



Effects of nitrogen flux on microstructure and tribological properties of in-situ TiN coatings deposited on TC11 titanium alloy by electrospark deposition

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Abstract: In order to improve the tribological properties of titanium alloys, the in-situ TiN coatings were prepared by electrospark deposition (ESD) on the surface of TC11 titanium alloy. The effects of nitrogen flux on the microstructure and tribological properties of TiN coatings were investigated. The results show that the coating is relative thin when the nitrogen flux is small and mainly consists of Ti_2N , α -Ti, TiO and TiN phases, and the metastable phase of Ti_2N is developed due to the rapid solidification of ESD. While in excessive nitrogen flux condition, many micro-cracks and holes might be generated in the coating. In moderate nitrogen flux, the coating is mainly composed of TiN phase, and is dense and uniform (50–55 μm). The average hardness is $HV_{0.2}$ 1165.2, which is 3.4 times that of the TC11 substrate. The TiN coatings prepared in moderate nitrogen flux perform the best wear resistance. The wear loss of the coating is 0.4 mg, which is 2/9 that of the TC11 substrate. The main wear mechanisms of the coatings are micro-cutting wear accompanied by multi-plastic deformation wear.

Key words: titanium alloy; TiN coating; electrospark deposition; friction and wear

1 Introduction

Titanium alloys have many advantages such as low density, high specific strength, excellent corrosion resistance and biocompatibility [1–3]. Thus, they have been widely applied to aerospace, chemical, metallurgy, medicine and nuclear industries. For example, the compressor disks and fan blades of aero-engine, submarine plane hatch wallboards and pump bodies, artificial joints and heart valves in medical field and other components have been made from titanium alloys [4–6]. However, titanium alloys limit their further application due to their poor tribological properties such as high friction coefficient and adhesive wear, leading to their failure in the early service stage. The surface modification and treatment of titanium alloys by using methods such as physical or chemical vapor deposition (PVD, CVD) [7,8], ion implantation [9], thermal oxidation [10], magnetron sputtering techniques [11] and laser cladding [12], have achieved good results. However, these methods require expensive equipments, specific room and it is difficult to produce large and complex shaped components.

Electrospark deposition (ESD) is a typical surface

modification technology with high energy density and low heat input, which has been widely used in the preparation of modified strengthening coatings [13–15]. By utilizing high energy pulsed discharge between electrode and metallic substrate, the ESD process can deposit the melting electrode materials onto the substrate to accomplish metallurgical reaction with substrate. Currently, several coatings, such as WC92–Co8 hard alloy coating [16], biocompatibility coating with graphite electrode in silicone oil dielectric [17] and TiN ceramic coating [18], have been developed by ESD process on titanium alloys. TiN coating with high hardness, high strength and low friction coefficient developed by ESD is a promising surface coating to modify the titanium alloy. Although the scholars have done a lot of work on ESD mechanisms, for example, the electrode material mass transfer mechanism [19], the single pulsed morphology formation mechanism [20] and the interface structure and diffusion behavior mechanism [21] have been studied systematically, the ESD mechanisms mentioned above are based on the reality that the coatings are developed by the electrode materials transferred to the metallic substrate with simple molten metallic compound. For TiN coating deposited by ESD, N_2 is applied not only as shielding gas but also as

reactive gas, in which N_2 will be decomposed and mixed with the molten electrode material and matrix material to achieve in-situ synthesis reaction. So, the mechanism to develop TiN coating by ESD is more complicated and it has not been investigated deeply.

From a large number of experiments on developing TiN coatings on titanium alloys by ESD, it is evident that N_2 has an important effect on the properties of TiN coatings and the complicated mechanism for forming TiN coatings. Thus, in this work, the TiN coatings were deposited under different nitrogen fluxes and the effects of nitrogen flux on the microstructure, mechanical properties and tribological properties of TiN coatings were studied systematically in order to reveal the ESD mechanism for developing TiN coatings, for providing a theoretical basis and a technical support for the preparation and engineering applications of TiN ceramic coating on titanium alloys.

2 Experimental

Titanium alloy plate of TC11 with dimensions of 10 mm×10 mm×3 mm was selected as the substrate material. The chemical composition of TC11 is listed in Table 1. The pure titanium TA2 rod with a diameter of 5 mm was used as the electrode.

Table 1 Chemical composition of TC11 titanium alloy (mass fraction, %)

Al	Mo	Zr	Si	Fe	O	Ti
6.32	3.29	1.79	0.23	0.077	0.096	Bal.

Prior to ESD process, the substrate specimens and the electrode tip were ground with 800 grit SiC paper to remove the oxide films and then rinsed with acetone to remove surface oil. The experiments were carried out by a 3H-ES ESD deposition machine. The reaction schematic diagram is shown in Fig. 1. In the ESD process, N_2 not only takes as shielding gas to prevent the oxidation of the titanium alloy, but also as reactive gas to develop TiN coating. In order to investigate the effects of nitrogen flux on the properties of the coatings, three typical flux values of N_2 (5, 10 and 15 L/min) were selected. The technological parameters of ESD are as follows: output voltage 80 V, discharge frequency 1200 Hz and specific strengthening time 3 min/cm².

In order to evaluate the bonding strength between the ESD coating and the substrate, scratch tests were carried out on an automatic scratch instrument of WS-2005. The scratch parameters are as follows: loading force 100 N, loading rate 20 N/min, indenter speed 2 mm/min and scratch length 10 mm. The scratch hardness H_{SL} was calculated according to the specification of ASTM G171–03 norm [22]:

$$H_{SL} = \frac{8L_c}{\pi d^2} \quad (1)$$

where L_c is the critical load that can be captured by acoustic signal and d is the corresponding scratch width that can be artificially measured. Scratch hardness H_{SL} is a fair indicator of coating cohesion.

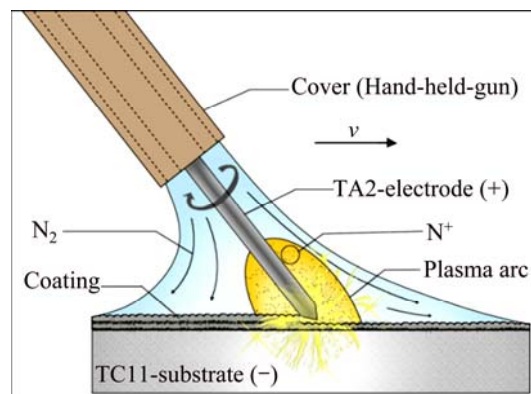


Fig. 1 Schematic diagram of preparing in-situ TiN coatings on TC11 by electrospark deposition (ESD)

The metallographic morphology was observed by an optical microscope of DMM-330C. The morphologies of the microstructure and the worn surface of ESD coatings were observed by a scanning electron microscope (SEM) of QUANTA 200. The elemental line scanning spectrum was tested by X-ray energy-dispersive analysis (EDAX) attached to the SEM. In addition, the phase composition was identified by a D/max 2500/PC type X-ray diffractometer with Cu target operated at 40 kV and 200 mA. The microhardness of the coatings was measured using a DHV-1000 microhardness tester under a load of 4.92 N with a dwell time of 15 s.

Tribological tests of the ESD coatings were evaluated by a ball-on-disc tribometer of HT-500. The upper specimens were GCr15 steel balls with the diameter of 4 mm and the surface roughness of 0.05 μ m. The down ones were the ESD coatings. The tribological tests were conducted at normal atmospheric temperature (25 °C) with a constant speed of 0.1 m/s under a norm load of 4 N. The sliding time was 30 min. The wear losses of the specimens were measured by an ATB120–4M electric analytical balance with an accuracy of 0.1 mg.

3 Results and discussion

3.1 Microstructure of coatings

Figure 2 shows the microstructure morphology of the TiN coating deposited on the surface of TC11 substrate by ESD. It shows that on the surface of TiN

coating, typical splash and sputter feature appear (Fig. 2(a)). When TA2 electrode approached TC11 substrate, a discharge channel might be generated between the electrode tip and the substrate, in which N_2 was ionized and generated high temperature of 8000–25000 °C in 1×10^{-5} – 1×10^{-6} s. Meanwhile, the molten droplets formed on the electrode tip were accelerated by the high plasma current and deposited on the substrate of TC11 substrate, resulting in the splash and sputter feature.

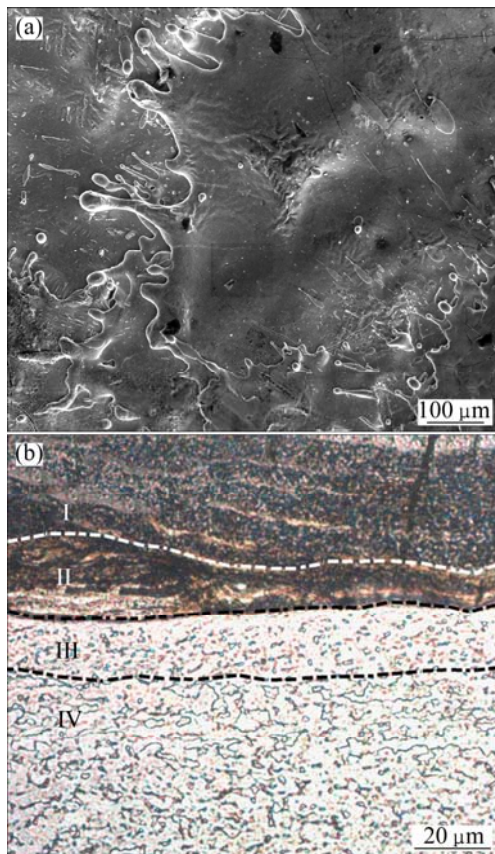


Fig. 2 Microstructural morphologies of TiN coating deposited at nitrogen flux of 10 L/min: (a) Top surface; (b) Cross-section

Figure 2(b) shows the cross-section metallographic micrograph of the TiN coating. It shows that the coating is dense and uniform throughout the cross-section. The evidently continuous interface proves the formation of metallurgical bond between the coating and the substrate. It is clear that the coating can be divided into four typical areas as shown in Fig. 2(b). Area I is the ESD coating and area II is the transition zone, while area III is the heat-affected zone and area IV is the bulk substrate of TC11. The microstructure in area I is fine and compact. In the ESD process, due to high energy pulsed discharge process, the molten pool generated on the surface of substrate was heated and cooled rapidly, which led to the increase of the super-cooling degree and the nucleation rate, then resulted in the grain refinement. The transition

zone II is inhomogeneous with the thickness of 10–15 μm . The heat-affected zone III is relatively thin and its thickness is 15–20 μm , in which there are no significant grain boundaries after being etched by Kroll solution. This means that there is little heat transmitting effect on the substrate of TC11 in the ESD process. The bulk substrate IV remains $\alpha+\beta$ biphasic morphology and apparent grain boundaries.

Figure 3 shows the morphologies of cross-section of the TiN coatings at nitrogen fluxes of 5, 10 and 15 L/min, respectively. When nitrogen flux is too small (5 L/min), the coating is thin with the thickness ranging from 20 to 25 μm and fewer micro-cracks (Fig. 3(a)). While in

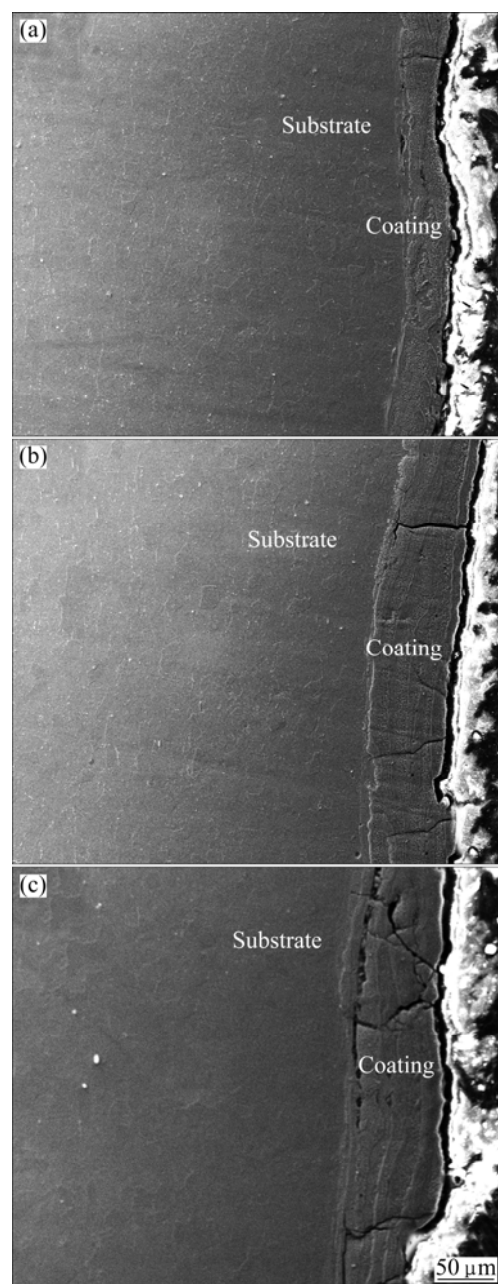


Fig. 3 Morphologies of cross-section of TiN coatings deposited at different nitrogen fluxes: (a) 5 L/min; (b) 10 L/min; (c) 15 L/min

moderate nitrogen flux (10 L/min) condition, the coating is dense and uniform with the average thickness of 50 μm , bonding with substrate metallurgically (Fig. 3(b)). Meanwhile, some micro-cracks are observed in the coating, which are approximately in the direction perpendicular to the coating surface. The molten pool generated on the surface of substrate rapidly solidifies to form a coating due to the ESD characteristics and results in much thermal stress in the deposited coating [23]. As a consequence, with increasing accumulation of the tensile thermal stress in the multi-repeat ESD process, the micro-cracks might develop gradually in the coating. Furthermore, low toughness of the deposited surface coating of TiN might also facilitate the development of the micro-cracks. When the nitrogen flux is excessively elevated (15 L/min), the thickness of the coating is increased to a certain extent, but the coating is not uniform with many micro-cracks and holes and delamination phenomena at the bonding interface between the coating and the substrate, which indicates that the deposited coating is in poor quality and low bonding strength (Fig. 3(c)). This can be attributed to the excessive flux of nitrogen gas, which results in severe chemical reaction between the titanium and nitrogen. Meanwhile, the turbulence is generated on the local reaction region of substrate surface, which might be involved in the molten pool and leads to the formation of micro-cracks and holes in the coating due to insufficient time for the air current to escape.

The element distribution across the section of the coating is illustrated in Fig. 4. It shows that elements of Ti, N and Al change continuously as a function of depth from the surface. The contents of elements Ti and N are relatively high and stable between the surface and the position 35 μm away from the coating, which indicates that this area is TiN coating. With the increase of the distance from the surface, the contents of elements Ti and Al increase while that of element N decreases between the position 35 and 50 μm from the coating, indicating that this area is transition zone, in which all the elements change continuously and slowly to prove the metallurgical bonding between the coating and the substrate. Also, the diffusion behavior can be verified by the changes of the element contents from the line scanning spectra in transition region. There is higher content of N in both the coating and the transition region. This reveals that nitrogen ions (or atoms) ionized by high-energy pulsed micro-arc have migrated into the coating when a localized melting pool forms and solidifies after cooling. Furthermore, there is certain content of element Al in the coating, which indicates that element Al has diffused into TiN coating from titanium alloy substrate during ESD process.

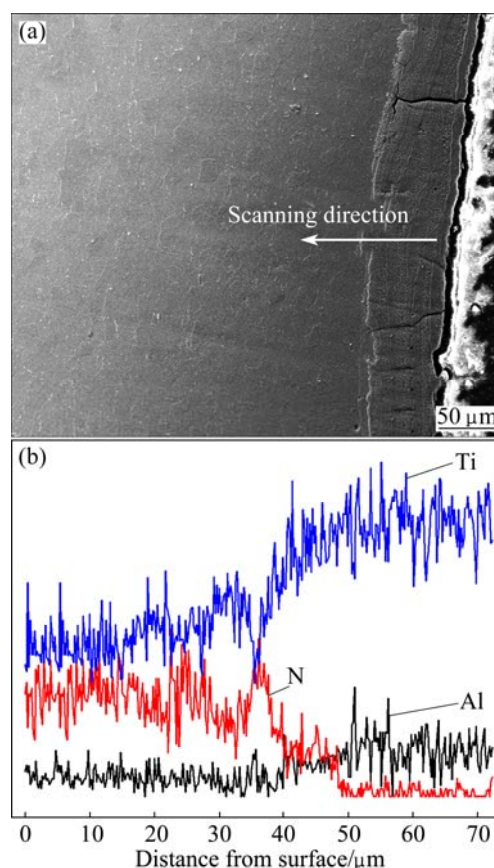


Fig. 4 Cross-section elemental line scanning distribution profile of TiN coating at nitrogen flux of 10 L/min: (a) SEM image; (b) Element distribution

In summary, the intermixing pattern among nitrogen ions (or N atoms), pure titanium electrode material of TA2 and TC11 titanium alloy substrate can be accomplished in two ways in the ESD process. One is the metallurgical in-situ synthesis reaction in the molten pool, the other is the diffusion behavior of elements at the interface. The active nitrogen ions ionized by high frequency pulsed discharge may be absorbed on the surface of molten pool and overcome the surface energy to diffuse into the molten pool rapidly. However, the intermixing is uneven due to the ultrahigh condensation rate of the molten pool, which restricts the diffusion of nitrogen ions (or atoms). For this reason, the upper portion of molten pool contains much more element N than the lower portion. Compared with element N, element Al diffuses into the interfacial region much more easily on account of the opposite direction of thermal gradient. So, there exists certain content of element Al in the upper and the lower portions of the coating.

The X-ray diffraction patterns of the coatings prepared at different nitrogen fluxes are illustrated in Fig. 5. The coating is mainly composed of TiN and Ti_2N phases in the moderate nitrogen flux (10 L/min) condition (Fig. 5). However, TiO and $\alpha\text{-Ti}$ peaks are also

found besides the TiN and Ti₂N phases as the nitrogen flux is too small (5 L/min), indicating that insufficient nitrogen flux exposes the molten titanium alloy to the atmosphere of high temperature and leads to the reaction between Ti and O in air, which ultimately leads to the generation of TiO phase. In excessive nitrogen flux (15 L/min) condition, the coating is mainly composed of TiN phase and Al₃Ti_{0.8}V_{0.2} compound.

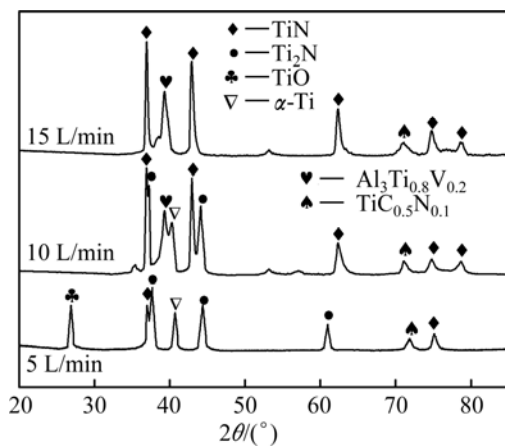


Fig. 5 XRD patterns of TiN coatings deposited in different nitrogen flux conditions

It is important to study the metallurgical reaction during the ESD process because of the complicated in-situ synthesis reaction occurring in the molten pool. The main elements Ti and N and their possible reactions are discussed primarily. For the Ti–N system, the following reactions are proposed:



The amount of nitrogen ions (or atoms) produced by high frequency pulsed discharge in low nitrogen flux condition is small, therefore, the amount of the nitrogen ions (or atoms) absorbed on the surface of molten pool at first and then diffused into the molten pool by overcoming the surface energy is small. However, the titanium alloy substrate with lower melting point generates a large volume of molten materials, so the mole ratio of N to Ti ($n(\text{N})/n(\text{Ti})$) is relatively small. According to the binary diagram of Ti–N system [24], the product mainly consists of α -Ti and Ti₂N phases. Although Ti₂N phase is a metastable phase, it is possible to be developed due to the kinetics of the ESD process. ESD is a high energy pulsed process accomplished with rapid solidification of the melting pool. Hence, it enables to generate and retain some metastable phases in the

coating. When the nitrogen flux is large, the amount of the nitrogen ions (or atoms) diffusing into the molten pool is large and so is the $n(\text{N})/n(\text{Ti})$ value, which results in the generation of TiN phase. And the above results are consistent with the XRD pattern analysis.

3.2 Mechanical properties of coatings

Figure 6 shows the microhardness distribution of cross-section of TiN coatings deposited in different nitrogen flux conditions. It shows that the microhardness values of the three different coatings increase significantly compared with that of the substrate. The highest values of microhardness appear on the top surfaces of coatings and decrease gradually along the depth direction of the coating. At moderate nitrogen flux of 10 L/min, the microhardness value of the coating is the highest, and the average microhardness is HV_{0.2} 1165.2, which is 3.4 times that of the substrate. This is attributed to high contents of TiN phase and Ti₂N phase in the coating as well as the strengthening effect of grain refinement due to the rapid solidification in ESD process [25]. In the excessive nitrogen flux condition (15 L/min), the average microhardness of the coating is HV_{0.2} 982.3, because the defects such as micro-cracks and holes in the coating decrease the microhardness of the coating. When the nitrogen flux is too small (5 L/min), the average microhardness of the coating is HV_{0.2} 842.1, which is the lowest compared with those of other coatings. This can be attributed to lower content of TiN phase in the coating. The chemical reaction between nitrogen and titanium becomes weak due to the low flux of nitrogen.

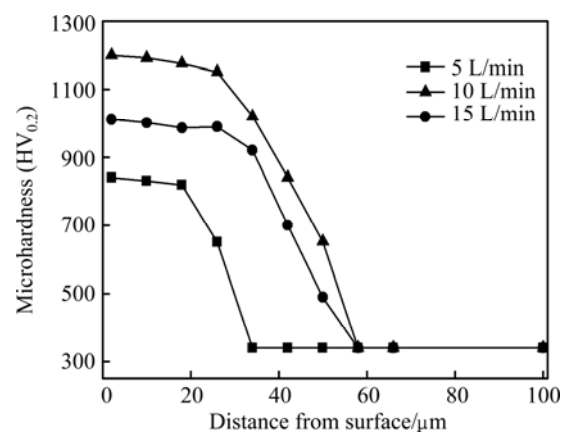


Fig. 6 Microhardness distribution of cross-section of TiN coatings at different nitrogen fluxes

The bonding strength between the coating and the substrate is an important parameter to evaluate the coating performance. Scratch tests were carried out on the apparatus of WS-2005 to measure the bonding strength of the coatings. The results are shown in Fig. 7.

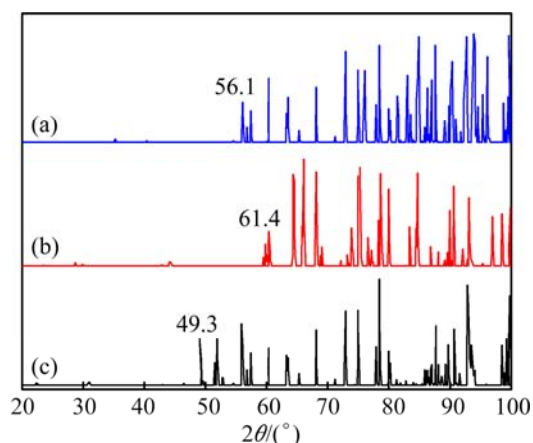


Fig. 7 Acoustic signal maps of TiN coatings deposited at different nitrogen fluxes: (a) 5 L/min; (b) 10 L/min; (c) 15 L/min

The critical normal load of L_c can be measured at the beginning of the occurrence of coating failure and it is a characteristic value for each coating. The critical load value of the coating deposited at moderate nitrogen flux (10 L/min) is 61.4 N, and the critical load values of the coatings deposited in the conditions of too small nitrogen flux (5 L/min) and excessive nitrogen flux (15 L/min) are 56.1 and 49.3 N, respectively.

The optical and SEM images of the scratches on the coatings deposited in different nitrogen flux conditions

after the scratch tests are illustrated in Fig. 8. From the SEM images, the coating fracture occurs under the dynamic load of nanoindenter and the contents of elements Ti and N change dramatically. In combination with acoustic signals demonstrated in Fig. 7, it is clear that the coating failure occurs at this location. The corresponding scratch widths were measured artificially. The scratch hardness values (H_{SL}) for the three coatings are calculated according to Eq. (1) and the results are shown in Table 2.

Table 2 Scratch testing results of TiN coatings

N_2 flux/(L·min ⁻¹)	d/m	L_c/N	H_{SL}/GPa
5	5.12×10^{-4}	49.3	0.479
10	5.34×10^{-4}	61.4	0.549
15	5.63×10^{-4}	56.1	0.451

The scratch hardness H_{SL} is an important index for coating adhesion. Consequently, the H_{SL} values of three coatings at different nitrogen fluxes of 5, 10 and 15 L/min are 0.479, 0.549 and 0.451 GPa, respectively, which demonstrates that the coating deposited at moderate nitrogen flux (10 L/min) is in the strongest bonding state compared with other two coatings. High H_{SL} value of scratch hardness is attributed to the thicker coating, denser structure, and higher microhardness as well as less micro-defects in the coating [4].

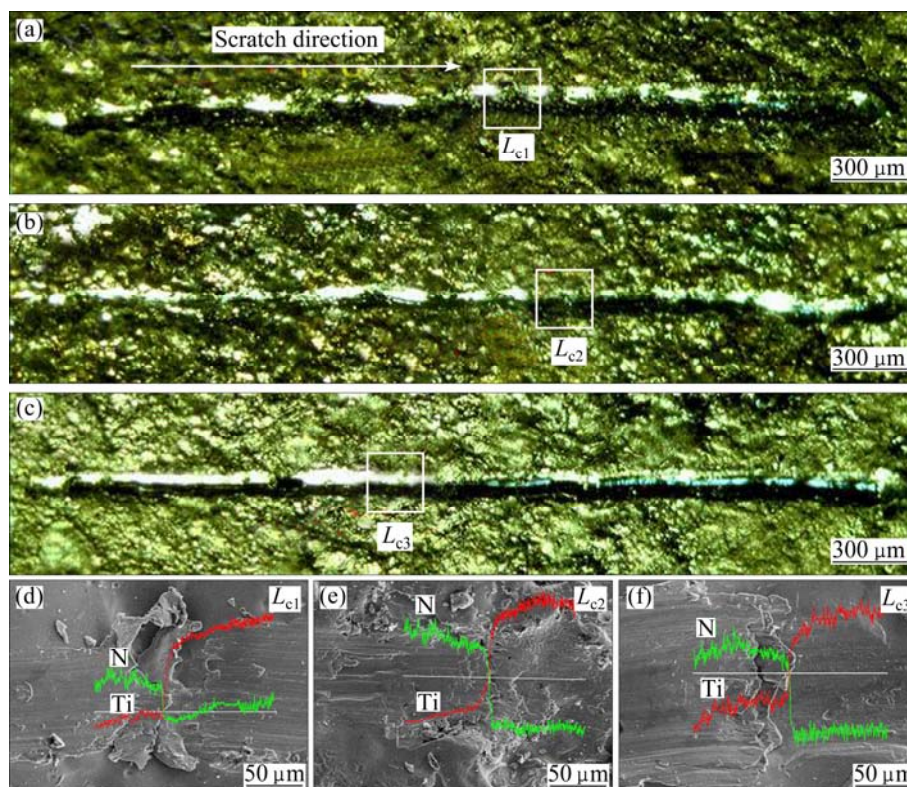


Fig. 8 Optical (a–c) and SEM (d–f) images of scratches after scratch testing on TiN coatings deposited at different nitrogen fluxes: (a, d) 5 L/min; (b, e) 10 L/min; (c, f) 15 L/min

3.3 Tribological properties of coatings

The friction and wear results of the TiN coatings in different nitrogen flux conditions are shown in Fig. 9. It shows that the coatings exhibit low friction coefficients and small wear losses compared with the TC11 samples. Especially, the coating deposited at nitrogen flux of 10 L/min has the lowest friction coefficient and the least wear loss. For the TC11 alloy, after the running-in period of 2 min, the friction coefficient sharply increases to a large value of 0.49 and its fluctuating range is relatively large (± 0.02). When the nitrogen flux is too small (5 L/min), the friction coefficient of coating increases slowly from 0.15 to 0.25 within 15 min, and then sharply reaches 0.49 which is as large as that of TC11 substrate after 15 min, which indicates that the coating has been worn out and results in the exposure of the TC11 substrate. In this situation, the friction between the coating and GCr15 ball has been changed into that between TC11 substrate and GCr15 ball, so, the friction coefficient increases in a great margin. In the moderate nitrogen flux condition (10 L/min), the friction coefficient of the coating maintains at 0.08, which reduces 83.4% compared with that of TC11 substrate, indicating that TiN coating has an excellent performance of reducing friction. But if the nitrogen flux becomes

excessive (15 L/min), the friction coefficient of the coating increases linearly from 0.07 to 0.13 as a function of time.

Figure 9(b) illustrates the variation of wear losses of the coatings deposited in different nitrogen flux conditions. It shows that the wear losses of the coatings are smaller than that of the TC11. Especially, the wear cost of coating deposited at the moderate nitrogen flux (10 L/min) is the least (0.4 mg), which is 2/9 that of the TC11. If the nitrogen flux is small (5 L/min) or excessive (15 L/min), the wear losses of the coatings are 0.8 and 1 mg, respectively, which are both lower than that of the TC11 substrate. So, the nitrogen flux has very important effect on the anti-wear properties of the coatings.

The morphologies of worn surfaces of the coatings deposited in different nitrogen flux conditions are shown in Fig. 10. It is obvious that there are many serious furrows and plastic deformation on the worn surface of TC11, which indicates that the main wear mechanisms are micro-cutting wear and multi-plastic deformation wear (Fig. 10(a)).

The morphology of worn surface of the coating deposited at a small nitrogen flux of 5 L/min is shown in Fig. 10(b). It can be seen that there are the traces of furrows and plastic deformation on the worn surface, which is similar to that of TC11 substrate (Fig. 10(a)). It is attributed to thin (20–25 μm) and low microhardness ($\text{HV}_{0.2}$ 842.1) of the coating. Due to small value of nitrogen flux which might result in weak chemical reaction between the nitrogen and the titanium, the friction coefficient of the coating sharply rises to 0.49 after 15 min (Fig. 9(a)), indicating that the coating has been worn out and the friction and wear between the coating and GCr15 have changed into those between TC11 and GCr15. The main wear mechanisms are multi-plastic deformation wear and micro-cutting wear.

Figure 10(c) shows the morphology of worn surface of the coating deposited at moderate nitrogen flux (10 L/min). It shows that the worn surface is smooth and covered by many shallow furrows, which indicates that the coating exhibits favorable wear resistance and its main wear mechanism is micro-cutting wear. Due to the splash and sputter morphology of ESD TiN coating, at the running-time of friction with the counterpart GCr15 ball, the hard particles peel off from the surface of TiN coating and transform to debris, leading to some ploughing furrows on the TiN coating. However, the role of furrow plough is small as a result of high hardness of TiN coating, which leads to micro-cutting wear ultimately. In addition, dense and uniform distribution of the coating throughout the cross-section and metallurgical bonding with substrate also provide the strong support for the coating to exhibit excellent wear resistance.

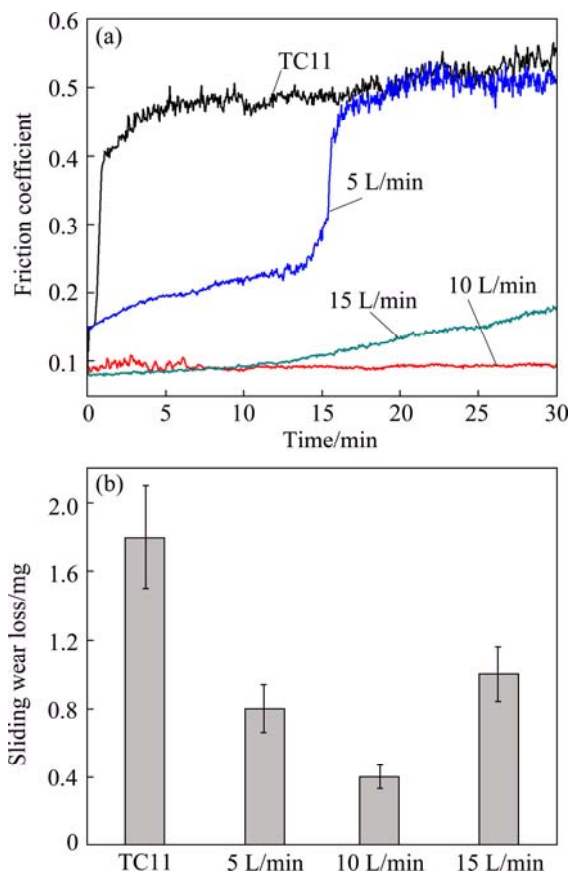


Fig. 9 Friction coefficients and wear losses of TC11 substrate and TiN coatings deposited at different nitrogen fluxes

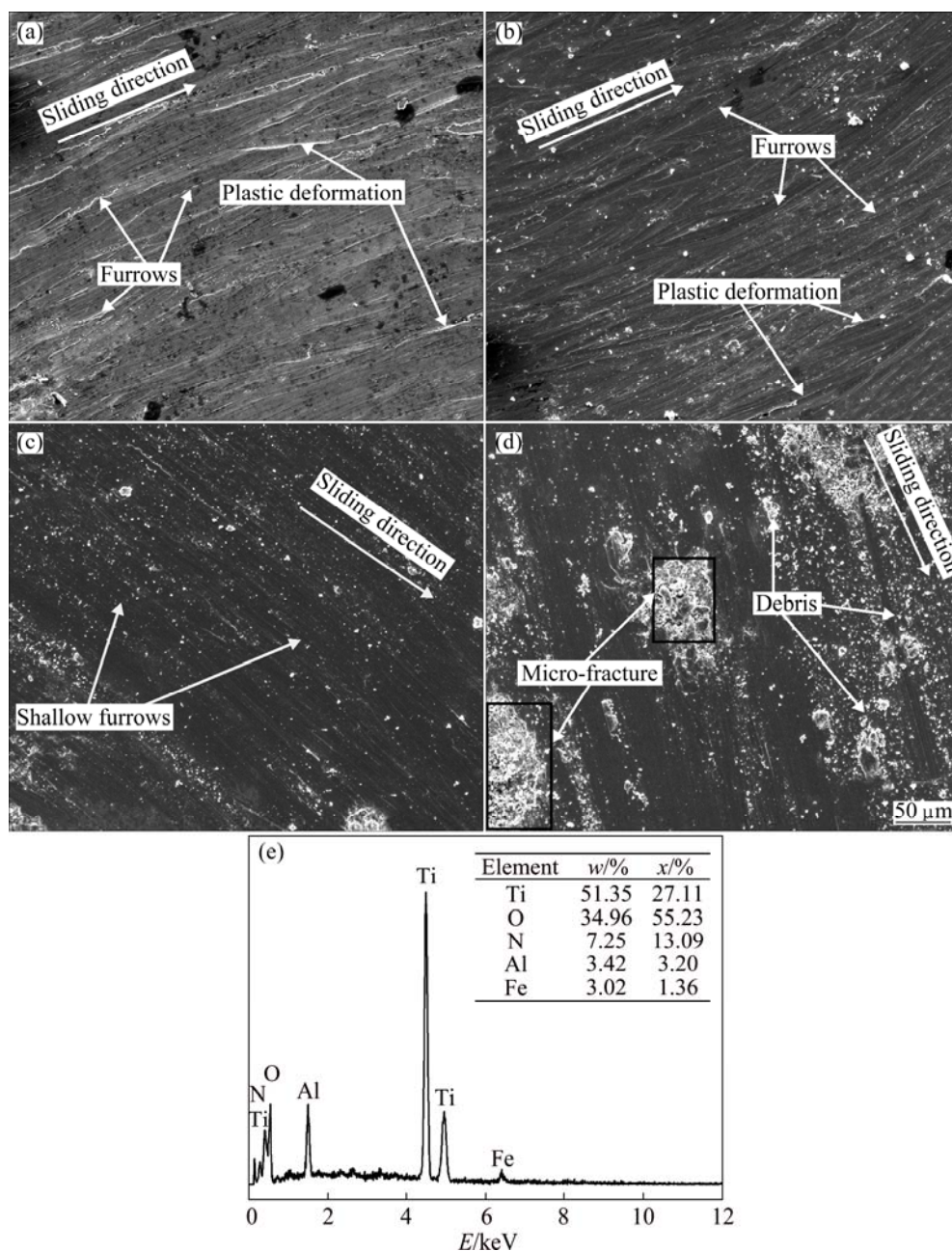


Fig. 10 Morphologies of worn surfaces of TC11 substrate and TiN coatings deposited at different nitrogen fluxes: (a) TC11; (b) 5 L/min; (c) 10 L/min; (d) 15 L/min; (e) EDAX spectrum of debris marked in Fig. 10(d)

As to the coating deposited at excessive nitrogen flux (15 L/min), the worn surface is rough, and there are many micro-fracture areas and micro-cutting traces as well as some desquamated debris as shown in Fig. 10(d). Figure 10(e) shows the EDAX of wear debris marked in Fig. 10(d). As can be seen, the major elements are Ti, N and O, which indicates that in the friction process, the coating element Ti with high chemistry activity generates oxide products when it contacts with O. Meanwhile, element Fe is transported from the GCr15 ball. As discussed above, although there are many hard phases of TiN and Ti₂N in the coating (Fig. 5), large amount of micro-cracks

and holes on the cross-section surface and delamination at the weakly bonded interface (Fig. 3(c)) due to excessive nitrogen flux may greatly decrease the wear resistance. In friction process, under the repeated action of normal load and friction forces of the counterpart, the defects in the coating such as micro-cracks and holes might propagate and finally result in the peeling off from the coating, which leads to much debris in composition with that deposited at nitrogen flux of 10 L/min. So, the wear loss increases significantly and leads to rough worn surface. The main wear mechanisms are micro-cutting wear and micro-fracture wear.

4 Conclusions

1) The in-situ TiN ceramic coatings were successfully deposited on the surface of TC11 titanium alloys by electrospark deposition (ESD). In the deposition process, the industrial pure titanium of TA2 was selected as the electrode material and high purity nitrogen gas as the reaction and protection gas.

2) The nitrogen flux has very important influence on the microstructure of the coatings. At moderate nitrogen flux, the coating is uniform and dense in a tight metallurgical bonding state. At small nitrogen flux, the coating is thin with the lowest hardness. And when the nitrogen flux is in excessive condition, there are many micro-cracks and holes on the cross-section surface as well as delamination at the interface between the coating and the TC11 substrate.

3) The TiN coating has excellent wear resistance and anti-friction properties, which is also greatly influenced by the nitrogen flux. As nitrogen flux increases, the main wear mechanism of the coating is transformed from micro-cutting wear to multi-plastic deformation wear accompanied with micro-cutting wear, and then the micro-facture wear.

References

- [1] STOJADINOVIC S, VASILIC R, PETKOVIC M, KASALICA B, BELCA I, ZEKIC A, ZEKOVIC L. Characterization of the plasma electrolytic oxidation of titanium in sodium metasilicate [J]. *Applied Surface Science*, 2013, 265: 226–233.
- [2] DURDU S, DENIZ O F, KUTBAY I, USTA M. Characterization and formation of hydroxyapatite on Ti6Al4V coated by plasma electrolytic oxidation [J]. *Journal of Alloys and Compounds*, 2013, 551: 422–429.
- [3] KUNG K C, YUAN K, LEE T M, LUI T S. Effect of heat treatment on microstructures and mechanical behavior of porous Sr–Ca–P coatings on titanium [J]. *Journal of Alloys and Compounds*, 2012, 515: 68–73.
- [4] DURDU S, AKTUG S L, KORKMAZ K. Characterization and mechanical properties of the duplex coatings produced on steel by electro-spark deposition and micro-arc oxidation [J]. *Surface and Coatings Technology*, 2013, 236: 303–308.
- [5] APACHITEI I, LEONI A, RIEMSLAG A C, FRATILA-APACHITEI L E, DUSZCZYK J. Enhanced fatigue performance of porous coated Ti6Al4V biomedical alloy [J]. *Applied Surface Science*, 2011, 257(15): 6941–6944.
- [6] WANG Y M, ZHANG P F, GUO L X, OUYANG J H, ZHOU Y, JIA D C. Effect of microarc oxidation coating on fatigue performance of Ti–Al–Zr alloy [J]. *Applied Surface Science*, 2009, 255(20): 8616–8623.
- [7] LECLAIR P, BERERA G P, MOODERA J S. Titanium nitride thin films obtained by a modified physical vapor deposition process [J]. *Thin Solid Films*, 2000, 376(1): 9–15.
- [8] LIN Xiao-xuan, ZHAO Gao-ling, WU Li-qing, DUAN Gang-feng, HAN Gao-rong. TiN thin films for energy-saving application prepared by atmospheric pressure chemical vapor deposition [J]. *Journal of Alloys and Compounds*, 2010, 502(1): 195–198.
- [9] KRISCHOK S, BLANK C, ENGEL M, GUTT R, ECKE G, SCHAWOHL J, LIEFEITH K. Influence of ion implantation on titanium surfaces for medical applications [J]. *Surface Science*, 2007, 601(18): 3856–3860.
- [10] ASHRAFIZADEH A, ASHRAFIZADEH F. Structural features and corrosion analysis of thermally oxidized titanium [J]. *Journal of Alloys and Compounds*, 2009, 480(2): 849–852.
- [11] XI Ying-xue, FAN Hui-qing, LIU Wei-guo. The effect of annealing treatment on microstructure and properties of TiN films prepared by unbalanced magnetron sputtering [J]. *Journal of Alloys and Compounds*, 2010, 496(1): 695–698.
- [12] MAN H C, CUI Z D, YUE T M. Corrosion properties of laser surface melted NiTi shape memory alloy [J]. *Scripta Materialia*, 2001, 45(12): 1447–1453.
- [13] FRANGINI S, MASCI A, BARTOLOMEO A. Cr₇C₃-based cermet coating deposited on stainless steel by electrospark process: Structural characteristics and corrosion behavior [J]. *Surface and Coatings Technology*, 2002, 149(2): 279–286.
- [14] FRANGINI S, MASCI A. FeAl based coatings deposited by the electrospark technique: Corrosion behavior in molten (Li+K) carbonate [J]. *Surface and Coatings Technology*, 2004, 184(1): 31–39.
- [15] AGARWAL A, DAHOTRE N B. Pulse electrode deposition of superhard boride coatings on ferrous alloy [J]. *Surface and Coatings Technology*, 1998, 106(2): 242–250.
- [16] WANG R J, QIAN Y Y, LIU J. Structural and interfacial analysis of WC92–Co8 coating deposited on titanium alloy by electrospark deposition [J]. *Applied Surface Science*, 2004, 228(1): 405–409.
- [17] TANG C B, LIU D X, WANG Z, GAO Y. Electro-spark alloying using graphite electrode on titanium alloy surface for biomedical applications [J]. *Applied Surface Science*, 2011, 257(15): 6364–6371.
- [18] HAO Jian-jun, PENG Hai-bin, HUANG Ji-hua, MA Yue-jin, LI Jian-chang. TiN/Ti composite coating deposited on titanium alloy substrate by reactive electric-spark [J]. *Transactions of the China Welding Institution*, 2009, 30(11): 69–72. (in Chinese)
- [19] GALINOV I V, LUBAN R B. Mass transfer trends during electrospark alloying [J]. *Surface and Coatings Technology*, 1996, 79(1): 9–18.
- [20] LIU Jun, WANG Rui-jun, QIAN Yi-yu. The formation of a single-pulse electrospark deposition spot [J]. *Surface and Coatings Technology*, 2005, 200(7): 2433–2437.
- [21] WANG R J, QIAN Y Y, LIU J. Interface behavior study of WC92–Co8 coating produced by electrospark deposition [J]. *Applied Surface Science*, 2005, 240(1): 42–47.
- [22] ASTM G171–03. Standard test method for scratch hardness of materials using a diamond stylus [S].
- [23] ZHENG C, ZHOU, Y H. Surface modification of resistance welding electrode by electro-spark deposited composite coatings. Part I: Coating characterization [J]. *Surface and Coating Technology*, 2006, 201(3): 1503–1510.
- [24] WANG W E. Partial thermodynamic properties of the Ti–N system [J]. *Journal of Alloys and Compounds*, 1996, 233(1): 89–95.
- [25] LUO Cheng, XIONG Xiang, DONG Shi-jie. TiB₂/Ni coatings on surface of copper alloy electrode prepared by electrospark deposition [J]. *Transactions of Nonferrous Metals Society of China*, 2011, 21(2): 317–321.

氮气流量对 TC11 钛合金表面电火花原位反应沉积 TiN 强化层显微组织和摩擦学性能的影响

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摘 要: 为提高钛合金表面耐磨性能, 运用电火花沉积技术在 TC11 钛合金表面原位反应沉积 TiN 强化层, 研究 N_2 流量对强化层显微组织和摩擦学性能的影响。结果表明: 当 N_2 流量过小时, 强化层厚度较薄, 主要由 Ti_2N 、 $\alpha-Ti$ 、 TiO 和 TiN 等相组成, 电火花快速放电导致基体表面产生的熔池急速冷凝, 使得亚稳态 Ti_2N 相保留在强化层中; 当 N_2 流量过大时, 强化层微裂纹和孔洞等缺陷较多; 而当 N_2 流量适中时, 强化层主要由 TiN 等物相组成, 且致密均匀($50\sim 55\ \mu m$), 平均显微硬度达 $HV_{0.2}\ 1165.2$, 是 TC11 钛合金基体的 3.4 倍。当 N_2 流量适中时, TiN 强化层的耐磨性能最好, 此时其磨损质量为 $0.4\ mg$, 是 TC11 基体的 $2/9$, 其主要磨损机理为微观切削磨损和多次塑变磨损。

关键词: 钛合金; TiN 涂层; 电火花沉积; 摩擦磨损

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