Adhesion strength and high temperature wear behaviour of ion plating TiN composite coating with electric brush plating Ni–W interlayer

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Abstract

Adhesion strength and high temperature wear behaviour of ion plating TiN composite coating with electric brush plating Ni–W interlayer deposited on a hot work die steel were investigated using a plate-on-ring test rig. The microstructure and wear characteristics of the coating were analyzed using XRD, TEM, SEM and EDS. The adhesion of the coating to the substrate was determined by scratch test. The results indicated that crystallization and precipitation-hardening in the electric brush plating Ni–W interlayer and formation of interface diffusion layer and duplex composite layer at the interface occurred due to thermal effects during TiN deposition. The Ni–W interlayer could provide an effective support for the TiN coating, thus the adhesion strength and hardness of the TiN composite coating increased significantly. In the temperature range 500–700°C, the TiN composite coating with Ni–W interlayer revealed high wear resistance as compared with the single TiN coating. The coefficient of friction and wear rate of the single TiN coating increased as the temperature increased, while the TiN composite coating exhibited the lowest coefficient of friction and wear rate at 600°C. Abrasive and adhesive wear were the predominant wear mechanisms of the coatings at elevated temperatures. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: TiN composite coating; Ni–W interlayer; Adhesion strength; High temperature wear

1. Introduction

Physical vapor deposition (PVD) TiN coatings are widely used in many engineering applications due to their high hardness, high adhesion strength, low coefficient of friction and good chemical stability [1–5]. In many practical situations such as high loads or high temperature atmosphere, however, severe wear and thermal fatigue occurred. The TiN coatings sometimes have a great tendency to failure, especially on softer substrates. One reason is that the softer substrate could not provide effective support for the TiN coating. Another is that poor adhesion to the substrate is present due to a difference in the properties between the coating and the substrate. Therefore, the applications for these coatings are limited.

To improve the adhesion and wear resistance, the composite coating with an interlayer, which has suitable hardness, composition and adhesion strength, have been obtained. It is found that electroless Ni–P [6,7], gas-nitriding [8], ion nitriding, plasma nitriding [9–11] have beneficial effects on mechanical properties of coatings, and have potential applications for the PVD TiN composite coatings. Although some investigations [8,12] have been conducted on microstructure, deposi-
tion technology and mechanical properties of the compo-
site coatings, very few studies on high temperature
wear behaviour of the composite coatings have been
reported.

There are many factors which influence the high
temperature wear of TiN coating, for example physical
and chemical properties, sliding speed, applied load
and test temperature. Sue et al. [13] characterized the
friction and wear behaviour of TiN, ZrN and CrN
coating in contact with Inconel 718 alloy at 500 and
600°C using a pin-on-disc type apparatus. This work
indicated that the wear of the coatings was extremely
small compared with that of Inconel alloy, and the
wear loss of Inconel alloy was considerably influenced
by the mating coating. Adhesive wear, oxidative and
chemical wear were predominant for the coating re-
moval. A more detailed investigation of dry sliding
wear behaviour of TiN coating deposited on stainless
steel against high speed steel below 500°C by Wilson
and Alpas [14] showed that the wear of the TiN coating
was small at lower temperature at low sliding speed
(< 1.0 m·s⁻¹). Above 450°C, however, failure of the
TiN coating occurred due to extensive plastic deforma-
tion. Yu et al. [15] evaluated the tribological properties
of TiN and TiC films in vacuum at high temperatures.
The investigation revealed a decrease in the friction
coefficient due to the formation of protective oxide
films on the worn surface of the TiN film below 623 K.
And then the friction coefficient increased at 673 K.
The increase of the friction coefficient may be induced
due to the deterioration of the oxide film on the TiN film
during dry sliding.

In this present work, a new composite coating (ion
plating TiN coating deposited on electric brush plating
Ni–W interlayer) was prepared. Based on the experi-
mental data and the results of microstructural studies,
the strengthening mechanism and sliding wear be-
aviour of the composite coating in the temperature
range 500–700°C are evaluated.

2. Experimental procedure

2.1. Preparation of coating

A hot work die steel [chemical composition (wt.%):
C: 0.35; Cr: 2.42; V: 0.32; W: 8.23; Si: 0.20; Mn: 0.25;
Fe: bal.] was used as the substrate material. The steel
used in this present work was heat-treated by austeniti-
sation at 1100°C, quenching in salt bath, followed by
tempering 3 h at 560°C, with a hardness of HV 660.
Prior to plating, all substrate surfaces were polished
degreased with acetone. The surface roughness of the
substrate was approximately 0.5 μm (Rₐ). The
composition of electric brush plating Ni–W (D) bath
was:

<table>
<thead>
<tr>
<th>Material</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄: 7H₂O</td>
<td>380–450 g/l</td>
</tr>
<tr>
<td>HCOOH</td>
<td>30–40 g/l</td>
</tr>
<tr>
<td>H₂BO₃</td>
<td>30–35 g/l</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>6–8 g/l</td>
</tr>
<tr>
<td>CoSO₄: 7H₂O</td>
<td>2–3 g/l</td>
</tr>
<tr>
<td>MgCl₂·12H₂O</td>
<td>2–3 g/l</td>
</tr>
<tr>
<td>NaWO₄: 7H₂O</td>
<td>20–30 g/l</td>
</tr>
<tr>
<td>H₂C₂H₂O·H₂O</td>
<td>20–30 g/l</td>
</tr>
<tr>
<td>CH₂COOH</td>
<td>18–25 g/l</td>
</tr>
<tr>
<td>NaF</td>
<td>4–6 g/l</td>
</tr>
<tr>
<td>MnSO₄·H₂O</td>
<td>2 g/l</td>
</tr>
<tr>
<td>Cl₂H₂NaSO₄</td>
<td>0.01 g/l</td>
</tr>
</tbody>
</table>

For this series of experiments, the value of pH of the
plating bath was 1.4–2.4. Electric brush plating was
operated at a working voltage of 12–14 V. The Ni–W
layers with a deposit thickness of 20 μm were obtained.

Ion plating TiN coatings were carried out in an ATC-
500 coating equipment (VAC-TEC). As comparison,
the TiN coatings were deposited on the die steel sub-
strate and on electric brush plating Ni–W interlayer
under the same conditions. Before deposition, the vac-
uum chamber was evacuated to 0.01 Pa. Then the
substrates were heated, Ar gas was fed into the vacuum
deposition chamber and the steered arc plasma source
with a titanium target was operated with an arc current
of 130 A. After the titanium ion bombardment at 600
V bias voltage, an argon–nitrogen mixture (N₂:Ar = 1:4) was fed into the chamber. The TiN coatings were
deposited on the substrates at a temperature of 450°C
and with a coating thickness of 3 μm. Microstructural
analysis of the single TiN and TiN composite coatings
were identified by X-ray diffraction and transmission
electron microscopy (TEM).

2.2. Adhesion and wear tests

A conventional scratch tester (WS-92 equipped with
an acoustic emission detector) was used to evaluate the
adhesion of a coating to substrate. The radius of the
diamond pin was 0.2 mm. All the tests were performed
employing a continuous increase in the normal load,
from 0 N to 100 N, at a loading rate of 100 N·min⁻¹.
Surface hardness of the coatings was determined with
Vickers microhardness indenter (HX-500), using a load
of 0.1 N.

High temperature wear tests were performed on a
plate-on-ring apparatus (Type MG-200) with the coated
specimen serving as the ring under dry condition. The
apparatus has been described in a previous publication
[16]. The ring specimen with a diameter of 66 mm was
mounted on the upper holder. The plate specimen with
a diameter of 70 mm was fixed to the rotating lower
holder. The plate specimen was fabricated from a high
carbon quenched-and-tempered steel (chemical compo-
sition (wt.%): C: 0.95; Cr: 1.5; Si: 0.15; Mn: 0.20; Fe: bal.) with a Rockwell C hardness of 40 HRC. Wear
tests were conducted at a sliding speed of 2.0 m·s⁻¹
and at applied loads between 29 and 69 N. In this work,
the testing temperatures were carried at 500, 600 and
700°C, respectively. The weight loss was measured with
an analytical balance at 2.5-min interval throughout the
test. The coefficient of friction was calculated by dividing the friction force which was recorded on line via torque as measured by the strain gauge. The worn surfaces of the specimens were examined using scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDS).

3. Results and discussion

3.1. Microstructure of TiN composite coating

X-Ray diffraction spectra show that the ion-plating TiN coating is composed mainly of TiN and an amount of Ti$_3$N$_2$ phase, and indicates several preferential orientations (Fig. 1). The TiN deposits forward the growth of the (111) plane, whereas the Ti$_3$N$_2$ deposits show preferential orientations of (112) and (200) planes. The XRD data represented that the electric brush plating Ni–W layer deposited on steel substrate was a mixture of crystalline and amorphous structure. After ion-plating TiN coating deposited on the Ni–W interlayer, the peak of TiN (111) reduced, but the peaks of Ti$_3$N$_2$ phase increased. There exists NiTi phase in the X-ray diffraction pattern, as shown in Fig. 1. The TEM diffraction of the TiN coating also confirms that the coating consists of two phases and presents preferential orientation to some extent (Fig. 2). A typical SEM micrograph of the surface of TiN composite coating is shown in Fig. 3. The microstructure of the composite coating reveals a dispersive distribution of the second particulate throughout the coating. The EDS analysis of the second particulate showed that the atomic ratio of Ni–W was approximately 4:1, indicating that the precipitation of Ni$_4$W phase occurred in the Ni–W interlayer during TiN deposition. Similar results have been found when the precipitation-hardening in Ni–W plating occurred above 400°C [17].

3.2. Adhesion strength and hardening mechanisms

Table 1 lists the critical load $L_C$ determined by scratch adhesion test and microhardness $HV$ of Ni–W layer, single TiN coating and TiN composite coating. As a comparison with the single TiN coating deposited on the steel substrate, the TiN coating deposited on the electric brush plating Ni–W interlayer presents the high critical load and microhardness.

Based on [18], the relationship between the critical shear stress $\tau_C$ for coating peeling and the critical load $L_C$ yields

$$\tau_C = 2^{1/2}KH_s^{1/2}L_C^{1/2}/(\pi^{1/2}R)$$

(1)

where $H_s$ is the hardness of substrate, $R$ is the radius.
Table 1 Critical load \( L_c \) and microhardness \( H V_{0.1} \) of the coatings

<table>
<thead>
<tr>
<th>Coating</th>
<th>Ni-W layer</th>
<th>Single TiN coating</th>
<th>TiN composite coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L_c ) (N)</td>
<td>No peeling</td>
<td>46</td>
<td>58</td>
</tr>
<tr>
<td>( HV_{0.1} )</td>
<td>850</td>
<td>1480</td>
<td>1650</td>
</tr>
</tbody>
</table>

of spherical stylus, \( K \) is the coefficient in relation to friction.

From Eq. (1), with increasing the critical load and microhardness, the critical shear stress for coating peeling increased. The electric brush plating Ni–W layer on the die steel led to an increase in the surface hardness of the substrate from 660 \( H V_{0.1} \) to 850 \( H V_{0.1} \). The substrate with higher hardness could provide a more effective support for the TiN coating and thus the critical shear stress increased. After deposition of TiN, a suitable distribution of hardness was presented throughout the composite coating. Fig. 4 shows the variation of microhardness with depth below the surface in the Ni–W layer, single TiN coating and TiN composite coating. Although the hardness of the single TiN coating high, the hardness grade in the single TiN coated specimen is steep due to its thin thickness. It is noted that the thickness of hardening layer for the TiN composite coating is increased though the surface hardness of the Ni–W layer is not enough. The ability to support loading may be improved owing to its higher surface hardness \( (1650 \ H V_{0.1}) \) and hard intermediate layer.

The strengthening mechanisms of the TiN composite coating are schematically shown in Fig. 5: (1) crystallization: the single electric brush plating which represents a mechanical adhesion to the steel substrate is a mixture of crystalline and amorphous structure. During the TiN deposition, an amount of amorphous Ni transfers to crystalline Ni in the Ni–W layer at the deposition temperature of 450°C. (2) Precipitation–hardening: some fine and dispersive intermediate phases or the second phases precipitate (mainly Ni\(_x\)W) within the Ni–W interlayer due to thermal effects, causing the increase in hardness of the interlayer. (3) Duplex layer composite strengthening: the variation of strain through the single TiN coating and substrate is continuous during deformation, while the variation of stress is not continuous because their Young’s modulus \( E \) are different. For the TiN composite coating, the Ni–W interlayer with high hardness and high adhesion strength as compared with the steel substrate modifies the stress discontinuity between the TiN coating and steel substrate. The stress through the composite coating presents a graded distribution. Therefore, the ability to support loading and resist plastic deformation is improved. (4) Formation of diffusion layer: because of the effect of high deposition temperature, the diffusion rates of the elements Ti, N, Ni and W at the interface and within the interlayer and steel substrate increase considerably. The investigation [7] confirmed that the
inter-diffusion occurred at the interface using AES analysis. The metallurgical adhesion at the interfaces enhanced the adhesion of the coating to the substrate and reduced the stress grade at the interfaces. By the effect of the intermediate hardening layer, the cracks can only propagate at the interface of the substrate. The path of crack propagation was prolonged and the depth of the effective hardening layer was increased.

3.3. Effect of temperature on wear rate and coefficient of friction

Fig. 6 shows the variation of wear rate for the Ni-W layer, single TiN coating and TiN composite coating with a test temperature at an applied load of 49 N and at a sliding speed of 2.0 m·s⁻¹. For the Ni-W layer, single TiN coating and TiN composite coating, however, the coefficients of friction first decreased with temperature then increased with further increasing temperature, thus producing the minimum values at 600°C. These results showed similar trends to those of wear rates. As shown in Fig. 7, the Ni-W layer reveals low coefficient of friction as compared with the TiN coating. The reason is that protective NiO film formed on the worn surface of Ni-W layer during dry sliding at high temperature. During high temperature wear, the temperature results in a change in surface adsorption, oxidation and mechanical properties [4]. According to the results of high temperature wear of the TiN coating [13], a stable oxide film on the worn surface of the TiN coating was formed and thus reduced the coefficient of friction below 350°C. When the test temperature was raised above 350°C to 400°C, however, the deterioration of the oxide film enhanced the coefficient of friction during dry sliding. In the present work, the test results agree with previous investigation. It is suggested that the hardness, compactness and wear resistance of TiO₂ film are lower than those of TiN coating above 500°C. Further increasing temperature up to 700°C, the loose TiO₃ film was easily fractured and peeled under friction force. Failure in protection of the surface layer, the tendency to adhesion between the counterface increased, resulting in an increase in the coefficient of friction of the TiN coating.

As the testing temperature was raised from 500 to 600°C, for the TiN composite coating with Ni-W inter-layer, the wear rates and coefficients of friction reduced. It would be attributed to the high hardness of the TiN composite coating because of the precipitation-hardening occurring in the Ni-W interlayer at 600°C. For the TiN coating without the Ni-W inter-layer, the hardness of the steel substrate dropped as the test temperature increased. The single TiN coating could not be supported by the soft steel substrate and easily damaged during dry sliding. Therefore, the wear resistance of the single TiN coating decreased with
increasing temperature. It has been reported that the hardness of the Ni–W layer remains at a high value between 500 and 600°C, but reduced dramatically at 700°C [17]. To confirm the above results, in this work, the Ni–W layer and the TiN composite coating were treated in vacuum furnace at 500°C, 600°C and 700°C for 1.5 h, respectively. Then the microhardness measurement was conducted at ambient temperature. The hardness of the Ni–W layer increased from 830 HV₀.₁ at 500°C to 920 HV₀.₁ at 600°C, then reduced to 760 HV₀.₁ at 700°C. For the TiN composite coating with Ni–W interlayer, the hardness increased from 1600 HV₀.₁ at 500°C to 1750 HV₀.₁ at 600°C. It was concluded that the second phases continuously precipitated in the Ni–W interlayer at 600°C. The increase in hardness of the composite coating resulted in the decrease in wear rate and coefficient of friction. With further increasing temperature, because of coarsening of the grain size and the second phase particulate occurring in the interlayer, the hardness reduced to 1350 HV₀.₁ at 700°C, and then the sliding wear resistance of the composite coating decreased dramatically.

3.4. Effect of applied load on wear rate

The variation of wear rates of the single TiN coating and TiN composite coating with applied load at 600°C is shown in Fig. 8. With increasing applied load, the wear rates of both the coatings increased. In contrast, the increase in wear rate for the single TiN coating is larger than that for the TiN composite coating. With Ni–W interlayer, the TiN composite coating had the higher surface hardness and adhesion strength, and ability to resist plastic deformation enhanced. After the TiN coating was worn away, the Ni–W interlayer with high hardness also remained higher wear resistant in comparison with the steel substrate. At higher applied loads, the TiN composite coating was superior to the single TiN coating in wear resistance at high temperature.

3.5. Worn morphology and wear mechanisms

Fig. 9 shows the morphology of the worn surfaces of the TiN composite coating after tests at an applied load of 49 N at various temperatures. In the case of temperature 500–700°C encountered in wear test, it is possible to see the occurrence of interfacial diffusion between the TiN coating and Ni–W interlayer. At 500°C, the worn surface exhibits some ploughed grooves, a little degree of peeling formation by adhesive wear in Fig. 9a. It indicated that the abrasive wear was the predominant mechanism, and slight adhesive wear also occurred. From Fig. 9b, the worn surface reveals slight grooves and increased adhesive regions at 600°C. With modified friction and high hardness, the TiN coating could resist against penetrating and cutting action during dry sliding. Otherwise, the hardness of the asperites on the high carbon steel counterface reduced at high temperature. In this case, the coating exhibited much slightly scratched regions. The relatively smooth regions on the worn surface are the transferred layers. By the EDS analyses of the smooth region on the worn surface, as shown in Fig. 9c, it has been found that there were elements Fe, Cr and Ti on the surface of the coating specimen. This result indicated that the materials on the steel counterface transferred to the surface of the TiN coating during unlubricated sliding wear. Similar transferred layer could also be observed on the worn surfaces of the TiN coatings tested at 500°C and 700°C. The formation of a transferred layer could also be observed in the cases of high temperature wear of the TiN coatings deposited on high speed steel and Inconel 718 alloy substrates. Because of the high testing temperature and high flashing temperature at the counterface, the adhesive transfer layer would be oxidized during sliding wear [19]. At 600°C, in this work, there was an amount of TiN debris in the transferred layer, indicating that the material removal resulted from adhesive and abrasive wear.

The SEM micrographs of the worn surfaces of the composite coating tested at 700°C are presented in Fig. 9d,e. From Fig. 9d, the worn surface is much rougher and exhibits severe adhesion and peeling, relatively slight grooves. It has been suggested that the abrasive wear is predominantly wear mechanism, while abrasive wear is suppressed during sliding wear at higher temperature. As shown in Fig. 9e, it can be observed that there exist a large amount of particles on the region of peeling. This also confirmed that the precipitation of the second phase occurred in the Ni–W interlayer.
Fig. 9. The SEM micrographs and EDS analysis of the worn surfaces of TiN composite coatings after tests at an applied load of 49 N at different temperatures: (a) 500°C; (b) 600°C; (c) EDS analysis of the smooth region in Fig. 9b; (d) 700°C; and (e) 700°C, showing a large amount of particles on the region of peeling.

4. Conclusion

Because of the effect of temperature during TiN deposition, the crystallization and precipitation–hardening in the electric brush plating Ni–W interlayer occurred. The formation of interface diffusion layer and duplex composite layer at the interfaces enhanced the adhesion strength and hardness of the TiN composite coating.

The wear resistance of the TiN composite coating...
was higher than that of the single TiN coating. With increasing temperature, the wear rate and coefficient of friction of the single TiN coating increased. At 600°C, the TiN composite coating exhibited the lowest wear rate and coefficient of friction in the test temperature range 500–700°C. As the test temperature increased, the predominant wear mechanism of the TiN coating transferred from abrasive wear to adhesive wear.

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References