JMEPEG (2012) 21:958–964
DOI: 10.1007/s11665-011-9971-7

©ASM International
1059-9495/$19.00

The Influence of Plasma Nitriding Pre-Treatment on Tribological Properties of TiN Coatings Deposited by PACVD

M.S. Mahdipoor, F. Mahboubi, Sh. Ahangarani, M. Raoufi, and H. Elmkhah

(Submitted June 27, 2010; in revised form February 2, 2011)

The aim of this study is to investigate the effect of plasma nitriding pre-treatment (PN) on mechanical and tribological behavior of TiN coatings produced by plasma-assisted chemical vapor deposition (PACVD). The heat treatment of quench and temper was carried out on hot work AISI H11 (DIN 1.2343) steel samples. A group of samples were plasma nitrided at 500 °C for 4 h in an atmosphere containing 25 vol.% nitrogen and 75 vol.% hydrogen. Then TiN layer was deposited on all of samples at 520 °C temperature, 8 kHz frequency, and 33% duty cycle. The microstructural, mechanical, and tribological properties of the coatings were investigated using SEM, WDS, AFM, microhardness tester, and pin-on-disc wear test. The load of wear test was 10 N and the samples were worn against different pins, ball-bearing steel (DIN 1.3505), and cemented tungsten carbide (WC-Co). The results indicate that the difference of hardness between the samples with PN-TiNlayer and those samples with only TiN layer without PN was 450 HV and the former samples showed a significant amount of wear resistance in comparison to the latter ones.

Keywords mechanical testing, surface engineering, tool steels, tribology

1. Introduction

Over the last few decades, requirements have grown steadily for tribological and corrosion-resistant layers for many industrial tools deposited by various methods. Recent progress in coating methods has led to the manufacture of a new group of adaptive and self-lubricating coatings (Ref 1). For instance, using plasma in some deposition methods such as PVD and CVD improves the properties of coating deposited with these methods and also removes their inherent limitations (Ref 2). The inability of PVD processes to coat the tools with complex shape and the high temperature deposition of CVD method are the problems that can be solved using plasma (Ref 3). Plasma-assisted CVD has been developed to combine the good adhesion of CVD and the low temperatures of PVD, while avoiding their typical drawbacks such as high temperature with deformations and poor adhesion, respectively (Ref 2).

Titanium nitride (TiN) is one of the most important coatings deposited by different methods on cutting tools or casting and forging dies to increase the corrosion and wear resistance. Indisputably, it can be so useful for wear resistance applications because this film has high hardness and low friction coefficient (Ref 4). TiN, TiC, TiCN, and TiBN are some of the coatings that can easily be produced using PACVD method (Ref 5). Many investigations have been carried out to improve the properties of coatings that are deposited by PACVD such as prior sputtering. Using pre-plasma nitriding can also be useful because deposition of TiN film with the hardness of about 1850 HV on 500 HV hard heat-treated steel forms an unstable and weak interface, due to a high hardness difference between steel substrate and TiN coating in the interface (Ref 6). This problem can be solved by an intermediate layer-like plasma nitrided layer with about 1000 HV hardness to lessen hardness profile gradient and to form CrN phase with the same crystal structure as TiN (Ref 3, 7).

The aim of this study is to investigate the influence of pre-plasma nitriding on the tribological behavior of TiN coating. The samples were tested using pin-on-disk tribometer against ball-bearing steel (DIN 1.3505) and cemented tungsten carbide (WC-Co) pins at room temperature. However, the several reports have been published dealing with the effect of pre-plasma nitriding on adhesion strength of the coatings deposited by PACVD method, the influence of pre-plasma nitriding on the tribological properties of these coatings has not been fully understood.

2. Experimental

The specimens in the form of 50 mm diameter and 8 mm thick discs were made from hot work steel (DIN 1.2343) rod. The chemical analysis of the steel, obtained by spark emission spectroscopy test, is presented in Table 1. A tempered

M.S. Mahdipoor and **F. Mahboubi**, Department of Mining and Metallurgical Engineering, Amirkabir University of Technology, Tehran, Iran; **F. Mahboubi**, New Technology Research Center, Amirkabir University of Technology, Tehran, Iran; **Sh. Ahangarani**, Department of Advanced Materials & Renewable Energies, Iranian Research Organization for Science and Technology, Tehran, Iran; **M. Raoufi**, Department of Metallurgical Engineering, Iran University of Science and Technology, Tehran, Iran; and **H. Elmkhah**, Nanomaterials Group, Tarbiat Modares University, Tehran, Iran. Contact e-mail: mahdipoor@aut.ac.ir.

Table 1 Chemical composition of hot work AISI H11 steel obtained by spark emission spectroscopy test

Element	C	Si	Mn	Cr	Mo	V	P	S
Weight percent	0.36	0.55	0.37	4.72	0.66	0.55	0.0043	0.0027

Table 2 PACVD process conditions for TiN coating

Parameter	Value
Pulsed voltage	550–600 V
Duty cycle	33, 40, 50%
H_2	1.6 NL/min
N_2	0.25 NL/min
Ar	0.05 NL/min
$TiCl_4$ (carrier H_2)	0.1 NL/min
Deposition time	4 h
Pressure	2 mbar
Temperature	520 °C
Duty cycle	33%

martensitic microstructure was emerged by austenitizing at 1050 °C for 30 min, quenching in oil, and then tempering at 550 °C for 45 min. The samples were ground and polished with standard metallographic techniques.

After preparation of the samples, some of them were plasma nitrided at 500 °C for 4 h in an atmosphere containing 25 vol.% nitrogen and 75 vol.% hydrogen. Then TiN layer was deposited on all samples, with pre-plasma nitriding (PN) and without pre-plasma nitriding, using PACVD under constant conditions (Ref 8) which are presented in Table 2. In this article, the steel samples with TiN coating will be presented as sample TiN and plasma nitrided steel samples with TiN coating will be presented as sample PN + TiN. The treated specimens were studied using scanning electron microscope (SEM), wavelength dispersive spectrometry (WDS), atomic force microscope (AFM), microhardness tester and pin-on-disk tribometer. The load of wear test was 10 N and the samples were worn against two different pins, ball-bearing steel (DIN 1.3505), and cemented tungsten carbide (WC-Co) with 0.1 m/s sliding speed. The relative humidity at room temperature during the test was in the range of 35–45%. At last, weight losses of the samples and pins are reported.

3. Results and Discussion

3.1 Structure and Morphology

The surface and cross section of the TiN film deposited on plasma nitrided steel were observed by SEM, Fig. 1. The thickness of the TiN coating is about 2.5 µm and it seems that the average grain size is about 150 nm. The dense microstructure of this coating may lead to better corrosion resistance (Ref 5).

The AFM micrographs of samples TiN and PN + TiN are indicated in Fig. 2. It can be seen that sample PN + TiN has long hills and deep valleys, but sample TiN has smooth surface. It is evident that the plasma nitriding caused the roughness of the surface to increase in comparison to untreated sample. This is due to the formation of cauliflower shape surface nitrides which have valley- and hill-like feature and as a result post-TiN coating roughness increases (Ref 6). So, these long hills can be broken during wear test and causes more weight loss, however, the surface roughness is not the only effective parameter (Ref 9).

3.2 Microhardness Measurements

Microhardness ($HV_{0.050}$) distributions on the cross section of the samples are presented in Fig. 3. It is observed that the microhardness profile of sample PN + TiN has lower slope in the interface in comparison to sample TiN which has a more steep change in hardness profile from surface to substrate. Moreover, using plasma nitriding treatment before deposition of TiN coating increases the surface hardness of samples so that the surface hardness of TiN sample is 1400 HV, but PN + TiN sample has 1810 HV surface hardness. This is due to the intermediate plasma nitrided layer with about 1050 HV hardness and almost 50 µm depth which removes the existed hardness shock in the interface between coating and substrate and mechanically supports the coating (Ref 6, 10). Furthermore, precipitation of CrN phase at the interface with the same crystal structure as TiN enhances the adherence of the subsequent TiN hard coating (Ref 3).

3.3 Tribological Properties

Friction coefficients of the specimens were exhibited against ball-bearing steel and WC-Co pins, using a pin-on-disk wear test machine. Figure 4 shows the friction curves over a sliding distance of 1000 m for different samples TiN and PN + TiN. The friction coefficient of sample TiN against ball-bearing steel pin starts with 0.82 and after 800 m, it increases to 0.95. In the same conditions, the friction coefficient of sample PN + TiN increases gradually up to 0.85. These samples showed different friction coefficients against WC-Co pins so that for sample TiN, after 500 m it reached from 0.6 to 0.85, whereas sample PN + TiN showed a constant friction coefficient of 0.6.

It should be mentioned that during TiN wear test, titanium, iron, and oxygen atoms can be detected on the wear tracks and due to the increase of temperature and preparation of essential conditions, the formation of iron oxides or titanium oxides as transfer layers are possible there.

It was found that the transfer layer on TiN coatings with low Cl content, one of the crucial factors in the TiN coatings deposited by PACVD to the formation of TiO_2, are composed of Fe_2O_3 and Fe_3O_4 that show high friction coefficients. Rutile phase of TiO_2 with iron oxides can be the transfer layers for higher Cl-containing TiN coatings (Ref 1). In this study, due to high deposition temperature of TiN coating, there is not enough Cl to the formation of rutile phase (Ref 4) and as a result, the low friction coefficients of TiN coatings (<0.2) are not expected.

For wear test in ambient air against steel pins the friction coefficients of the samples TiN and PN + TiN are approximately 0.9 (Fig. 4).This can be attributed to the adhesion of some particles of steel pin as transfer materials to the coatings and the formation of thin iron oxide layers on the wear track of

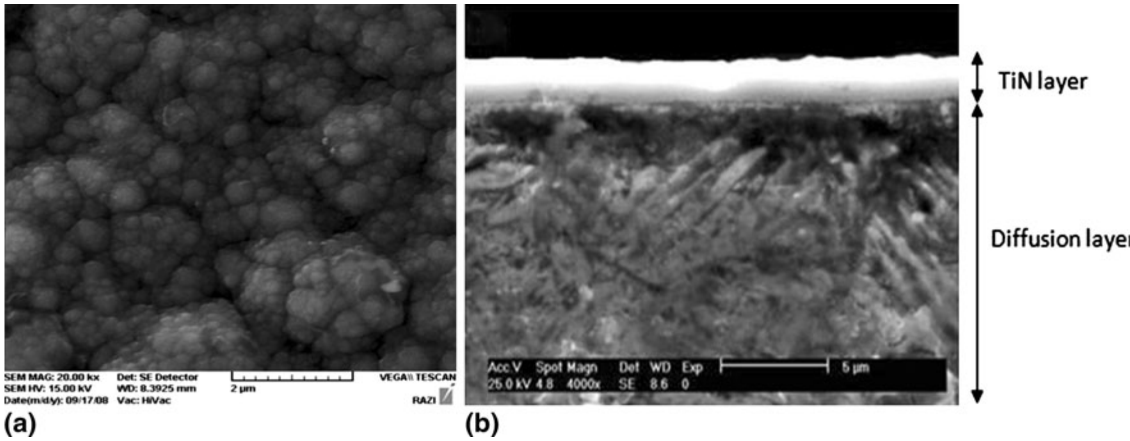

Fig. 1 SEM micrographs of the PN + TiN sample (a) surface (b) cross section

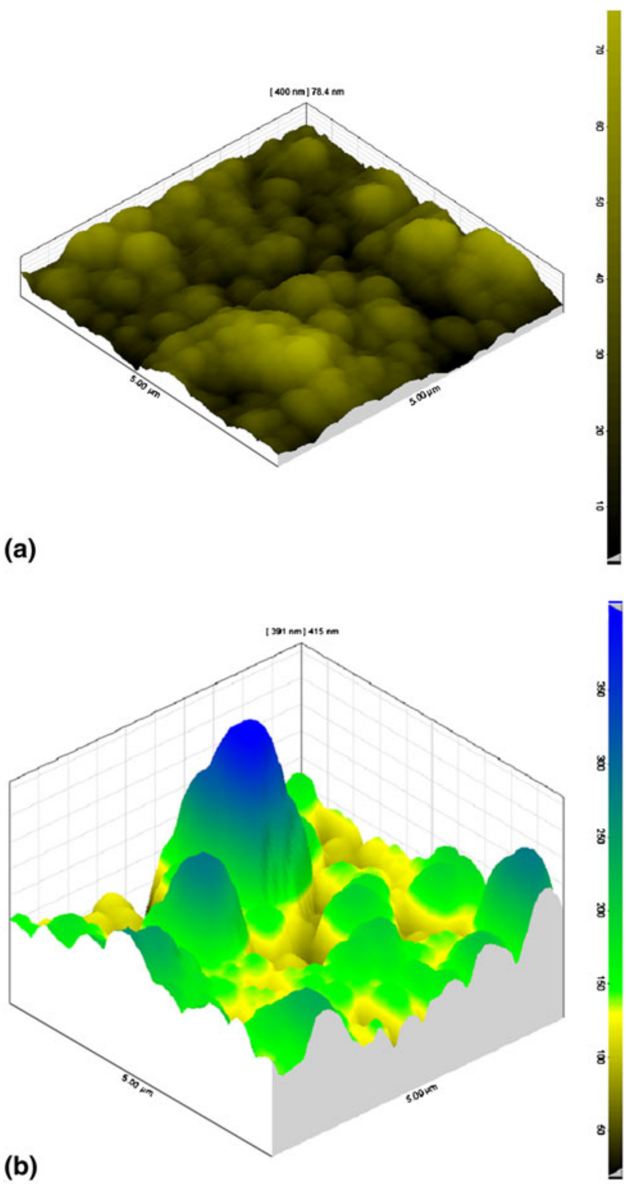

Fig. 2 AFM micrographs of (a) TiN sample (b) PN + TiN sample

TiN coating (Ref 11). Moreover, it is inferred that the pre-plasma nitriding does not have a crucial effect on reducing of friction coefficient in this condition. The situation is different when WC-Co pins are used. In this condition, friction coefficients of the samples are in the range of 0.6–0.8 (the TiO_2 layer has not been formed on the wear track for this pin) (Ref 12). When WC-Co pin was used, the adhesion of pin particles on the TiN coating should be very low because of their ceramic natures. As a result, the lower friction coefficient curves are completely reasonable in this condition.

Plasma nitriding pre-treatment decreases the friction coefficient from 0.8 to 0.6. In fact, during wear test against WC-Co pin, TiN layer can be removed and its particles cause to increase the contact area and as a result due to the increase of contact area between two surfaces, rising of the friction coefficient in some regions of its curve is reasonable. Therefore, when TiN sample was worn against WC-Co pin, friction coefficient rises after 500 m sliding distance because TiN coating was removed and the contact of ceramic pin with steel substrate increased. This theory is in good agreement with the weight loss of the samples. Indeed, the instability of interface, due to high hardness difference between steel substrate and TiN coating is harmful for tribological properties of the samples. To sum up, although TiN is high wear resistance coating, it will be ineffective if the coating removes from the surface during wear test. So, pre-plasma nitriding plays an important role to keep TiN coating on the substrate.

When testing against ball-bearing steel pin, the predicament wear mode could be abrasion due to high fluctuation in their friction coefficient curves and broad wear tracks on the samples (Ref 13). When the sample PN + TiN was worn against WC-Co pin, abrasive wear could be observed on a narrow wear track, but it is different for the sample TiN. The wear track of the specimen TiN against WC-Co pin is shown in Fig. 5. Some cracks on the surface of the TiN layer (Fig. 5a) and its cross section as well as its TiN-substrate interface (Fig. 5b) can be seen. The crack formation in the TiN coating and its propagation can be attributed to brittleness and weak adhesion of TiN coating to the substrate. The cracked and detached TiN particles can boost the wear rate in TiN samples. As can be seen in Fig. 5, the TiN coating cracked into small pieces and detached from the substrate. The coating crack is undoubtedly started from weak and unstable region that can be the interface between TiN coating and substrate. In addition, there are many

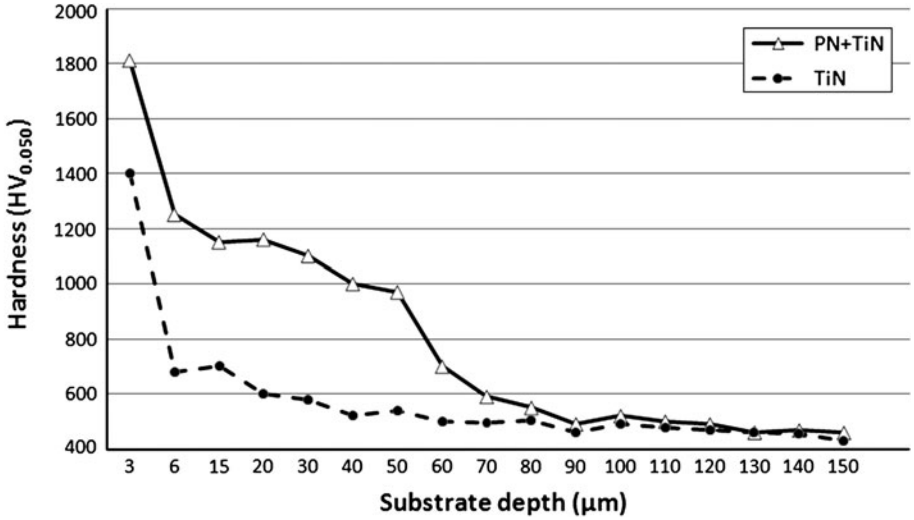

Fig. 3 Microhardness (HV0.05) profiles of the TiN coated samples with pre-plasma nitriding (PN + TiN) and without pre-plasma nitriding (TiN)

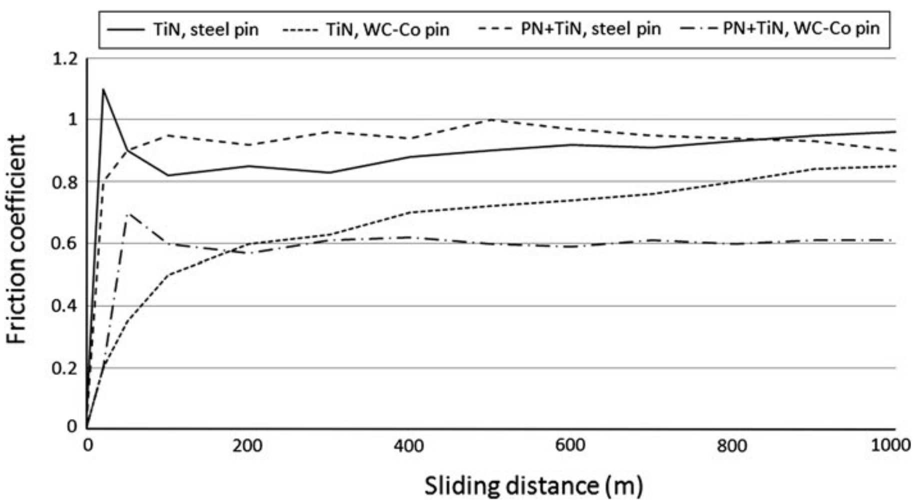

Fig. 4 Friction coefficients obtained in pin-on-disc testing of the TiN coated samples with pre-plasma nitriding (PN + TiN) and without pre-plasma nitriding (TiN) against different pins

cracks in the remained parts of TiN on the wear track and beneath it. Thus, it seems that there is fatigue wear by crack initiation from the interface and its propagation to the sample's surface. The schematic illustration of this mechanism is shown in Fig. 6. According to this figure, initiation of cracks can be formed from the interface and propagates into coating or substrate during wear test. Moreover, spreading of these cracks can remove more parts of TiN coating from surface and increase contact areas between pin and substrate. So, the detached TiN particles can be so harmful and increase the wear rate due to their high hardness.

The SEM images and WDS map of worn surfaces against ball-bearing steel and WC-Co pins are shown in Fig. 7. From the image of wear traces and the maps for Ti and Fe elements, investigating of their wear is possible.

It can be seen that PN + TiN samples have an excellent wear resistance against steel pin so that the TiN layer were not removed. Ti atoms are detected on the whole wear path and some Fe atoms that are present there are attributed to steel pins debris that were transferred on the wear track. This specimen showed a good resistance to WC-Co pin in comparison to sample TiN because as Fig. 7 indicates, the detected Fe elements on the wear track for sample TiN are much more than those detected for sample PN + TiN. Indeed, detection of Fe atoms in this condition can be attributed to removing of TiN coating and detecting Fe atoms from substrate. As a result, the high amount of identified Fe atoms on wear path of the TiN sample can be good account for the important role of stable and adhesive interface on tribological behavior of TiN coating on the steel substrate (Ref 6). According to SEM micrographs of the wear tracks of sample PN + TiN against steel pin, it sounds that the wear tracks are broad and they may not deep, at least not deeper than the thickness of the TiN coating. However, these tracks after wear against WC-Co pin seem narrower and deeper. These situations can be ascribed to hardness of the used pins (Ref 8) and are in good agreements with their weight losses.

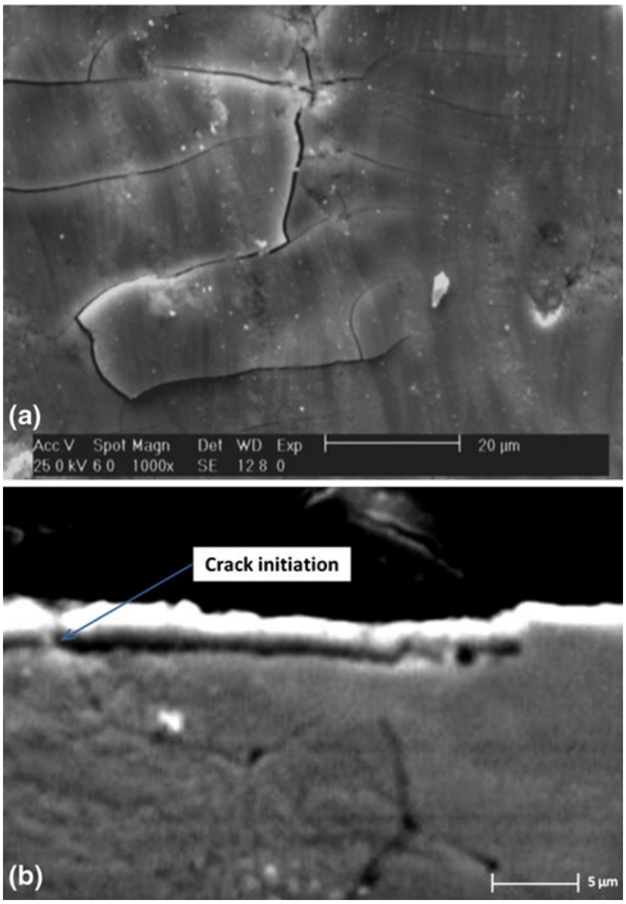

Fig. 5 (a) SEM micrograph of a remain part of TiN layer on the wear track, (b) SEM micrograph of cross section of wear track

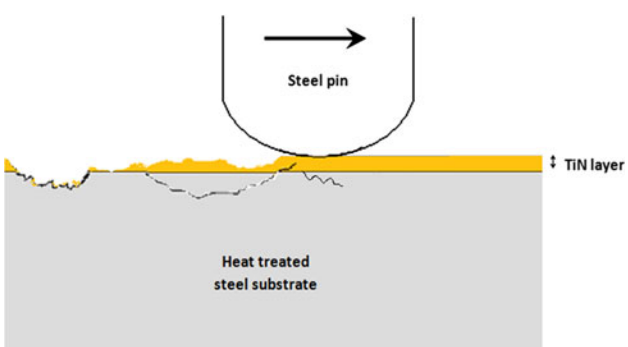

Fig. 6 Schematic illustration of fatigue wears for TiN sample

Weight loss of the samples and their counter pins after wear tests are presented in Fig. 8. There is a large difference of this parameter for samples TiN and PN + TiN so that the weight loss of sample TiN is 1.6×10^{-5} kg against ball-bearing steel pin and is 4.5×10^{-5} kg against WC-Co pin, while for specimen PN + TiN, they are 0 kg and 2×10^{-6} kg. It can be seen that when the specimens were plasma nitrided, their weight loss reduced considerably. The weight loss of sample TiN after wear against steel pin is 1.6×10^{-5} kg, while there is almost no mass loss for sample PN + TiN in this condition. This is due to the weakness of interface between TiN coating and substrate that cause the thin TiN layer to be removed during wear test by crack initiation and its propagation along the interface. As a result, pin wears the steel substrate at the end of the test. Fe map of the wear track (Fig. 7) shows that after wear test, TiN layer has been removed completely and pin contacts with steel substrate, so this amount of weight loss was expected, but for the sample PN + TiN, tiny amount of steel pin is transferred to the sample which compensates its weight loss (Fig. 8). When the WC-Co pin is used, the weight losses of specimens increase because this pin has a high hardness and can wear TiN coating much more than steel pin. The influence of pre-plasma nitriding is noticeable in this condition, so that mass losses of samples decrease from 4.5×10^{-5} to 2×10^{-6} kg (Ref 14). These results are in good agreement with Fe map of the sample TiN (Fig. 7) because in those pictures, a lot of Fe atoms were detected in wear track and it means that TiN coating have been removed during wear test. There is another point about wear rate of pins and specimens that presented in Fig. 8. The weight losses of steel pins in comparison to samples are very high. As a matter of fact, it means that when steel pin was used, TiN worn steel pin (Ref 15), but using WC-Co pin leads to wear of TiN coating due to their hardness (Ref 13).

As it is indicated in Fig. 8 for sample TiN against WC-Co pin, in spite of high wear resistance of TiN coating, the wear behavior is not favorable. In this test, TiN layer was removed completely from surface and specimen's weight loss is high in comparison to other sample's weight loss. Therefore, pre-plasma nitriding plays a significant role for improving wear resistance.

4. Conclusions

The main objective of this investigation was to recognize the effect of pre-plasma nitriding on mechanical and tribological properties of TiN coating deposited on hot work steel (DIN 1.2343) by PACVD. Based on the results the following conclusions can be derived:

1. Pre-plasma nitriding treatment due to formation of a nitrided intermediate layer with 1050 HV hardness between substrate and TiN coating causes to hamper the hardness shock in the interface and the TiN coating is mechanically supported by the nitrided layer, leading to 400 HV increase in the surface hardness of TiN layer.
2. The weight loss of PN + TiN sample is much lower than the weight loss of TiN sample. In this condition, the coating has good adhesion strength and it is not removed during wear test. Hence, the wear resistance (mass loss) is more than 10 times better.
3. For TiN samples, removing of TiN coating during the wear test increases the friction coefficient from 0.6 to 0.8 due to an increase in the contact areas between the two surfaces.
4. The wear resistance of binary PN + TiN coatings is much better than others samples so that after 1000 m it does not remove against ball-bearing steel pin at all and it wears slightly against WC-Co pin.

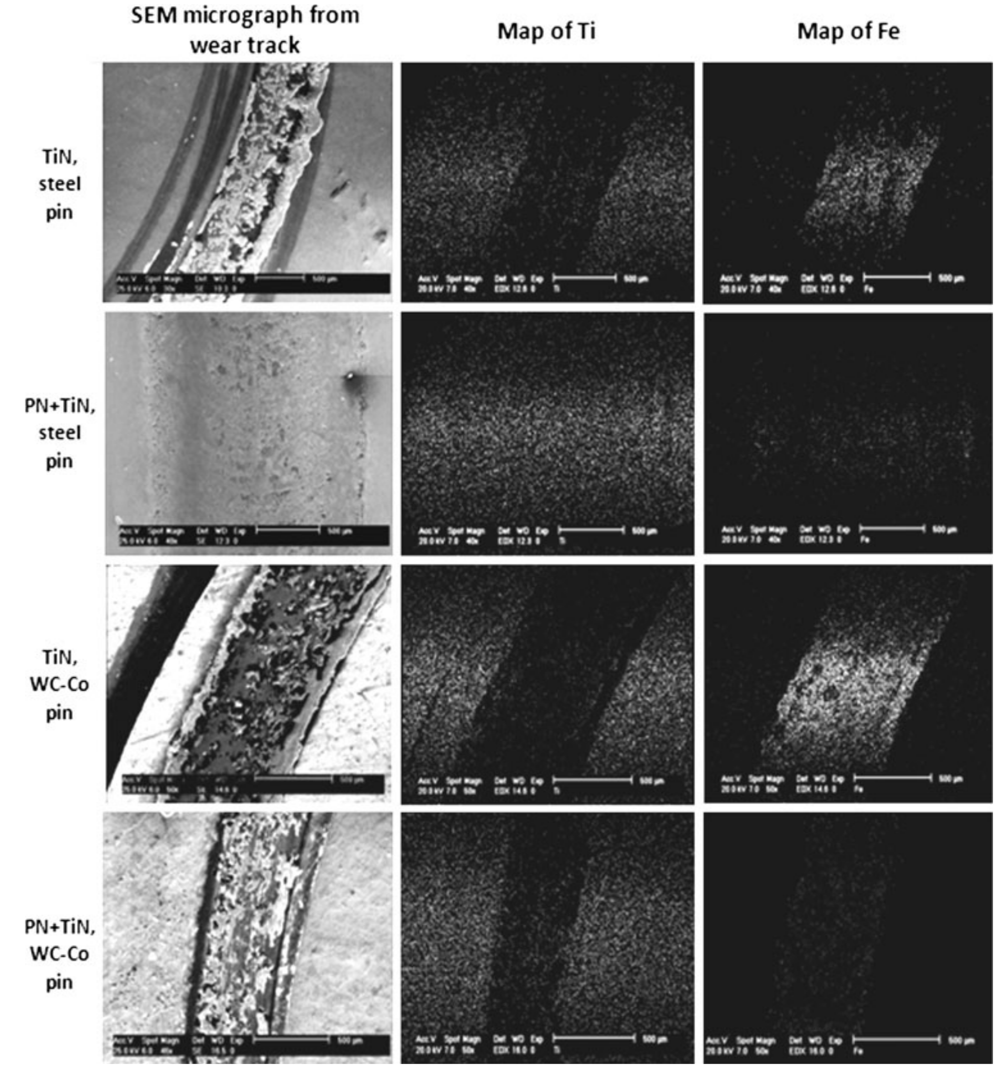

Fig. 7 SEM images and WDS analyses for the worn surfaces of the TiN coated specimens with pre-plasma nitriding (PN + TiN) and without pre-plasma nitriding (TiN) against ball bearing steel and WC-Co pins after 1000 m

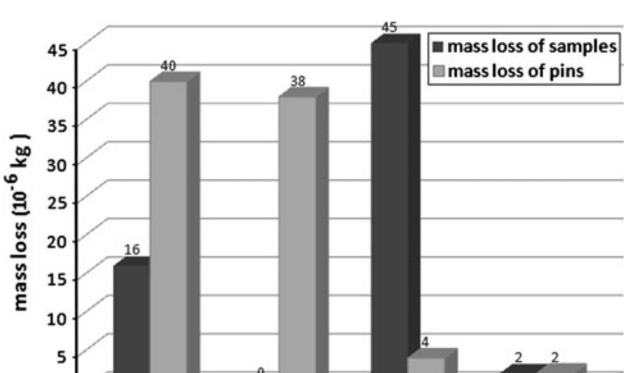

Fig. 8 Mass loss of the TiN coated samples with pre-plasma nitriding (PN + TiN) and without pre-plasma nitriding (TiN) and their abrasive pins after pin-on-disk wear test

References

1. E. Badisch, C. Mitterer, P.H. Mayrhofer, G. Mori, R.J. Bakker, J. Brenner, and H. Stori, Characterization of Tribo-Layers on Self-Lubricating PACVD TiN Coatings, *Thin Solid Films*, 2004, **460**, p 125–132
2. S.S. Eskildsen, C. Mathiasen, and M. Foss, Plasma CVD: Process Capabilities and Economic Aspects, *Surf. Coat. Technol.*, 1999, **116–119**, p 18–24
3. M. Stoiber, J. Wagner, C. Mitterer, K. Gammer, H. Hutter, C. Lugmair, and R. Kullmer, Plasma-Assisted Pre-Treatment for PACVD TiN Coating on Tool Steel, *Surf. Coat. Technol.*, 2003, **174-175**, p 687–693
4. M. Stoiber, E. Badisch, C. Lugmair, and C. Mitterer, Low-Friction TiN Coatings Deposited by PACVD, *Surf. Coat. Technol.*, 2003, **163–164**, p 451–456
5. S. Ma, K. Xu, and W. Jie, Plasma Nitrided and TiCN Coated AISI, H13 Steel by Pulsed dc PECVD and Its Application for Hot-Working Dies, *Surf. Coat. Technol.*, 2005, **191**, p 201–205
6. Y. He, I. Apachitei, J. Zhou, T. Walstock, and J. Duszczyk, Effect of Prior Plasma Nitriding Applied to a Hot-Work Tool Steel on the

Scratch-Resistant Properties of PACVD TiBN and TiCN Coatings, *Surf. Coat. Technol.*, 2006, **201**, p 2534–2539

7. X. Zhu, H. Huang, K. Xu, and J. He, Influence of the Interface Preparation on Properties of PECVD TiN, *Surf. Coat. Technol.*, 1999, **116–119**, p 1029–1032
8. P. Hardt, M. Eckel, M. Schmidt, and H. Wulff, Influence of Process Parameters on the Growth of TiN in Different Sized Plasma-Assisted Chemical Vapor Deposition Reactors, *Surf. Coat. Technol.*, 1999, **120–121**, p 238–243
9. P.J. Kelly, T. Vom Braucke, Z. Liu, R.D. Arnell, and E.D. Doyle, Pulsed DC Titanium Nitride Coatings for Improved Tribological Performance and Tool Life, *Surf. Coat. Technol.*, 2007, **202**, p 774–780
10. K.S. Mogensen, C. Mathiasenn, S.S. Eskildse, H. Stori, and J. Bottiger, The Time Development of Pulsed-DC Production Plasmas Used for Deposition of TiN, *Surf. Coat. Technol.*, 1998, **102**, p 35–40
11. A. Azushima, Y. Tanno, H. Iwata, and K. Aoki, Coefficients of Friction of TiN Coatings with Preferred Grain Orientations Under Dry Condition, *Wear*, 2008, **265**, p 1017–1022
12. Y. Tanno and A. Azushima, Effect of Counter Materials on Coeficients of Friction of TiN Coatings with Preferred Grain Orientations, *Wear*, 2009, **266**, p 1178–1184
13. E. Badisch, G.A. Fontalvo, and C. Mitterer, The Response of PACVD TiN Coatings to Tribological Tests with Different Counterparts, *Wear*, 2004, **256**, p 95–99
14. Y. He, I. Apachitei, J. Zhou, T. Walstock, and J. Duszczyk, The Influence of the Depth of a Plasma Nitrided Layer in Tool-Steel Substrate on the Scratch-Resistant Properties of PACVD TiBN Coating, *Surf. Coat. Technol.*, 2007, **201**, p 7036–7042
15. K.S. Klimek, A. Gebauer-Teichmann, P. Kaestner, and K.-T. Rie, Duplex-PACVD Coating of Surfaces for Die Casting Tools, *Surf. Coat. Technol.*, 2007, **201**, p 5628–5632