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## High temperature sliding wear behaviors of ion plating TiN composite coating with ion nitriding as interlayer on hot work die steel <sup>①</sup>

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**[Abstract]** High temperature sliding wear behaviors of ion plating TiN composite coating with ion nitriding interlayer on 3Cr2 W8 V hot work die steel substrate during 500 ~ 700 °C were investigated. Phase structure was analyzed by XRD and adhesion strength of TiN coating was measured by scratch test. The worn morphologies and wear mechanism of TiN composite coating were observed and analyzed by using SEM. The results showed that both adhesion strength and hardness of TiN composite coating with ion nitriding interlayer are higher than those of single TiN coating. Ion nitriding interlayer provides a stronger support for TiN coating. With increasing temperature, the wear rates and friction coefficient of all tested coatings increase. The wear resistance of TiN composite coating is better than that of single TiN coating. The wear mechanisms of TiN composite coating are mainly adhesion-transfer wear and abrasive wear. The adhesion-transfer wear becomes more severe as the test temperature increases.

**[Key words]** TiN; composite coating; interlayer; high temperature wear

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### 1 INTRODUCTION

Physical vapor deposition (PVD) TiN coating has been widely used in many industrial fields because of its high hardness, high adhesion strength, low friction coefficient and good chemical stability. In tool and die industry, TiN coating can greatly improve both service life and surface properties of cutting tools and some cold working dies<sup>[1~3]</sup>. Because of the severe working conditions of high temperature accompanied with high loads, hot working dies, as well as some high speed cutting tools, often fail due to severe thermal wear and thermal fatigue. Earlier failure of the TiN coating on the hot working die substrate occurs because of softening and plastic deformation of the substrate, which can no longer provide any support for the coating. Therefore, application of the TiN coating on hot work dies and high speed cutting tools is limited. In order to further improve the adhesion strength and hence the wear resistance of the material, composite coatings with interlayer were introduced in 1990s, to obtain a better matching of hardness with microstructure and adhesion strength. Although PVD TiN composite coatings with electroless plating Ni-P<sup>[4,5]</sup>, electric deposition nickel, gas nitriding<sup>[6]</sup>, ion nitriding and plasma nitriding interlayers<sup>[7~9]</sup> have found some applications, TiN composite coating, ion nitriding and plasma nitriding techniques have been highlighted. However, most of the research works on composite coatings have been focused

on either the microstructure and technology optimization of coatings or their mechanical properties at room temperature. Few works has been carried out on the thermal fatigue and wear behavior of the TiN composite coating at elevated temperature. Furthermore, investigation of the high temperature wear behaviors of the single TiN coating is also very limited, and there exhibits controversy, for instance, different tendency of friction coefficient with temperature has been reported<sup>[10~12]</sup>. In this paper, high temperature wear behaviors of the composite coating of ion plating TiN with ion nitriding as interlayer during 500 ~ 700 °C, comparing with those of the ion nitriding layer and the single TiN coating, are investigated.

### 2 EXPERIMENTAL

#### 2.1 Specimens preparation

Chemical compositions of 3Cr2 W8 V hot work die steel as substrate (%) were: 0.35 C, 2.42 Cr, 0.32 V, 8.23 W, 0.20 Si, 0.25 Mn, respectively. 3Cr2 W8 V steel was treated by salt bath quenching at 1100 °C and tempering at 560 °C, 1 h for three times. The specimens with surface roughness of Ra 0.5 μm were cleaned before deposition to eliminate oil and rust, followed by nitriding in LD-75 ion nitriding furnace at 550 °C for 3 h with an NH<sub>3</sub> pressure of 2 kPa. The TiN coating with thickness of about 2.5 ~ 3.0 μm was deposited on the nitrided specimen with ATC-400 ion plating device (VAC-TEC company, USA) at a temperature of 500 °C.

## 2.2 High temperature wear tests

Wear tests were carried out on an MG-200 high speed, high temperature wear test machine under dry sliding conditions with ring-disk contact. The specimen contact form of test machine was schematically shown in Fig.1. Rings with sizes of  $d66\text{ mm} \times 8\text{ mm}$  (thickness 6 mm) scratched against the GCr15 steel disk, which was treated by quenching and tempering to a hardness of HRC40, for up to 750 s with an interval of 150 s at 500 °C, 600 °C and 700 °C, respectively. The linear velocity was kept at 2.0 m/s and the applied normal load is 49 N. Four kinds of specimens were tested: the substrate, the ion nitriding coat, the single TiN coat and the TiN composite coat.

Mass loss of the ring was measured using an electronic balance with an accuracy of 0.01 mg. Wear rate of the TiN coating was defined as the mass loss per sliding distance. Average friction coefficients were calculated from the measured friction torque. Phase structure of the TiN coating was determined using Rigaku D/max-3B X-ray diffractometer. The micro-hardness distribution in the hardened layer was measured with an HX-500 micro-hardness instrument. The worn surface was examined by a JSM-35C scanning electron microscopy (SEM) equipped with EDAX energy dispersive spectrometry. The adhesion strength of the TiN coating was characterized by the critical load, which was measured in a WS-92 acoustic emission scratching instrument.

## 3 RESULTS AND DISCUSSION

### 3.1 Phase structure of TiN composite coat

XRD patterns in Fig.2 show that the TiN film is

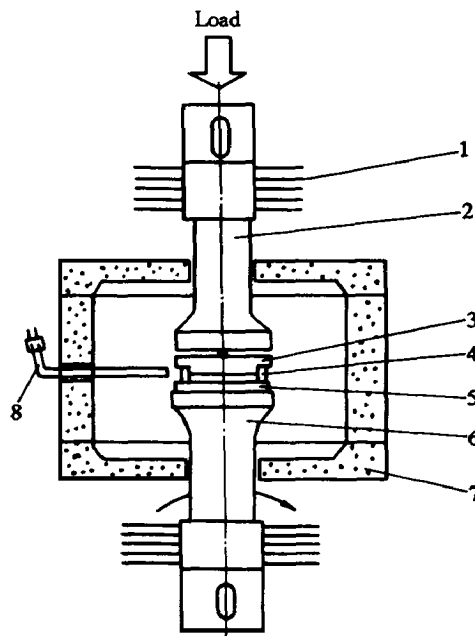


Fig.1 Schematic sketch of specimen contact form of test machine

- 1 — Cooling sheet; 2 — Stationary upper specimen axle;
- 3 — Upper specimen holder; 4 — Upper ring specimen;
- 5 — Lower disk specimen; 6 — Rotary lower specimen axle;
- 7 — Furnace; 8 — Thermocouple

consisted of TiN and  $\text{Ti}_2\text{N}$  phase. TiN phase is the dominant one in the coat with strong orientation of (111). The  $\text{Ti}_2\text{N}$  phase shows (112) and (200) orientation (Fig.2(a)). However, at 600 °C diffraction peak of  $\text{Ti}_2\text{N}$  (200) orientation is enhanced and diffraction peaks of TiN(111) and TiN(220) are decreased. At high temperature titanium oxide  $\text{TiO}_2$  phase occurs (Fig.2(b)).

The critical load ( $L_c$ ) and micro-hardness of

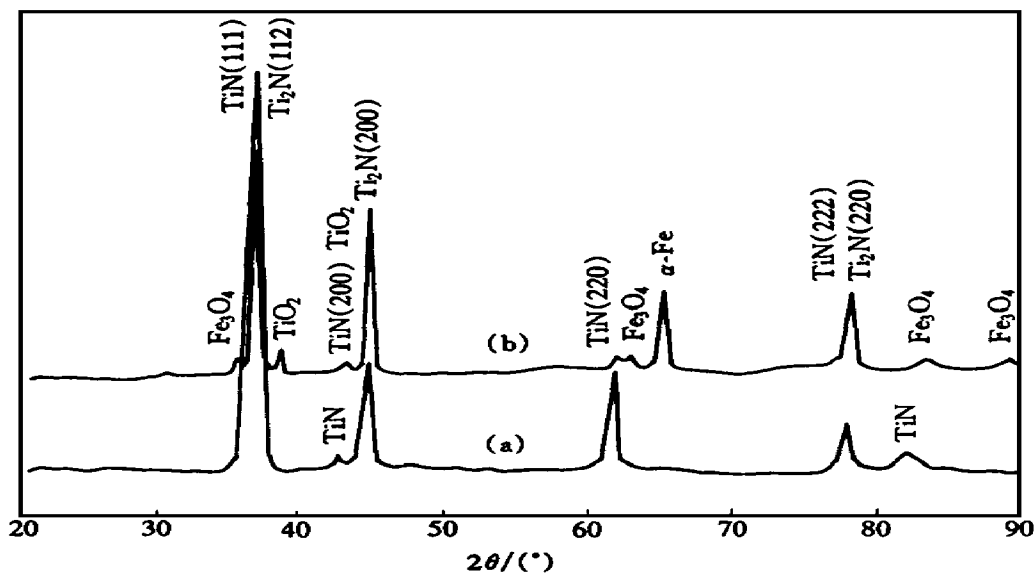


Fig.2 XRD analyses of TiN composite coats at room temperature and after wear at 600 °C  
(a) — Room temperature; (b) — 600 °C

TiN coats are listed in Table 1. It should be pointed out that the observed hardness actually presents the combined hardness of both the coat and the substrate. The critical load of TiN is improved with combined treatment of ion nitriding and ion plating, and hence the adhesion strength and surface hardness are also improved.

**Table 1** Critical load ( $L_c$ ) and micro-hardness HV(0.1) of TiN composite coat

Coat	Single TiN coat	TiN composite coat
$L_c/N$	42 ~ 46	54 ~ 58
HV(0.1)	1 018	1 236

Based on the fully plastic indentation and plowing-cutting theory<sup>[13]</sup>, relationship between the critical shear stress of the coat removal  $\tau_c$  and  $L_c$  is given by Ref.[14]:

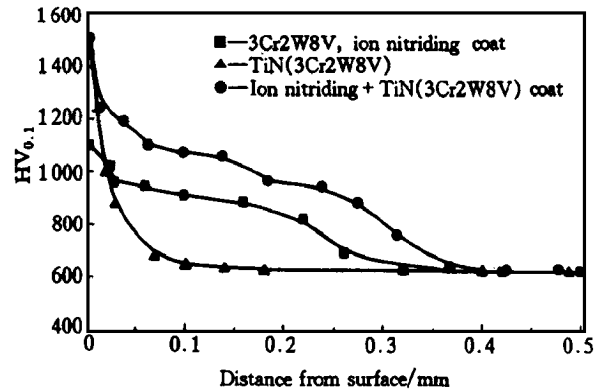
$$\tau_c = 2 K H_s^{1/2} L_c^{1/2} \pi^{1/2} R \quad (1)$$

where  $H_s$  is the substrate hardness,  $R$  is indenter radius and  $K$  is a constant related to the friction process. From Eqn.(1), it is clear that  $\tau_c$  increases with increasing  $L_c$  and  $H_s$ .  $\tau_c$  of the composite coat is improved since ion nitriding treatment improves hardness of the 3Cr2W8V substrate from HV660 to HV900, which provides a much stronger support for the TiN top coat. Improvements of the adhesion strength of the composite coat can be attributed to the following cases<sup>[9,14~16]</sup>:

- 1) Ion nitriding treatment eliminates surface oxide of the substrate.
- 2) Formation of the inner diffusion layer composed of Fe, Ti, N and Cr elements, which reduces the stress gradient of the interface.
- 3) Developing of cracks in the TiN is limited within the interface owing to the effect of the hardening interlayer, and thus the path of crack propagation is prolonged.
- 4) Deposition of the TiN layer reduces the content of the  $\epsilon$ -Fe<sub>2-3</sub>N phase in the nitriding layer and at the same time increase the relative content of the  $\gamma$ -Fe<sub>4</sub>N phase. Meanwhile, the diffusion reaction in the interface is beneficial to the improvement of the adhesion strength.

In addition, the composite treatment of combining ion nitriding with TiN coat also produces a hardness gradient distribution. It can be seen from Fig.3 that although the TiN film itself possesses high hardness, the hardness gradient along the cross-section is too steep due to the much thinner layer of about 20 ~ 30  $\mu$ m. Ion nitriding treatment has a hardening layer of 250  $\mu$ m, but the external layer hardness is not high enough. Composite coat possesses not only a higher surface hardness up to HV1 500, but also a beneficial strengthening interlayer of 350  $\mu$ m. Because the Ti and N elements diffuse into the inner layer during de-

position and interact with it, the hardness of ion nitriding interlayer is about HV100 higher than that of the single ion nitriding layer, which improves the capacity of supporting load and hence wear resistance of the coating.

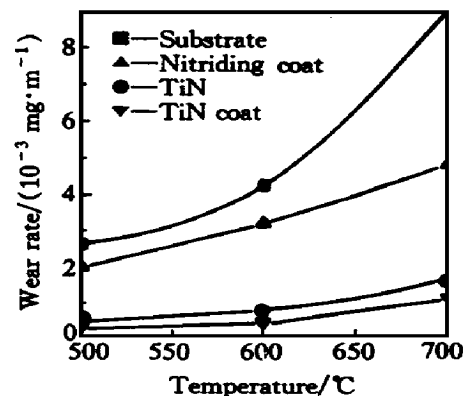


**Fig.3** Micro-hardness distribution over cross-section of samples

### 3.2 Influence of temperature on wear rate and friction coefficient of TiN coating

Relationship between the wear rate and the test temperature is shown in Fig.4. It is evident that the wear rate of different coats, including the substrate, increased with increasing test temperature. At the same temperature, the wear rate of the single TiN coat was obviously lower than that of the 3Cr2W8V substrate and ion nitriding specimens, but was higher than that of TiN composite coat. The wear rate difference between the ion nitriding layer and the composite coat became greater at 700 °C. Thus, it is believed that the TiN composite coat possesses the highest wear resistance at elevated temperature.

It can be seen from Fig.5 that the friction coefficient decreased in the order of substrate, ion nitriding coat, single TiN coat and TiN composite coat when tested at the same temperature. It can be attributed to that the TiN coat, one of hard ceramic compounds, decreased the friction force and reduced the



**Fig.4** Relationship between wear rate of coat and temperature

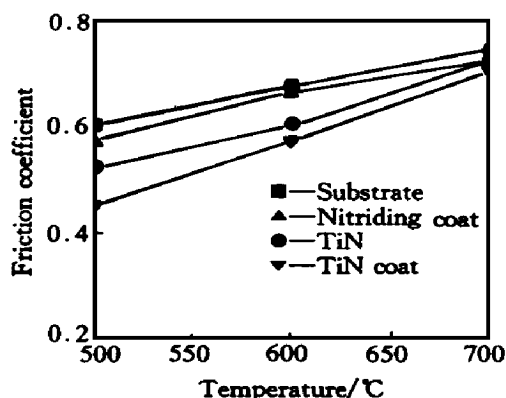


Fig.5 Influence of temperature on friction coefficient

adhesion tendency between the upper specimen and the disk during the wear process. With increasing temperature, the friction coefficient of the substrate and TiN coating rose and approached to the similar values of 0.72 ~ 0.74, because of the facts that the higher the test temperature is, the severer the TiN coat is oxidized<sup>[13]</sup>. It was reported that the TiN coat was oxidized slightly at 500 °C, and began to develop titanium oxide TiO<sub>2</sub> at 600 °C, but was oxidized severely at 700 °C. YU et al<sup>[12]</sup> studied the high temperature wear properties of the coat below 400 °C, they found that the friction coefficient  $\mu$  of the TiN coat decreases with increasing temperature up to 350 °C, due to the formation of a stable oxidation film on the TiN coating surface. Above 350 °C up to 400 °C, the friction coefficient increases again because of deterioration of the oxide film. These phenomena are in accordance with our results. The hardness, density and wear resistance of the TiO<sub>2</sub> oxidation layer developed are lower than those of the TiN film above 500 °C, and will delaminate partly, leading to strong adhesion of the friction couple at 700 °C. Therefore, the friction coefficient of the TiN coat increased with increasing test temperature.

### 3.3 Morphology of worn surface

Fig. 6 shows morphologies of the worn surface of the TiN composite coat at different test temperatures. Traces of both the adhesive wear and the abrasive wear with plowing groove on the worn TiN coat was obvious (as illustrated in Fig. 6(a), (b)). The deep colorful plain area in Fig. 6(a) was characterized of the adhesion transfer layer, which was consisted of Ti, Fe and Cr elements with no W and V elements found by EDAX (Fig. 7). This proves that the transfer layer was caused by adhesion and transfer of the GCr15 disk materials to the TiN coat and delamination of the TiN coat at high temperature wear. In the adhesion-transfer layer debris of the TiN coat was also found. Due to the higher test temperature and flash

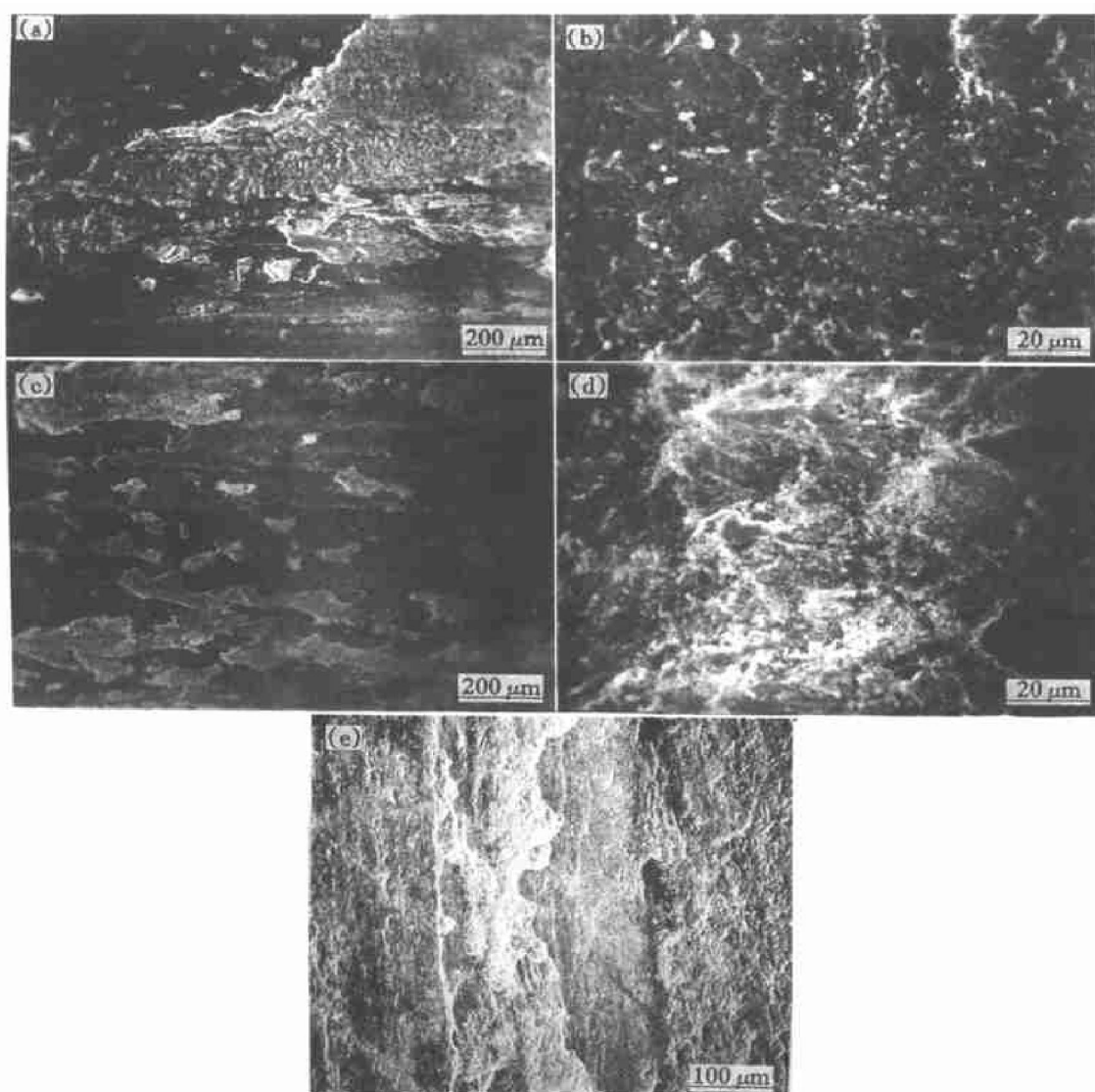
temperature between the sliding surfaces, this transfer layer developed a thin oxide film<sup>[10]</sup>, as can be seen in the XRD pattern shown in Fig. 2(b). XRD analyses proved the existing of Fe<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub> on worn surfaces. This adhesion-transfer layer has also been observed on the worn surface of the TiN coat on high speed steel and Inconel 718 alloy substrates<sup>[10,17]</sup>.

The adhesion-transfer layer existed even up to 600 °C and 700 °C. Therefore, the adhesion-transfer wear is one of the main wear mechanisms under high test temperature. At the earlier stage of wear, the adhesion-transfer layer plays the role of "smear layer", which decreases the roughness of the original friction surface and reduces friction force. With prolonging wear process, this adhesion-transfer layer improves the adhesion tendency between the sliding surfaces. Thus, the lower friction force at the earlier stage rises and the wear process gets severer, which leads to further increasing of the friction coefficient. Fig. 6(b) shows the worn morphology of the delamination area of the adhesion layer and the rougher surface. In addition, during the wear process, asperities and hard particles in the disk surface, as well as the debris become the abrasive, which cut and plough the sliding surface, as illustrated in Fig. 6(a), (e). Therefore, the abrasive wear is another predominant wear mechanism at high temperature.

Fig. 6(c), (d) show the worn morphology of the composite coat at 700 °C. It can be seen that with increasing temperature, the adhesive area got wider obviously. This indicates that the adhesion-transfer wear becomes harsher and the abrasive wear also gets severer (Fig. 6(d)). Therefore, the friction coefficient and the wear rate rises. Two main causes should be emphasized here. On one hand, softening of the substrate and reduction of the surface shear strength induce severer adhesion wear; on the other hand, accelerating oxidation of the TiN film and thickening of the TiO<sub>2</sub> layer deteriorate the wear resistance of the TiN coating. However, compared with the 3Cr2W8V substrate and ion nitriding layer, the wear rate of the composite coating increased very slowly with increasing temperature. Except for the much sever wear, the high temperature sliding wear behaviors of the substrate and ion nitriding layer were very similar to that of the TiN composite coat. Thus, the detail will not be described.

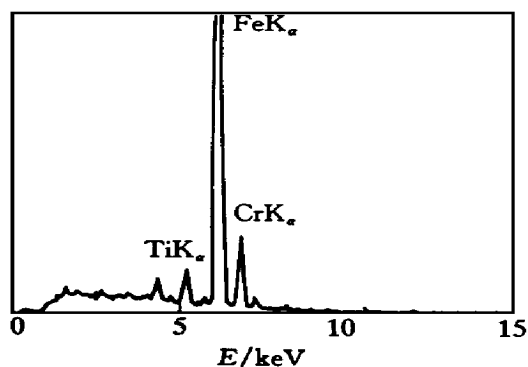
### 3.4 Influence of ion nitriding interlayer on wear property

As described in section 3.1, strong support of the ion nitriding interlayer to the TiN coating, enhances the adhesion strength between the TiN coat and the substrate. The interlayer also forms a beneficial matching of microstructure, hardness gradient, stress distribution and so on. Therefore, the ion ni-



**Fig.6** Worn surface morphologies of TiN composite coats

(a) —500 °C ; (b) —500 °C , no adhesion area ; (c) — 700 °C ; (d) —700 °C , no adhesion area ; (e) —600 °C



**Fig.7** EDAX result of transfer layer

triding interlayer has improved the plastic deformation resistance, the ability of sustaining the applied load, and the high temperature wear resistance for the TiN composite coat. Meanwhile, it also prohibits

the substrate softening. Even if the TiN film is worn out, this interlayer itself can also behave as good wear resistance layer. The effects become more noticeable as the test temperature increases. Therefore, the composite coat is better than that of the single TiN coat and ion nitriding layer.

#### 4 CONCLUSIONS

1) Both the adhesion strength and the hardness of the TiN composite coat with ion nitriding interlayer are higher than those of the single TiN coat. Ion nitriding interlayer provides strong support for the TiN coat.

2) The wear rates and the friction coefficient of all the tested coats increase with increasing test temperature. The wear resistance of the TiN composite coat is better than that of the single TiN layer, and

much better than that of the ion nitriding layer.

3) The main wear mechanisms of the TiN composite coat are determined to be the adhesion-transfer wear and the abrasive wear. The adhesion-transfer wear becomes severer as test temperature increases.

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