ELSEVIER

Surface and Coatings Technology 132 (1998) 26–30

SURFACE & COATINGS TECHNOLOGY

www.elsevier.nl/locate/surfcoat

Plasma CVD of hard coatings Ti(CNO) using metallo-organic compound $Ti(OC_3H_7)_4$

Shi Yulong*, Peng Hongrui, Xie Yan, Xie Guangwen, Zhao Cheng, Li Shizhi

Thin Films Laboratory, Qingdao Institute Chemical Technology, 53 Zhengzhou Road, 266042 Qingdao, PR China

Received 29 November 1999; accepted in revised form 19 June 2000

Abstract

The use of the metallo-organic compound $Ti(OC_3H_7)_4$ with auxiliary heating plasma CVD (MOPCVD) of hard coatings Ti(CNO) is reported. The harmful effect of chlorine on the film properties and on the PCVD equipment could be avoided in this way. The deposition rate decreased from 2.4 to 1.2 μm/h when the oven temperature ranged from 120 to 420°C, and the maximum microhardness value of the Ti(CNO) coatings can reach 16 000 MPa. The coatings were analyzed with SEM and XRD. The coatings showed the typical columnar structure. The XRD analysis revealed that the d(200)-values of the Ti(CNO) films decreased from 0.2130 to 0.2123 nm with increasing the oven temperature. The chemical composition of the films was measured by XPS. The films were mainly composed of titanium, carbon, nitrogen and oxygen. The bonding energies of Ti2p3/2 and Ti2p1/2 of the Ti(CNO) films were 458.70 and 463.75 eV, respectively. The cutting tests have shown that the average lifetime of ϕ65 mm HSS drills coated with the MOPCVD-Ti(CNO) was 7.3 times as long as that of uncoated ones; the average lifetime of ϕ65 × 5 mm HSS milling cutter coated increased by a factor of 8. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Plasma CVD; Hard coatings; Metallo-organic compound

1. Introduction

Plasma CVD (PCVD) is an appropriate method for the deposition of wear-resistant coatings because it can provide the lower deposition temperature and is convenient to adjust and alternate the precursors, which results in the growth of different hard coatings, such as TiN, TiC, Ti(CN), Al_2O_3, etc. [1,2]

However, the precursor used for the deposition of TiN, TiC and Ti(CN) is $TiCl_4$ and the chlorine is harmful to the coatings properties and the PCVD equipment. Recently the metallorganic compounds, such as $Ti(OC_2H_5)_4$, $Ti(OC_3H_7)_4$, $Ti(N(CH_3)_2)_4$ and $Ti(N(C_2H_5)_2)_4$, are used for the deposition of hard coatings, and the deposition temperature can be lowered, and the harmful effect of chlorine on the coatings properties and on the equipment could be avoided [3–7].

* Corresponding author. Tel.: +86-532-4022664; fax: +86-532-4870041.
E-mail address.: ylshi@public.qd.sd.cn (Y.L. Shi).

0257-8972/00/$ - see front matter
PII: S0257-8972(00)00743-X

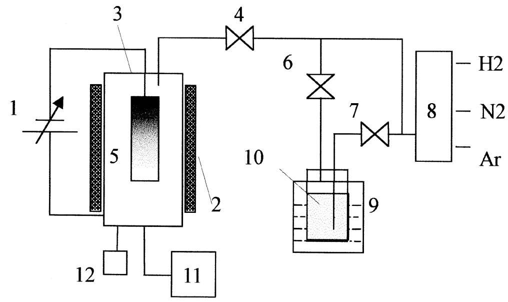


Fig. 1. Experimental set-up of MOPCVD equipment: (1) d.c. power supply; (2)auxiliary heating; (3) reactor; (4,6,7) valves; (5) workpiece; (8) mass-flow meter; (9) thermostat; (10) MO precursor; (11) vacuum pump; (12) vacuum gauge.

In this paper the Ti(CNO) coatings deposited by means of metallo-organic compound $Ti(OC_3H_7)_4$ and their applications are reported.

2. Experimental

A d.c.-plasma apparatus used in this study is shown schematically in Fig. 1, which was earlier reported in detail [7]. The reactive gases were $Ti(OC_3H_7)_4$ (99% purity), H_2 and N_2 (both 99.999% purity).

The HSS(W18Cr4V: C 0.70–0.80; Mn 0.10–0.40; $P \leq 0.030$; $S \leq 0.030$; Si 0.20–0.40; Cr 3.80–4.40; V 1.00–1.40; W 17.50–19.0; Mo ≤ 0.30; the others Fe) specimens ($12 \times 10 \times 3$ mm) with base hardness of 64–65 HRC were polished with emery paper. The surface roughness was Ra 0.4 μm. The HSS specimens were ultrasonically cleaned in acetone. After cleaning, they were mounted on the cathode in the reaction chamber. The twist drills, 6 mm in diameter, and the milling cutters with an outer diameter of 65 mm made of HSS with base hardness of 63–65 HRC, also were mounted on the cathode after cleaning. The deposition parameters are summarized in Table 1.

After the deposition the morphology and crystal structure of the films were investigated by means of scanning electron microscopy (model: JSM-840, made in Japan) and X-ray diffraction (model: D/max-rA, made in Japan). X-Ray photoelectron spectroscopy (model: MICROLAB MKII, made in UK) was used to determine the chemical composition of the films. A Vickers indenter (model: Hv-1000, made in China) was used to measure the hardness of Ti(CNO) films. The tests of the twist drills and milling cutters were carried out in factories.

3. Results and discussions

The color of the films deposited by MOPCVD is dark gray. The deposition rate changed with deposition parameters. The films hardness was measured with a Vickers indenter at a load of 0.196 N. The measurements were performed on the surface of the films of more than 3 μm thickness. The microhardness varied between $Hv_{0.2}$ 9000 and 16 000 MPa (for a detailed report see earlier work [8]), which is lower than that of PCVD with precursor $TiCl_4$.

Fig. 2 shows the effect of the oven temperature on the deposition rate of the Ti(CNO) films. With increasing the oven temperature, the deposition rate varied from 2.4 to 1.2 μm/h, this is because adsorption of the substrate decreased with the temperature increment.

The cross-sectional and surface morphology of the Ti(CNO) films on HSS substrates examined by scanning electron microscopy (SEM) were shown in Fig. 3a,b. It was found that the columnar structure, and grain size was approximately 1–2 μm, which is the same as TiN coated with PCVD using $TiCl_4$.

Fig. 4 shows the diffraction pattern of the films deposited from $Ti(OC_3H_7)_4$, determined by X-ray diffraction (XRD), using CuKα radiation. The reflections in the spectrum were in accordance with the various planes (111), (200) and (220) of the Ti(CNO) phase. In addition to those reflections related to the film, the sharp reflections of the substrate material αFe also appear in the pattern. Because some C–H fragments or crack products of the metallorganic precursors have been incorporated in the films [4,6], the crystallization is not as good as TiN coated with PCVD using $TiCl_4$.

Through XRD examination, it is found that the deposition temperature effected the crystallization of the Ti(CNO). Fig. 5 showed that d(200)-values of the films Ti(CNO) decreased from 0.2130 to 0.2123 nm. It is assumed that with increasing the oven temperature, the undissociated organic impurities in the films decreased, and the crystallization was better.

Table 1
The deposition parameters of MOPCVD — Ti(CNO)

Oven Temp. (°C)	Pressure (Pa)	H_2 to N_2	Voltage (V)	Current (mA/cm^2)	Time (min)	$Ti(OC_3H_7)_4$ (mol/min)
120–420	133–266	4:1–1:10	650–1200	0.3–1.2	60–180	0.8×10^{-3}

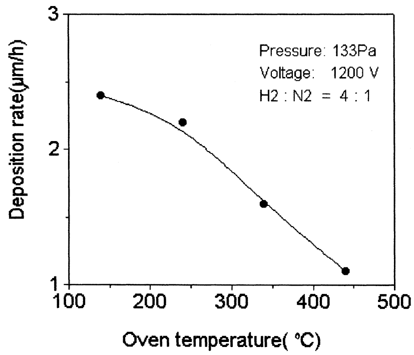


Fig. 2. The effect of oven temperature on the deposition rate of Ti(CNO) film.

The chemical composition of the films were measured by X-ray photoelectron spectroscopy (XPS). The films were mainly composed of titanium, carbon, nitrogen and oxygen. Two peaks of Ti2p were found at 458.70 and 463.75 eV, which corresponded to Ti2p3/2 and Ti2p1/2, respectively. According to Louw et al. [9], the Ti2p3/2 and Ti2p1/2 positions of TiN films coated by PVD are at 454.95 and 460.55 eV, respectively. The involvement of strong electronegative element O into the film would increase the binding energies and shift them toward higher energy side. Owing to this, we attribute the 458.70 and 463.75 eV peaks to the chemical state of Ti2p in the Ti(CNO), as shown in Fig. 6.

4. Tests of MOPCVD-Ti(CNO) coatings

4.1. Twist drills

Twist drills can be used to justify the feasibility of using MOPCVD-Ti(CNO) for coating HSS tools at a relatively low cost. The formal test was carried out in The Measurement and Cutting tools factory of Beijing, China. Six twist drills made of HSS with diameters of 6 mm were tested, three of them were coated in our apparatus to give a Ti(CNO) coating 3 μm thick, and three were uncoated for comparison. The test conditions and results are listed in Tables 2 and 3, respectively. The failure criterion is that the flank wear of the drill is equal to 0.4 mm.

From the test the improvement in tool performance is obvious. The average lifetime of the coated drills was approximately 7.3 times that of the uncoated ones.

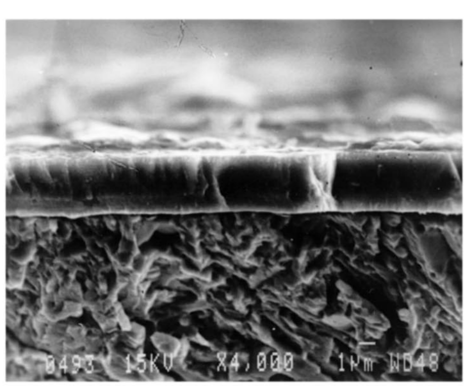
4.2. Three-face milling cutter

Three-face mills made of high speed steel(W18Cr4V) with outer diameter of 65 mm were coated with MOPCVD-Ti(CNO) films to give 3 μm thickness. The working conditions are listed in Table 4 and working results in Table 5. The failure criterion is that the surface roughness of the workpiece is equal to 6.3 μm. It is found that the lifetime of three-face milling cutters coated with MOPCVD-Ti(CNO) increased by a factor of 8.

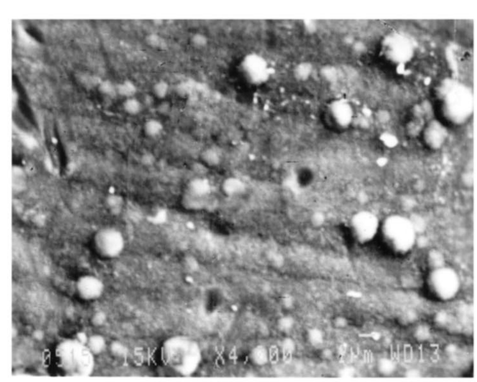
5. Conclusions

Ti(CNO) coatings have been successfully deposited on HSS substrates by means of plasma chemical vapor deposition (MOPCVD) with auxiliary heating using the metallo-organic compound $Ti(OC_3H_7)_4$. The maximum microhardness of the coatings can reach 16 000 MPa. The coatings showed the typical columnar structure. The d(200)-values of the films varied with the oven temperature.

The cutting tests have shown that the average lifetime of ϕ6-mm HSS drills coated with MOPCVD-Ti(CNO) was 7.3 times as long as that of uncoated ones; the



(a)



(b)

Fig. 3. SEM micrographs of cross-sectional and surface morphology of the film Ti(CNO) on HSS substrates.

average lifetime of $\phi 65 \times 5$ mm HSS milling cutter coated increased by a factor of 8.

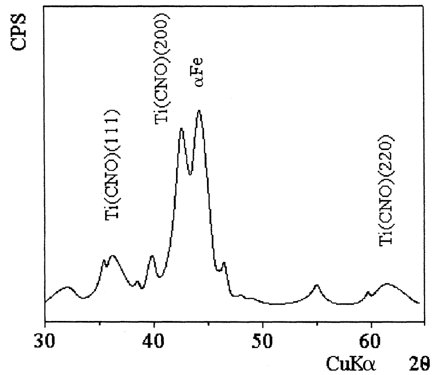


Fig. 4. X-Ray diffraction pattern of Ti(CNO) film.

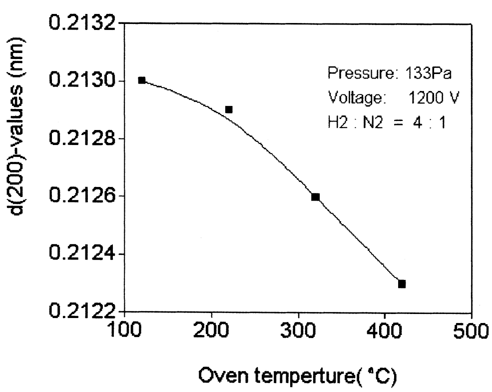


Fig. 5. The d(200)-values varied with the oven temperatures.

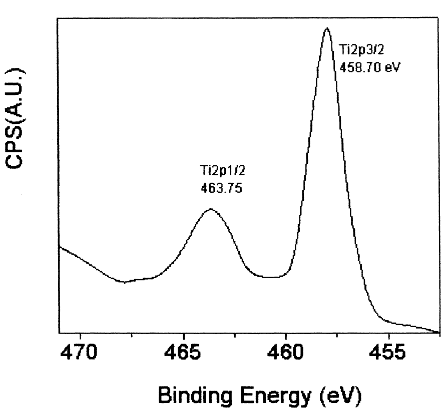


Fig. 6. XPS analysis of the Ti(CNO) film.

Table 2
Test conditions for twist drills

Item	Specification
Material	40Cr (C 0.37–0.44, Si 0.17–0.37, Mn 0.50–0.80, Cr 0.80–0.10, the others Fe)
Hardness	HB213
Rotation speed of main spindle	1850 rev./min
Cutting speed	35 m/min
Feed	0.2 mm/r
Cooling	Emulsion
Working mode	Blind hole; hole depth 18 mm

Table 3
Test results for twist drills

Test no.	Holes drilled by	
	Coated drills	Uncoated drills
1	19	5
2	28	2
3	34	4
Average	27	3.7

Table 4
Test condition for three-face milling cutters

Item	Specification
Workpiece name	Cotton drum
Material	Aluminum alloy ZL 106 (Fe 0.6–0.8; Zn 0.2; Sn 0.01; Pb 0.05; the others Al)
Cutting conditions	
Rotation speed of main spindle	600 rev./min
Cutting speed	120 m/min
Feed	475 mm/min
Cooling	Air
Cutting depth	5 mm

Acknowledgements

We would like to acknowledge the sponsorship of The Natural Science Foundation of Shandong Province of China.

Table 5
Test results for three-face mills

Workpieces cutt by coated milling cutter						Average
1	2	3	4	5	6	
300	260	180	240	220	240	240
Workpieces cutt by uncoated milling cutter						30

References

[1] S.Z. Li, W. Huang, H.S. Yang, Z.S. Wang, Plasma Chem., Plasma Process. 4 (1984) 147.

[2] K.T. Rie, T. Lampe, S. Stramke, Z. Werkstofftech. 17 (1986) 109.

[3] H.R. Stock, P. Mayr, in: G.W. Gullen (Ed.), Proc.10th. Int.Conf. CVD, , 1987, pp. 1174–1180.

[4] C. Taeschner, K. Bartsch, A. Leonhardt, Surf. Coat. Technol. 59 (1993) 207–211.

[5] K.-T. Rie, A. Gebauer, J. Woehle, Surf. Coat. Technol. 74-75 (1995) 362–368.

[6] H. Berndt, A.-Q. Zeng, H.-R. Stock, P. Mayr, Surf. Coat. Technol. 74-75 (1995) 369–374.

[7] Y.L. Shi, H.R. Peng, S.Z. Li, Surf. Technol., in Chinese 5 (1997) 4–6.

[8] Y.L. Shi, H.R. Peng, S.Z. Li, Vac. Sci. Technol., in Chinese 20 (1) (2000) 60–62.

[9] C.W. Louw, I. LeR. Strydom, K. van den Heever, Surf. Coat. Technol. 49 (1991) 348–352.