Reactive HVOF sprayed TiN-matrix composite coating and its corrosion and wear resistance properties

Jing MA[1,2,3], Dong-qing YAN[1], Jian-wen HU[1], Xin ZHANG[1], Yang LI[1]

1. School of Materials, Hebei University of Science and Technology, Shijiazhuang 050018, China;
2. Hebei Key Laboratory of Material Near-Net Forming Technology,
Hebei University of Science and Technology, Shijiazhuang 050018, China;
3. State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China

Abstract: TiN-matrix composite coating was prepared on 45# steel by reactive high-velocity oxy-fuel (HVOF) spraying. Its microstructure, phase composition, micro-hardness, corrosion resistance in 3.5% NaCl solution and wear resistance were analyzed. The results suggest that the TiN-matrix composite coating is well bonded with the substrate. The micro-hardness measured decreases with the increase of applied test loads. And the micro-hardness of the coating under heavy loads is relatively high. The TiN-matrix composite coating exhibits an excellent corrosion resistance in 3.5% NaCl solution. The corrosion potential of coating is positive and the passivation zone is broad, which indicates that the TiN-matrix composite coating is stable in the electrolyte and provides excellent protection to the substrate. The wear coefficient of the coating under all loads maintains at 0.49−0.50. The wear mechanism of the coating is revealed to be three-body abrasive wear. Yet the failure forms of TiN-matrix composite coating under different loads have an obvious difference. The failure form of coating under light loads is particle spallation due to the stress concentration while that of coating under heavy loads is cracking between inter-lamellae.

Key words: reactive HVOF spraying; TiN-matrix composite coating; corrosion resistance; wear resistance

1 Introduction

Titanium nitride (TiN) coatings have been widely used as decorative coatings, wear-resistant coatings, diffusion barriers and electrodes for their superior wear resistance, erosion resistance, heat resistance and a low friction coefficient. At present, TiN coatings are mainly obtained by physical vapour deposition (PVD) or chemical vapour deposition (CVD) [1,2]. However, their deposition efficiency is relatively low.

In recent years, much attention has been paid to reactive thermal spraying for its promising synthesizing composite coatings [3−5]. During spraying, hard ceramic phases, such as carbides, borides and nitrides are formed in-situ in a metallic or inter-metallic matrix by the reactions between the injected powder and the reactive gas.

Reactive plasma spraying (RPS) technique has been applied to getting a thick TiN coating through reaction between titanium powders and nitrogen plasma jets [6−13]. BACCI et al [6] prepared a TiN coating with a thickness of 60 μm using reactive plasma spraying, and the spraying was performed in a pure nitrogen atmosphere chamber at 50 MPa. KOBAYASHI [7], using a gas tunnel-type plasma jet, prepared a TiN coating whose thickness was over 200 μm. FENG et al [8] prepared a TiN coating with 500 μm in thickness by reactive plasma spraying in a nitrogen-containing environment. Reactive spraying TiN coatings have a considerable hardness, up to HK1500, without the characteristic brittleness of pure TiN coatings obtained by PVD or CVD techniques. Moreover, considerable thickness (>200 μm) can be fabricated within a few minutes of deposition. Compared with plasma spraying, the spraying particles' velocity of high-velocity oxy-fuel

(HVOF) spraying is faster and can reach up to two times of sonic speed. So, the porosity of reactive HVOF spraying coating should be denser. And the approach about TiN coating prepared by reactive HVOF spraying has not been reported.

We recently prepared TiN-matrix coating by reactive HVOF spraying. Its micro-hardness and fracture toughness are superior [14]. As a promising cutting tool coating, its wear resistance properties were studied. The aim of this work is to research the corrosion and wear resistance properties of TiN composite coating prepared by reactive HVOF spraying.

2 Experimental

Medium carbon steel (0.42%−0.50%C steel) was selected to be the substrate. The specimens were machined into the sample dimensions of d60 mm×3 mm and then ground with 600 grit SiC paper. Before spraying, the surface was ultrasonic cleaned with alcohol and de-ionized water and then sand (corundum) blasted to obtain the fresh surface. The grit size was about d0.6 mm. The blast pressure and angle were 0.4−0.5 MPa and 70°, respectively. The residual sands were removed by compressed air. Commercial Ti powders (+44−74 μm) were used as spraying powders. Nitrogen was selected as feeding gas. The coating was prepared by JP5000 HVOF spraying instrument produced by America. The spraying parameters are shown in Table 1.

Table 1 HVOF spraying parameters used in experiments

Flow rate of kerosene/ (L·min^{-1})	Flow rate of O$_2$/ (L·min^{-1})	Flow rate of H$_2$/ (L·min^{-1})	Powder feed rate (N$_2$)/(g·min^{-1})	Spraying distance/ mm
0.32	822	10	70	380

A CHI600C electrochemical analyzer was used to study polarization behavior. A saturated Ag/AgCl electrode and Pt wire were used as counter electrode and auxiliary electrode, respectively. 3.5% NaCl solution was selected as electrolyte. Scanning rate of 0.05 V/s, sampling interval of 0.001 V, sensitivity of 0.1 A/V, and quiet time of 2 s were selected in all the polarization tests. TiN-matrix coating was used as the working electrode with an exposing area of 1.0 cm^2 and nonworking surface was covered with epoxide resin.

Wear test was presumed according to metal wear experimental test (GB 12444.1—90). MM200 type wear tester was used (Fig. 1). TiN-matrix coating was prepared on a butterfly type substrate. GCr15 ring (about 60HRC) was used as counterpart wear ring. The rotation speed was 200 r/min. Three loads (196, 294 and 735 N) were chosen. Masses before and after wear test were weighed. Wear coefficient was calculated from frictional torque, according to the following formula:

$$\mu = 0.1 \times \frac{M}{RF} \cdot \frac{a + \sin a \cos a}{2 \sin a}$$

where M is frictional torque; F is the load; R is semi-diameter of opposite wear ring; a is half of the contact angle for wear friction couples, which can be calculated as follows:

$$a = \arcsin(b/2R)$$
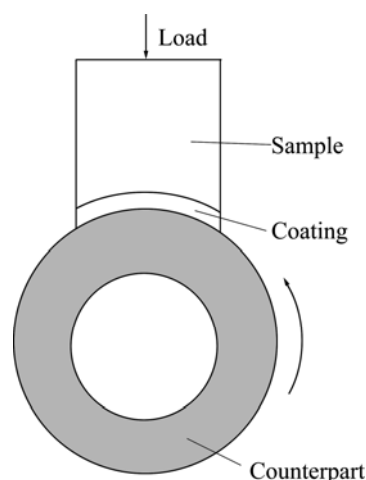
where b is the width of wear track.

Fig. 1 Illustration of wear test

The phases and composition of the coating were analyzed by X-ray diffraction instrument (Bruker D8 ADVANCE XRD, Cu K$_\alpha$ 1.5406 Å) and EDS. Micro-hardness of TiN coating was measured with a HX−1000 micro-hardness tester. Loads were ranged from 0.49 to 9.8 N and a dwell time of 40 s was selected. To avoid the stress field effect near the indentation, the distance between every two indentations was controlled to be three times longer than the indentation diagonal. The cross-section morphologies of the HVOF coatings were examined by scanning electron microscopy (SEM).

3 Results

3.1 Phase and morphologies of HVOF spraying coating

Figure 2 shows the XRD pattern of reactive HVOF sprayed TiN-matrix coating. The coating consists of TiN, TiN$_{0.3}$, Ti$_2$O$_3$ and TiO$_2$. The main phase was TiN so that the reactive HVOF sprayed coating may be called TiN-matrix composite coating. Figures 3 and 4 show the cross-section morphologies of HVOF sprayed TiN-matrix composite coating. The coating is well bonded with the substrate. Even without bond coating, the thickness of coating reaches about 300 μm. The coating
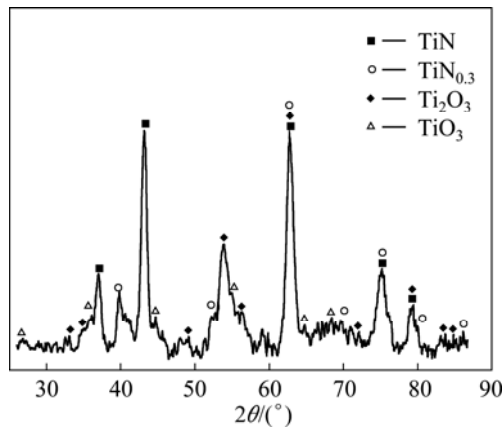
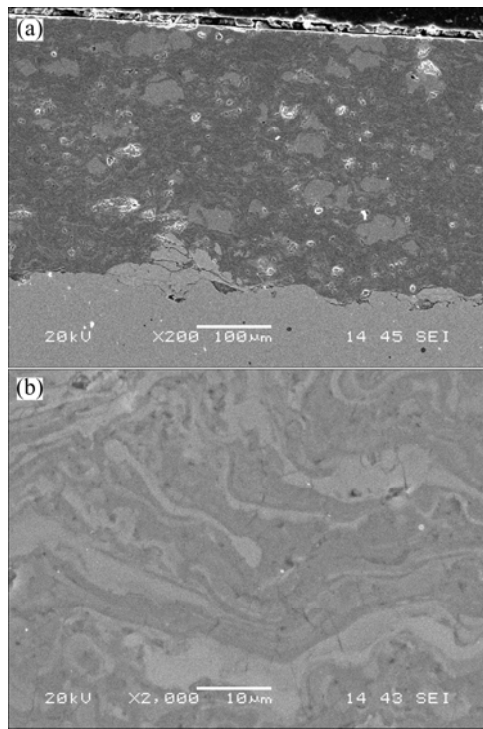**Fig. 2** XRD pattern of HVOF sprayed TiN-matrix composite coating

Fig. 3 SEM images of HVOF sprayed TiN-matrix composite coating: (a) Lower magnification; (b) Higher magnification
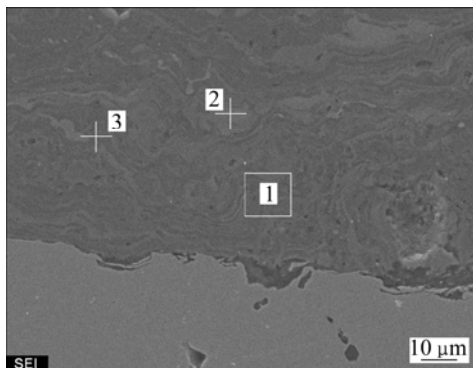

Fig. 4 SEM image of HVOF sprayed TiN-matrix composite coating

was composed of two phases: dark phase and light phase. EDS analysis (Table 2) indicates that the light phase consists of Ti and N while the dark phase consists of Ti, N and O. Therefore, the light phase may be titanium nitrides (TiN and $TiN_{0.3}$) and the dark phase may be the mixture phase of titanium nitrides (TiN and $TiN_{0.3}$) and titanium oxides (Ti_2O_3 and TiO_2).

Table 2 EDS analysis of TiN-matrix composite coating

Element	$x/\%$		
	Point 1	Point 2	Point 3
N	11.22	10.98	10.76
O	17.10	−	16.45
Ti	71.67	89.02	72.79

3.2 Micro-hardness analysis

Table 3 shows the micro-hardness analysis of HVOF sprayed TiN-matrix composite coating. As shown in Fig. 5, the micro-hardness measured decreases with the increase of applied test loads, which was so called the indentation size effect (ISE). With applied load ranging from 0.49 N to 9.8 N, the corresponding hardness decreased from $HV_{0.49N}$ 1136.5 to $HV_{9.8N}$ 810.4. Reactive plasma sprayed TiN coating was studied by FENG et al [8]. The microhardness of reactive plasma sprayed TiN

Table 3 Micro-hardness of HVOF sprayed TiN-matrix composite coating

Load/N	Hardness (HV)			
	Mean	Standard	Minimum	Maximum
9.8	810.4	109.4	730	970
4.9	962.6	76.7	870	1075
2.74	971.4	197.5	690	1410
1.96	1122.0	211.0	914	1584
0.98	1124.4	260.2	625	1533
0.49	1136.5	171.7	927	1486

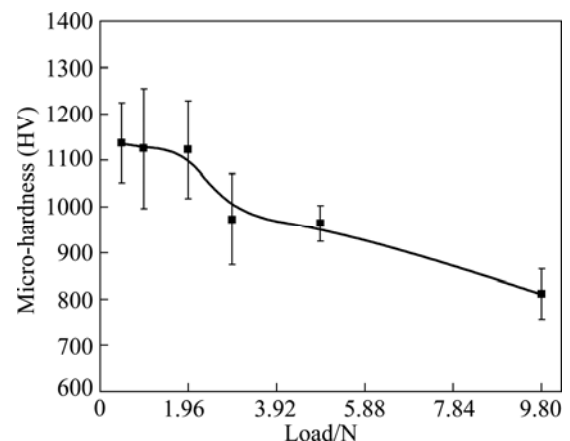**Fig. 5** Relationship between micro-hardness and applied load

coating drops from $HV_{0.245 N}1267.8$ to $HV_{9.8 N} 485.8$. Compared with the TiN coating prepared by reactive plasma spraying [8], the hardness of TiN coating prepared by reactive HVOF spraying under high loads is higher.

3.3 Corrosion potential curves

Figure 6 shows the polarization behavior of HVOF sprayed TiN-matrix composite coating in 3.5% NaCl solution. Compared with carbon steel, the corrosion resistance of TiN-matrix composite coating was improved remarkably. The open potential of carbon steel was −0.749 V (vs Ag/AgCl electrode). For HVOF sprayed TiN-matrix composite coating, the open potential was about −0.018 V, which is relatively positive. The anode polarization of TiN-matrix composite coating can be parted into three zones: active dissolution zone *AB*, passivation zone *BC* and trans-passivation zone *CD*. No active-passive zone was present. The passivation zone was relatively board. The critical passive potential was about 0.35 V and the current density decreased slowly at passivation zone. When the polarization potential was about 1.5 V, the current density reached its minimum value. After that, the potential current density increased greatly and trans-passivation occurred. Compared with carbon steel, the potential of TiN coating was positive. Even at a higher potential, the current density can maintain a lower level, which indicates the excellent corrosion resistance of the coating.
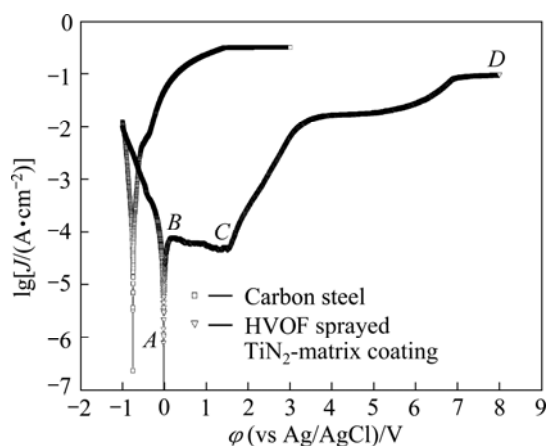

Fig. 6 Polarization curves of HVOF sprayed TiN-matrix composite coating in 3.5% NaCl solution

3.4 Wear tests

Figure 7 shows the wear torque curves of TiN-matrix composite coating wearing against GCr15 ring under loads of 196, 274 and 735 N. For TiN-matrix composite coating, the wear torque turned to a constant value after initial unstable wear. For 45# steel, the wear torque was very fluctuant in the whole wear process and

the swing was large. Table 4 shows the mass loss and wear coefficient calculated of TiN-matrix composite coating against GCr15 ring under loads of 196, 294 and 735 N. For the sample without coating, the wear mass loss was 1.5814 g, three magnitudes higher than that of sample with TiN-matrix composite coating, which was just several milligramme. Compared with coating under light loads, the mass loss of TiN-matrix composite coating under high loads was not increased, which indicates that the wear resistance of coating is excellent. For sample without coating, the wear coefficient is 0.64 while that of TiN coating at different loads maintains at 0.49−0.50.
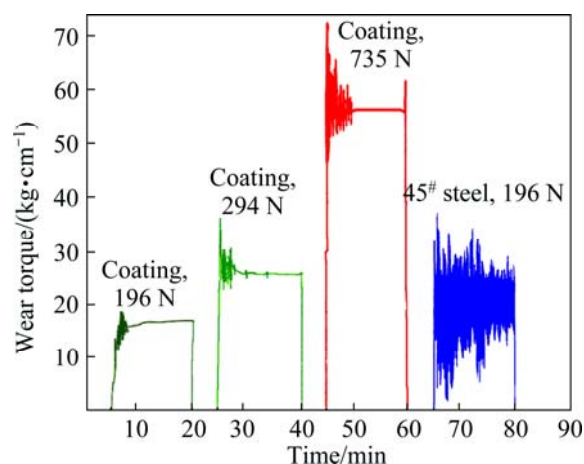

Fig. 7 Wear torque curves of TiN-matrix composite coating wearing against GCr15 ring under loads of 196, 294 and 735 N

Table 4 Wear test result of HVOF sprayed TiN-matrix composite coating

Load /N	Mass loss/g	Wear coefficient
196 (without coating)	1.5814	0.64
196 (with coating)	0.0013	0.49
294 (with coating)	0.0036	0.49
735 (with coating)	0.0021	0.50

Figure 8 shows the surface and cross-section morphologies of TiN-matrix composite coating under loads of 294 N and 735N. The surface was even for sample under 294 N. At local zone, particles were spalled from the coating. Cracks were formed on the surface of coating under a load of 735 N, extending in parallel to the surface of coating. The breakage form of the coating under high loads was lamellar spallation. EDS analysis of point *A* of TiN-matrix composite coating under 294 N (Fig. 9) shows that the composition of spalled particle is Ti, O and N, which indicates the spallation of local coating. Figure 10 shows the EDS analysis of TiN-matrix composite coating under 735 N. On the surface of the TiN-matrix composite coating, a Fe-rich film was formed,

which indicates that the composition of GCr15 steel ring was smeared on the surface of TiN-matrix composite coating during the wear test. Figure 11 shows the surface morphology of GCr15 steel ring after wear test under 735 N. Obvious furrows (about 200 μm in width) were formed. Some metal oxides were also found.
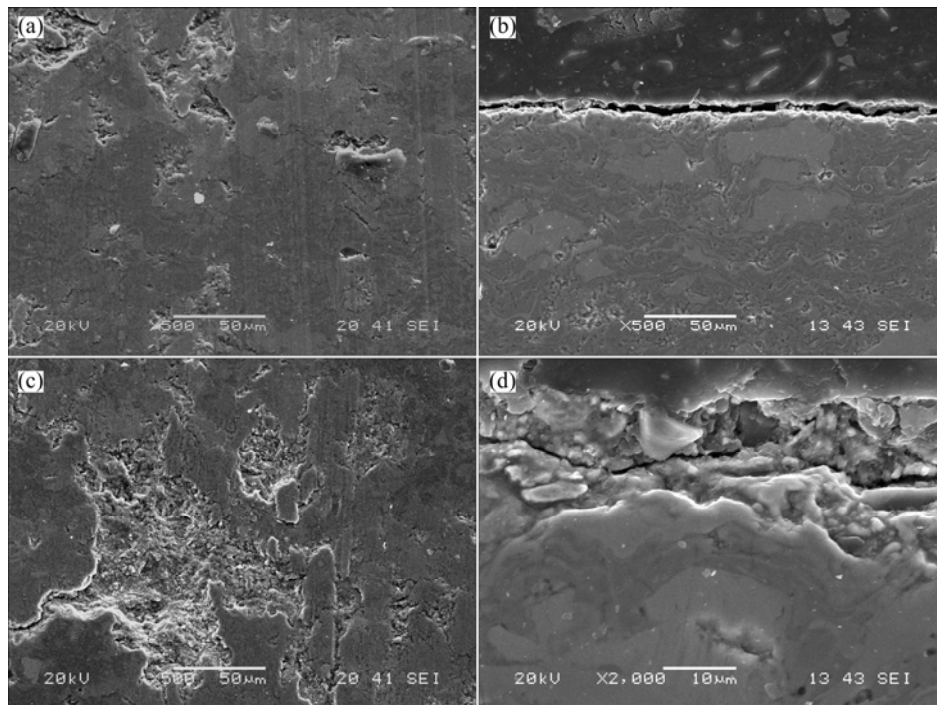

Fig. 8 Surface (a, c) and cross-section (b, d) morphologies of TiN-matrix composite coating under different loads: (a), (b) 294 N; (c), (d) 735 N
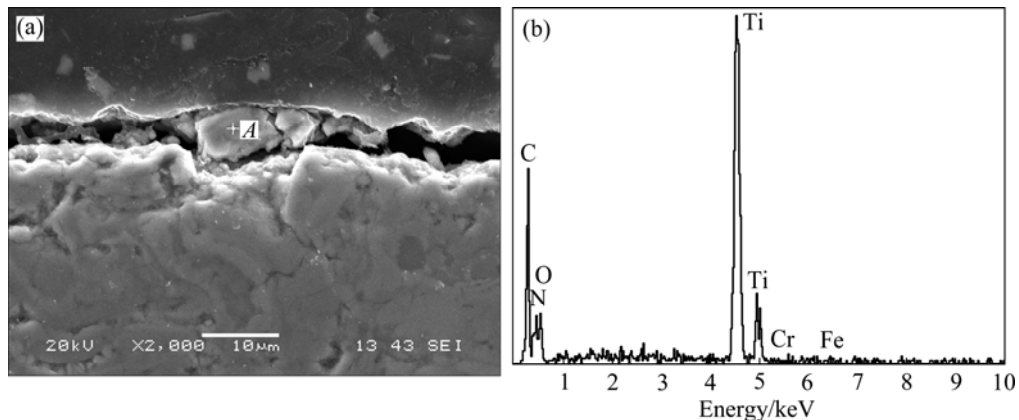

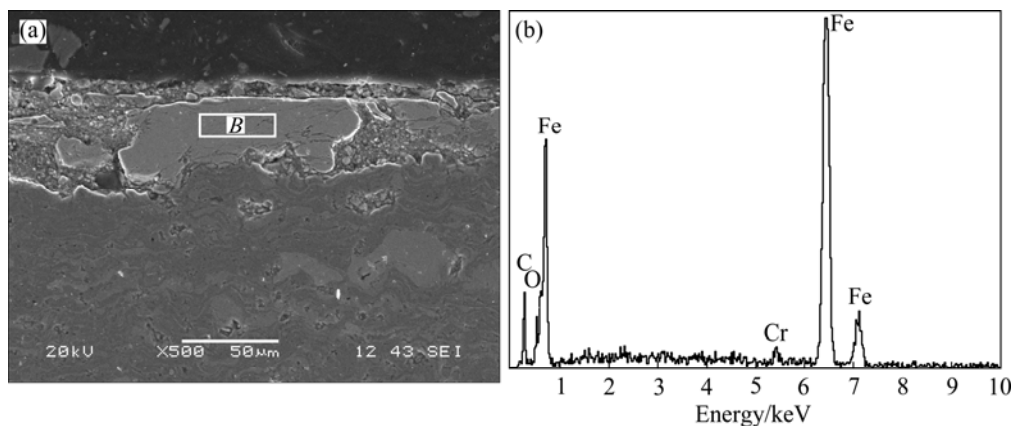**Fig. 9** SEM image (a) and EDS analysis of point *A* (b) in TiN-matrix composite coating under 294 N

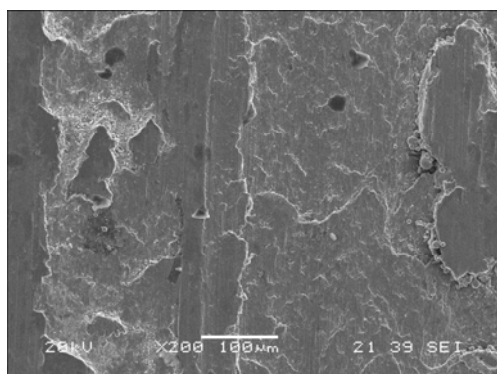**Fig. 10** SEM image (a) and EDS analysis (b) of area *B* TiN-matrix composite coating under 735 N

Fig. 11 Surface morphology of GCr15 ring under 735 N

4 Discussion

4.1 Formation of TiN-matrix composite coating

For a self-propagating high temperature synthesis reactive spraying, the adiabatic temperature of reactive system must be higher than 2500 K [15,16]. In this study, two reactions should be considered:

$$Ti(s) + 0.5N_2(g) = TiN(s) \tag{1}$$

$$Ti(s) + O_2(g) = TiO_2(s) \tag{2}$$

To calculate the adiabatic temperature (T_{ad}) of above reactions, several hypotheses should be set:

1) Reaction will happen solely, that is, no other reactions happen;

2) Reaction will happen totally according to equation, and no reactant remains;

3) Reaction system has no energy exchange with environment.

If reaction happens at 298 K, then,

$$\Delta H_{298}^{\Theta} + \sum_i n_i (H_{T_{ad}}^{\Theta} - H_{298}^{\Theta})_{i,\text{resultant}} = 0$$

or

$$\sum_i n_i (H_{T_{ad}}^{\Theta} - H_{298}^{\Theta})_{i,\text{resultant}} = -\Delta H_{298}^{\Theta}$$

where ΔH_{298}^{Θ} is the heat of reaction at 298 K; n_i is the stoichiometric number; $(H_{T_{ad}}^{\Theta} - H_{298}^{\Theta})_{i,\text{resultant}}$ is the relative mole enthalpy of resultants. It can be expressed as

$$H_{T_{ad}}^{\Theta} - H_{298}^{\Theta_i} = B_1 T + 10^{-3} B_2 T^2 + 10^5 B_3 T^{-1} + 10^{-6} B_4 T^3 + 10^8 B_5 T^{-2} + B_6$$

Then, the adiabatic temperatures of reactions (1)

and (2) are 4909 K and 10556 K, respectively, which are both higher than 2500 K, that is, all reactions satisfy the condition for SHS spraying. The data for calculation are shown in Table 5 [17].

From the above analysis, Ti is very reactive. And Ti is easier to be oxidized compared with nitriding. Yet during HVOF spraying, the ratio of titanium nitride to titanium oxides in coating depends on the partial pressures of oxygen and nitrogen. For nitrogen was used to feed titanium powders, Ti was nitrided in HVOF flame, giving out a lot of heat. The overlap of reaction heat and HVOF flame make TiN melt and deposit as TiN-matrix coating.

For oxygen was used to assist combustion during HVOF spraying, the content of oxides in the TiN-matrix composite coating is higher than that prepared by reactive plasma spraying. In former studies [18], the oxides existing in the coating are regarded as a phase harmful to the properties of TiN-matrix composite coatings because these oxides have a much lower hardness and strength than the pure TiN material in the coating. Yet in our studies, even under heavy loads, the microhardness of TiN-matrix composite coating is still high.

4.2 Indentation size effect

Like other coatings, the HVOF sprayed TiN-matrix composite coating also has indentation size effect (ISE). ISE is probably attributed to the fact that hardness corresponds to the energy consumed during the plastic deformation of unit volume of materials. Since some changes occur inevitably on the free surface area during indentation, and the work done by the indentation load is partially consumed in the indentation volumetric deformation, the hardness obtained by calculation shows a phenomenon of the indentation size effect [19]. Yet different materials have different ISE rules. In Ref. [8], there are two stages in the curves of micro-hardness vs load. At the first stage for the load from 0.245 to 1.96 N, Vickers micro-hardness declines sharply for its relatively high work hardening degree; at the second stage when the load surpasses 1.96 N, Vickers micro-hardness declines slowly for the light work hardening level. In our studies, Vickers micro-hardness of TiN-matrix coating decreases slowly under applied loads of 0.49−9.8 N. Under 9.8 N, the micro-hardness is HV810.4, which is

Table 5 Thermodynamics data for calculation

Sample	B_1	B_2	B_3	B_4	B_5	B_6	Temperature/K	$\Delta H_{298}^{\Theta_i}$/kJ
TiN	11.91	0.47	2.96	0	0.00	−4583.00	298−3223	−339.15
	16.00	0.00	0.00	0	0.00	2207.00	3223−3500	
TiO$_2$	15.02	1.35	2.38	0	0.00	−5393.00	298−2143	−948.36
	21.00	0.00	0.00	0	0.00	4123.00	2143−3000	

much higher than HV485.8 of RPS TiN coating [8]. This indicates that the microhardness of HVOF TiN-matrix coating is super.

For lower indentation loads, the indentation mark is very small, close to the thickness of layer. So, the microhardness is mainly affected by intrinsic hardness of TiN coating and elastic modulus of crystals inside the splats. While several splats were probed under higher loads, interlamellar cracking will have effects on the indenter, resulting in a lower measured hardness. Compared with plasma spraying, HVOF flame produces a faster but colder particle stream [20]. The high droplet impacting velocity produces sufficient high interface contact strength between impacting droplets and the substrate so that regular disk-like splats with low fragmentation are formed [21]. Therefore, reactive sprayed HVOF TiN-matrix coating has a higher hardness due to its lower defect and better inter-lamellar cohesion vs RPS one.

4.3 Corrosion behavior

Compared with carbon steel, the corrosion potential of TiN-matrix composite coating was shifted positively (about 0.731 V), which indicates that the coating is very stable in 3.5% NaCl solution. After the active polarization, a thin passivation film may be formed on the surface of TiN coating. With the increase of polarization potential, the passivation film is thicker and thicker. So, the current density in passivation zone is decreased steadily. The passivation zone is very broad (the potential voltage from 0.35 V to 1.5 V). When the polarization voltage is very high, the coating is broken down. The current density sharply increases and overpassivation occurs.

The corrosion behavior of reactive plasma-sprayed Ti−TiN coatings in 0.5 mol/L NaCl solution has been discussed by VALENTE and GALLIANO [22]. It was found that its corrosion resistance was strictly dependent on coating porosity. The interconnected porosity directly induced crevice corrosion attack. Compared with reactive plasma-sprayed Ti−TiN coating, the corrosion potential of reactive HVOF sprayed TiN-matrix composite coating is more positive and an obvious passivation zone is present, which shows that the protective ability of HVOF sprayed TiN-matrix composite coating is superior to that of TiN coating prepared by plasma spraying. The reason is that the HVOF sprayed TiN-matrix composite coating is very dense. For HVOF spraying, the velocity of melt powders is extra high as well as the flame velocity. The flame velocity can reach twice higher than that of sound. The velocity of melt powders can also reach 300−700 m/s when the powders leave the "de Laval" nozzle. So, the HVOF sprayed TiN-matrix composite coating is very dense. Moreover, the overlap of reactive heat and flame heat will increase the temperature of powders. So, the bond strength between the coating and the substrate is very high. Therefore, the corrosion resistance of HVOF sprayed TiN-matrix composite coating is superior.

4.4 Wear mechanism

Much heat is generated for its high speed friction during wear test so that the surface of GCr15 steel is oxidized. The oxide film on the surface of GCr15 steel is cut and ploughed by the hard particles of TiN-matrix composite coating, forming abrasive oxide dust. On the other hand, stress may be concentrated at the local zone of coating, which causes the expanding of the micro-cracks and the spallation of partial coating. Particles of coating spall and abrasive debris form. The wear converts into abrasive wear and the wear condition is more severe. So the wear mechanism of TiN-matrix composite coating against GCr15 ring at steady stage is three-body abrasive wear. For GCr15 ring, the wear mechanism is micro-cutting and ploughing plastic deforming.

Under different loads, the wear mechanism may be different. Under light loads, micro-cracks may be generated due to the contacting stress. Micro-cracks then spread at the repeating action of stress. Some hard particles spall. While under the severe wear condition of heavy loads, the surface of GCr15 ring is cut and smeared to the surface of TiN-matrix composite coating, which acts as lubricant [23]. So, the wear coefficient under heavy load does not increase, just maintaining a value almost equal to that under light loads. However, the contacting stress at the wearing interface is high. On the influence of high stress repeated rolling, cracks generate between the layers of coating. Thus the failure form of TiN-matrix composite coating under heavy loads is cracking between inter-lamellae.

5 Conclusions

1) TiN-matrix composite coating with about 300 μm in thickness was prepared by reactive HVOF spraying. The TiN-matrix coating has lamellar structure and is well bonded with the substrate. The micro-hardness of the coating under heavy loads is relative high.

2) TiN-matrix composite coating prepared by reactive HVOF spraying exhibits an excellent corrosion resistance. Its corrosion potential is positive and passivation zone is broad, which indicates that the coating has a good stability and an excellent protection.

3) The wear coefficient of TiN-matrix composite coating under loads of 196, 294 and 735 N maintains at 0.49−0.5. The wear mechanisms under light loads and heavy loads are three-body abrasive wear. The failure

form of TiN-matrix composite coating under light loads is particle spallation due to the stress concentration, while that of coating under heavy loads is cracking between inter-lamellae.

References

[1]   STOIBER M, PANZENBŐCK M, MITTERER C, LUGMAIR C. Fatigue properties of Ti-based hard coatings deposited onto tool steels [J]. Surf Coat Technol, 2001, 142−144: 117−124.

[2]   MOTTE P, PROUST M, TORRES J, GOBIL Y, MORAND Y, PALLEAU J, PANTEL R. TiN-CVD process optimization for integration with Cu-CVD [J]. Microelectronic Eng, 2000, 50: 369−374.

[3]   OZDEMIR I, HAMANAKA I, HIROSE M, TSUNEKAWA Y, OKUMIYA M. In situ formation of Al−Si−Mg based composite coating by different reactive thermal spray processes [J]. Surf Coat Technol, 2005, 200: 1155−1161.

[4]   BORGIOLI F, GALVANETTO E, GALLIANO F P, BACCI T. Sliding wear resistance of reactive plasma sprayed Ti–TiN coatings [J]. Wear, 2006, 260: 832−837.

[5]   INGO G M, KACIULIS S, MEZZI A, VALENTE T, CASADEI F, GUSMANOA G. Characterization of composite titanium nitride coatings prepared by reactive plasma spraying [J]. Electro Acta, 2005, 50: 4531−4537.

[6]   BACCI T, BERTAMINI L, FERRARI F, GALLIANO F P, GALVANETTO E. Reactive plasma spraying of titanium in nitrogen containing plasma gas [J]. Mater Sci Eng A, 2000, 283: 189−195.

[7]   KOBAYASHI A. Formation of TiN coatings by gas tunnel type plasma reactive spraying [J]. Surf & Coat Tech, 2000, 132: 152−157.

[8]   FENG W R, YAN D R, HE J N, ZHANG G L, CHEN G L, GU W C, YANG S Z. Microhardness and toughness of the TiN coating prepared by reactive plasma spraying [J]. Appl Surf Sci, 2005, 243: 204−213.

[9]   GRENIER S, SHANKER K, TSANTRIZOS P, AJERSCH F. Deposition of TiN films using a thermal plasma reactive forming technology [J]. Surf Coat Technol, 1996, 82: 311−316.

[10]   FENG W R, YAN D R, HE J N, LI X Z, DONG Y C. Reactive plasma sprayed TiN coating and its tribological properties [J]. Wear, 2005, 258: 806−811.

[11]   LI J F, LIAO H, NORMAND B, CORDIER C, MAURIN G, FOCT J, CODDET C. Uniform design method for optimization of process parameters of plasma sprayed TiN coatings [J]. Surf Coat Technol, 2003, 176: 1−13.

[12]   GALVANETTO E, GALLIANO F P, BORGIOLI F, BARDI U, LAVACCHI A. XRD and XPS study on reactive plasma sprayed titanium-titanium nitride coatings [J]. Thin Solid Films, 2001, 384: 223−229.

[13]   XIAO L S, YAN D R, HE J N, ZHU L, DONG Y C, ZHANG J X, LI X Z. Nanostructured TiN coating prepared by reactive plasma spraying in atmosphere [J]. Appl Surf Sci, 2007, 253: 7535−7539.

[14]   MAO Z P, MA J, SUN B D, WANG J. Properties of TiN-matrix coating deposited by reactive HVOF spraying [J]. J Coat Technol Res, 2009, 6(2): 243−250.

[15]   MERZHANOV A G. History and recent developments in SHS [J]. Ceram Int, 1995, 21: 371−379.

[16]   MERZHANOV A G. Combustion processes that synthesize materials [J]. J Mater Process Tech, 1996, 56: 222−241.

[17]   YE Da-lun. Handbook of mineral thermodynamic data [J]. Beijing: Metallurgical Industry Press, 1981. (in Chinese)

[18]   YING Sheng. Advanced ceramics and their applications [M]. Beijing: Beijing Science and Technology Press, 1990. (in Chinese)

[19]   GONG J H, GUAN Z D. Effect of microcracking on the energy-balance relationship for hardness testing of ceramics [J]. Mater Let, 2001, 49: 180−184.

[20]   BOLELLI G, LUSVARGHI L, MANFREDINI T, PIGHETTI MANTINI F. Comparison between plasma- and HVOF-sprayed ceramic coatings. Part I: Microstructure and mechanical properties [J]. Int J Surf Sci Eng, 2007, 1(1): 38−61.

[21]   DHIMAN R, CHANDRA S. Freezing-induced splashing during impact of molten metal droplets with high Weber numbers [J]. Int J Heat Mass Trans, 2005, 48: 5625−5638.

[22]   VALENTE T, GALLIANO F P. Corrosion resistance properties of reactive plasma-sprayed titanium composite coatings [J]. Surf Coat Technol, 2000, 127: 86−92.

[23]   BOLELLI G, CANNILLO V, LUSVARGHI L, MANFREDINI T. Wear behaviour of thermally sprayed ceramic oxide coatings [J]. Wear, 2006, 261: 1298−1315.

反应超音速喷涂制备 TiN 基复合涂层及其
腐蚀磨损性能

马 静 [1,2,3]，闫冬青 [1]，胡建文 [1]，张 欣 [1]，李 扬 [1]

1. 河北科技大学 材料科学与工程学院，石家庄 050018；
2. 河北科技大学 河北省材料近净成形技术重点实验室，石家庄 050018；
3. 北京理工大学 爆炸科学与技术国家重点实验室，北京 100081

摘　要：采用反应超音速喷涂方法在 45#钢基体上制备 TiN 基复合涂层，并对涂层的显微结构、相成分、显微硬度和在 3.5%NaCl 溶液中的腐蚀行为和耐磨性进行研究。结果表明，TiN 复合涂层与基体结合良好，在较大载荷下显微硬度较高。TiN 基复合涂层的耐蚀性优异，其腐蚀电位较正，钝化区很宽，这表明涂层在电解液中很稳定，有效地保护了基体。磨损实验表明在 196、294 和 735 N 的载荷下摩擦因数基本保持在 0.49~0.5。磨损机制为三体磨料磨损，轻载荷下的失效形式为应力集中造成的涂层颗粒剥落，而在重载荷下为涂层间的开裂。

关键词：反应超音速喷涂；TiN 基陶瓷涂层；耐腐蚀性；耐磨性

(Edited by Xiang-qun LI)