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Pulsed DC plasma enhanced chemical vapor deposited TiN/ Ti(C,N) multilayer coatings①

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[Abstract] TiN single coatings and TiN/ Ti(C,N) multilayer coatings deposited on Cr12MoV substrate have been completed by pulsed DC plasma enhanced chemical vapor deposition(PCVD) process. The SEM, XRD and microvicker's hardness as well as the indentation test were used to study the microstructure and mechanical properties of TiN/ Ti(C,N) multilayer coatings. The results show that TiN/ Ti(C,N) coatings are fine and have free-column structure, and carbon atoms take the place of some nitrogen atoms in Ti(C,N) coatings when lower flow ratio of CH_4 is used. The microvicker's hardness and interfacial adhesion between TiN/ Ti(C,N) coatings and Cr12MoV substrate increases more obviously than that of TiN single hard coatings due to the more dense and free-column structure when process is optimized.

[Key words] PCVD; TiN/ Ti(C,N) multilayer coating; microstructures; properties
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1 INTRODUCTION

Various coatings deposition techniques, such as PVD, CVD, PCVD, IBED and PSII have been used to improve the wear-resistance, corrosion-resistance as well as elevated anti-oxidation behavior of surface of steels, for instance, cutting tool or die steels and non-ferrous metals in recent years[1~3]. Among them PCVD has been considered as the promising method for hard coatings deposition. The advantages of this process mainly include the low deposition temperature, ability of suppressing arc problem, process parameters being chosen widely, independently of temperature. Especially the small hole and narrow stitch can be coated uniformly. Therefore, some authors[4,5] have investigated this technique. Up to now, the hard coatings, for example TiN, TiC, TiCN, TiSiN and TiAlN deposited on different substrates by this technique have been synthesized[6~8]. However, the structure and properties of the above single coatings are still not satisfied. For instance, the poor adhesion result from the marked difference of mechanical and physical properties between substrate and coatings materials is still not well solved, which will limit the application of coatings[9].

The multilayer coatings TiN/ Ti(C, N) by PCVD is developed in this paper to optimize the properties of coatings. Prior to deposition, the plasma nitriding has been performed for the substrate so that the high load-carrying capacity has been obtained.

2 EXPERIMENTAL

The plasma nitriding and TiN/ Ti(C,N) coatings were performed in industrial scale set-up (reactor space d450 mm × 650 mm) with pulsed DC power. The working gases were H_2, N_2, CH_4 and Ar, which are adjusted by mass flow controller (MFC). The $TiCl_4$ was led into the reactor as a precursor by a H_2 carrier gas. The plasma was generated by a pulsed DC discharge power. Fig.1 shows the output of pulsed DC voltage. Its frequency changed from 0 to 33 kHz. The ratio of pulse on time∶ pulse off time is 1∶1. Pulse voltage varies within 0 ~ 1 200 V.

The samples made from cold-working die steel Cr12MoV (d30 mm × 10 mm) were polished as a substrate materials. After quenched and tempering at 530 ℃, its hardness was HRC53 ±2. Prior to deposition, the samples were cleaned and sputtered in H_2 + Ar gases with a high voltage (about 1 000 V). Then plasma nitriding with $V(N_2)∶V(H_2) = 1∶3$, pressure 500 ~ 600 Pa, nitriding temperature 520 ℃ for 1 h is completed.

The deposition condition for TiN and TiN/ Ti(C,N) coatings was listed in Table 1. Effect of flow ratio of CH_4 on the structure and properties of TiN/ Ti(C,N) were investigated.

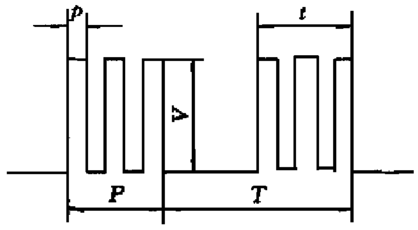

Fig.1 Voltage output for pulsed DC plasma

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Table 1 Process parameters for TiN and TiN/Ti(C, N) hard coatings

Coating	Pulse votage / V	Pulse frequency / kHz	Pulse on time : off time	Deposition temperature/ ℃	Deposition time/ h	$V(H_2)$: $V(N_2)$: V(Ar) : V(TiC)l_4
TiN	650	17	1 : 1	530	2.0	6 : 3 : 1 : 1
TiN of TiN/Ti(C, N)	650	17	1 : 1	530	0.5	6 : 3 : 1 : 1
Ti(C, N) of TiN/Ti(C, N)	650	17	1 : 1	530	1.5	6 : 3 : 1 : 1

$V(CH_4)$: $V(N_2 + CH_4)$ are 20 %, 30 %, 50 %, respectively

In this paper, the X-ray diffraction (XRD), scanning electron micrographs (SEM) were employed to analyze the crystallogram and structure of coatings. Hardness was measured with Vickers hardness meters. The indentation test, i.e. a modified hardness tester of using a diamond-spherical stylus under different load pressed to the surface of the coatings was used to evaluate the adhesion of coatings. The critical load was corresponding to the coatings being spalled off from the substrate was defined as adhesion of the coatings.

3 RESULTS AND DISCUSSION

3.1 Structure of TiN/Ti(C,N) multilayer coatings

The SEM fractographs of TiN single coatings and TiN/Ti(C, N) multilayer coatings are presented in Fig.2. The non-compact and typical column structure could be found in TiN coatings. However, the dense and free-column structure appeared in TiN/Ti(C, N) coatings. There was also not obviously separated layer between TiN and Ti(C, N). It implies that the transition of deposition from TiN to Ti(C, N) was continuous. Because the TiN and Ti(C, N) were all FCC compounds, the carbon and nitrogen atoms could displace each other. As a result, the Ti(C, N) compound was formed[11]. A comparison of surface morphology between TiN and Ti(C, N) is shown in Fig.3.

The grain size of TiN and TiN/Ti(C, N) were close when 20 % CH_4 was used. The grain size increased with increasing the flow ratio of CH_4 (> 30 %). This was probably due to the disconnection of Ti(C, N) to TiN and TiC (Fig.4). But from Fig.2, it could be seen that the deposition rates of TiN and Ti(C, N) were almost same.

The XRD patterns of TiN and Ti(C, N) with different CH_4 flow ratio are given in Fig.4. They all show the same diffraction peaks and NaCl crystalline structure could be characterized in these cases. They also exhibit the (200)-preferred orientation. So it could be suggested that the carbon atoms would take the place of some nitrogen atoms in Ti(C, N). On the other hand, the radius of carbon atom ($R_c = 0.077$ nm) is larger than that of nitrogen atom ($R_n = 0.071$ nm), the diffraction peaks of Ti(C, N) tended to deviate to low degree compared with that of TiN. The deviation extent increased with increasing the CH_4 flow ratio. But the diffraction peaks (111) and (200) of Ti(C, N) were broadened when CH_4 flow ratio was greater (30 %). The reason may be due to the disconnection of Ti(C, N) to TiN and TiC, the

Fig.2 SEM fractographs of TiN and TiN/Ti(C, N) coatings
(a) —TiN; (b) —TiN/Ti(C, N) with 20 %CH_4; (c) —TiN/Ti(C, N) with 50 %CH_4

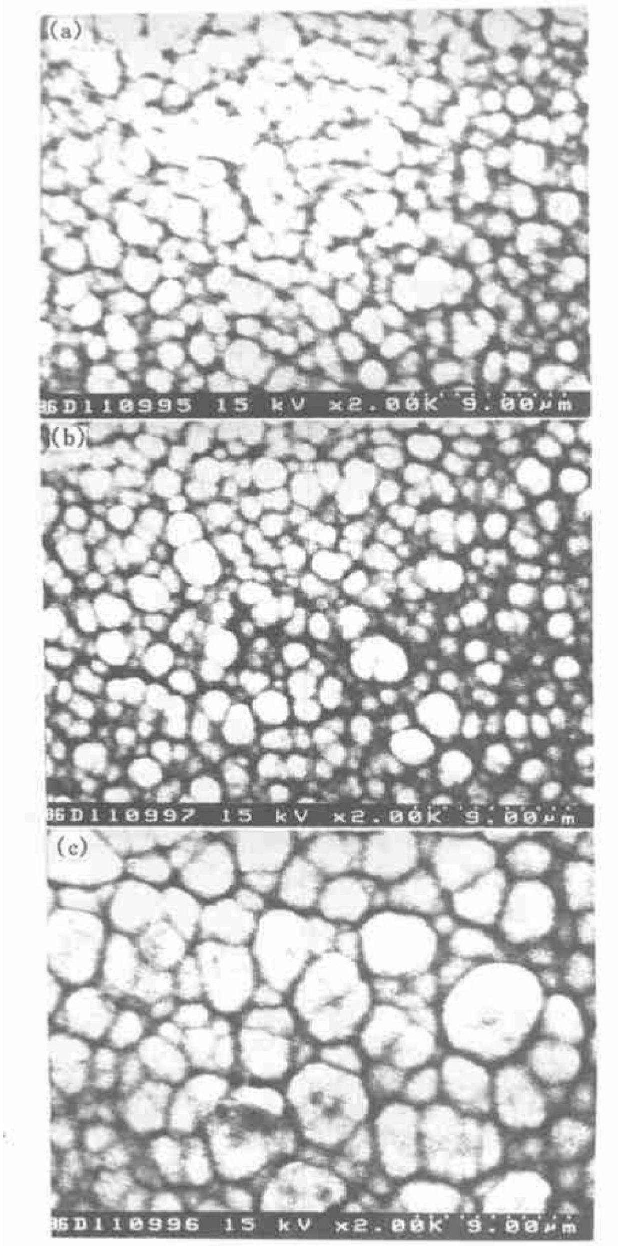

Fig.3 SEM surface micrographs of TiN and TiN/ Ti(C, N) coatings
(a) —TiN; (b) —TiN/ Ti(C, N) with 20 %CH_4 ;
(c) —TiN/ Ti(C, N) with 50 %CH_4

diffraction peaks of TiN and TiC would lead to the brooding of the peaks.

3.2 Microhardness of TiN/ Ti(C,N) coatings

Fig.5 shows the effects of flow ratio of CH_4 on Vickers hardness of TiN / Ti(C, N) multilayer coatings. The hardness was almost linearly increased with increasing the flow ratio of CH_4. So the hardness of TiN coatings could be enhanced with TiN/ Ti(C, N) multilayer coatings. It is certainly useful to improve the wear resistance of hard coatings.

3.3 Adhesion of TiN/ Ti(C,N) coatings

The indentation adhesion of TiN and TiN/ Ti (C, N) coatings deposited on Crl2MoV substrate is presented in Fig.6. The adhesion of TiN/ Ti (C, N)

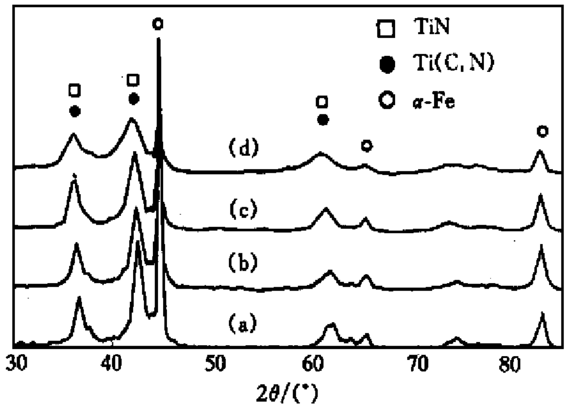

Fig.4 XRD patterns of TiN and TiN/ Ti(C, N) hard coatings
(a) —TiN; (b) —TiN/ Ti(C, N) with 20 % CH_4 ;
(c) —TiN/ Ti(C, N) with 30 % CH_4
(d) —TiN/ Ti(C, N) with 50 % CH_4

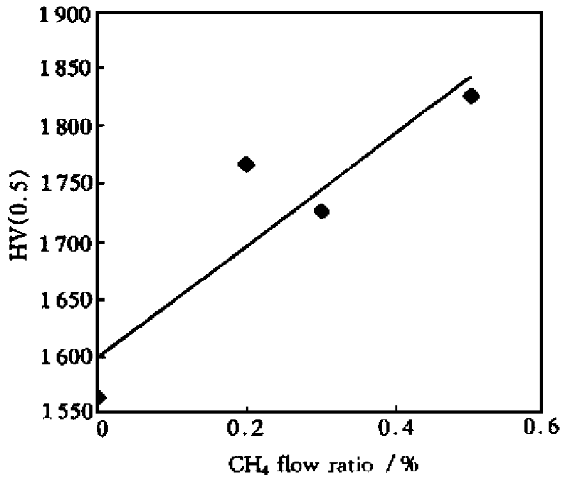

Fig.5 Relation of microhardness of TiN/ Ti(C, N) coatings vs CH_4 flow ratio

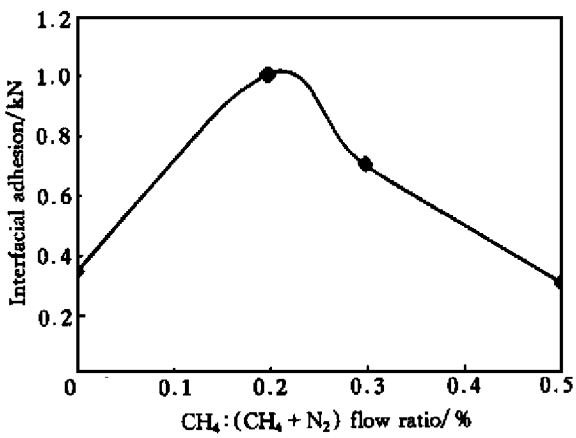

Fig.6 Effect of CH_4 flow ratio on interfacial adhesion between TiN/ Ti(C, N) and Crl2MoV

coatings was enhanced more obvious than that of TiN coatings. One reason is the moderate transition of mechanical properties from substrate to TiN/ Ti(C, N) coatings due to the plasma nitriding and multilayer coatings design. In addition, it could be found from Fig.2 that the dense and free-column structure of TiN/ Ti(C, N) coatings will attributed to the increase of adhesion. Fig.7 gives the comparison of indentation morphology between TiN and Ti(C, N) with 20 % CH_4 used. It shows the spalling off and radial cracks for TiN coatings. However, the indentation morphology of TiN/ Ti(C, N) is still perfect. It indicates that the adhesion of TiN/ Ti(C, N) is greater than that of TiN. But with the increase of CH_4 flow ratio, the adhesion of TiN/ Ti(C, N) was increased first and then decreased, the maximum adhesion was reached when 20 % CH_4 was used. The poor adhesion of TiN/ Ti(C, N) coatings when 50 % CH_4 was used may be resulted from the grain coarsening of TiN/ Ti(C, N) (Fig.3(c)). Therefore, in order to improve the wear-resistance of hard coatings, the hardness and adhesion of hard coatings should be considered together. The plasma nitriding and PCVD TiN/ Ti(C, N) duplex treatment are suggested to be the promising techniques for surface modification.

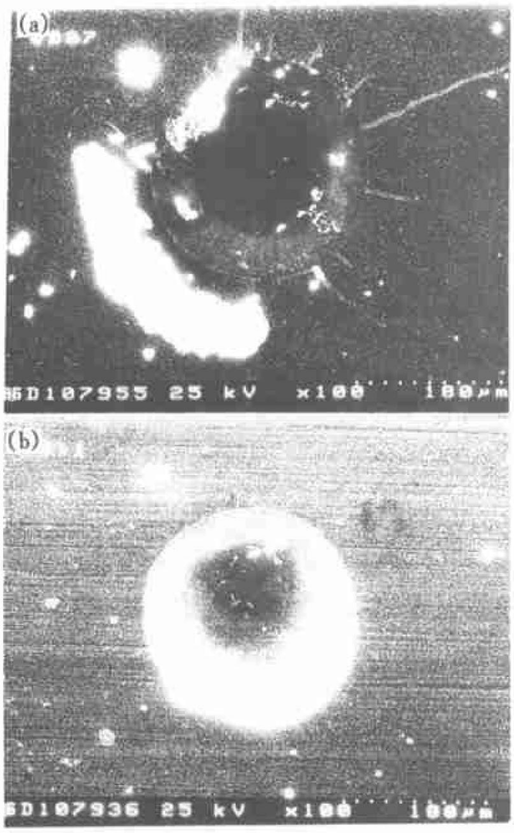

Fig.7 Comparison of indentation morphology between TiN and TiN/ Ti(C, N) coatings at pressing load of 1 kN
(a) —TiN; (b) —TiN/ Ti(C, N) with 20 % CH_4

4 CONCLUSIONS

1) The high quality coatings of TiN/ Ti(C, N) deposited by pulsed DC plasma chemical vapor deposition has been obtained. When process is optimized, the vickers hardness and indentation adhesion of TiN/ Ti(C, N) multilayer coatings are increased compared with that of TiN single coatings. In this case, the dense and free-column structure of TiN/ Ti(C, N) coatings and moderate transition of properties between substrate and coatings play an important role.

2) XRD analyses indicate that the TiN/ Ti(C, N) multilayer coating is FCC crystalline structure. The carbon atoms get into the Ti(C, N) coatings by taking the place of some nitrogen atoms at low flow ratio of CH_4; but Ti(C, N) will disconnect to the TiC and TiN phases at high flow ratio of CH_4.

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