Microstructure and friction and wear behaviors of the low temperature iron electroplated titanium alloy

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Abstract: Titanium alloys are popular used in many fields such as spaceflight and car manufacturing. However, titanium alloy has disadvantages of being easy to scoring, scratching or seizure and low wear resistance. Iron electroplating coating is an important technique for repairing defective surface, and structures which usually been provided by this way greatly influence the tribological characteristics of the specimens. When it lays over the Ti or Titanium alloy specimens' surface, the properties defects of Ti and Titanium alloys can been fetched up. On the basis of the tested tribological characteristics and microstructure of the plated specimens, it further discussed: (i) the reasons of forming the surface microstructure; (ii) the relationship between the surface microstructure of iron electroplating coating and its properties. (iii) The characteristics iron electroplating coating and Titanium alloy. Results show that: (a) nanocrystalline grains is achievable in iron electroplating coating at low temperature, hydrogen gassing is likely the direct reason to cause crack of iron electroplating coating; (b) the impurities and the surface stress of iron electroplating coating are likely the factors to accelerate the propagation of crack; (c) iron plating on Titanium alloy piece can increase the surface hardness and its wear resistance.
Keywords: Titanium alloy; iron electroplating; microstructure; nanocrystalline grains; tribological characteristic

0 Introduction

Titanium alloy is well known for its good properties such as excellent low temperature plastic property, good machining property, high relative intensity, excellent anti-oxidation, anti-erosion and passivation property under 550℃. Therefore, titanium alloy has been used in many fields such as chemical equipments, spaceflights, weapon manufacturing[1~3]. However, the application of titanium alloy is limited by some disadvantages of being easy to scoring, scratching, or seizure. The wear resistance of titanium alloy is relative low, and the anti-erosion property is poor over 550℃. In order to improve the wear resistance of titanium alloy, the technicians have searched some new surface technologies， such as Carburizing technology, Ionitriding technology and Ion Spraying technology, to treat with Titanium alloy work pieces, but these methods all have their limitations: Carburizing coating and Ionitriding coating can't work at high temperature. Combinative intensity between Titanium alloy and Ion Spraying coating is poor.

Iron electroplating coating is a kind of effective surface engineering technique to enhance the wear resistance and anti-corrosion property. When an iron layer is coated on the titanium alloy substrate, the scratching between the contacting surfaces of the component will be encountered by iron layer, the results of which is that it gets higher wear resistance than pure titanium alloy. On the other hand, the electroplated iron layer can isolate the titanium substrate exposure to oxygen, carbon and nitrogen environments, so its anti-corrosion property will be improved. Recently, low temperature iron electroplating has developed as an effective surface repairing technology. Much attention has been paid to this technique: Gomes. A discussed the effect of the substrate on the electrodeposition of iron sulphides [4], and point out some good substrates for iron plating coating, magnetic thin iron plating coating were studied by Charles F and Lowrie, this kind of coating could be used in some electronic building bricks[5], Jartych. E and Feng Wang got different

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Fe-alloys films by different technology [6,7], Tremmel discussed bright nickel-iron alloy electroplating bath and process[8], this coating has a good anti-erosion property, and Kang Yu-ping observed the microstructure and property of iron plating layer without pre-etching[9]. The iron electroplating coating has been tried in some new fields: vitreous state iron plating coating were studied by Sisolak[10], for the vitreous state iron plating coating has excellent magnetism, be expected to used in some transformation place between electricity and magnetism. Tsubouchi had a patent about how to get porous iron plating coating, hoped it can be used in future industry[11].

In this paper, the technique of low temperature iron electroplating coating on the titanium alloy is studied, in order to enhance the wear resistance and anti-corrosion property of titanium alloy. For nanocrystalline grains owned excellent properties, so the study intended to get nanocrystalline grains iron plating coating. Then the microstructure and surface topography of the coating is observed. Friction and wear test results are presented. Moreover, the wear mechanism is discussed.

1 Experiment

1.1 Iron electrodepositing technique

Ti-6Al-4V alloy was selected as the coating substrate in this paper. Iron electroplating coating was conducted by using JZDA-100/12 plating D-AC power source. The positive electrode was pure iron. The temperature of electroplating bath was 25℃. The chemical composition of the electrolyte is shown in Table1. The pH value of the solution is 0.8～1.0. The current density at cathode is 30 A/dm^2. The iron electrodepositing duration is 1 hour.

Table 1. The chemical composition of electrodepositing solution

composition	$FeCl_2 \cdot 4H_2O$	KCl	$MnCl_2$	H_3BO_3	Wetting agent
Concentration /(g/L)	360	10	5	6	0.01

1.2 Iron electrodepositing technique

Combinative intensity between titanium alloy and iron electroplating coating was measured by annular shearing tests and thermal shock tests. Thermal shock tests were done by heating iron electroplated titanium alloy to 500℃, then cooling it sharply in water to 20℃. Annular shearing test specimens were prepared in the principle shown in Fig.1a. The iron coating layer in 5mm width on the titanium alloy rod was obtained. When the specimen was electroplated, the other places were protected by nonconducting materials. The negative electrode was connected from Titanium alloy rod, the positive electrode was a ring which was made of pure iron. The thickness of iron coating was stipulated over 0.5 mm. The specimen rod was put into a die, which had a hole to fit the rod as shown in Fig.1b. Then the iron coating could be crutched by the die, give an increscent pressure on rod by a pressure tester show as Fig.1 (b), when the iron plating coating flaked away from Titanium alloy rod, the combinative intensity between Titanium alloy and iron electroplating coating was measured, the value which the pressure tester denoted was the value of combinative intensity.

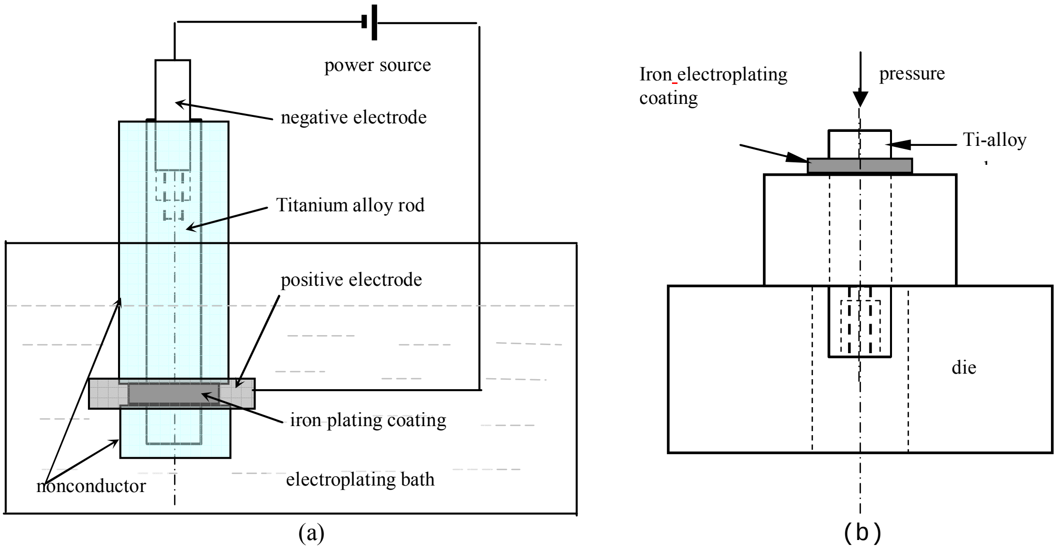


Fig 1. The principle of shearing test specimen preparartion (a) and test apparatus (b)

The surface topography and cross section view of the iron electroplated titanium alloy specimens were observed by using JSM-5610 LV scanning electro-microscope. The chemical elements of the coating was examined by using EDX techniques.

In order to evaluate the friction and wear properties of the iron electroplated titanium alloy, a block sliding on ring tribometer was applied to perform wear tests. The size of the block is 1.20 mm×1.20 mm×1.40 mm, which is made from Ti-6Al-4V alloy, and there was iron plating coating on one of its surface. The radius of the ring is 46 mm, which is made from 1045 carbon steel, the composition of the carbon steel is C (0.42~0.50), Mn (0.5~0.8), Si (0.17~0.32), the other is Fe. The set up of the block on ring is shown as Fig.2. The surface roughness of the contact surfaces of ring and block specimens was polished to Ra=0.32 μm. Two kinds of test condition were chosen in this paper. Tests 1 were performed under dry condition with the load of 10 N, and the sliding velocity is 0.24 m/s, the test duration lasts one hour. Tests 2 were performed under lubrication for the duration of 1.5 hours. The lubricant is 46 base oil having kinematic viscosity under 50℃ of 46 mm^2/s, flash point of 180℃ and pH value of 7~8. The contact load was applied to 100 N. The sliding velocity is 0.24 mm/s.

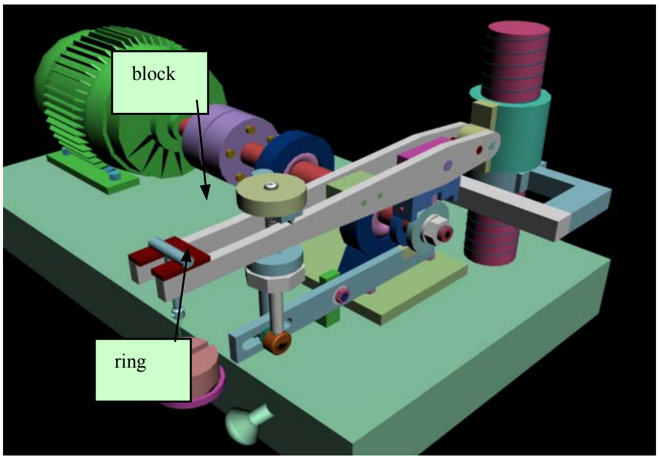


Fig.2 The schematic set up of block on ring wear tester.

2 Results and discussion

2.1 Combinative intensity between Titanium alloy and iron electroplating coating

Thermal shock tests were done by heating iron electroplated titanium alloy to 500℃, then cooling it sharply in water to 20℃, the coating could be resistant to five times thermal shock and keep in integrity. Annular shearing test show the results that the shearing strength between Titanium alloy and iron electroplating was 225 MPa, it was a high strength for a coating and its substrate.

2.2 Surface topography of iron electroplating coating

SEM analysis revealed some scattering anomalistic microcosmic meshy cracks and eroded holes appearing on the smooth and clear surface of the iron electroplating coating (Fig.3). The major cause of these cracks and holes was likely due to the action of hydrogen molecules. Generally, hydrogen molecules are likely to be evolved in the course of iron electroplating, and some of which may be adsorbed by coating surface of metal. The process of such hydrogen evolution and absorption would deplete the deposition of iron atoms onto the substrate, which led to the formation of some voids in the crystalline lattices of the plated coating. In addition, some hydrogen molecules would also merge to form microbubbles that may further grow to become bigger bubbles that are then large enough to break away from the surface of metal. En route of breaking away from the surface, the pressure of the bubbles would be so large to push away those oncoming iron atoms and prevent them adhering onto the overlaying substrate, thus forming some barrows in the coating. However, there would be some relatively low pressure bubbles being sealed to form porosities (micro-holes) in the plated coating. Impurities are likely to gather in these micro-holes.

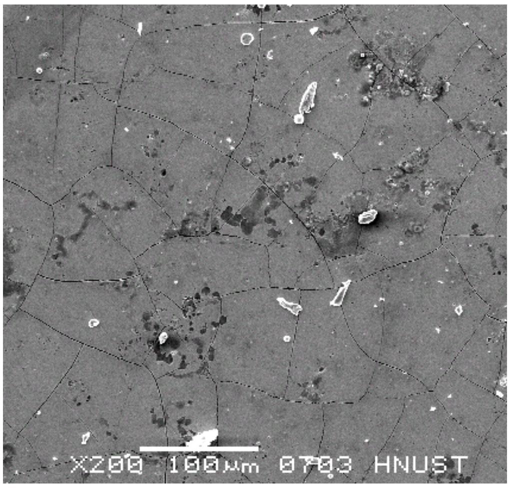


Fig. 3. SEM image of the iron electroplating coating, 200×

EDX results (Figs.4 and 5) on a smooth plating location with some eroded holes confirmed that there were some impurity elements besides Fe, such as O, K and Cl, in the eroded holes. The presence of these elements tends to offset the balance of the electrode potentials, to accelerate electrochemical corrosion and stress corrosion. However, it was found only the Fe element presented in the smooth plating locations. The results indicated that the plating chemicals like KCl, $MnCl_2$, H_3BO_3 and wetting agent were not actively participating in composing the iron electroplating coating, they were only serve for the auxiliary deposition. Crack is generally appeared when internal stress reaches certain critical value. The uniform cracking lines and the propagation of cracking feature on the surface of the plated coating (Fig. 3) suggest that the crack in the iron electroplating coating is likely to occur along the grain boundaries where the binding force of iron lattices is the least, viz. the location of air holes.

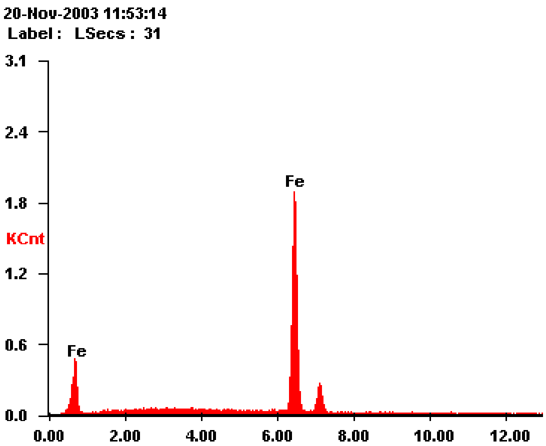


Fig4 EDX result of smooth location of the iron electroplating coating

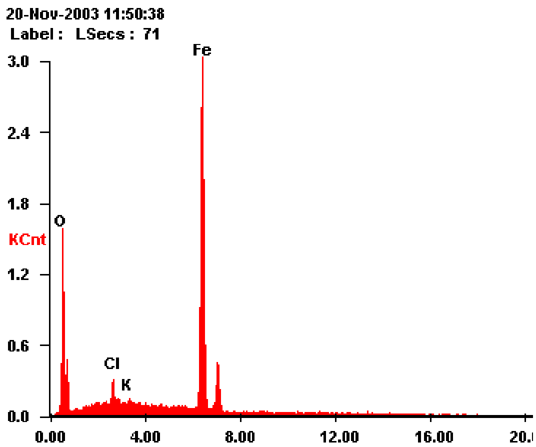


Fig.5 EDX result of eroded holes of the iron electroplating coating

2.3 Surface of the iron electroplating coating

The sectional plane structure of iron electroplating coating was analysised by SEM was shown in Fig.6. Analysis indicated that a specific microstructure characteristic of iron electroplating coating at low temperature which has the obviously distinct structures differs from the crystalline grains at the incipience of transitional plating and en-route of the plating process. It was observed that the crystalline grains at the incipience of transitional plating were in small columnar structure; their size was getting smaller as plating was progressing. At the stage when the plating was transiting from the end of the transitional plating stage towards the en-route plating, the small columnar crystallization grains were replaced by infinitesimal equiaxed crystalline grains. Another characteristic of the microstructure (Fig.7) shows that the average diameter of crystalline grains of the coating surface in infinitesimal size was approximately 100nm. Microstructure characteristics of iron electroplating coating are mainly determined by the growing nature of grains in the course of electro-deposition, and the forming orientation and behaviors of the iron crystallization in the electric field of the plating. The low current density and weak electric field at the initial stages of transitional plating normally leads to low electron transportation velocity, and small driving force to activate the nucleation of crystalline nucleus. Subsequently, the crystallization of iron in the electroplating coating emanates mainly from the grains of basis material and grows along the direction of electric field as known as "upright growing"[12], results in the columnar-crystallization grains. In the last stage of transitional plating and the beginning of formal plating, the current density, the electron transportation velocity and the driving force in forming crystalline nucleus were all increasing. As a result, it increased the growth velocity both the crystal nucleation rate and the crystal grains, likely with the former being faster. Then the grains became smaller. As the current density value increased to certain critical value, the rapid crystal nucleation and grows led to the instant touching of the grains that was favorable for the growth of equiaxed crystallization grains rather than for that of columnar-crystallization grains.

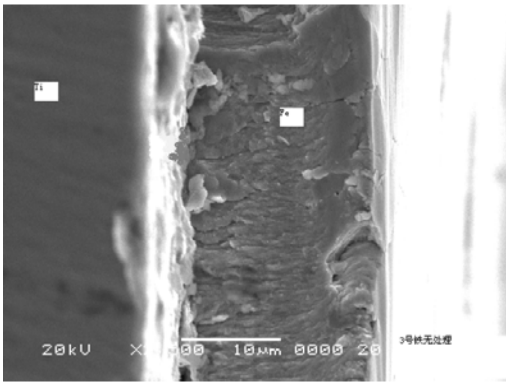


Fig6 Sectional plane structure of iron electroplating coating, 2500×

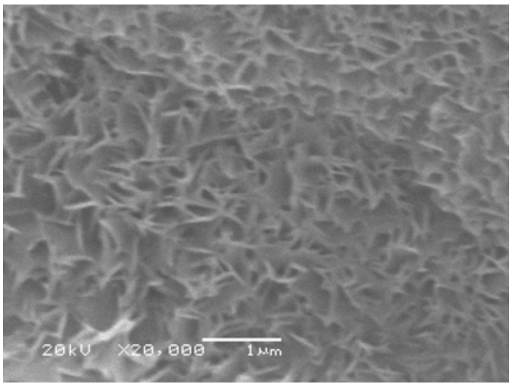


Fig.7 SEM image of iron electroplating coating, 20000×

2.4 Friction and wear behaviors

For the pure iron with the same chemic component, its tribological characteristics were compared with iron plating. Fig.8 shows friction coefficient behavior of iron electroplating coating at low temperature and that of pure iron and Ti-ally, obtained under the same test conditions (Sliding tests 1). The values of friction coefficient for the iron electroplating coating were generally lower than those for pure iron and Titanium alloy. The developing trends of the three curves vary with the sliding time. The mean friction coefficient of iron electroplating coating was at low value in the beginning of test and then quickly rising until stabilized at certain value. Whereas, its counterpart for pure iron and Titanium alloy showed trends of small rise followed with the test going on. It was almost linearly until reaching certain value at which it was fluctuating. Test results showed the wear resistance of the iron electroplating coating was better than that of pure iron and Titanium alloy too (Fig.9): typically, the volume wear of the iron electroplating coating was 0.014 mm^3 whilst that of pure iron was 0.046 mm^3 and Titanium alloy was 1.064 mm^3. The worn surfaces also can show the result that the wear resistance of the iron electroplating coating was better than that of pure iron and Titanium alloy (Figs.10 (a), (b), (c)): the wear trace of iron electroplating was shallower than those of pure and Titanium alloy at the same test condition.

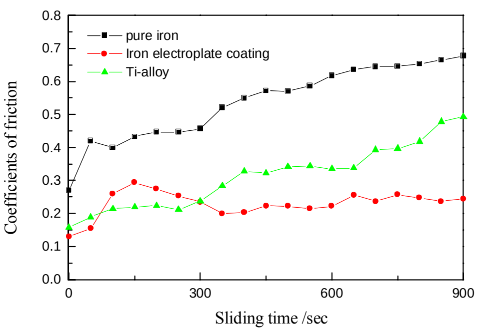


Fig.8 Friction coefficient specimen at sliding tests 1

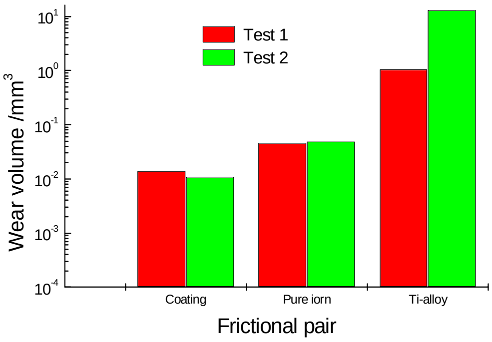
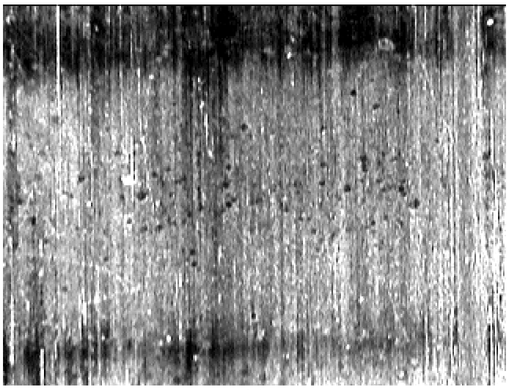
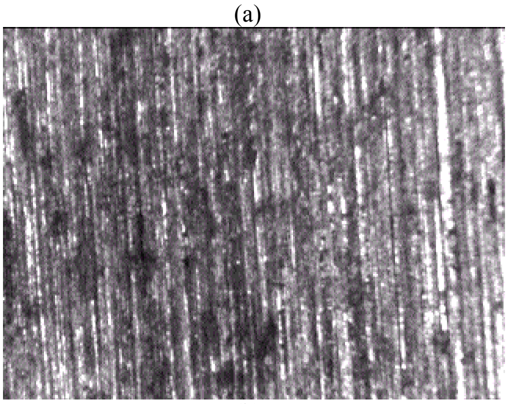


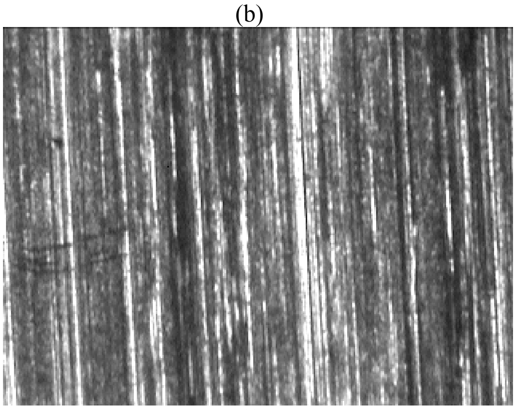
Fig. 9 Wear volume of specimen at sliding tests



(a)



(b)



(c)

Fig.10 The optical observation of the worn surfaces of (a) iron electroplating coating, (b) pure iron and (c) titanium alloy in test 1., the magnification is 100×, and the sliding direction is downward.

Analysis of coating and mating surfaces indicated that cold-welding occurred between the surfaces of frictional sliding pair in dry frictional condition. According to molecule-mechanical theory of friction, friction is always synthesized by surface engagement and molecular adhesion between two friction surfaces. For metal rubbing pair, molecular adhesion would be the dominant mechanism prompting for interfacial friction. At the beginning of friction test, the existence of oxide films on the friction surface led to low friction coefficient. When the oxide films were broken down, the friction coefficient was subsequently gradually increasing. Owing to its very fine crystal grains, the strength of the iron electroplating coating was greater than that of the pure iron (the microhardness value of the iron electroplating coating being prepared is about $HV_{0.1}$ 579, the microhardness of pure iron is about $HV_{0.1}$ 190 and that of Titanium alloy is $HV_{0.1}$ 120), thus leading to relatively lower wear. Study indicated that the topography of iron electroplated coating almost remained unchanged throughout the frictional test duration. This implies that the real rubbing area of sliding pair likely also remained unchanged. Consequently, steady force of molecular adhesion was achieved after a period of sliding that then gave almost steady value of friction coefficient. Contrast to the iron electroplating coating, the friction coefficient of pure iron increased immediately after the breaking down of oxide films because the crystal grains of pure iron are generally coarser which led to have lower hardness. The effect of surface engagement for pure iron was more influential at the beginning of the frictional test. The rubbing off of the peak of surface asperities after running-in stage of the pure iron and 45 steel mating pair reduced the effect of such types of surface engagement which led to the decrease of frictional coefficient. When the sliding test was going on, the real rubbing area of the mating pair was gradually enlarging and the exposing mating surface of pure iron had similar mechanical properties as its mating 45 steel ring specimen. The force of molecular adhesion was thus increasing gradually which led to the occurrence of adhesion wear and the increase of frictional coefficient. Otherwise, the scattering anomalistic microcosmic meshy cracks and eroded holes on iron electroplating coating can deposit the wear particles, then the friction coefficient and wear of iron electroplating coating was low.

Fig.11 shows friction coefficient behavior at Sliding tests 2. The values of friction coefficient for the iron electroplating coating were generally lower than those for pure iron and Titanium alloy. The developing trends of the three curves were stable with the sliding time. Test results shows the wear resistance of the iron electroplating coating was better than that of pure iron (Fig.9): typically, the volume wear of the iron electroplating coating was 0.011 mm^3 whilst that of pure iron was 0.049 mm^3 and Titanium alloy was 13.253 mm^3. The worn surfaces also can show the result that the wear resistance of the iron electroplating coating was better than that of pure iron and Titanium alloy (Figs.12 (a), (b), (c)): the wear trace of iron electroplating was shallower than those of pure and Titanium alloy at the same test condition.

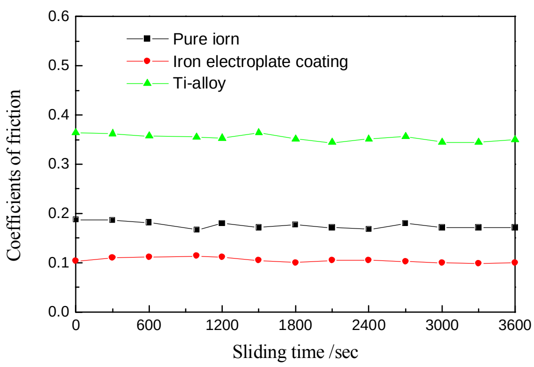
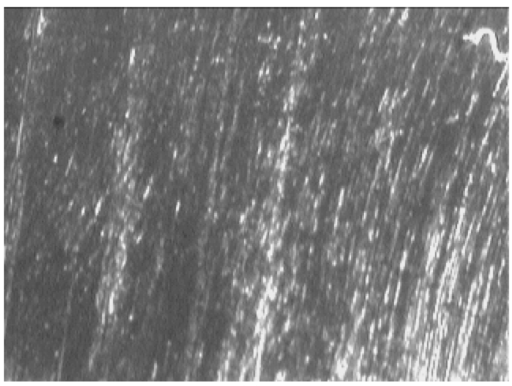
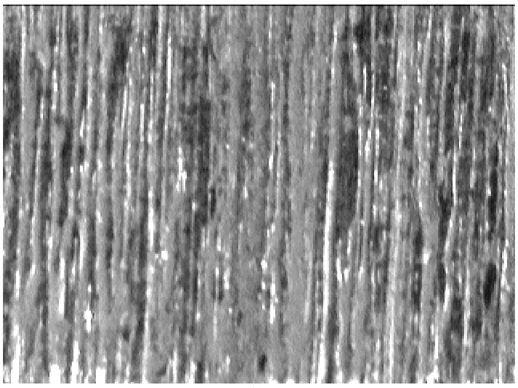


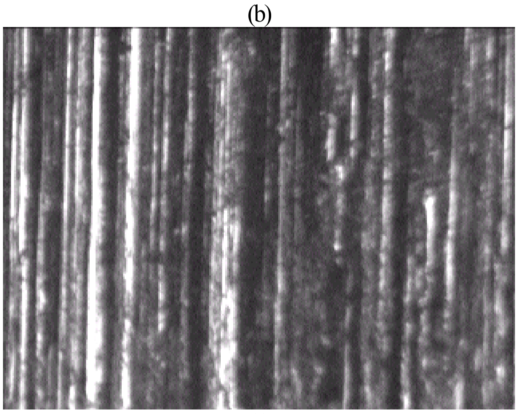
Fig.11 Friction coefficient specimen at sliding tests 2



(a)



(b)



(c)

Fig.12 The optical observation of the worn surfaces of (a) iron electroplating coating, (b) pure iron and (c) titanium alloy in test 2., the magnification is 100×, and the sliding direction is downward.

Analysis of tribological characteristics of iron electroplating coating, pure iron and Titanium alloy indicated in lubricating condition that Titanium alloy was sensitive to the pressure at the test, so its volume wear was much bigger than those of iron electroplating coating, pure iron. Besides molecule mechanical theory of friction, the scattering anomalistic microcosmic meshy cracks and eroded holes on iron electroplating coating can not only deposit the wear particles, but also deposit the lubicating oil, increasing lubricating effect, then the friction coefficient and wear of iron electroplating coating was lower than those of others.

3 Conclusion

（1）By thermal shock test and annular shearing test, Iron electroplating coating owns high combinative intensity.

（2）Infinitesimal crystal grains with average diameter about 100nm was achievable from iron electroplating coating at low temperature. Iron coating on Titanium alloy piece can increases the surface hardness.

（3）Crack in iron electroplating coating was directly due to the formation of micro-holes by evolution of hydrogen in the plating process. The impurities in the so-formed micro-holes and the surface stress generated in the iron electroplating coating expedited the propagation and the enlargement of the crack.

（4）Experimental analysis showed the chemicals like KCl，$MnCl_2$，H_3BO_3 and wetting agent in the iron electroplating were not actively participating the composition of iron electroplating coating. They played their role only in the process of auxiliary deposition.

（5）The tribological Characteristics of the iron electroplating coating were better than those of pure iron and Titanium alloy; they gave lower frictional coefficient and smaller wear amount under the same testing conditions.

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低温下钛合金镀铁的摩擦磨损性能

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摘要：钛合金被广泛用于在各个领域，如航空，汽车制造。然而，钛合金综由于自身易刮伤和低磨损的缺点而限制了其使用，钛合金镀铁可克服其缺陷。根据钛合金镀铁的摩擦磨损性能测试结果，可得出以下结论：（i）形成表面微观形貌的原因；（ii）钛合金镀铁表面微观形貌与其性能的关系；（iii）钛合金镀铁表面特征。结果表明：（a）铁电镀涂层在低温下可形成纳米晶粒，氢气处理可能造成铁电镀涂层裂纹的直接原因；（b）钛合金镀铁中的杂质和铁电镀涂层表面应力是加快传播裂纹的可能因素；（c）钛合金镀铁可以增加表面硬度和耐磨性。

关键词：钛合金；镀铁；微观形貌；纳米粒子；摩擦性能
中图分类号：TB3