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PLASMA ASSISTED CVD USING METALLO-ORGANIC COMPOUNDS AS PRECURSORS

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Abstract-In this work the use of three metallo-organic compounds was investigated with the pulsed DC plasma assisted CVD process to deposit layers on steel substrates and hard metals. The layers have been studied by SEM, XRD, WDX and ESCA. It is shown that chlorine free adhesive titanium carbonitride coatings can be obtained by MOCVD even at substrate temperatures less than 400 °C.

1. Introduction

The TiN-, TiC-, Ti(C,N)- layers or multilayers using TiCl_4 as metal donor have opened up many industrial applications. But for several applications the coating temperatures are still too high and the chlorine from the metal donor causes undesired side effects. Cracking the TiCl_4 in plasma chlorine and chlorine compounds are formed.

For wear and corrosion resistance it is very important to suppress the chlorine which will be built up into the layer during the coating process. With decreasing substrate temperature the chlorine content in the layer increases and reduces the layer quality. Investigations by KIKUCHI et al. /1/ on TiN coated inserts showed an increased flank wear for chlorine content higher than 5 % mass.

The harmful effect of chlorine on layer and on PACVD equipment can be avoided by using a non-chlorinated metallo-organic compound as metal donor. By employing this kind of metallo-organic compounds (MOC) therefore chlorine free layers can be achieved and decreasing of substrate temperature below 500 °C due to the low energy of bonds in molecule can be expected. MOCVD offers the advantages of mild process conditions, control over microstructure and composition, and high deposition rates /2/.

2. Apparatus

Figure 1 shows a schematic layout of the equipment which is described elsewhere /3/. The pure gases N_2 , H_2 and Ar are made available by the gas supply system and fed into the reactor via pressure reducing valves and mass flow controllers. The liquid or solid metal donor used is evaporated or sublimed and led into the reaction chamber by carrier gas. The power supply generates a pulsed DC-power up to 900 V. Thus the pulsed plasma exists between an anodic metal plate and the cathodic substrates. Additional heating allows uniform temperature distribution in the reactor. This heating enables an independent adjustment of the substrate temperature and the plasma parameters.

Fig. 1: Schematic layout of the pulse plasma CVD system

3. Metallo-organic-Compounds as Precursor

The critical factor in the CVD process is the selection of a precursor with suitable properties. The following properties must be considered:

1. The precursor should be either a liquid or a solid, with sufficient vapor pressure and mass transport at the desired temperature.
2. The precursor should be chemically and thermally stable at its evaporation temperature.
3. The precursor should be relatively easy to synthesize and to handle.
4. The key to the success of the MOC as a precursor is the ease of removal of the organic groups in the form of volatile nonreactive products of reaction.

Here as titanium donor the metallo-organic compounds Tetrakis(di-alkylamido)titanium $-\text{Ti}[\text{N}(\text{R})_2]_4-$ ($\text{R} = \text{Me}$ or Et , called TMT or TET, fig. 2a) were used. For comparison a low chlorine-content MO compound Bis(methylcyclopentadienyl)methyltitaniumchloride $-(\text{H}_3\text{C}-\text{C}_5\text{H}_4)_2\text{TiCl}-(\text{CH}_3)-$ (called BCMT, $\text{Cp}^* = \text{H}_3\text{C}-\text{C}_5\text{H}_4$, fig. 2b) was used. Compared to TiCl_4 these compounds contain relatively less titanium (table 1). Using MOC one must take more of these compounds to offer the same amount of titanium in process as using TiCl_4 .

Fig. 2: Structure of used metallo-organic compounds

Table 1: Titanium content in donor substances

compound	TiCl_4	$\text{Ti}(\text{NMe}_2)_4$	$\text{Ti}(\text{NEt}_2)_4$	$\text{Cp}^*_2\text{TiClMe}$
<u>Ti-content</u> mass%	25,2	21,3	14,2	18,7
weight factor	1	0,85	0,56	0,74

Table 2: Precursor Volatility Data

precursor	boiling point /°C, pressure / Pa	reference
$\text{Ti}(\text{NMe}_2)_4$	56/100	/4/
$\text{Ti}(\text{NEt}_2)_4$	103/100	/4/
$\text{Cp}^*_2\text{TiClMe}$	sublimes 120/50	/4/

For the choice of coating parameters it is very important to consider the energy of the bonds in the molecule. Unfortunately only limited information is available on this. However it is expected that the bonds can be split selectively by varying the plasma power. No vapour pressure diagrams of these metallo-organic compounds are known, but some volatility data are reported (table 2).

4. Experimental

The objective of the study is to investigate the formation of titanium containing layers using metallo-organic compounds by varying the coating parameters such as gas composition, gas flow rate, plasma power and coating temperature. Typical coating parameters are listed in table 3.

The treatment gas is composed of Ar, H_2 and N_2 , with a total flow rate of 30 - 60 l/h. One example for the gas composition is 50 vol% H_2 , 26,7 vol% N_2 and 23,3 vol% Ar. Here the amount of the metal donor is very small because the fraction of the metal donor is very low in comparison to those of the other gases. N_2 or Ar is the carrier gas. Gas pressure was varied between 50 and 300 Pa.

The layers are produced on tempering steel Ck 35, cold work steel 1.2379 (X 155 CrV Mo 12 1) and hard metal P 30. The layer composition was determined by EDX and WDX analysis. The microstructure and properties of the surface layers were investigated by means of light- and electron-optical microscopy, X-ray diffraction and hardness measurements. ESCA was used to determine the chemical bondings of the layers.

5. Results and Discussion

The substrate temperature was varied between 250 °C and 450 °C. Flat samples were used for the tests. The chemical composition was examined by EDX. An example is shown in figure 3, where the coating was carried out at 150 Pa, 360 °C and 550 volt, with a precursor of $\text{Ti}(\text{NMe}_2)_4$. In the tests the growth rate was 0.5 to 4 $\mu\text{m}/\text{h}$. Figure 3 reveals that the layer on hard metal contains titanium. Obviously the titanium peak of the coated sample exceeds the peak of the base material. Using $\text{Cp}^*_2\text{TiClMe}$ as precursor EDX-analysis detected no chlorine in the layer though the precursor contains chlorine. By WDX-analysis carbon and nitrogen in the layer could be detected indicating that the

Table 3: Typical MO-PACVD Conditions

precursor	temp. of precursor C	substrate temperature C	gas pressure Pa	plasma voltage V	pulse/ pulse repetition ratio
$\text{Ti}(\text{NMe}_2)_4$	40	250	150	400	1/13
$\text{Ti}(\text{NMe}_2)_4$	70	350	150	500	1/4
$\text{Ti}(\text{NMe}_2)_4$	80	400	150	500	1/4
$\text{Ti}(\text{NEt}_2)_4$	110	280	150	500	1/4
$\text{Ti}(\text{NEt}_2)_4$	120	350	150	500	1/13
$\text{Cp}^*_2\text{TiClMe}$	130	280	80	500	1/4
$\text{Cp}^*_2\text{TiClMe}$	130	350	80	500	1/4

layers are composed of $\text{Ti}(\text{C},\text{N})$. The C and N concentrations in the layer varied depending on the process parameters and metal donor used. $\text{Ti}(\text{C}_x\text{N}_y)$ layers exist for $0.33 < x + y < 1.04$ /5/. e. g. one of the layers had the composition $\text{Ti}(\text{C}_{0.59}\text{N}_{0.23})$; deposition conditions: precursor $\text{Ti}(\text{NMe}_2)_4$, substrate temperature 300°C , plasma voltage 400 V. Thus the lattice constant varies between 0.4306 and 0.4286 nm. Besides Ti, C and N, in some cases oxygen was found in the layer, which was also detected by FIX et al. /6/. Oxygen incorporation probably results from traces of O_2 and/or H_2O in the carrier gas or absorbed in the walls of the reactor. The titanium amides are very sensitive to moisture and oxygen.

5.1 Microstructure and Morphology

The microstructure and morphology of the surface layers were investigated. The surface topography is shown in figure 4a. The coating has a domed appearance as found on TiN or TiC layers produced with TiCl_4 in a PACVD process /7/. The profile of the surface roughness demonstrates that the surface is rather smooth with amplitudes about 0.1 to 0.15 μm (fig. 4b). The characteristic value R_a amounts to 0.025 μm for this layer. Figure 5 shows a calotte grinding of a $\text{Ti}(\text{C},\text{N})$ layer with a scratch track. This track has no porous flaking. The layer thickness amounts to about 8 μm . The grooves on the surface of the layer indicate that the layer follows exactly the topography of the substrate.

Fig. 3: EDX analysis of a coated hard metal, precursor: $\text{Ti}(\text{NMe}_2)_4$, 150 Pa, 360°C , 550 V

(a)

(b)

Fig. 4: Surface topography of a layer with roughness profile, precursor: $\text{Ti}(\text{NMe}_2)_4$

The fracture surface of a layer on hard metal is represented in figure 6. The compact layer has columnar crystals formed by the growth of grains with preferred crystallographic orientation. Here the parallelism to the PACVD coating with TiCl_4 as metal donor is again obvious. No such features were found using thermal CVD. Thus one can conclude that the surface topography depends on the process parameters, but not on the metal donor.

Fig. 5: Calotte grinding with scratch track; precursor: $\text{Ti}(\text{NMe}_2)_4$

Fig. 6: Fracture Surface of a layer, precursor: $\text{Ti}(\text{NMe}_2)_4$

The microhardness measurements were performed on polished samples. Values of about 1200 to 2000 HV 0.01 were obtained. Two tendencies of the hardness appear. The hardness increased with increasing temperature and it seemed that using $\text{Ti}(\text{NEt}_2)_4$ as precursor the layer is somewhat harder than using $\text{Ti}(\text{NMe}_2)_4$.

5.2 X-Ray Diffraction

Figure 7 shows an example of a X-ray diffraction analysis of a layer on Ck 35. Additional to the peaks of cubic $\text{Ti}(\text{C,N})$ of the layer one can see the peaks of α -Fe of the

base material. The lattice constant of the Ti(C,N) varied depending on the concentration of C and N in this ternary system /5/. The peaks became broader at low deposition temperature and reduced plasma power. The broad peaks indicate an increase of amorphous material and/or the existence of internal stress. The flaking of layer suggests the existence of internal stress (see table 4).

Fig. 7: X-ray diffraction pattern (Cu-Kα) of Ti(C,N) layers on Ck 35, precursor: Ti(NMe₂)₄

Fig. 8: Surface topography of a layer produced by thermal CVD, precursor: Ti(NMe₂)₄

5.3 Variation of Plasma Power

In this study the influence of the plasma on the layer quality was examined. Conventional CVD without any plasma at 350 °C substrate temperature formed a layer with poor adhesion to the base material (fig. 8). Some areas have powdery appearance, as previously reported by FIX et al. /6/. It should be mentioned that the coating temperature was high enough to split the C-C, C-H, C-N and Ti-N bonds in the molecule of the initial substance /8/.

Table 4: Influence of plasma power vs layer

Temperature °C	Process	Pulsed DC-Plasma Power	Product Layer
350	thermal CVD	none	flaking
350	PACVD	high	adherent
280	PACVD	high	adherent
280	PACVD	low	flaking

Superposing a pulsed DC plasma while the coating temperature was kept constant the layer quality was improved. The layer has a compact appearance, good adhesion (30 - 40 N) to the base material and a structure as described before. Table 4 shows schematically the effect of superposing the plasma on layer quality. At a lower coating temperature of 280 °C layers of comparable quality to those of 350 °C can be obtained by using high

plasma power. The growth rate amounts to 1-2 $\mu\text{m/h}$.

Further decreasing of plasma power by variation of pulse duration and pulse repetition time led to the deterioration of the layer quality. Thus it is shown that a successful deposition is possible by superposing a pulsed DC plasma under the conditions described above.

5.4 Optical Emission Spectroscopy

In this investigation the optical emission spectroscopy (OES) was used as a qualitative in-situ process analysis. Measuring the intensity of spectral lines it is possible to identify the density of each excited state which will be helpful to control and optimize the coating parameters.

Figure 9 shows a small part of an emission spectrum from coating process at 410 °C and 550 V, precursor $\text{Ti}(\text{NMe}_2)_4$. The Ti^+ peak is clearly recognizable. Beside Ti^+ in the plasma Ti was found. Indeed KUTYREVA et al. /8/ have shown that the thermal split of the bonds in the $\text{Ti}(\text{NET}_2)_4$ molecule will occur even at lower temperature. Also KULAKOWSKA et al. /9/ detected Ti^+ in addition to Ti, but no TiN. In /10/ the TiN formation has been expected and the mechanism discussed in detail. In our study no TiN was observed in case of metallo-organic precursors used.

Fig. 9: Optical emission spectrum 367-369 nm, precursor: $\text{Ti}(\text{NMe}_2)_4$, 410°C, 550 V, 150 Pa

5.5 Features of using the different Precursors

Generally $\text{Ti}(\text{NR}_2)_4$ and $\text{Cp}^*_2\text{TiClMe}$ as precursors led to the same results, i. e. deposition of $\text{Ti}(\text{C}_x\text{N}_y)$ layers. Mechanistic considerations /6/ show two problems associated with the use of $\text{Ti}(\text{NR}_2)_4$ amido complexes as precursors: The strong N-C bonds do not break easily, and there is facile Ti-C bond formation via β -hydrogen activation. An ESCA analysis of a layer shows that the carbon is both Ti bound and organic (fig. 10).

In the $\text{Cp}^*_2\text{TiClMe}$ -compound β -hydrogen activation may be hindered because the β carbons are tied back in a ring. This suggests that complete cyclic groups are leaving and can lead to TiC_xN_y layer with less C content than a layer produced with $\text{Ti}(\text{NR}_2)_4$. The carbon deposition at the reactor walls is another indication for the stability of cyclic groups. Using $\text{Ti}(\text{NR}_2)_4$ more carbon is de-

Fig. 10: ESCA analysis of carbon bonds in a layer, precursor: $\text{Ti}(\text{NET}_2)_4$

posited at the reactor walls than using Cp^*TiClMe . Further investigations on the mechanistic aspects are necessary to realize some "molecular engineering".

6. Conclusion

This work has illustrated the usefulness of the titaniumtetrakis(dialkylamides) and bis-(methylcyclopentadienyl)methyltitaniumchloride for Ti(C,N) coating since

- 1) the substrate temperature can be reduced to below 400 °C
- 2) further reduction of substrate temperature can be realized by the superposition of a plasma to thermal CVD
- 3) formation of chlorine free layers can be obtained
- 4) Ti(C,N) with different C and N concentration can be readily achieved and influenced by the process parameters and precursor.

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