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Tribology behavior of double-glow discharge Mo layers on titanium alloy in aviation kerosene environment

TANG Jin-gang¹, LIU Dao-xin¹, TANG Chang-bin¹, ZHANG Xiao-hua¹, XIONG Hua², TANG Bin³

1. Corrosion & Protection Research Institute, Northwestern Polytechnical University, Xi'an 710072, China;

2. Xi'an Aviation Power Control Technology Limited Company, Xi'an 710072, China;

3. Institute of Surface Engineering, Taiyuan University of Technology, Taiyuan 030024, China

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Abstract: In order to improve the tribology behavior in aviation kerosene, molybdenum (Mo) modified layers were fabricated on Ti6Al4V base alloy using a double-glow plasma surface alloying technique. The morphology, microstructure, microhardness and element depth distribution of the Mo modified layers were studied. The tribology properties of Ti6Al4V base alloy, Mo modified layers and 5CrMnMo tool steel sliding with GCr15 steel or QSn4-3 copper alloy counterparts in aviation kerosene were comparatively researched. The effect of roughness on the sliding wear behavior was discussed. The results indicate that the Mo modified layers with polishing treatments not only reduce the friction coefficient of Ti6Al4V base, but also enhance the wear resistance of the counterparts. The Mo modified layers have better tribology behavior than 5CrMnMo steel. It is also found that the wear volume loss of the counterparts is proportional to the value of roughness of Mo modified layers, which is related directly to the ploughing wear between micro convex bodies of the layers and counterparts.

Key words: wear; friction coefficient; Ti6Al4V; aviation kerosene; Mo

1 Introduction

In order to enhance the wear resistance and reliability of components (valves and sleeves) in aviation engine fuel control system, it is quite general to use high speed steels or tool steels for their high strength and good wear resistance, such as X40CrSiMo10-2 [1], SUH36 [2] and Cr12MoV [3]. However, because of the high density and low ratio of specific strength, the ratio of pull/weight of aviation engines decreases and the energy consume increases. So, it is becoming a hot research to use aluminum or titanium alloys to replace structural steels in recent years [4,5]. Titanium alloy is one of the best light materials for its high ratio of specific strength, excellent corrosion resistance and high fatigue resistance. But its poor wear resistance and high friction factor limit its application in sliding operational environment. It is necessary to improve the tribology behavior of titanium alloy in the aviation kerosene environment using surface modification technologies for its practical use to fabricate valves or sleeves [6,7]. PVD hard coatings can efficiently raise the wear resistance of titanium alloys, while the poor cohesive strength between the base and the coatings limits its use in valves and sleeves operating with precision assembly. Plasma nitriding could gain a metallurgy layer with the base, while NH3 or H2 used as work medium in nitriding could cause titanium hydrogen brittleness. A double-glow plasma surface metallurgy technique could broaden the surface metallurgy application field [8], and has a good prospect in improving the wear resistance of metals [9,10]. Mo coatings could efficiently heighten the tribology behavior of titanium alloy because Mo coatings have good tribology behavior and can solute with Ti element without the limit of element ratio [11-13]. In addition, the double-glow plasma surface metallurgy technique generally influences the surface roughness of the components. However, there is less study about the effect of the surface roughness on the tribology behavior of counterparts in the aviation kerosene environment.

In this study, a Mo metallurgy layer was gained by a double-glow plasma surface metallurgy technique on

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Corresponding author: LIU Dao-xin; Tel: +86-29-88491479; E-mail: liudaox@nwpu.edu.cn DOI: 10.1016/S1003-6326(11)61415-5

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Ti6Al4V base to replace tool steel in the aviation fuel control system. The effect of roughness on the wear behavior of counterparts was also discussed.

2 Experimental

2.1 Materials

The Ti6Al4V alloy used in this work was tempered at 820 °C with a composition of 6.70 Al, 4.21 V, 0.10 Fe, 0.14 O, 0.07 Si, 0.03 C, 0.015 N, 0.003 H and balance Ti (mass fraction, %). The microhardness was $HK_{0.025}422$. The 5CrMnMo was tempered at 960 °C+720 °C in air with a composition of 0.50 C, 0.60 Cr, 0.15 Mo, 1.2 Mn, 0.25 Si and balance Fe (mass fraction, %). The microhardness was $HK_{0.025}1127$.

2.2 Preparation of surface metallurgy Mo layers

Ti6Al4V discs with dimensions of $d30 \text{ mm} \times 8 \text{ mm}$ were ground to a 2000 grit finish using SiC papers, and then diamond polished. This procedure achieved a roughness R_a of 0.04 µm.

Figure 1 shows the sketch of the double-glow plasma surface metallurgy equipment. Mo alloying process was conducted by a double-glow plasma surface alloying technique [10]. L is the distance between the targets, E_1 is the source voltage and E_2 is the cathode voltage. A Mo plate (99.95%) and specimen worked as sputtering target and substrate, respectively. The base vacuum of the system was 50-100 Pa. On establishing the vacuum, pure argon was let in as the work medium to sputter-clean the surface of the base and target for 30 min, and then the alloying proceeded. Mo atoms were sputtered out and deposited on the surface of the substrate which was heated to a high temperature by ion bombardments. A Ti-Mo metallurgy alloy layer was formed through the following diffusion process of Mo on the surface of the Ti6Al4V base. The process was operated at 850 °C for 3 h. The process parameters were E_1 of 700–1000 V, E_2 of 300–700 V and pressure of 50-70 Pa. The power supply was a DC pulse source with a pulse frequency of 10 kHz at 80% duty cycle.



Fig. 1 Sketch of double-glow plasma surface metallurgy equipment

2.3 Characterization of Mo alloying layers

The surface micro-morphology was characterized

by scanning electron microscopy (SEM, Hitachi S–570). The cross-section microhardness of the alloying layer was measured by an HV–1000 Knoop microhardness tester under a load of 0.245 N lasting for 20 s. The phase transformation of the Mo alloying layer was determined by X-ray diffraction (XRD, D/max–RB). The cross-section element distribution of the Mo alloying layer was determined by a glow discharge optical emission spectrometer (GDS, GDA 750), and the ductility of alloying layer was researched by a tester with a Vickers diamond penetrator squeezing researched layers reciprocally [14,15].

The wear test was carried out by a ball-on-disk tester under a load of 10 N in 3# aviation kerosene at room temperature. The counterpart was a GCr15 sphere with 5 mm in diameter ($HK_{0.025}757$) and QSn4–3 copper alloy pin with 5 mm in diameter. The wear trace diameter was 7 mm. The sliding velocity was 200 r/min and the wear time was 120 min. Each test was carried out 3 times. Samples were diamond polished to different values of roughness. The wear volume loss was measured with a SJ–201 profile meter.

3 Results and discussion

3.1 Characterizing of Mo layers

Figure 2 shows the surface and cross-section SEM morphology of the Mo layers. Figure 3 shows the



Fig. 2 SEM images showing surface (a) and cross-section (b) of Mo alloying layers



Fig. 3 Element (a) and micro-hardness (b) depth distribution of Mo alloying layers

element and microhardness depth distribution, and Fig. 4 shows the XRD result of the Mo layers. There are cellular micro pits on the Mo layer surface, and this is related intensively with ion bombardments in the double-glow surface metallurgy process [9,16]. The Mo layer consists of a pure Mo layer and a diffusion layer. The pure Mo layer is about 10 μ m and the diffusion layer is 25 μ m in thickness. The gradient distribution of Mo and Ti elements along the depth indicates that a metallurgical cohesion occurs between Ti6Al4V base and Mo layers.



Fig. 4 XRD pattern of Mo alloying layers

The microhardness of Mo layer (HK_{0.025}1264) is about 3 times that of the Ti6Al4V base (HK_{0.025}422) and the depth of microhardness improving layer is about 200 μ m. This is favorable for the load-carrying ability and tribology properties. The XRD analysis shows that the Mo layer is homogeneous and compact with preferential orientation of (211).

Figure 5 shows the fatigue micrograph of the dynamic repeating presses of the Mo alloying layers. In the oscillating squeezing process, Mo layer surface is always in contact with Vickers diamond penetrator and bore fatigue compress load. Mo layers could bear a maximum fatigue load of 40 N at 1000 cycles without cracks. This indicates a high ductility for the Mo layers on titanium alloy. However, because of the variance of the ductility between the Mo alloying layers and titanium alloy base, there are obvious cracks on the corner of indentation due to the great stress concentration after 3000 cycles of fatigue squeezing load.



Fig. 5 SEM images showing fatigue microstructures of dynamic repeating presses of Mo alloying layers under maximum load of 40 N: (a) 1000 cycles; (b) 3000 cycles

3.2 Tribology behavior

3.2.1 Tribology behavior sliding with GCr15 counterparts

To be convenient, the Mo layer on titanium alloy is labeled "M" and the Mo layer with a polishing treatment following is labeled "M+P". The initial roughness R_a of the double-glow Mo layer is 0.56 µm. Figure 6 shows the wear test results of 5CrMnMo steel and Ti6Al4V with different surface treatments sliding with GCr15 counterparts. It can be seen that the wear track of Ti6Al4V base is the worst and the friction coefficient is the highest. This is due to the severe abrasive and adhesive wear of Ti6Al4V base with low microhardness. However, the friction coefficient for both Mo modified layers and 5CrMnMo is obviously lower due to the sufficient lubricating effect of aviation kerosene. Compared with Ti6Al4V, the wear resistance of 5CrMnMo is raised obviously, due to the high microhardness and low friction coefficient.



Fig. 6 Comparison of wear resistance of 5CrMnMo steel and Ti6Al4V with different surface treatments sliding with GCr15 counterparts: (a) Wear volume loss; (b) Friction coefficient vs time

Because the microhardness of Mo layers is much higher than that of 5CrMnMo, the wear volume loss of Mo modified layers is increased about 14 times than that of 5CrMnMo. However, the wear volume of GCr15 counterparts sliding with Mo modified layers is very huge. After the polishing treatment following, the roughness R_a of Mo alloying layers drops to the level of polished 5CrMnMo. So, the abrasive wear volume and the friction coefficient of GCr15 counterparts decrease. The wear volume of GCr15 sliding with the polished Mo alloying layers is much lower than that with 5CrMnMo. In addition, the wear volume of Mo modified layers is much little.

Figure 7 shows the wear morphology of 5CrMnMo steel, Ti6Al4V and Mo alloying layers with or without polishing treatments following sliding with GCr15 counterparts. It can be seen that the wear tack of 5CrMnMo is slight with little abrasive wear and polishing feature. In contrast, the wear track of Ti6Al4V sliding with GCr15 conterparts is wide and deep with obvious abrasive and adhesive wear charactertics. There are less erasing feature on the wear track of Mo layers than 5CrMnMo. So, it is feasible to fabricate Mo alloying layers on Ti6Al4V to replace 5CrMnMo with Ti6Al4V for anti-attrition of component mass and improving the service life of valves or sleeves in aviation engines.



Fig. 7 SEM images showing wear morphology of 5CrMnMo steel (a), Ti6Al4V (b) and M+P (c) (R_a =0.04 µm) sliding with GCr15 counterparts

3.2.2 Tribology behavior sliding with Cu alloy counterparts

Figure 8 shows the wear test results of 5CrMnMo steel and Ti6Al4V with different surface treatments sliding with Cu alloy counterparts. Due to the low microhardness of Cu alloy (HK_{0.025}197), the wear volume loss of Ti6Al4V is much little. The friction coefficient of T6Al4V sliding with Cu alloy counterparts is low. This is partially attributed to the solid lubricating effect of Cu alloy transferred to the surface of Ti6Al4V. Owing to the high microhardness of 5CrMnMo and the good lubricating effect, the abrasive wear is reduced. The wear volume loss and the friction coefficient of 5CrMnMo is lower than that of Ti6Al4V. Because of the high initial roughness of Mo alloying layers (R_a =0.56 µm), the wear volume loss and the friction coefficient of Cu counterparts sliding with Mo layers are high, although the wear volume loss of Mo layers is negative with Cu alloy transferred. With Mo alloying layers polished following, the roughness R_a is reduced from 0.56 to 0.04 µm and the friction coefficient from 0.15 to 0.11 without the loss of wear resistance of Mo alloying layers.



Fig. 8 Comparison of wear resistance of 5CrMnMo steel and Ti6Al4V with different surface treatment sliding with Cu alloy counterparts: (a) Wear volume loss; (b) Friction coefficient versus time

With Mo alloying layers polished following, the wear volume loss of Cu alloy counterpart is reduced to be less than that of 5CrMnMo. So, the system friction coefficient, surface roughness and microhardness are vital for reducing the wear volume loss of both samples and counterparts. It is essential not only to enhance the wear resistance of titanium but also not to influence the wear resistance of wear counterparts by replacing high strength steel with titanium alloy to fabricate valves or sleeves. It shows favorable tribology behavior to fabricate a Mo alloying layer on Ti6Al4V without raising the wear volume of counterparts with a polishing treatment following.

Figure 9 shows the wear morphology of Ti6Al4V and 5CrMnMo steel sliding with Cu counterparts. It can be seen that the wear mechanism of Ti6Al4V base is abrasive and adhesive with Cu alloy transferred from the counterparts. The wear track of 5CrMnMo is characterized by adhesive wear and slight erasing wear. It is indicated that soft Cu alloy is transferred from the counterparts to Ti6Al4V base or 5CrMnMo surface and forms a thin solid lubricating film under the synergistic effect of mechanical and chemical actions.



Fig. 9 SEM images showing wear morphology of Ti6Al4V and 5CrMnMo steel sliding with Cu alloy counterparts: (a) Ti6Al4V alloy; (b) 5CrMnMo steel

3.2.3 Effect of roughness on tribology behavior of Cu alloy counterparts

As shown by the above results, although the wear

resistance of titanium alloy is improved obviously, the roughness has an important effect on the wear resistance of the counterparts. So the effect of the polishing treatment for Mo alloying layers on the wear behavior of Cu alloy counterparts was researched in this study. Figure 10 shows the wear test results of Cu alloy counterparts sliding with Mo layers versus roughness. It is indicated that the wear volume loss ΔV of Cu alloy counterparts is proportional to the value of surface roughness. In addition, to reduce the wear volume loss of Cu alloy counterparts sliding with Mo layers to be lower than that with 5CrMnMo, the roughness of Mo layers must be polished to be equal to or less than 0.17 µm.



Fig. 10 Wear volume loss of Cu alloy counterparts versus surface roughness of Mo alloying layers

The effect of roughness of Mo layers on the wear behavior of Cu alloy counterparts is determined by the abrasive wear mechanism and lubricating effect in aviation kerosene [17]. A parameter which is commonly used to establish the lubrication regime is the so-called factor λ , defined by the ratio of the thickness of elastohydrodynamic films (h_{min}) and the composite roughness of the mating surfaces, and is expressed as [18]:

$$\lambda = \frac{h_{\min}}{\left((R_q^1)^2 + (R_q^2)^2\right)^{1/2}}$$
(1)

where R_q^1 and R_q^2 are the roughness of one contact surface and the other, respectively. In general, λ is used to predict the transition of fluid-film lubrication (FFL) and mixed lubrication (ML). It can be stated that if λ is higher than 3, full fluid lubrication is established, contact between the asperities of the mating surfaces is impeded by the lubricant film and the wear tends to be zero. If λ is equal to or less than 1, the surfaces are lubricated by the boundary lubricating film and thus wear cannot be avoided. If $1 < \lambda < 3$, varying degrees of ML exist. The value of the factor λ reflects the ratio of contact area impeded by the lubricant film or micro asperities. The high roughness value R_a of the initial Mo alloying layers (R_a =0.56 µm) induces a larger ratio of asperity contact wear area in the contact zone. The factor λ for Mo alloying layers is increased with the polishing treatment reducing roughness of Mo modified layers. More area is impeded by the lubricant film in the contact zone and the wear volumes loss of Cu alloy counterparts is prevented with abrasive wear induced.

In addition, although the roughness of initial polished Ti6Al4V is low, the factor λ increases due to the severe abrasive wear of soft Ti6Al4V base in the wear test. Therefore, the ratio of elastic FFL decreases and the wear volume loss of Cu alloy counterparts is aggravated.

Figure 11 shows the wear morphology of Cu alloy counterparts sliding with Mo alloying layers with or without polishing treatments following. It can be seen that the wear track of Cu alloy counterparts sliding with Mo alloying layers is 2.5 mm wide in diameter. This is attributed to the harsh abrasive wear of Mo alloying layers with high initial roughness. With the roughness of Mo alloying layers is reduced to be 0.5 mm wide in diameter. So, the roughness of Mo alloying layers has an important effect on the wear behavior of Cu alloy counterparts through influencing the wear mechanism.

4 Conclusions

1) A 35 μ m thick Mo alloying layer is fabricated on Ti6Al4V surface by the double-glow plasma discharge technique. The Mo alloying layer consists of a Mo depositing layer and a diffusion layer with good ductility. The surface microhardness is increased by twice. The gradient distribution of microhardness and Mo element depth distribution indicates that a metallurgical cohesion occurs between Ti6Al4V base and Mo layers.

2) The Mo alloying layer enhances the wear resistance of Ti6Al4V in aviation kerosene. With polishing treatments following, its wear resistance is higher than that of 5CrMnMo. The wear volume loss of GCr15/QSn4–3 alloy counterparts sliding with polishing Mo layers is lower than that with 5CrMnMo. It is feasible to fabricate Mo alloying layers on Ti6Al4V to replace 5CrMnMo for reducing the mass and improving the service life of valves or sleeves in aviation engines.

3) The roughness of Mo alloying layers has an important effect on the wear volume loss of QSn4–3 alloy counterparts. In aviation kerosene environment, the wear volume loss of QSn4–3 counterparts is proportional to the value of roughness of Mo alloying layers.



Fig. 11 SEM images showing wear morphology of Cu alloy counterparts sliding with M (a, b) and M+P (c, d) (R_a =0.04 µm)

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钛合金表面辉光离子渗 Mo 合金化层在 航空煤油环境中的摩擦学行为

汤金钢1, 刘道新1, 唐长斌1, 张晓化1, 熊 华2, 唐 宾3

1. 西北工业大学 腐蚀与防护研究所, 西安 710072;

2. 西安航空动力控制科技有限公司, 西安 710072;

3. 太原理工大学 表面工程研究所,太原 030024

摘 要:为改善钛合金在航空煤油中的摩擦学性能,采用辉光离子渗技术在 Ti6Al4V 合金表面制备 Mo 合金化层。 分析合金化层的表面形貌和微观结构,测试合金化层的显微硬度和元素沿层深的分布,对比研究钛合金基体、渗 Mo 合金化层和 5CrMnMo 工具钢在航空煤油中分别与 GCr15 钢及 QSn4-3 铜合金配副对磨时的耐磨性能,并探 讨渗 Mo 合金化层的表面粗糙度对摩擦磨损行为的影响。结果表明:经表面抛光处理后,钛合金表面辉光离子渗 Mo 合金化层不仅显著降低了钛合金的摩擦因数,而且有效增强了摩擦配副的耐磨性。渗 Mo 合金化层的摩擦性 能优于 5CrMnMo 工具钢。实验还发现铜合金配副的磨损体积损失与 Mo 合金化层的表面粗糙度成正比,这主要 是由合金化层与配副表面之间微凸体的磨粒磨损作用决定的。

关键词: 磨损; 摩擦因数; Ti6Al4V; 航空煤油; Mo

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