.8um thick, and it is tightly bound to the substrate and coating without pores. The component analysis results of cross section energy spectrum of composite coating are shown in Figure 1(b). The coating composition is W, the transition layer composition is Cu, and the matrix composition is mainly Ti. Using magnetron sputtering Cu transition layer combined with CVD method can effectively improve the defect of low adhesion of coating, and can realize the rapid deposition of tungsten coating at a low temperature (deposition rate of 20um/min at 450℃), and the critical load between Cu/W composite coating and substrate can reach 184.2N.
Fig. 2 shows the cross section microstructure and energy spectrum of the WS₂/W composite coating. After curing, the surface of the composite coating forms a sulfide layer of 10-16μm, and there is an obvious interface between the sulfide layer and the tungsten coating. Point scanning energy spectrum component analysis results are shown in Fig. 2(b), and the ratio of W atom to S atom is 1:2. As shown in Fig. 2(c), the surface layer is a W and S compound layer with constant W and S content, and the subsurface layer is pure tungsten coating. The Cu transition layer almost disappears due to diffusion to the Ti matrix at high temperature. Because S has no solubility in W, diffusion of S atom does not occur. As showed in Fig. 2(d), W and S are uniformly distributed in the whole composite coating with the same distribution characteristics, and there is no element S in the tungsten coating.

Fig. 3 shows the surface X-ray diffraction spectrum of WS₂/W composite coating. It can be seen that WS₂ is formed on the surface of the sample after vulcanization, and the phase structure is single. Through
the process, the experimental temperature is maintained above 700 ℃ and the added S powder reacts, which can avoid the reaction of the unreacted S powder with WS2 to produce WS3 in the cooling process.

Fig.3 XRD patterns of WS2/W composite coating

3.2 Microhardness analysis of composite coating
The microhardness test results of WS2/W composite coating are showed in Fig. 4. The microhardness of WS2 coating is low, which is 110.4HV. The average microhardness of tungsten coating is 740.1HV. The Cu transition layer disperses, and the microhardness of the transition zone near CVD tungsten coating is 206.1HV. However, with the increase of the distance from the surface, the Cu content decreases gradually and the hardness value increases consistently to the average microhardness of titanium substrate 289.2HV.

Fig.4 Hardness curve of titanium matrix and WS2/W composite coating

3.3 Analysis of wear resistance of composite coating
Fig. 5 shows the friction performance test curve of WS2/W composite coating. The friction of WS2/W composite coating is in the running-in stage within 0-4 minutes, and the friction test enters the stable stage after 4min. The friction coefficient stabilizes at about 0.15 (curve B). Compared with the friction coefficient of titanium matrix, which is about 0.85 (curve A), the WS2/W composite coating significant reduces the initial running-in time on the surface of titanium alloy. The friction coefficient is very low, showing excellent lubrication effect.

The results of wear weightlessness test are showed in the Table 1. The wear rate is defined as the weight lost of wear divided by the density of the titanium alloy (4.5g/cm3) and the sliding distance. The wear weight loss of titanium substrate is 0.0011g, and the wear rate is 1.628×10^{-6}mm^{3}·mm^{-1}, while the wear weight loss of titanium alloy surface prepared by WS2/W composite coating is 0.0005g, and the wear rate is 0.74×10^{-6}mm^{3}·mm^{-1} under the same test conditions. Compared with the titanium substrate, the surface wear rate of the composite coating is reduced sharply and the wear resistance is dramatic improved.
Fig.5 Friction performance curve of WS<sub>2</sub>/W composite coating

Table 1 Test results of weight loss on sample wear

| Sample                         | Weight loss/g | Wear rate/mm<sup>3</sup>·mm<sup>-1</sup> |
|-------------------------------|---------------|-------------------------------------------|
| Titanium substrate            | 0.0011        | 1.628×10<sup>-6</sup>                     |
| WS<sub>2</sub>/W composite coating | 0.0005       | 0.74×10<sup>-6</sup>                     |

4. Conclusions
(1) The method of combining magnetron sputtering Cu transition layer with CVD tungsten coating can realize rapid deposition at lower temperature. In addition, the critical load between Cu/W composite coating and matrix can reach 184.2N.

(2) After curing, the structure of Cu/W composite coating is WS<sub>2</sub>/W/ diffusion layer/ matrix. The interface between each layer is clear, the bonding is close, and there are no cracks and holes. The average microhardness of WS<sub>2</sub> layer and W layer is 110.4HV and 740.1HV respectively. The surface hardness of titanium alloy is significantly improved by W layer.

(3) The friction coefficient of WS<sub>2</sub>/W composite coating surface is 0.15, which is about 18% of the substrate (0.85). The wear rate is 1.184×10<sup>-6</sup>mm<sup>3</sup>·mm<sup>-1</sup>, about 45% of the matrix (1.628×10<sup>-6</sup>mm<sup>3</sup>·mm<sup>-1</sup>). It has excellent wear resistance and antifriction properties.

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