

## Effects of the gas mixture on the characteristics of PACVD TiN coating of hot-work tool steel

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Titanium nitride (TiN) coatings were deposited on hot-work steel (DIN 1.2367) by plasma-assisted chemical vapor deposition (PACVD) and the influence of different N<sub>2</sub>/H<sub>2</sub> gas flow ratio on the layer properties were investigated. Scanning electron microscopy studies shows that the growth rate increases with increasing N<sub>2</sub>/H<sub>2</sub> gas flow ratio. It was learned the TiN layers are nearly stoichiometric, except for low N<sub>2</sub> gas flows. Grazing incidence X-ray diffraction (GIXRD), scanning electron microscopy (SEM) and pin-on-disk test were used to evaluate the microstructure as well as tribological properties such as friction, wear, and hardness. It was also revealed that by increasing the flow ratio, the grain size of the TiN coatings decreased. A hardness of 1710 HV<sub>0.05</sub> was obtained when the layer was fabricated at the higher flow ratios.

**Key words:** PACVD, TiN coating, Tribology, Gas mixture

### Introduction

Steel alloy DIN 1.2367 (X38CrMoV5) is currently one of the most often used chromium-molybdenum tool steels, which contains higher molybdenum content. This steel has various applications, such as gears, shear blades, mandrels punches and tooling dies. The mechanical, friction and wear properties of this have been extensively investigated as a function of tempering treatment and associated microstructure [1, 2].

The PACVD technique is an appropriate method to deposit wear and corrosion resistant hard coatings which have excellent properties for several applications. In comparison to PVD methods, it offers the possibility of coating work pieces with complicated shapes homogeneously. Other advantages of PACVD method are the high adhesion and the good morphology of the layers. Tools deposited with hard coatings, like TiN, TiCN, TiC, have already been used successfully for many industrial applications [3-5]. The PACVD process is influenced by several process parameters, like discharge voltage, current density, gas pressure and gas composition and flow rate [6, 7].

In the present research, the influence of the N<sub>2</sub>/H<sub>2</sub> gas flow ratio on properties of PACVD TiN coating on the hot-work tool steel has been investigated.

### Experimental Details

TiN coatings with compositional gradients were deposited on a DIN 1.2367 (X40CrMoV53) hot-work tool steel substrate using a PACVD coating system equipped with a voltage-controlled pulse generator. The spectrometric analysis of the substrate is shown in Table 1.

During coating, process parameters such as gas flow, wall temperature, voltage duration of pulse-on and pulse-off time and total pressure were monitored. H<sub>2</sub>, Ar, N<sub>2</sub> and TiCl<sub>4</sub> vapor were used as process gases for coating deposition. Total pressure was kept at 2 mbar and substrate temperature was controlled at 420 °C in

**Table 1.** Chemical composition of hot work steel (DIN 1.2367).

ELEMENT	C	Mn	W	Ni	Si	Cr	V	Mo
Wt%	0.49	0.50	0.02	0.24	0.48	5.42	0.52	2.65

**Table 2.** PACVD parameters.

Parameters	Value
Pulsed voltage	650 V
Duty cycle	33%
Temperature	420 °C
PACVD time	1 hr
N <sub>2</sub> /(N <sub>2</sub> +H <sub>2</sub> ) flow ratio	25% , 38%
Total pressure	2 mbar
nitriding time	2 hr
nitriding temperature	420 °C

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order to avoid exceeding the tempering temperature of the hot-work tool steel. Plasma nitriding was used as pre-treatment to decrease hardness gradient between substrate and coating. The processing parameters for plasma nitriding are listed in Table 2. The  $N_2/H_2$  gas flow ratio ( $N_2/(N_2+H_2)$ ) was varied. The crystalline structure of the coating was determined by grazing incidence X-ray diffraction (GIXRD) in the continuous scanning mode using  $CuK_{\alpha}$  radiation ( $\lambda = 0.154056$  nm). The full-width at half-maximum (FWHM) of the Bragg peaks is used to approximate grain size base on the Scherrer formula [8]:

$$D = \frac{0.9\lambda}{\beta \cdot \cos\theta'} \quad (1)$$

Where  $D$  is grain size,  $\beta$  is the FWHM of the Bragg peak, and  $\theta$  is the Bragg reflection angle. The film morphology studied by scanning electron microscopy (SEM). The Vickers hardness of the TiN coatings was measured using a micro-hardness test, within the loading range of 50 g; five micro-hardness tests were performed for each sample to obtain the average values of the hardness. Friction coefficients were measured by pin-on-disc method in normal conditions with loads 10 N and velocity of 0.1 m/s.

## Results and Discussions

Fig.1 illustrates the GIXRD patterns of the coatings deposited at 420 °C using the two gas mixtures. The (200) plane is revealed to be the preferred structure, implying that the TiN coating is deposited via kinetics-limited crystal growth [12] and under thermodynamically stable conditions because the lowest energy surface in the TiN crystal is the (200) plane. The GIXRD pattern also indicates an exclusively face-center-cubic (fcc) structure. TiN possesses a face-centered cubic (fcc) lattice with  $a_0 = 0.4242$  nm. The structure of TiN is closely related to Ti. Nitrogen can be incorporated on the octahedral sites of both the hexagonal close-packed lattice of titanium and the fcc sublattice in titanium nitride and thus form  $TiN_x$ . In stoichiometric TiN, it is assumed that all the octahedral sites are filled with nitrogen [9]. Titanium nitride is an intercalation compound whose stoichiometry in  $TiN_x$  can vary in the range  $0 < x < 1$ .

Fig. 1 shows that by increasing the flow ratio from 25% to 38%, the (220) plane is not thermodynamically stable relative to the (200) and (111) planes and the broad peak of the (220) plane indicates that the grain size decreases. Hence, the specific surface of TiN increases.

Fig. 2 shows that the grain size of TiN decreases nearly linearly with increasing  $N_2$  gas flow.

Only for an  $N_2/H_2$  gas flow ratio of 0.38, the colour of the TiN layers is golden. At lower  $N_2$  gas flows the colour of the TiN layers becomes increasingly brown. Fig. 3 shows the SEM pictures of the TiN layers. A

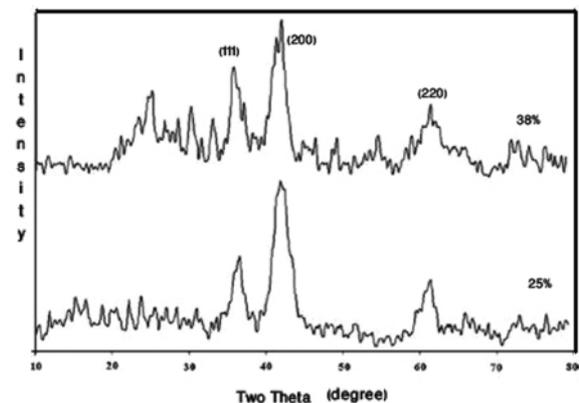


Fig. 1. GIXRD diffraction patterns acquired from the TiNX coatings using the two gas mixtures.

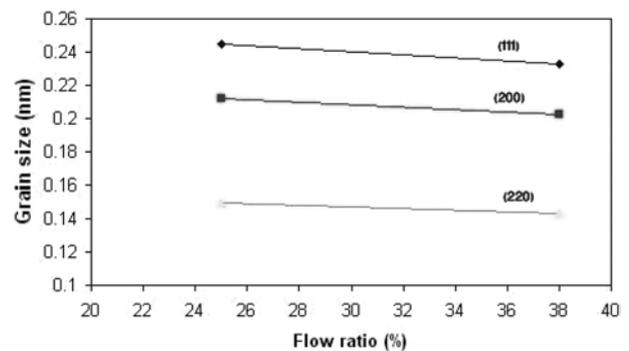


Fig. 2. the grain size changes of TiN coating for different values of flow ratio.

similar effect is obtained in the morphology of the TiN layers. High  $N_2$  gas flows lead to a high surface roughness of the TiN layers, as can be seen in the right-hand pictures. An influence of the flow ratios cannot be observed, although the growth rates are different. The left-hand pictures show the TiN layers deposited at low  $N_2/H_2$  gas flow ratios. A dense TiN layer is grown in 38% but not in 25%, where the TiN layer has a very rough structure.

Current density of TiN layers depends on the  $N_2/H_2$  gas flow ratio. TiN layers deposited in the 38% were shown a current density of 2 mA/cm<sup>2</sup> but in the 25% current density was 1.4 mA/cm<sup>2</sup>. This may correspond to the composition of the TiN layers, as shown in Fig. 4. This proves relation between the Ti/N ratio and the  $N_2/H_2$  gas flow ratio. Two later layers mentioned are not stoichiometric. The Ti/N ratios are nearly 1.8 and 1.3 for the 25% and the 38% respectively. In contrast to the results of Crummenauer *et al.* [10], the variation of the  $N_2/H_2$  gas flows only shows an influence on the Ti/N ratio of the coatings for small values. Because of the similar results in different gas ratios, this result confirms our assumption that the total amount of material in the gas phase is less important for the deposition than the gas composition. The Cl content of the TiN layers shows no apparent dependence on the  $N_2/H_2$  gas flows (Fig. 4).

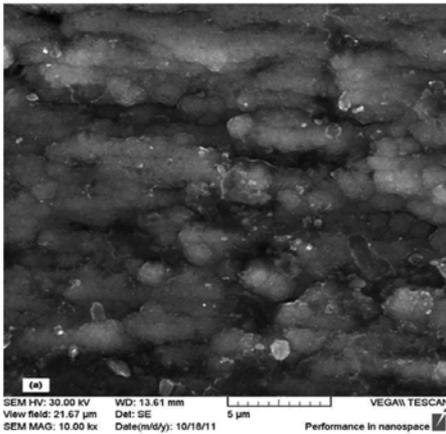


Fig. 3a

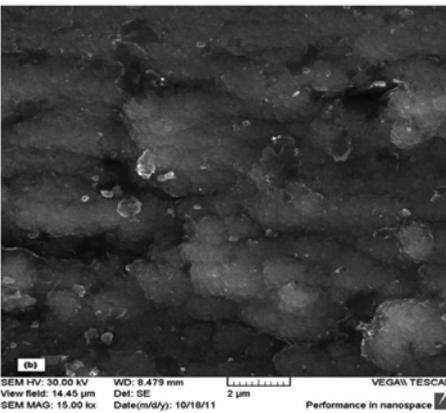


Fig. 3b

Fig. 3. Morphology of TiN layers dependence on the N<sub>2</sub>/H<sub>2</sub> gas flow ratio, evaluated by SEM. a) 38% b) 25%.

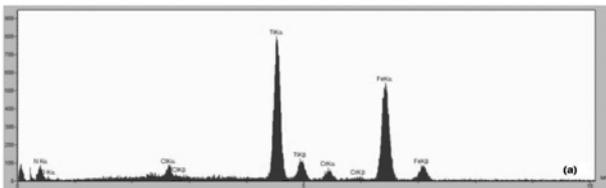


Fig. 4a

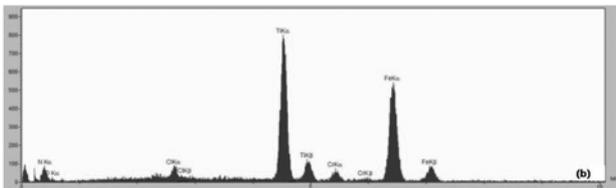


Fig. 4b

Fig. 4. Relation between EDS of TiN layers measured by SEM and the N<sub>2</sub>/H<sub>2</sub> gas flow ratio a) 38% b) 25%.

Fig. 3 shows that films deposited at high N<sub>2</sub>/H<sub>2</sub> ratios are much more homogeneous than those deposited at low ratios.

The friction behaviour of the TiN coatings against ball-bearing steel in ambient air at room temperature is

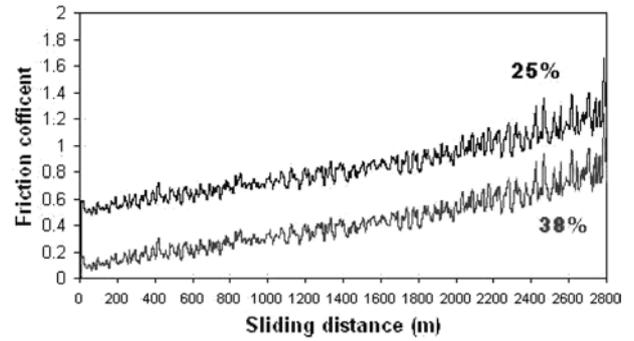


Fig. 5. Friction coefficients of TiN coatings against ball bearing steel at room temperature.

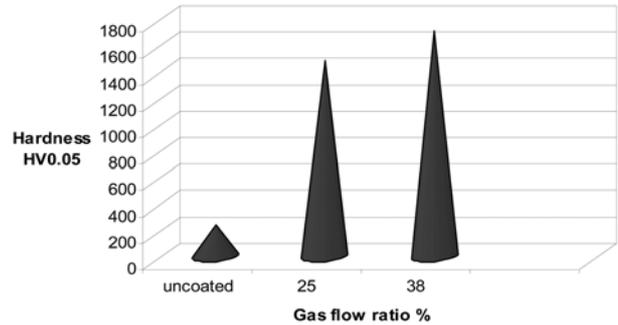


Fig. 6. the hardness of TiN coatings for various flow ratios.

summarized in Fig. 5.

TiN coating friction coefficient containing the lower flow gas remains constant at 1.3 without significant fluctuations, over the whole test period of 2800 m. A similar friction behavior was observed for the TiN coating with 38% with a constant friction coefficient of approximately 0.6. The friction coefficient starts at a value of approximately 0.6, where it remains constant for a sliding distance of approximately 2800 m. After this running-in period, where the friction coefficient is mainly a result of ploughing and polishing of the surfaces in contact, a sharp drop to a value of 0.6 occurs. Then, the friction coefficient remains constant until the end of the test period of 2800 m without significant fluctuations.

The resulting hardness values of the TiN coatings deposited at a temperature of 420 °C with various flow ratios are illustrated in Fig. 6. They varied from the flow ratio of 25% with a hardness of 1485 HV<sub>0.05</sub> to the flow ratio of 38% with a hardness of 1710 HV<sub>0.05</sub>. The hardness of the TiN coatings increased as the flow ratio increased. The reduction of hardness can be attributed to two reasons. By the flow ratio increased, the grain size of the TiN coatings had also decreased (as shown in Fig. 2). Due to the decrease in the grain size, the hardness of the TiN coatings increased. Furthermore, during the growth of the grain size, the chlorine atoms diffused into high angle grain boundaries after exceeding the solubility limit of chlorine in the TiN lattice [11]. Thus, the hardness of the thin films decreased.

## Conclusions

The following conclusions can be drawn from this research:

Applying higher flow ratio of  $N_2/(N_2+H_2)$  resulted in modification of the film morphology as well as its grain size.

The films grown using plasma-assisted processes at 0.38 flow ratios, were generally fine-grained and had a denser structure than 0.25.

Finally, it was found that the surface hardness increased with the flow ratio.

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