

Improvement of the Wear Resistance of Ti-Based Coating Sliding against Copper Alloy

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The multilayer coating, Ti10%-C:H/TiC/TiCN/TiN, was deposited on cemented tungsten carbide (WC-Co) substrate by an unbalanced magnetron sputtering system. Tribological characteristics of this coating were compared with the coatings of TiN, TiCN, and TiC/TiCN/TiN deposited on WC-Co substrates and the WC -Co substrate itself. The coating displayed excellent tribological properties, *i.e.*, both low value and smooth curve of friction coefficient, and also, compared with the other tested materials, yielded the lowest wear depth when sliding against bronze under dry conditions. The coating thus protects against the high wear experienced when Ti-based coatings rub against copper alloy.

Keywords copper alloy, multilayer coating, tribology

1. Introduction

Surface modification techniques have proven to be effective methods for improving the wear resistance properties of materials. In general, these surface techniques can be divided into two categories: antiwear coatings characterized by high hardness and antifriction coatings characterized by low friction coefficients. Hard coatings such as titanium nitride (TiN), titanium carbide (TiC), and titanium carbonitride (TiCN)[1–4] are widely used in industrial applications. Recent research has proven that using diamond-like carbon (DLC) or amorphous hydrogenated carbon (a-C: H) and metal-containing a-C: H (Me-C: H) films can reduce friction coefficients without applying liquid lubricants to the sliding interface.[5–8] A potential coating design is the multilayer system. These coatings not only reveal their positive performance over comparable single-layer coatings, but also tend to synthesize the attractive properties of the different materials they contain. It is well known that Ti-based coatings (TiN, TiC, and TiCN) rubbing against copper alloy display high wear rates.[9,10] This study is aimed at the improvement of the tribological properties of Ti-based coatings sliding against copper alloy by the design of multilayer Ti10%-C: H/TiC/TiCN/TiN coating.

2. Experimental Details

2.1 Coatings Deposition

Ti10%-C: H/TiC/TiCN/TiN and TiC/TiCN/TiN Coatings Deposition. Ti10%-C: H/TiC/TiCN/TiN and TiC/TiCN/TiN were deposited on tungsten carbide-cobalt (WC + 6% Co) disks *via* UBM sputtering (UDP- 450, Teer Coatings, Worcestershire, United Kingdom) and a closed-loop optical emission monitoring (OEM) control system. Sputtering was performed in an Ar atmosphere, with N_2 and C_2H_2 as the reaction gases. The process of Ti10%-C: H/TiC/TiCN/TiN coating deposition is as follows.

First, a layer of Ti of about 0.1 μm is deposited on the specimens. After the Ti layer is deposited, nitrogen is introduced to produce a thickness of 1 μm of TiN. Then, C_2H_2 is introduced gradually to produce a thickness of 1 μm of TiCN. Next, the nitrogen supply is gradually turned off and the flow of C_2H_2 is increased, producing a thickness of 0.5 μm of TiC. Finally, the C_2H_2 flow is further increased gradually to cause more “poisoning” of the Ti target. An optical emission spectrometer is used to measure the intensity of Ti emission from the target. The C_2H_2 flow is then admitted through a piezoelectric valve until the intensity of the Ti emission line has dropped to a preselected value. The spectrometer and the piezoelectric valve are then switched into a closed-loop system to stabilize the partial pressure of the reactive gas at this level. As a result, the Ti metal and hydrocarbon are sputtered simultaneously from the poisoned target surface to produce a Tix%-C: H layer on the specimens. The OEM control allows the deposition of films with the required metal composition to be formed by monitoring the ratio, x%, of target poisoning in the relative intensity of the selected titanium emission line with reference to the intensity from a nonpoisoned target. Additionally, a sample was prepared of TiC/TiCN/TiN deposited on the WC-Co substrate. The TiC/TiCN/TiN coating was composed of sequential layers of 0.1 μm Ti, 1.25μm TiN, 1.25μm TiCN, and 2.5μm TiC from the substrate to the outmost layer. Table 1 displays the deposition parameters.

TiN and TiCN/TiN Coating Deposition. Coatings of TiN and TiCN/TiN were deposited on tungsten carbide disks using a Arc-PVD system mode by Hauzer Techno Coating (HC-1000, Venlo, Holland). The deposition parameters are listed in Table 2. To enhance adhesion, interface layers, about 0.1 μm Ti for TiN and TiCN/TiN, were deposited between the WC-Co substrate and the coating. The deposition procedure for TiN, for instance, is described as follows: (1) the target was preheated to evaporation temperature, and then pure Ti was evaporated and grown on the specimens using an arc deposition process; (2) nitrogen gas was subsequently introduced into the deposition chamber, and then TiN began to grow on the pure Ti layer. The film thickness was controlled by adjusting the deposition

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Table 1 Deposition parameters for Ti10%-C:H/TiC/TiCN/TiN and TiC/TiCN/TiN

Parameters	
Reaction gases	N_2 and C_2H_2
Chamber pressure (Pa)	1
Substrate bias voltage (V)	−50
Target current (A)	6
Target voltage (V)	300–400
Substrate temperature (°C)	150
Deposition rate (μm/h)	2

Table 2 Deposition parameters for TiN and TiCN/TiN

	Films	
Parameters	TiN	TiCN
Partial pressure of N_2 (Pa)	1	0.4
Partial pressure of CH_4 (Pa)	…	0.6
Chamber pressure (Pa)	1	1
Substrate bias voltage (V)	−120	−120
Arc current (A)	80	80
Arc voltage (V)	80–120	80–120
Substrate temperature (•)	400	400
Deposition rate (μm/h)	4	4

time. Formation of TiCN was achieved by introducing CH_4 into the TiN-deposition chamber and the pressure ratio of N_2:CH_4 was held at 2:3. In this study, the TiCN/TiN coating was composed of sequential layers of 0.1 μm Ti, 2.5μm TiN, and 2.5μm TiCN, from the substrate to the outmost layer.

2.2 Characterization of Coating

The microhardness of the coatings were measured by a nanoindentation tester (Fischerscope H100B, Fischer Technology Inc., Sindefinger, Germany). Herein, the force at initial contact was 0.4 mN, the time between two load steps was 1 s, the total time for loading was 39 s, and the force at final contact was 100 mN. In this work, for each case, five to ten indents were performed.

Surface wear and fracture mechanisms of the coatings were observed by scanning electron microscopy (SEM) and x-ray mapping (using a energy dispersive spectrometer (EDS))

2.3 Wear Tests

Wear tests were also performed using a Schwingung Reibung Venschleib (SRV) oscillation friction and wear tester (Optimol, München, Germany), which consisted of a fixed lower specimen supporter and a replaceable upper specimen holder. The upper specimen was a bronze rod (diameter: 15 mm, length: 22 mm), with a hardness of HRB 94 (Rockwell B scale). The lower specimen was a coated disk. Figure 1 shows the real dimensions of the test specimens and a schematic diagram of the experimental setup.

The arrangement of a rod mated with a disk generated a rod-on-disk line contact wear mode. Tests were performed at room temperature, at atmospheric pressure, and under unlubricated conditions. The relative humidity of the laboratory was in the range 45 to 55%. In addition, a constant 1 mm stroke, 100 N normal load, 24 min test duration (144 m sliding distance), and 50 Hz frequency were employed. The maximum depth of the wear scars on the coated sample was measured by a surface profilometer (Surfcorder SE-30H, Kosaka Laboratory Ltd., Tokyo) with a precision of ± 0.005 μm at a magnification of $\times 10^6$. All tests were performed twice, and three different measurements at different places were taken from each test pass. Then, the six measurements from each test were averaged and shown as the measured result of the test.

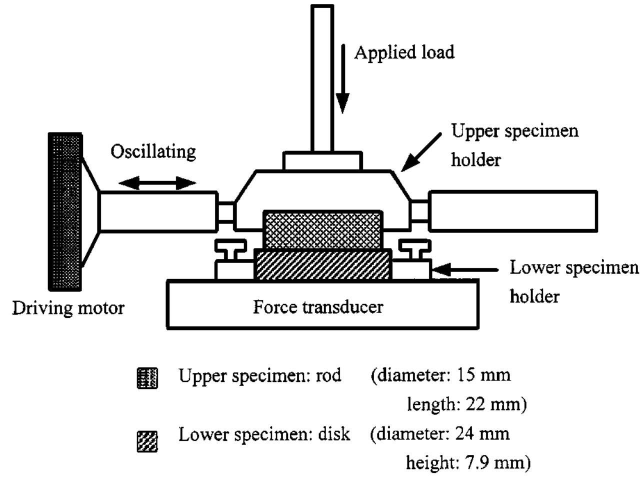


Fig. 1 SRV wear test

3. Result and Discussion

The Ti10%-C: H/TiC/TiCN/TiN (931 kg/mm^2) coating has lower microhardness than the TiC/TiCN/TiN (2983 kg/mm^2), TiCN/TiN (2850 kg/mm^2), and TiN (2760 kg/mm^2) coatings. Ti10%-C: H/TiC/TiCN/TiN and TiC/TiCN/TiN have the highest and lowest microhardnesses, respectively.

The wear depths for TiN, TiCN/TiN, TiC/TiCN/TiN, and Ti10%-C: H/TiC/TiCN/TiN coatings as well as uncoated WC are shown in Fig. 2. It can be seen that the multilayer Ti10%-C: H/TiC/TiCN/TiN shows excellent wear resistance. Compared with the Ti10%-C: H/TiC/TiCN/ TiN coating, the wear depths of the TiN, TiCN/TiN, and TiC/TiCN/TiN coatings and the WC substrate are 3.5, 3.1, 2.3, and 1.7 times greater, respectively.

The friction coefficients were also continuously recorded during the wear tests. The friction trace can be classified into two different types. The Ti10%-C: H/TiC/TiCN/TiN coating against bronze rod shows low friction coefficients (the average value 0.319) and a smooth friction trace. In addition, the TiC/TiCN/TiN, TiCN/TiN, and TiN coatings and WC substrate against the bronze rod contain high friction coefficients (the average values 0.64, 1.1, 1.0, and 1.0, respectively) and a large fluctuation trace. The typical friction coefficient variations of the TiN and Ti10%-C: H/TiC/TiCN/TiN coatings and the WC

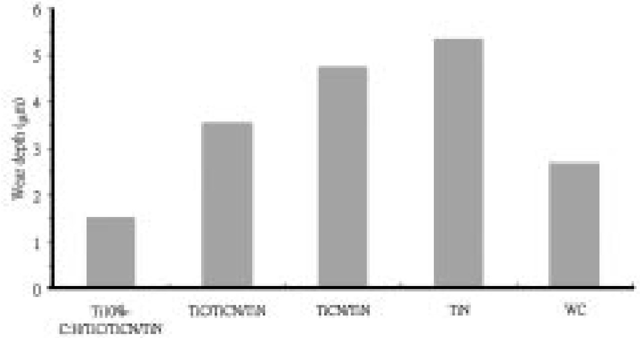


Fig. 2 Wear depth of coatings and WC substrate sliding against bronze rod after sliding time of 24 min

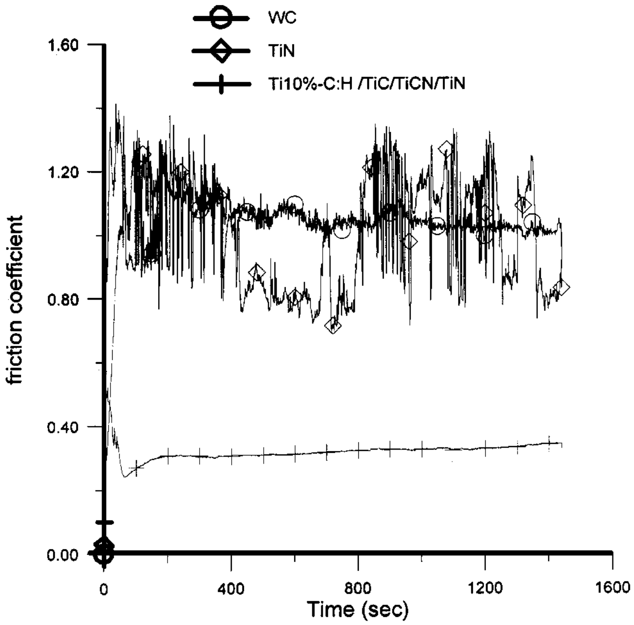


Fig. 3 Plot of friction coefficients of coatings and WC substrate sliding against bronze rod

substrate are shown in Fig. 3. It can be seen that the Ti10%-C: H/TiC/TiCN/TiN coating yields a much lower and smoother friction coefficient curve. The other curves display higher general values and continuous fluctuations throughout the test. Figure 4 shows a typical worn TiN surface, indicating a surface formed by an agglomeration of wear debris. Energy dispersive spectrometry (EDS) analysis of Fig. 4 showed that its content is 30.7 at.% oxygen, 45.9% Ti, and 23.4% Cu, which indicates an oxidation mechanism and Cu transfer on the worn surface because of tribo-chemical reaction and adhesion. The similar worn surface and wear behavior were observed in TiCN/TiN and TiC/TiCN/TiN coatings. The main reason for high wear of these coatings is the oxidation of the Ti-based coating *via* the catalytic action of copper.[9]

As mentioned, Ti10%-C: H/TiC/TiCN/TiN sliding against the bronze rod yields a friction coefficient trace that is smooth and low (Fig. 3). Microscopic observation of the wear surface of the coated disk shows a few light rubbing traces and no

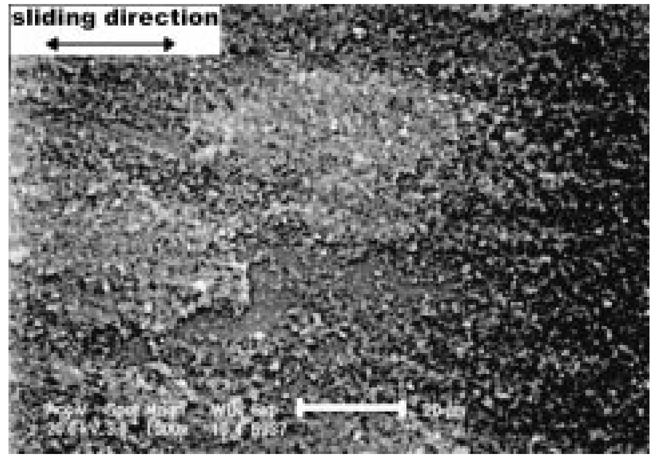
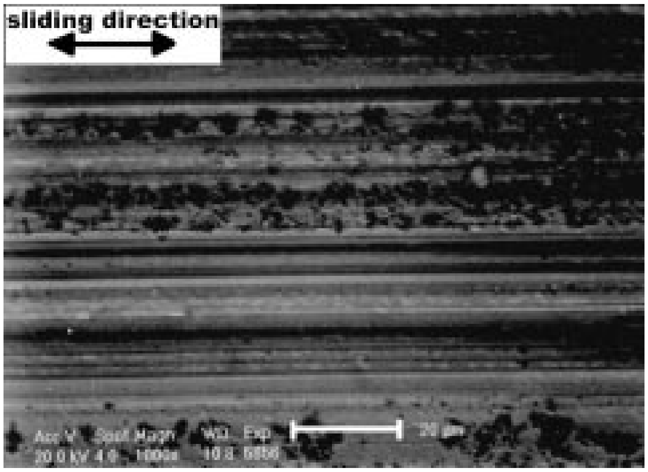


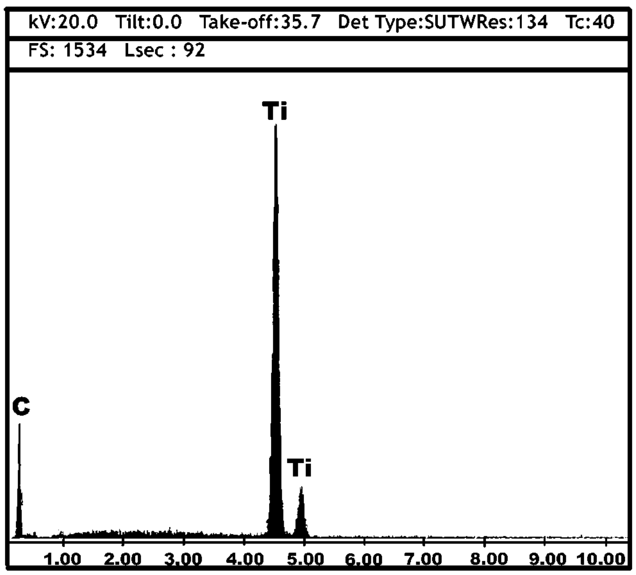
Fig. 4 Typical wear surface of TiN coating sliding against bronze rod after sliding time of 24 min

wear debris, as seen in Fig. 5(a). In addition, the noise level during testing is very slight compared with the TiN, TiCN/TiN, and TiC/TiCN/TiN coatings. Figure 5(b) presents the EDS analysis corresponding to the wear surface of Fig. 5(a). As can be seen, no Cu element transfer occurred from the counterbody bronze rod, and no oxidation occurred in the wear surface of the coated disk. On the other hand, a transfer layer formed on bronze rod from the coated disk. Figure 6 displays the typical wear scars on the bronze rod after testing 24 min. The original machining marks (perpendicular to sliding direction) on the bronze rod can be clearly observed below a protective transfer layer. It is assumed that the protective transfer layer accounts for the improvement in the tribological behavior.

For further analysis, the wear pair contact surface tribological behavior at different testing times was analyzed to discover why the multilayer coating Ti10%-C: H/TiC/TiCN/TiN wore so mildly during wear testing. The wear behavior can be classified into the three stages shown in Table 3, which lists the average friction coefficients and elemental composition of the wear surface of the bronze rod at different testing times. At stage 1, the wear traces of the bronze rod show mere plastic deformation along with a high friction coefficient (0.53 to 0.40), with no material adhering to the wear surface from the coated disk. Figure 7(a) displays the typical wear scars of the bronze rod after testing 30 s. The contact surface of the bronze rod is deformed along the sliding direction. The original machining marks (perpendicular to the sliding direction) can be clearly seen below the deformed surface, as shown in Fig. 7(b) (magnification of Fig. 7(a)). No elemental transfer occurred from the coated disk to the wear scars on the bronze rod, as verified by EDS analysis of the wear region of Fig. 7(a) (Table 3). At stage II, the wear scars on the bronze rod show the formation of a transferred layer; the content of the transferred layer included carbon, which increases while the friction coefficient (0.32 to 0.31) simultaneously decreases. Figure 7(c) shows a typical micrograph after 300 s of testing. The EDS analysis of Fig. 7(c) verifies that the transferred layer is carbon rich, composed of about 30 at.% carbon (Table 3). At stage III, after 600 s of testing, the friction coefficient achieved a stable value of about 0.31, while the transferred layer area and thickness increased



(**a**)



(**b**)

Fig. 5 (**a**) Typical wear surface of Ti10%-C:H/TiC/TiCN/TiN coated disk sliding against bronze rod. (**b**) Corresponding EDS analysis after sliding time of 24 min

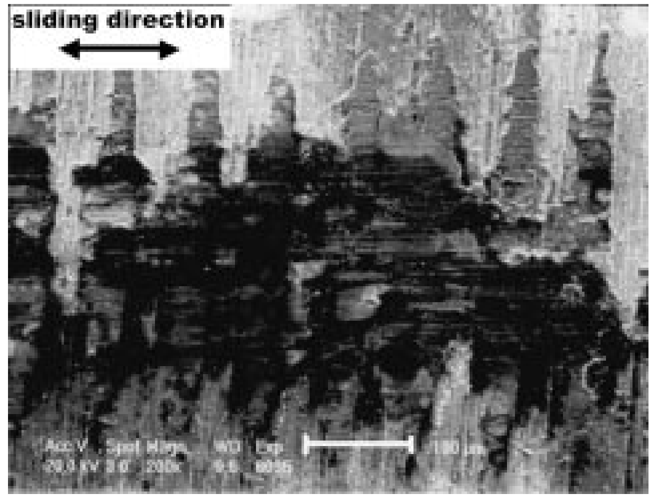


Fig. 6 Typical wear scar of bronze rod sliding against Ti10%-C:H/TiC/TiCN/TiN coated disk after sliding time of 24 min

Table 3 The average friction coefficient and elemental composition of transfer layer on wear surface of bronze rod by EDS analysis at different test times

			Elemental composition (at.%)			
Stage	**Test time (s)**	**Friction coefficient**	**C**	**Cu**	**Ti**	**O**
I	10	0.53	0	100	0	0
	30	0.47	0	94.2	0	5.8
	60	0.40	0	92.3	0	7.7
II	180	0.32	24.6	58.8	2.3	14.3
	300	0.31	30.1	45.8	7.5	16.6
III	600	0.31	37.2	12.4	19.3	31.1
	1440	0.32	32	13.7	20.5	33.8

to the levels displayed in Fig. 7(d). In addition, EDS analysis of the transferred layer shows that the amount of carbon increased to a high value of 37.2 at.%, while the amount of titanium and oxygen increased to 19.3 and 31.2%, respectively, and the amount of copper decreased to 12.4%, as shown in Table 3. Finally, at the end of this experiment (1440 s), the transferred layer carbon content was about 32% (EDS analysis of Fig. 6). Obviously, a carbon-rich transfer layer formed on the counterbody bronze rod, providing a solid lubricant effect and protecting the Ti10%-C: H/TiC/TiCN/TiN coating from severe adhesive and oxidative damage.

Durability lifetime is defined as the testing time until a sudden and large increase in the friction coefficient (above 0.4) occurs, followed by continuous large fluctuations. Because the TiN, TiCN/TiN, and TiC/TiCN/TiN coatings and substrate WC have a high friction coefficient along with large fluctuations throughout the test, the durability tests were performed only for the bronze and Ti10%-C: H/TiC/TiCN/TiN sliding pair. The durability lifetime was found to be about 6996 s. After durability testing, the wear scar depth on the coated disk was 7.4 μm, worn completely through the coating and deep into the WC substrate. Obviously, although the top coating of Ti10%-C: H was worn through, carbon-rich debris remained inside the wear trace, and new carbon-rich debris were continuously supplied from the gradually enlarging wear traces on the coating film. Further, the carbon- rich transferred layer on the counterbody bronze produced a solid lubricant effect, providing a friction coefficient of low value and smooth curve, and generating only slight noise during the test.

4. Conclusions

- (The TiN, TiCN/TiN, and TiC/TiCN/TiN coatings sliding against bronze display high wear and a high friction coefficient due to the severe oxidation and adhesion.
- (The tested multilayer coating Ti10%-C: H/TiC/TiCN/TiN

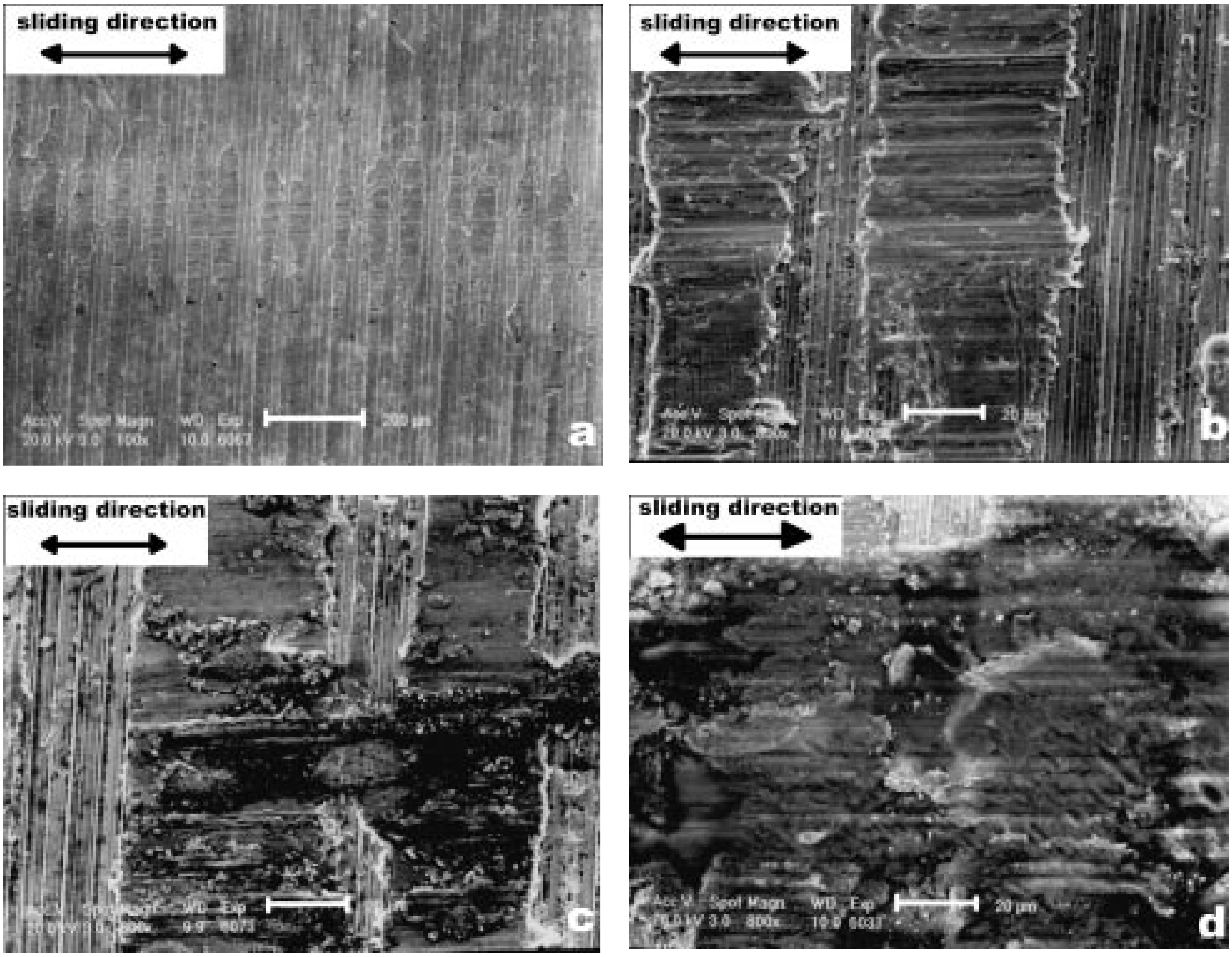


Fig. 7 Typical worn scars of bronze rods sliding against Ti10%-C:H/TiC/TiCN/TiN coated disk after sliding times of (**a**) 30 s, (**b**) magnification of (**a**), (**c**) 300 s, and (**d**) 600 s

is found to protect against the high wear found when Ti-based coatings rub against copper alloy. A transferred carbon-rich layer is formed on the counterbody, acting as a solid lubricant that reduces friction and wear of the sliding pairs.

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