Ceramics International **21** (1995) 421–425

Deposition of Adherent Hard Coatings on Steel by Plasma-Enhanced CVD

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(Received 9 December 1994; accepted 18 January 1995)

Abstract: Wear resistant TiN_x- and TiC_xN_y-layers were deposited on various pretreated steel substrates in the temperature range 673–773 K. The influence of the process parameters and substrate pretreatment on the deposition rate, layer composition, interface and layer structure, microhardness and stress have been investigated. With optimized process parameters, layers with a low oxygen and chlorine impurity content, high microhardness and a good adhesive strength are obtained. Usually, the TiN_x- and also the TiC_xN_y-layers with low carbon content deposited at 773 K have a columnar structure with a <200> texture. Nevertheless for TiC_x a <111> texture is observed. TiN_x-layers prepared below 773 K have a <111> preferred orientation or they are textureless. The adhesion of the coatings on plasma nitrided steel substrates is remarkably higher than on non-nitrided substrates. The critical loads for nitrided and non-nitrided S6-5-2 steel are 44 N and 14 N, respectively.

1 INTRODUCTION

One of the major problems of current low temperature deposition technologies, plasma-enhanced CVD (PECVD) and PVD, is to guarantee a sufficiently good adhesion for hard coatings deposited at temperatures below 773 K.[1,2] The deposition of TiN_x-PVD coatings on nitrided steel leads to an increased adhesion compared to non-nitrided steel substrates.[3]

In the present work, the influence of process parameters and substrate pretreatment on adhesion, composition, interface and layer structure, microhardness and stress of PECVD-coatings are studied. TiN_x- and TiC_xN_y-coatings are deposited at temperatures between 673 and 773 K using a PECVD-process working with a pulsed dc discharge, with titanium tetrachloride ($TiCl_4$) as titanium source. It is known that the use of $TiCl_4$ leads to an increased amount of chlorine impurities with decreasing deposition temperature and these impurities impair the coatings properties.[4,5]

A first important question is the dependence of the layer properties and the adhesion in the above-mentioned temperature range on the chlorine content and which process parameters prove to be suitable for a minimization of the chlorine concentration in the layers.

Another problem is the optimal substrate pretreatment. Investigations are necessary to find out the mechanical grinding and polishing pretreatment which result in better adhesion strength and to enlighten the effect of plasma nitriding of the steel substrates on the adhesion of hard coatings.

2 EXPERIMENTAL

The apparatus is schematically shown in Fig. 1. The reaction chamber is a hot wall reactor with an outer 3-zone resistance furnace. A pulsed dc glow discharge is generated between two parallel electrodes. The upper electrode which is used for introducing the gas mixture and the wall are the earthed anode. The substrates are held on the lower cathode. The substrate temperature is controlled by the furnace temperature and the plasma power and it is measured by a thermocouple near the cathode surface.

TiN_x is deposited using a gaseous mixture of $TiCl_4$, N_2, H_2 and Ar, TiC_xN_y with additional

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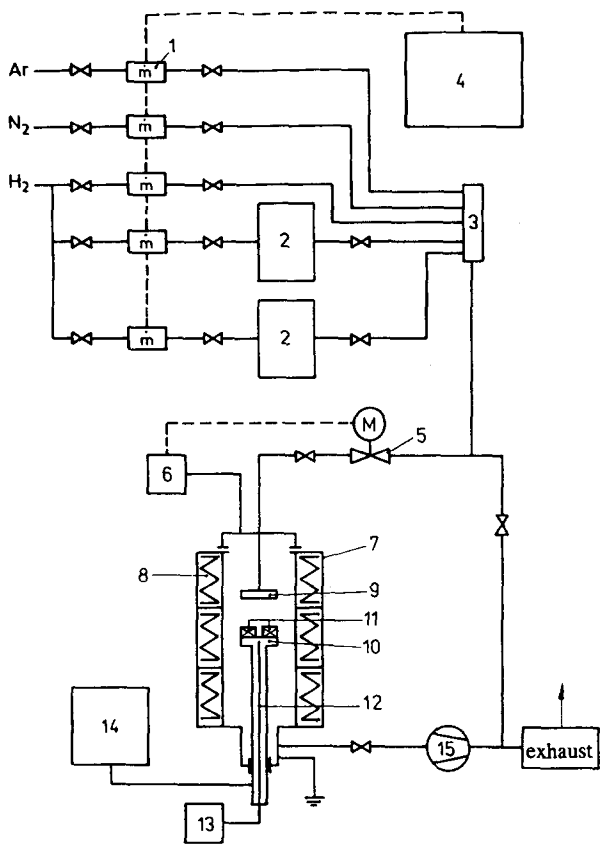

Fig. 1. Scheme of the PECVD apparatus: 1 — mass flow controller, 2 — $TiCl_4$ liquid source, 3 — gas mixing box, 4 — computer for the gas mixing system, 5 — gas inlet valve, 6 — pressure control unit, 7 — chamber, 8 — 3-zone resistance furnace, 9 — anode, 10 — cathode, 11 — substrates, 12 — thermocouple, 13 — device for substrate temperature measurement, 14 — pulsed dc power supply, 15 — vacuum pump.

methane. Experiments were carried out in the temperature range of 673–773 K, at a pressure of 330 Pa and a total gas flow rate of 17 $cm^3\ s^{-1}$.

The deposition was carried out on the high-speed steel S6-5-2 and the cold-work steel X155CrVMo12·1. Both of them are used either hardened only or additionally plasma-nitrided. The plasma-nitrided substrates were prepared without a compound layer and have a nitriding depth of 25–30 μm.

3 RESULTS AND DISCUSSION

3.1 Deposition rate and composition of TiN_x and TiC_xN_y layers

The deposition rate and the composition of TiN_x-layers depend on process parameters such as $TiCl_4$-flow, hydrogen/nitrogen partial pressure ratio $(p_{H_2}/p_{N_2})_0$ of the source gas, substrate temperature, plasma power density and pulse/pause ratio of the pulsed dc glow discharge.

The deposition rate at 773 K shows a linear increase with the plasma power density, if the plasma power density is increased from 0·4 W/cm^2 to 0·8 W/cm^2 while decreasing the reactor's wall temperature. The TiN_x-deposition rate increases with increasing $TiCl_4$ flow rate and hydrogen/nitrogen partial pressure ratio and finally reaches constant values, depending on substrate temperature (see Fig. 2), the plasma power density being held constant and the reactor's wall temperature being adjusted according to the substrate temperature.

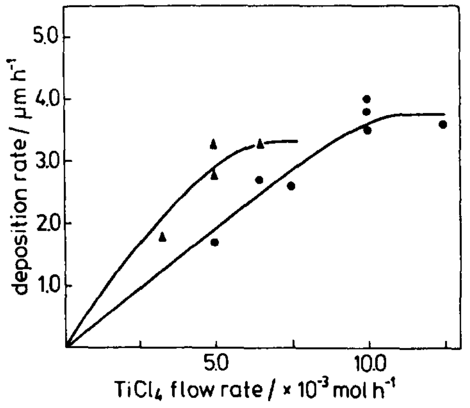

Fig. 2. Dependence of the TiN_x deposition rate on the $TiCl_4$ flow rate at substrate temperatures of 773 K (●) and 723 K (▲) at a partial pressure ratio $(p_{H_2}/p_{N_2})_0$ of the input gas of 9–13.

This indicates a transition from a mass-transport controlled to a kinetically controlled process.[6] The attainable maximum deposition rates were 4 μm/h at 773 K and 3·4 μm/h at 723 K, as Fig. 2 shows. At 673 K a deposition rate of 3 μm/h was observed.

The difference between both curves in the lower range of $TiCl_4$ flow rate is probably caused by the higher chlorine incorporation at 723K leading to a reduced density of the layers.

Nearly stoichiometric layers, of low oxygen content, were obtained in the kinetically controlled range at a $TiCl_4$ flow rate higher than 7 × 10^{-3} mol/h for 773 K (see Fig. 3) and 5 × 10^{-3}

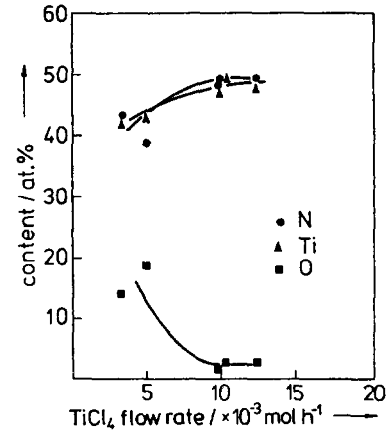

Fig. 3. Dependence of the N- and O-content on the $TiCl_4$ flow rate at a substrate temperature of 773 K and a partial pressure ratio $(p_{H_2}/p_{N_2})_0$ = 9·5 (titanium balance to 100%).

mol/h for 723 K, respectively, and on principle at $(p_{H_2}/p_{N_2})_0 > 9$. Partial pressure ratios $(p_{H_2}/p_{N_2})_0$ higher than 13 lead to an increase of hydrogen concentration in the layers, the hydrogen presumably being hydridically bound.[7] The increased oxygen content in the mass-transport controlled range is due to the influence of the residual gas and also to desorption of impurities containing oxygen off the reactor wall.

In order to deposit stoichiometrical layers, low in oxygen content, it is necessary to choose a pause length of less than 50 μs for a pulse duration of 10–40 μs.

The chlorine content is mainly influenced by the substrate temperature and the plasma power density. It increases from 1·9–2·2 at% at 773 K to 2·0–2·5 at% at 723 K and 3·3 at% at 673 K. In the case of low plasma power densities, the chlorine content grows rapidly. It must be higher than 0·5 W/cm^2 at 773 K because the chlorine concentration at a power density of 0·4 W/cm^2 was already 3·8 at%.

TiC_xN_y-layers have so far only been deposited at 773 K. The $TiCl_4$ flow rate was fixed to $6{\cdot}5 \times 10^{-3}$ mol/h and by varying the mole ratio $[n_C/(n_C + n_N)]_0$ in the source gas different C/N-concentrations in the layers could be realized.

The deposition rate of TiC_xN_y continuously decreases from 4 μm/h for the N-rich case to 2·5 μm/h for TiC_x. The reason is the thermodynamical more favourable formation of TiN_x compared to TiC_x. The composition of the TiC_xN_y layers does not only depend on the molar gas phase ratio $[n_C/n_C + n_N)]_0$, but also on the plasma power density, pulse/pause ratio and the partial pressure ratio $(p_{H_2}/p_{Ar})_0$ in the source gas. As discussed for the TiN_x layers, a higher power density of the dc discharge leads to lower chloride contents, as well as decrease of the $(p_{H_2}/p_{Ar})_0$ ratio. With an increasing carbon content of TiC_xN_y layers deposited at 773 K, an increase of the chlorine content from 2 at% for TiN_x to 4 at% for TiC is observed. It can be supposed that this derives from a change in the reaction mechanism. Similar chlorine data are related in the literature.[8] A decrease of the carbon content and an increase of the oxygen content in the layers is the result of pause lengths of more than 100 μs. In this case, hydrocarbon radicals with short life-time presumably no longer participate in layer deposition. Therefore, only pause lengths below 40 μs were used. A major problem of TiC_xN_y deposition is to avoid the formation of free carbon, which depends on the molar ratios $(n_C/n_{Ti})_0$ and $(n_N/n_{Ti})_0$ in the gas phase. In order to deposit almost stoichiometrical TiC_x, $(n_C/n_{Ti})_0$ must be less than 4. The deposition of TiC_xN_y layers, containing no free carbon, is only possible if the $(n_C/n_{Ti})_0$ ratio is decreased for increasing $(n_N/n_{Ti})_0$ ratio.

3.2 Structure of TiC_xN_y layers on nitrided and non-nitrided steels

Homogeneous TiN_x- and TiC_xN_y-layers were obtained on both kinds of steel, as can be seen from Fig. 4. A sharp substrate–layer transition can be observed.

At a substrate temperature of 773 K a columnar structure with <200> preferred orientation can be found for TiN_x- and nitrogen-rich TiC_xN_y-layers. This preferred orientation is enforced by nitriding of the steel substrates (see Fig. 5).

The <111> reflex in the X-ray diffraction pattern becomes more and more important for decreasing substrate temperatures, so that layers deposited at 723 K either have a columnar structure with a <111> preferred orientation, or non-textured, granular layers are observed, the latter especially for high $TiCl_4$ flow values. At 673 K, the layers show very broad diffraction reflexes and they are textureless.

Lattice parameters for TiN_x were found to be 4·252–4·264 Å at a substrate temperature of 773 K and 4·256–4·280 Å at 723 K. These values are generally higher than those reported for stoichiometric TiN_x (a = 4·240 Å[9]), deposited by conventional

Fig. 4. Cross section polish of a TiN_x layer on nitrided S6-5-2 deposited at 773 K.

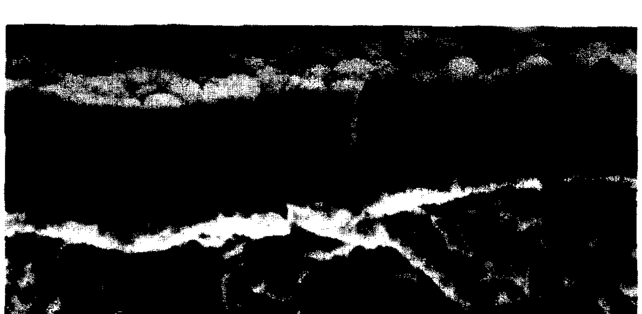

Fig. 5. SEM-fractograph of TiN_x-coated steel (substrate temperature 773 K).

thermal CVD. Oxygen impurities lead to smaller lattice constants, whereas chlorine and hydrogen as well as over stoichiometrically solved nitrogen and stress lead to higher values.[10,11] Because of their low content of chlorine and hydrogen (≤2 at%), the increased lattice constant in optimized TiN_x-layers is probably due to additionally solved nitrogen and stress.

The same applies to TiC_xN_y-layers, where lattice constants between 4·250 and 4·360 Å were found depending on the C/N ratio. The greater deviation of lattice parameters in TiC_xN_y layers in the carbon-rich case can be explained by a more important incorporation of chlorine, as was found experimentally (literature data: a (TiC) = 4·33 Å).

3.3 Microhardness and stress of the coatings

Microhardness was measured with a Vickers-indenter. For decreasing substrate temperature, the HV [0·02] value is lowered from 3050 at 773 K to 2550 at 723 K and 1920 at 673 K. For TiC_xN_y-coatings, values between 2640 and 3220 HV [0·02] were found, with higher values for carbon-rich coatings. For TiN_x-coatings, deposited by PVD at low temperatures, microhardness values as high as those of PECVD–TiN_x-coatings deposited at 773 K were found. Stress and lattice defects have been discussed as a possible reason for the high hardness.[10] In X-ray stress measurements, values between -2 and -3 GPa were found, i.e. remarkable compressive stress, for layers deposited at 773 K as well as for those deposited at 723 K. Therefore, decrease of microhardness with decreasing substrate temperature cannot be explained by reduced stress. However, it can be caused by an increasingly disturbed TiN_x-lattice and higher impurity contents, especially of chlorine and hydrogen.

3.4 Adhesion of TiN_x and TiC_xN_y layers on nitrided and non-nitrided steels

Adhesive strength was evaluated in scratch-test studies. The scratch trace was investigated microscopically and the critical load was used as a value for adhesive coating failure. First the influence of mechanical surface treatment and the resulting roughness on the critical load were studied. Results are shown in Table 1.

Table 1. Influence of surface treatment and roughness of nitrided steel S6-5-2 on the adhesive strength of TiN_x-coatings deposited at 773 K (thickness 5–6 μm)

Type of mechanical treatment	Surface roughness R_Z (μm)	Critical load (N)
Wet emery paper 240	0·94	30
Wet emery paper 500	0·75	27–44
Polished with alumina suspension	0·89	15
Polished with diamond paste 1.0	0·57	17

Table 2. Adhesion of TiN_x layer deposited at 773 K on nitrided and non-nitrided steel

Steel type	Steel treatment	Critical load (N)
S6-5-2	only tempered	14
S6-5-2	tempered, plasma-nitrided	44
X155CrVMo12·1	only tempered	22
X155CrVMO12·1	tempered, plasma-nitrided	31

Polishing with wet emery paper 500 proved to be the most adequate mechanical pretreatment, therefore it was used for the following experiments. Coatings on substrates polished with alumina suspension or diamond paste show less adhesive strength, obviously due to polishing material residues, even after cleaning in the ultrasonic bath using several solvents. This could be proved by GDOES depth profile analysis, where increased aluminum concentrations could be found in the interface region.

A higher adhesion strength was observed for TiN_x layers deposited on nitrided steel substrates (see Table 2).

The increase of the adhesion strength is more visible for the steel type S6-5-2 than for the cold-work steel X155CrVMo12·1. The TiC_xN_y layers don't reach such high critical loads as the TiN_x coatings. For nitrogen-rich TiC_xN_y layers on nitrided S6-5-2 only a value of 26 N was measured which further falls with increasing carbon content. Additional investigations are necessary to solve this problem. A possibility to improve the adhesion of TiC_xN_y layers is the deposition of a TiN_x interlayer.

The higher adhesion on the nitrided steels can be explained by the contribution of nitrogen of the plasma-nitrided steel surface to the initial state of TiN_x layer growth. Because both of the steels contain chromium the (Fe, Cr)-oxynitride surface layer discussed in the literature[12] can also cause an increase of the adhesion by the formation of a $Ti(O,N)_x$ interlayer. GDOES depth profiles of TiN_x-coated, nitrided steels show a significant oxygen enrichment on the interface.

Both of these effects lead to a higher chemical interaction between substrate and layer and therefore to an improved adhesion.

4 CONCLUSIONS

TiN_x and TiC_xN_y layers were deposited on nitrided and non-nitrided steels using pulsed dc plasma-assisted CVD. The following results are obtained:

(1) Nearly stoichiometric TiN_x layers with low oxygen and chlorine content can be prepared with optimized process parameters. TiC_xN_y layers containing no free carbon require a $(n_C/n_{Ti})_0$ gas phase ratio below 4.

(2) The microhardness of TiN_x layers decreases from 3050 *HV* [0·02] at 773 K to 1960 *HV* [0·02] at 673 K caused by increasing lattice defects and impurity content of chlorine and hydrogen. TiC_xN_y microhardness is somewhat higher with values up to 3220 *HV* [0·02].

(3) The preferred orientation of the layers depends on substrate temperature, $TiCl_4$ flow rate and carbon content.

(4) A remarkable improvement of the adhesion was found for TiN_x coatings on nitrided steel compared with non-nitrided steel.

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