Substrate effects on the micro/nanomechanical properties of TiN coatings

T.H. Zhang* and Y. Huan

*State Key Laboratory of Nonlinear Mechanics (LNM), Institute of Mechanics, Chinese Academy of Sciences,
Beisihuan West Road 15, Beijing 100080, China*

Received 10 October 2003; accepted 11 June 2004

Nanoindentation and nanoscratch tests were performed for titanium nitride (TiN) coatings on different tool steel substrates to investigate the indentation/scratch induced deformation behavior of the coatings and the adhesion of the coating–substrate interfaces and their tribological property. In this work, TiN coatings with a thickness of about 500 nm were grown on GT35, 9Cr18 and 40CrNiMo steels using vacuum magnetic-filtering arc plasma deposition. In the nanoindentation tests, the hardness and modulus curves for TiN/GT35 reduced the slowest around the film thickness 500 nm with the increase of indentation depth, followed by TiN/9Cr18 and TiN/40CrNiMo. Improving adhesion properties of coating and substrate can decrease the differences of internal stress field. The scratch tests showed that the scratch response was controlled by plastic deformation in the substrate. The substrate plays an important role in determining the mechanical properties and wear resistance of such coatings. TiN/GT35 exhibited the best load-carrying capacity and scratch/wear resistance. As a consequence, GT35 is the best substrate for TiN coatings of the substrate materials tested.

KEY WORDS: nanoindentation, nanoscratch, titanium nitride, mechanical properties, adhesion, wear resistance

1. Introduction

Owing to its excellent mechanical properties and wear resistance, titanium nitride (TiN) is commercially used on steels as a protective film to extend their working lifetime. The properties of TiN vary with preparation techniques, deposition conditions and substrates. Therefore, a thorough understanding of the mechanical response of a coated component to applied loads is of both fundamental and technical importance to evaluate the surface hardening and interfacial bonding strength for different materials. The deposition techniques and resulting coating properties have been studied extensively [1–4]. The mechanical properties of the coating are strongly influenced by the substrate on which it are deposited [5,6]. The nanoindentation and nanoscratch techniques are commonly used for evaluating the mechanical properties of such sub-micron coatings.

In the present research, a systematic investigation of the mechanical properties of TiN coatings on different steel substrates was performed. The aim of this study is to understand the predominant deformation mechanism that occurred in response to indentation and scratching. It then critically assesses the ways in which the information can be used to understand the deformation of these coatings.

2. Experimental details

The substrate materials were GT35 alloy tool steel (with composition in wt. %: Fe 60, TiC 35, Cr 2, Mo 2, C 1), 9Cr18 bearing steel (Si 0.8, Mn 0.72, P 0.035, S 0.03, C 0.96, Cr 17.8, Fe 79.655), and 40CrNiMo alloy structure steel (Si 0.25, Mn 0.70, C 0.41, Cr 0.82, Ni 1.45, Mo 0.18, Fe 96.19). The specimens were cut from real bearing rings that had been quenched and tempered. All samples were polished to a mirror finished surface and ultrasonically cleaned prior to coating deposition. TiN coatings with a thickness of about 0.5 μm were deposited onto the substrates using the vacuum magnetic-filtering arc plasma method. Finally, a DJB-823 organic film (Institute of Chemical Prevention, Beijing University of Posts and Telecommunication, Beijing, China) of approximately 1.0 μm in thickness was deposited on the TiN. The organic film is a solid film protective agent, and plays a lubrication role.

Nanoindentation tests were conducted using a MTS Nano Indenter[®] XP (MTS Systems Corp., Oak Ridge, TN, USA) with a Berkovich diamond tip. Hardness and elastic modulus were measured using the continuous stiffness measurement (CSM) option. Fused silica was used as a standard sample for the initial calibration. In the present study, a typical indentation experiment consists of seven subsequent steps: approaching the surface; determining the contact point; loading to

*To whom correspondence should be addressed.
E-mail: zhangth@lnm.imech.ac.cn

peak load; holding the tip for 10 s at the peak load; unloading 90% of peak load; holding the tip for 50 s at 10% of the peak load for thermal drift correction; and finally unloading completely. The experimental parameters were chosen as follows: strain rate, 0.05 s^{-1} ; allowable thermal drift rate, 0.05 nm/s ; depth limit, $1.0 \text{ }\mu\text{m}$. The hardness and elastic modulus were obtained from the curves using the Oliver–Pharr method [7]. Nanoscratch tests were performed using the lateral load measurement (LFM) option of the Nano Indenter[®] XP. A different diamond Berkovich tip was used with face forward. During a scratch test, the ramp normal load on the indenter was held. For these tests, the ramping normal loads were max 40, 100 and 300 mN . A scratch velocity of $10 \text{ }\mu\text{m/s}$ was used by controlling the stage movement. A typical scratch experiment is performed in nine subsequent steps: approaching the surface; first profile with normal load $20 \text{ }\mu\text{N}$ for $700 \text{ }\mu\text{m}$ in Y direction; return profile; pre-profile for $100 \text{ }\mu\text{m}$; scratch profile with ramping normal load for length $500 \text{ }\mu\text{m}$; unload; post-profile for $100 \text{ }\mu\text{m}$; return profile; final profile with normal load $20 \text{ }\mu\text{N}$ for $700 \text{ }\mu\text{m}$. Five indents or scratches were performed for each test conditions. All tests were carried out at room temperature. Surface observation was performed by a POLYVAR MET[®] optical microscope (Reichert-Jung, Vienn Austria).

3. Results and discussion

3.1. Nanoindentation properties

Nanoindentation tests with max indentation depth 1000 nm were performed for the steel samples (40CrNiMo, 9Cr18, GT35) and the coatings (TiN/40CrNiMo, TiN/9Cr18, TiN/GT35). The results are shown in table 1. p_m , δ_m , δ_r , H , E are the peak load on sample, max indentation depth, and residual indentation depth, hardness and modulus from unload, respectively. At the same depth (1000 nm) for all samples, p_m exhibits the load-carrying capacity; $1-\delta_r/\delta_m$, the indentation recovery capacity. H/E can provide important information on the mechanical resistance of the material. The relative high value of H/E ratio reveals the high elastic deformation during contact, making it an excellent candidate for applications where both

wear resistance and elasticity are required [8]. It has been found that the max load, $1-\delta_r/\delta_m$, hardness, modulus, and H/E of GT35 were highest, followed by 9Cr18 and 40CrNiMo. In general, the harder the substrate, the better are the load-carrying capacity and wear resistance. Thus, GT35 steel is the best substrate material. In addition, the residual indentation depths for TiN/steels were shallower than for the related steels. As a consequence, the TiN film exhibits a better elastic recovery capacity.

Figure 1 shows the hardness values as a function of indentation depth for all above samples. Each point represents the average of five separate indents, and the error bars were calculated from the standard deviation of these five results. The error values could be correlated with the non-homogeneous component distribution in the samples. Note the hardness in the topmost 20 nm . This is probably an artifact of the data reduction method—when the indentation depth is sufficiently shallow, the load–depth curve shows almost complete elastic recovery [9]. Variations in surface topography also led to the scatter in measured values within 50 nm of the film surface [10]. The hardness values of 40CrNiMo, 9Cr18 and GT35 samples were approximately independent of indentation depths. Their hardness and modulus values at 1000 nm depth are shown in table 1. In contrast, those of TiN/GT35, TiN/9Cr18, and TiN/40CrNiMo were dependent on indentation depths. In any coatings, all data show max hardness of about 38 GPa at depths from 50 nm to 100 nm , consistent with the general practice of keeping depth $<20\%$ of the film thickness to minimize substrate effects [11]. Therefore, the hardness values of TiN films on the three substrates were approximately 38 GPa . With the depth increasing, the hardness values decrease due to substrate effects, and gradually approach those of the corresponding steel substrates. Among the three coatings, the hardness curve for TiN/GT35 reduced the most slowly around the film thickness 500 nm with increasing indentation depth. It is shown that the mechanical properties of GT35 steel and TiN film corresponding the most closely. That is, the interface properties change only gradually. The deformation around the TiN/GT35 interface is more consistent under the load. The internal stress field around interface doesn't change abruptly, which

Table 1.
The load/unload-depth data of each sample and the corresponding hardness, and modulus and ratio of H/E .

	P_m/mN	δ_m/nm	δ_r/nm	$1-\delta_r/\delta_m/\%$	Hardness/GPa	Modulus/GPa	H/E
GT35	250	1000	760	19	14.3	368.5	0.039
TiN/GT35	300	1000	620	38			
9Cr18	200	1000	800	17	9.1	266.8	0.034
TiN/9Cr18	250	1000	640	36			
40CrNiMo	120	1000	840	15	5.8	203.3	0.029
TiN/40CrNiMo	160	1000	800	20

Figure 1. Hardness as a function of displacement into surface curves with five separate indents to about 1000 nm into the six samples: 40CrNiMo, 9Cr18, GT35, TiN/40CrNiMo, TiN/9Cr18, TiN/GT35 (about 500 nm-thickness TiN).

improves adhesion properties of coating and substrate. So, the combination of coating/substrate properties is important in determining the overall mechanical response of the system.

3.2. Nanoscratch properties

To explain the scratch measurement process, the TiN/9Cr18 example is shown in figure 2 for a ramping normal load of max 100 mN. In figure 2(a), the first-profile curve corresponds to the roughness of the initial surface, the scratch-profile curve corresponds to the tip penetration depth during testing, and the final-profile curve represents the residual depth after

scratching, assessing the surface damage and any elastic/plastic deformation. A negative depth corresponds to the scratch tip being pushed into the sample. It is evident that the scratch profile increases linearly as a function of the ramping increase of the normal load from 0 to 28 mN or scratch distance from 100 μm to 240 μm , marked as range L1. The final-profile curve nearly coincides with the first-profile over the range L1, although the scratch depth goes up to 100 nm. This indicates that the TiN coatings almost fully recover at these loads, in which the initial elasticity is coating-dependent and is hardly related to the substrate. The coefficient of friction remain constant at 0.15 in figure 3(c). Then over the range L2 from 240 μm to 600 μm , the slope of the scratch-profile curve increases, and the final-profile curve separates from the first-profile curve. It indicates that the substrate and TiN coating deformed plastically under these loads. The related coefficient of friction increases gradually until approaching the curves of its substrate 9Cr18 (see figure 3(a) and (c)). It is shown that the tip scratched into the substrate. Both lateral load as a function of the normal load and the scratch distance during the scratch profile are shown in figure 2(b).

Figure 3 shows the coefficient of friction as a function of the scratch distance under various ramping normal loads: (a) 9Cr18 with 40 mN; (b) TiN/9Cr18 with 40 mN; (c) TiN/9Cr18 with 100 mN; (d) organic/TiN/9Cr18 with 100 mN; (e) organic/TiN/9Cr18 with 300 mN. The friction coefficients of 9Cr18, TiN film, and organic film are approximately 0.40, 0.15 and 0.11, respectively. The friction coefficients of GT35, 40CrNiMo, TiN, and organic film are approximately 0.25, 0.45, 0.15, and 0.11, respectively. Thus, the solid lubricative effects are very marked.

In order to understand the deformation mechanism of the organic/TiN/GT35, organic/TiN/9Cr18, organic/TiN/40CrNiMo, it needs to be recognized that three

Figure 2. The scratch with a ramping normal load of max 100 mN for TiN/9Cr18: (a) The scratch depth as a function of the scratch distance and normal load; (b) The lateral load as a function of the scratch distance and normal load.

Figure 3. Coefficient of friction as a function of the scratch distance under various ramping normal loads: (a) 9Cr18 with 40 mN; (b) TiN/9Cr18 with 40 mN; (c) TiN/9Cr18 with 100 mN; (d) organic/TiN/9Cr18 with 100 mN; (e) organic/TiN/9Cr18 with 300 mN.

processes occurred successively during the ramping of the normal load up to 300 mN: fully elastic recovery (marked as range L1), plastic deformation (L2), and delamination/fracture (L3) of the films. Figures 4(a)–6(a) are the curves for the lateral load as a function of the normal load and scratch distance. The initial point of range L2 corresponds to the commitment of plastic deformation and the initial residual scratching in figures 4(b)–6(b). The normal and lateral loads associated with this event are called, N_p , F_p . In addition, the cracking or delamination of a hard coating is marked by a sudden increase in lateral load versus normal load and scratch distance curves. The normal and lateral loads associated with this event are called the critical load, N_c , F_c [11], corresponding to the initial points of the range L3. The data of three films are shown in table 2. The range L1 of organic/TiN/GT35 is the widest, and the values of N_p and F_p are the highest, followed by organic/TiN/9Cr18, and organic/TiN/40CrNiMo, showing that TiN/GT35 exhibited the best

Figure 4. The scratch of organic/TiN/GT35 with ramping normal load of max 300 mN: (a) The lateral load as a function of the scratch distance or the normal load; (b) The optical image of the scratch trace; (c) The optical image of the top of the scratch trace.

load-carrying capacity. The range L3 of organic/TiN/GT35 is the narrowest, and the critical load is the highest, followed by organic/TiN/40CrNiMo, and organic/TiN/9Cr18, showing that TiN/GT35 also exhibited the best adhesive capacity and scratch/wear resistance.

The damage or failure modes were different for the above samples. It is observed in figures 4(c)–6(c) that the small debris for organic/TiN/GT35 peeled off around the top of the scratch trace, but the small debris of TiN for organic/TiN/9Cr18 and organic/TiN/40CrNiMo was pressed entirely into the substrates. In particular, the micrograph in figure 6(c) clearly shows that the organic/TiN films were ploughed by the scratch tip, whose scratches were like a fish vertebrae, associated with the plastic flow of 40CrNiMo. For a hard substrate, the main failure mode of TiN film is brittle fracture. The debris of the broken film is larger than that on soft substrates.

Table 2.
The deformation range of each sample and the corresponding load.

	$L_1/\mu\text{m}$	$L_2/\mu\text{m}$	$L_3/\mu\text{m}$	N_p/mN	F_p/mN	N_c/mN	F_c/mN
Organic/TiN/GT35	100–220	220–496	496–600	72.0	8.0	237.6	64.8
Organic/TiN/9Cr18	100–193	193–417	417–600	55.8	4.9	190.2	46.2
Organic/TiN/40CrNiMo	100–156	156–440	440–600	33.6	2.8	204.0	96.8

Figure 5. The scratch of organic/TiN/9Cr18 with ramping normal load of max 300 mN: (a) The lateral load as a function of the scratch distance or the normal load; (b) The optical image of the scratch trace; (c) The optical image of the top of the scratch trace.

4. Conclusion

In this study, we studied the micro/nanomechanical properties of solid-lubricative TiN films on three different types of substrates. The main conclusions may be summarized as follows:

1. Compared with the substrate steels, the mechanical and wear resistance properties of TiN/steels are significantly improved. The lubricative effects of TiN coatings and the organic coatings are marked.

Figure 6. The scratch of organic/TiN/40CrNiMo with ramping normal load of max 300 mN: (a) The lateral load as a function of the scratch distance or normal load; (b) The optical image of the whole scratch trace; (c) The optical image of the top of the scratch trace.

2. GT35 steel is the best substrate. On one hand, the load-carrying capacities of GT35 and TiN/GT35 are the highest. On the other hand, the tendency to fracture of TiN/GT35 is the lowest. This may be due to the interface properties between TiN and GT35 steel, which can reduce the internal stress field and improve the critical load.
3. The nanoindentation and nanoscratch tests can provide very useful information on the near-surface elastic-plastic deformation, fracture, friction and wear properties.

Acknowledgments

The authors would like to thank Ms. Xiulan Wang in Beijing Research Institute of Aerospace Materials & Technology for the preparation of TiN films and Dr. Cunyi Xie in MTS Systems (China) Inc. for helpful discussion. This project was supported by the National Natural Science Foundation of China (10372103 and 10172086) and the Chinese Academy of Sciences (KJCX2-SW-L2).

References

- [1] C. Quaeys, J. D'Haen, L.M. Stals, et al., *Surf. Coat. and Technol.* 61 (1993) 227.
- [2] K. Xu, J. Chen, R. Gao and J. He, *Surf. Coat. and Technol.* 58 (1993) 37.
- [3] M.G. Hocking, V. Vasantasree, P.S. Sidky, *Metallic and Ceramic Coatings: Production, High Temperature Properties and Applications* (Wiley, New York, 1989) 86.
- [4] J.H. Huang, Y.P. Tsai and G.P. Yu, *Thin Solid Films* 355/356 (1999) 440.
- [5] J.C. Knight, T.F. Page and I.M. Hutchings, *Thin Solid Films* 177 (1989) 117.
- [6] S.V. Hainsworth and W.C. Soh, *Surf. Coat. Technol.* 163/163 (2003) 515.
- [7] W.C. Oliver and G.M. Pharr, *J. Mat. Res.* 7 (1992) 1564.
- [8] C. Charitidis, Y. Panayiotatos and S. Logothetidis, *Diam. Rel. Mat.* 12 (2003) 1088.
- [9] K.W. Lee, Y.-W. Chung, C.Y. Chan, I. Bello, et al., *Surf. Coat. Technol.* 168 (2003) 57.
- [10] N.R. Moody, A. Strojny, D.L. Medlin, et al., *J. Mat. Res.* 14 (1999) 2306.
- [11] B. Bhushan, *Handbook of Micro/Nanotribology*, 2nd ed. (Boca Raton, CRC Press, 1999).