Hard material layers on the basis of the system Ti-Al-C-O-N deposited by pulsed DC-plasma

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Abstract

The influence of plasma power density and gas phase composition on the composition of TiN, TiCN, TiC and TiAlN layers has been investigated. It is demonstrated that TiAlN and TiAlOCN layers are obtainable by pulsed DC-discharges. Further characterization results are given and discussed.

1. Introduction

So far, the deposition of wear resistant hard material layers by plasma CVD has been focussed on the system Ti-N-C with predominant research activities in TiN. However, the insufficient knowledge of the relationships between deposition conditions and layer properties is unfavourable for the optimum application of these hard layers. Furthermore, there is a lack in the development of new layer compositions, especially of ternary and multicomponent layers known from PVD (e. g. TiAlN [1, 2]).
The aim of this study was to investigate, more in detail, the influence of some important deposition parameters (e. g. plasma power density) on the formation and properties of conventional Ti-C-N layers and to demonstrate the possibility of deposition of new aluminium containing layers. Apart from the deposition of Al_2O_3, only a few studies are known concerning the deposition of Al-containing hard material layers. Lee, Ryoo and Lee [3] investigated the deposition of (Ti,Al)N layers from $TiCl_4$, $AlCl_3$, NH_3 gas mixtures using an rf-discharge. Other than Lee et al., we tried to use nitrogen instead of NH_3 because of its better convenience in the case of Cl-containing gas phases.

2. Experimental

The experimental set up used for the deposition experiments is schematically shown in Fig. 1. The deposition chamber, which was warmed up by an oil thermostat (wall temperature: 473 K), was outlined as parallel plate reactor powered by a DC-pulse source. Independent of the plasma power the temperature of the cathode could be fixed by controlling the air temperature of a hot air blower installed in the cylindrical cathode.

Usually, the layers were deposited on thin flat cold working steel (S6-5-2) plates, hard metal (WC/Co) cutting plates and tungsten sheet. $TiCl_4$, $AlCl_3$, CH_4, CO, N_2, H_2 and Ar were used as reaction gases.

Prior to the deposition the substrates have always been pretreated in the same manner in an $Ar/N_2/H_2$-plasma. During layer deposition only one parameter was changed, either the plasma power density or the gas phase composition. The fixed parameters were set as follows: total pressure 170 Pa, cathode temperature 763 ± 2 K and pulse/pause ratio 16 µs/32 µs. The gas flow rates were in the ranges 850 - 980 sccm H_2, 48 - 87 sccm N_2, 442 sccm Ar, 1.6 - 3.2 sccm $TiCl_4$, 0 - 80 sccm CH_4, 12 - 24 sccm CO and 1 - 4 sccm $AlCl_3$.

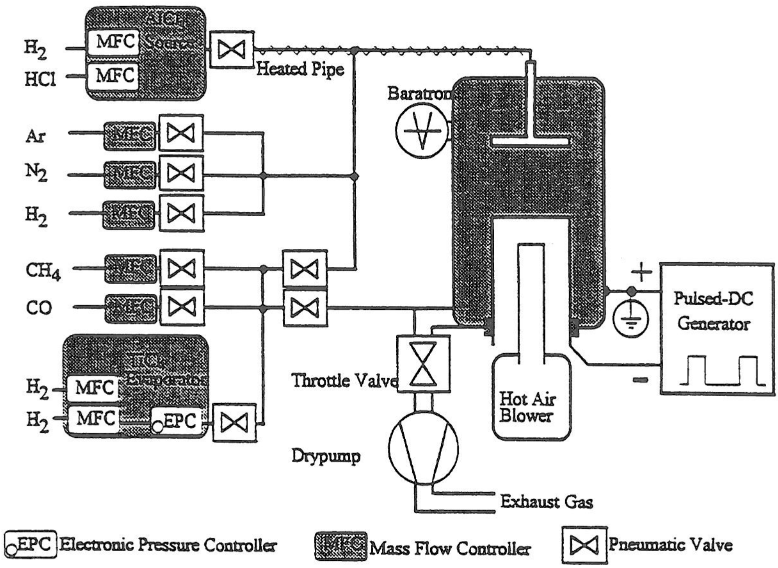

Fig. 1 Experimental set up (schematically)

The layers on the steel and WC/Co substrates have been characterized by SEM, XRD, GDOES and metallographic techniques. Layers deposited on tungsten were used for the determination of N, O and C content in TiN, TiCN and TiC, resp., by combustion and hot extraction methods. Element analyses were also performed by EDX and WDX. Furthermore, hardness, adhesion and sliding coefficients were determined.

3. Results and discussion

3.1. TiN, TiCN and TiC layers

For the deposition of TiN the influence of plasma power density on the layer composition, especially on the incorporation of O and Cl, was investigated. In Fig. 2 the

N, O and Cl-content of the layers is given in dependence on plasma power density. As expected and known from literature [4] the nitrogen content increases with increasing power density until a constant level, whereas the chlorine content decreases. Above about 0.9 W/cm^2 the chlorine content can no longer effectively decreased. The slope of the oxygen content is more surprising. The maximum of the oxygen content could be caused by the reverse effects of activated gaseous oxygen impurities and resputtering of surface adsorbed or bonded oxygen on the O-incorporation with increasing power density.

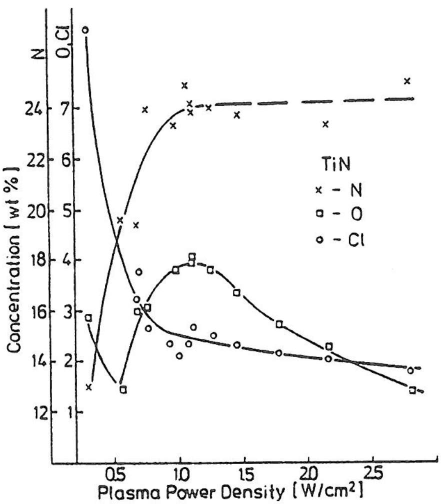

Fig. 2 Influence of plasma power density on the composition of TiN

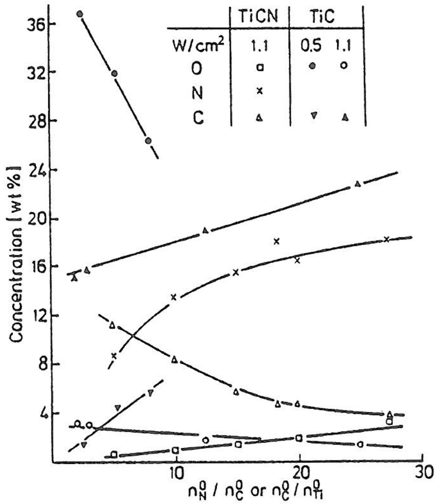

Fig. 3 Dependence of TiCN and TiC composition on the gas phase composition

In the case of TiCN and TiC the influence of gas phase composition on layer composition has been investigated. The results are given in Fig. 3. In comparison with the TiN deposition a remarkable higher plasma power density is necessary for a sufficient activation of the TiC forming carbon species. At low power density the oxygen incorporation in the TiC layers is extreme, which points to a lack of reactive carbon species. At higher plasma power density the carbon content can be changed in a wide range without deposition of larger oxygen amounts.

By considering these results the deposition of TiCN has been performed at higher plasma power. The n_C^0 / n_{Ti}^0-ratio was kept constant at 2, whereas the n_N^0 / n_{Ti}^0-ratio was changed between $10 < n_N^0 / n_{Ti}^0 < 54$ (n^0-mol numbers of used gas mixtures).

For the higher n_N^0 / n_{Ti}^0-ratios the TiCN composition is dominated by the nitrogen incorporation.

With increasing nitrogen content in the layers the oxygen content increases, too, and reaches the level of the pure TiN-layers deposited at the same power density.

3.2. TiAlN and TiAlOCN layers

For deposition of aluminium containing layers the same gas flow conditions as in the case of TiN were used with exception of the $TiCl_4$ flow, which was halved. The additional small amounts of $AlCl_3$ and CO, resp., do not essentially change the total gas flow.

In order to achieve an effective Al incorporation in the layers the plasma power density has to be enhanced over the level suitable for TiN or TiC deposition. The influence of the plasma power density on the Ti/Al-atom percent ratio in the layer is shown in Fig. 4. Unfortunately, there was a difference of the Al incorporation in the center of cathode (position 1) and the peripheral positions (position 2), which presumedly is caused by the velocity profile of the gas flow between the electrodes. Fig. 5 demonstrates the dependence of Al incorporation on the Al concentration of the gas phase.

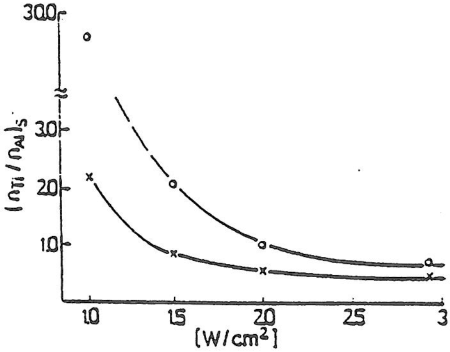

Fig. 4 Influence of plasma power density on the Al incorporation inTiN (x - position 1, o - position 2)

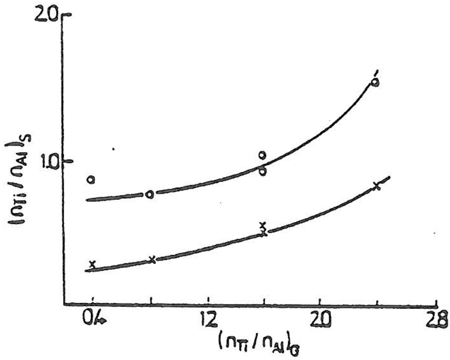

Fig. 5 Dependence of Al incorporation in TiN on the Al content of the gas phase (S - solid state, G - gaseous state)

Measurements of the concentration profiles perpendicular to the surface by GDOES proved the Al incorporation to be constant over the time. In most cases the O and Cl content of the layers amounted to 1.0 - 2.5 wt.%. The layers revealed a cubic face centred structure, as it was confirmed by X-ray diffraction. Some typical compositions obtained for additional presence of CO in the deposition atmosphere are summarized in Table 1, (the N-content was taken by difference).

At comparable oxygen content the layer hardness seems to increase with the aluminium content, whereas a strong rise of oxygen content causes a decrease of hardness at similar concentrations of the remaining elements. According to metallographic investigations these layer were monophase.

Table 1 Composition and hardness of (Ti,Al)C,O,N-layers

Layer composition (at. %)						HV [0.02]
Ti	Al	N	O	C	Cl	
6.2	38.3	33.8	16.6	3.7	1.3	1480
3.2	23.8	59.0	10.0	3.1	0.9	2062
9.2	38.8	35.5	10.4	4.4	1.7	2230
21.6	10.3	55.9	6.3	4.5	1.4	2640
13.7	31.9	40.9	7.7	4.1	1.7	3400

4. Layer characterization

In Table 2 characterization results and properties interesting for application are summarized. Some of the features (for example texture and microhardness) are very similar, but there are also clear differences. Opposite TiN for TiAlN lower compressive stresses were measured (layers deposited on S6-5-2), and the Al containing layers (deposited on WC/Co) yielded a lower friction coefficient (measured in air against Si_3N_4), too. The best results of adhesion on cold working steel (measured by scratch test) were obtained for TiN and TiCN. It is remarkable that in the case of TiN, TiCN and TiAlN a large scatter of microhardness has been observed, even if the composition was nearly constant. Small changes in oxygen content were found, which already has an influence on microhardness (s. Fig. 6) of TiN and TiAlN, resp.. Considering this effect the dependence of microhardness on the Ti/Al-atom percent ratio of the obtained layers is shown in Fig. 7.

Table 2 Typical characterization results

Feature	TiN	TiCN	TiC	(Ti,Al)N
Lattice constant (nm)	0.425 - 0.428	0.429 - 0.434	> 0.434	0.419 - 0.424
Texture	<200>	<200>	<200>	<200>, (<220>)
Stress (Gpa)	- 0.5 to - 1.5	-	-	- 0.2 to - 0.4
Adhesion on S6-5-2, L_C (N)	50 - 60	50 - 60	30 - 40	40 - 50
Friction coefficient	0.35	0.47	0.34	0.26
Microhardness, HV 20	1500 - 3100	1500 - 3200	2700 - 3400	2200 - 3100

5. Conclusions

Summarizingly, you should consider that the presented results were obtained for a limited window of the possible parameter field. Further activities are necessary to study the importance of other parameters (for example the pulse/pause ratio). On the basis of the obtained results the following general conclusions can be drawn:

1. To realize hard layers on the basis of the system Ti-Al-N-C-(O) it is recommended to vary the plasma power density in the range 0.7 - 2.0 W/cm^2, with increasing power density proceeding from TiN to TiC and TiAlN, resp.
2. More attention should be payed to the influence of power density on the impurity incorporation, especially of oxygen.
3. Further investigation has to be done to clear up the influence of the flow conditions on the Al incorporation in TiAlN layers.
4. With respect to the differences between the properties relevant for wear protection a combination of Ti-C-N-layers with TiAlN layers seems to be meaningful.

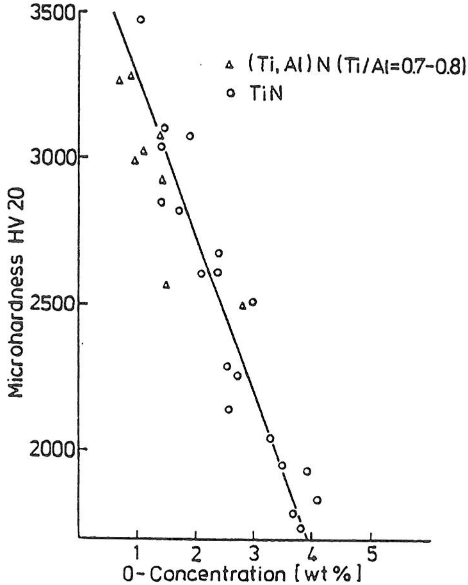

Fig. 6 Microhardness of TiN and (Ti,Al)N layers versus oxygen content

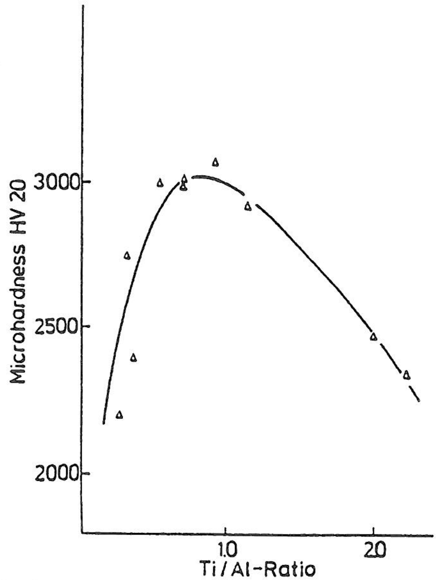

Fig. 7 Microhardness of (Ti,Al)N layers versus Ti/Al-atom percent ratio

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