Preparation, characterization and wear behaviour of TiN$_x$-coated cermets obtained by plasma-enhanced chemical vapour deposition

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Commercial cermet inserts were coated with titanium nitride by plasma-enhanced chemical vapour deposition (PECVD) using a pulsed direct current (d.c.) glow discharge. The influence of the coating parameters on the deposition rate, on the layer composition, on the layer–substrate interface, on the structure and on the microhardness of the layers was investigated for deposition temperatures in the range 500–700 °C. The adhesive strengths, and some mechanical properties, of the coated cermets were characterized by scratch tests, by friction wear investigations and by measurement of the transverse rupture strength. The wear behaviour was examined in the cutting tests. It was found that TiN$_x$-coatings deposited with a sufficiently high deposition rate and plasma power density have a low oxygen and chlorine content and that they are nearly stoichiometric. The layers usually have a columnar structure with a $\langle 2\,0\,0 \rangle$ texture. A granular, equiaxed structure was observed within a small range of deposition conditions. In interrupted and continuous turning tests with steel and grey cast iron, a high cutting performance of the coated inserts, which depended on the coating thickness and on the deposition temperature, was achieved.

1. Introduction

Cermets are a class of cutting materials which are increasing in importance and in their share of the market. Modern cermet tools have wider application fields and are superior in the finish cutting of steel and cast iron than uncoated hard metals [1, 2].

Coating cemented carbides (such as titanium carbide, titanium nitride and alumina) by chemical vapour deposition (CVD) and physical vapour deposition (PVD) processes resulted in a remarkably higher wear resistance [3]. Attempts were also made to coat the cermets, but conventional CVD processes are usually associated with high deposition temperatures, which lead to the formation of brittle intermetallic phases [4]. TiN$_x$-coated cermets obtained at lower temperatures by PVD have remarkably higher wear resistance in continuous cutting tests on unalloyed and alloyed steel [1, 5]. Lower deposition temperatures are also possible using plasma-enhanced chemical vapour deposition processes (PECVDs). In this work, TiN$_x$-coated cermets were prepared by PECVD. The deposition process was studied and the samples were characterized by chemical and structural analysis. Some mechanical properties and the wear resistance for the turning of steel and cast iron were also investigated.

2. Experimental procedure

2.1. PECVD process

Titanium nitride was deposited using a gaseous mixture of TiCl$_4$, N$_2$, H$_2$ and Ar. The apparatus is shown schematically in Fig. 1. The reaction chamber (with an inner diameter of 200 mm) was a hot-wall reactor with an outer three-zone resistance furnace allowing a maximum temperature of 800 °C. A pulsed direct current (d.c.) glow discharge was generated between two parallel electrodes. The upper electrode, which is used for introducing the gas mixture, and the wall comprise the earthed anode. The substrates were held on the lower cathode. The substrate temperature was maintained by the furnace temperature and by the plasma power, and it was measured by a thermocouple near the cathode surface. The gas-mixing system was controlled by a computer. TiCl$_4$ was vaporized from a thermostated liquid source.

2.2. Deposition conditions

Experiments were carried out in the temperature range 500–700 °C, at a pressure of 330 Pa (one experiment at 450 Pa) and at d.c. power densities between 0.4 and 0.8 W cm^{-2}. The flow rates of N$_2$, H$_2$ and TiCl$_4$ were varied in the ranges

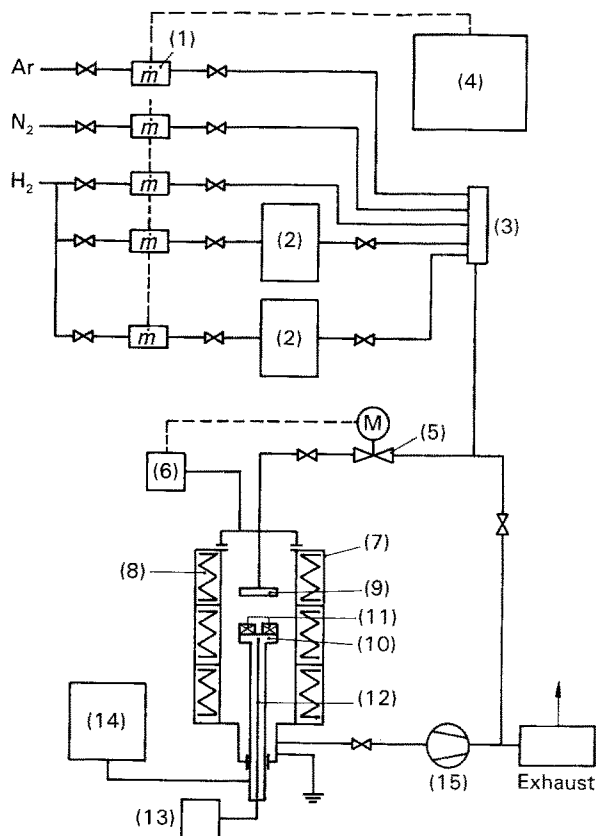*Figure 1* The PECVD apparatus: (1) a mass-flow controller, (2) the TiCl$_4$ liquid source, (3) a gas-mixing box, (4) a computer for the gas-mixing system, (5) a gas-inlet valve, (6) a pressure-control unit, (7) the recipient, (8) a threezone resistance furnace, (9) the anode, (10) the cathode, (11) the substrates, (12) a thermocouple, (13) a device for substrate-temperature measurement, (14) a pulsed d.c. power supply, and (15) a vacuum pump.

TABLE I The physical and mechanical properties of the cermet substrate materials, TCN27 and TCN54

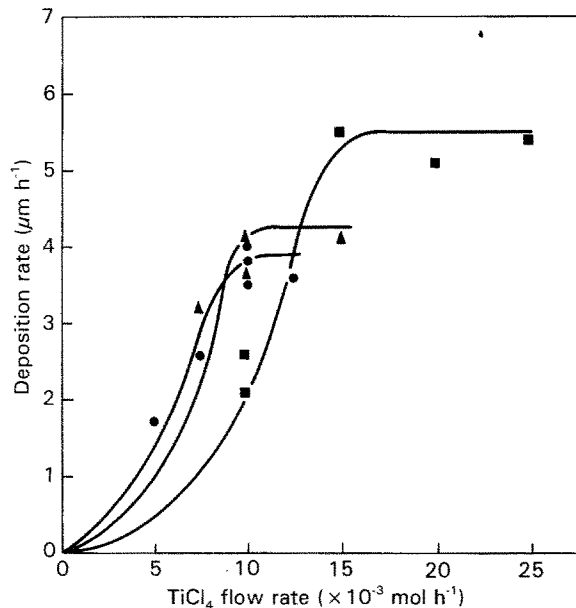| Properties	TCN27	TCN54
Density (kg m^{-3})	6450	6400
Hardness H_{V10}	1770	1650
Transverse rupture Strength (MPa)	1600	2000
Fracture toughness (MPa m$^{1/2}$)^2	7.3	9.1

Figure 2 The dependence of the TiN$_x$-deposition rate on the TiCl$_4$ flow rate for a partial-pressure ratio in the input gas of $(p_{H_2}/p_{N_2})_0$ = 9 − 13 at substrate temperatures of: (●) 500 °C, (▲) 600 °C, and (■) 700 °C.

70–250 s.c.cm., 650–1100 s.c.cm. and 2–10 s.c.cm. $(5–25 \times 10^{-3}$ mol h$^{-1})$, respectively; the argon flow rate was kept constant at 500 s.c.cm. The purity of the nitrogen and the argon was about 99.999%, the purity of the hydrogen was about 99.9% and that of the liquid TiCl$_4$ was about 99%. The gases were further purified by contact columns (with a palladium or a nickel catalyst), molecular-sieve columns and an aerosol filter. Some physical and mechanical properties of the commercial (Ti,W,Mo) (C,N)–Ni–Co cermet inserts (Cerametal) used as the substrates are given in Table I. The binder-rich substrate TCN54 was favoured for the wear investigations in order to combine the high toughness of the substrate material with the high wear resistance of the coatings.

3. Results and discussion

3.1. The influence of the process parameters on the deposition rate

The most important parameters for the deposition rate of titanium nitride are the TiCl$_4$ flow rate, the partial-pressure ratio $(p_{H_2}/p_{N_2})_0$, the substrate temperature and the power density of the pulsed d.c. glow discharge. The deposition rate is shown in Fig. 2 as a function of the TiCl$_4$ flow rate at different substrate temperatures, and it is shown in Fig. 3 as a function of the hydrogen/nitrogen partial-pressure ratio.
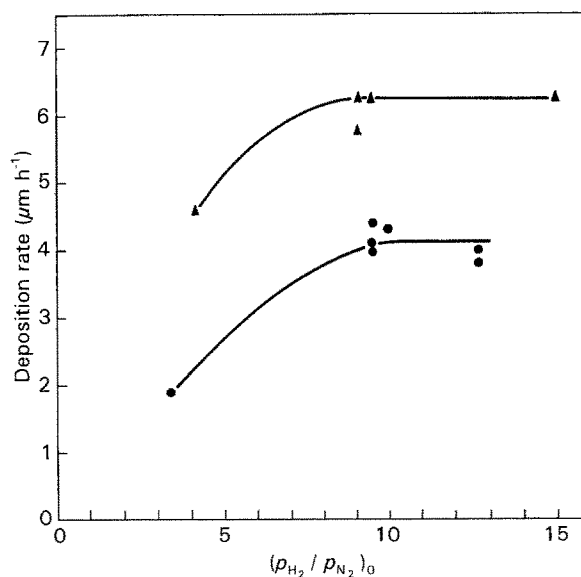

Figure 3 The dependence of the TiN$_x$-deposition rate on the hydrogen/nitrogen partial pressure ratio, $(p_{H_2}/p_{N_2})_0$ in the feed gas at substrate temperatures of (●) 500 °C and (▲) 700 °C. (The TiCl$_4$ flow rate was 1×10^{-2} mol h^{-1} at 500 °C, and it was 1.5×10^{-2} mol h^{-1} at 700 °C.

The deposition rate increased as the TiCl$_4$ flow rate and the hydrogen/nitrogen partial-pressure ratio increased to constant values which depended on the temperature. The TiCl$_4$ flow-rate influence points to a

transition from a mass-transport-controlled to a kinetically controlled process [6]. A high nitrogen partial pressure probably leads to a blockade of active reaction sites, because adsorbed nitrogen prevents the adsorption of Ti species [7] and thus it decreases the deposition rate. Furthermore, a decrease in the hydrogen concentration is connected with a lower concentration of NH_x species [8], which are supposed to be one of the most important plasma species in the PECVD of TiN_x [9].

Increasing the plasma power density from 0.5 to 1.5 $W\,cm^{-2}$ gave a nearly linear growth of the deposition rate.

3.2. The influence of the process parameters on the layer composition

The layer composition depends on the $TiCl_4$ flow rate (Fig. 4), on the partial-pressure ratio $(p_{H_2}/p_{N_2})_0$ (Fig. 5), the plasma power density (Table II) and on the pulse/pause ratio. The substrate temperature influenced only the chlorine content, which was lowered from 1.9 to 2.2 at % at 500 °C and to 0.9 at % at 700 °C. If the plasma power density is too low there is a remarkable increase in the chlorine content (Table II). This can be explained by the high dissociation energy of nitrogen (9.76 eV) [10]. The quantity of dissociated nitrogen, and therefore of the TiN which is formed is strongly correlated with the plasma power level. The chlorine compounds have lower dissociation energies, and chlorine can be more easily incorporated as the plasma power decreases.

A strong correlation has been observed between the deposition rate and the oxygen content as well as the stoichiometry of the TiN_x layers. Oxygen-poor and
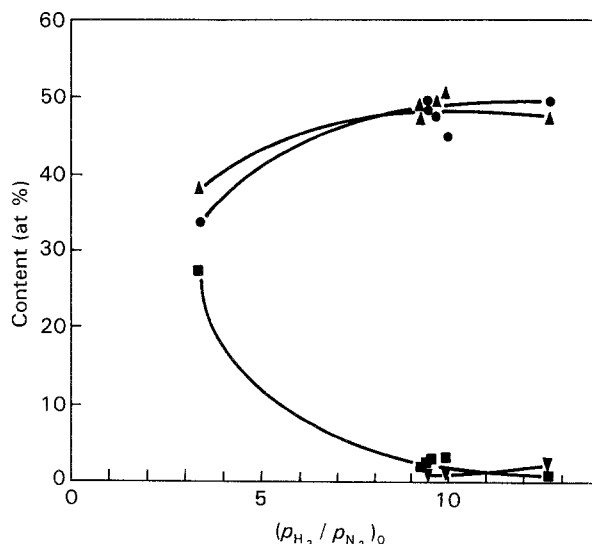
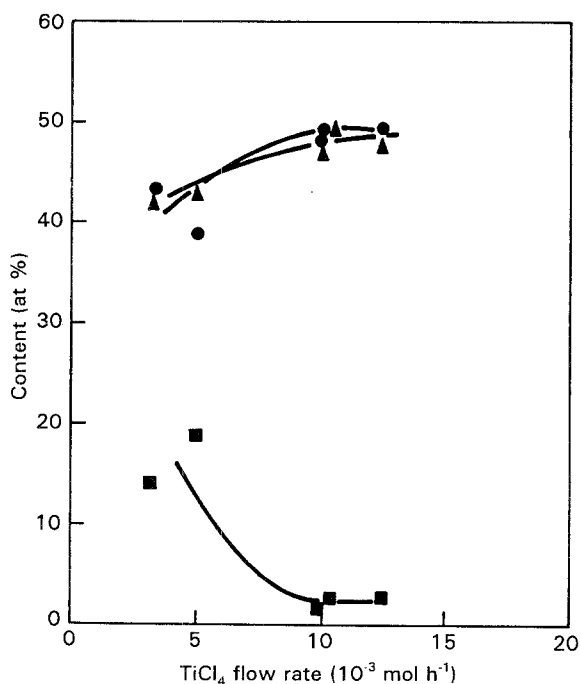Figure 5 The dependence of the N, O and H contents of the TiN_x layers on the hydrogen/nitrogen partial-pressure ratio $(p_{H_2}/p_{N_2})_0$, in the input gas at a substrate temperature of 500 °C and at a $TiCl_4$ flow rate of 1×10^{-2} mol h^{-1} (the Ti made up the balance to 100 at %) : (●) N, (▲) Ti, (■) O and (▼) H.

TABLE II The dependence of the chlorine content in the TiN_x film on the plasma power density for a substrate temperature of 500 °C

Plasma power density $(W\,cm^{-2})$	Cl content (at %)
0.40	3.8
0.52	1.9
0.72	2.2

nearly stoichiometric layers were obtained in the kinetically controlled deposition range with $TiCl_4$ flow rates above 1×10^{-2} mol h^{-1} (Fig. 4) and with $(p_{H_2}/p_{N_2})_0$ partial-pressure ratios above 9 (Fig. 5). Partial-pressure ratios above 13 lead to an increase in the hydrogen content in the layers, which is probably hydridically bounded [11, 12]. Higher oxygen contents observed in the mass-transport deposition range are probably due to a residual-gas influence and to hot-wall desorption effects. It is necessary for the deposition of stoichiometric oxygen-poor TiN_x layers to maintain pause periods below 50 µs in the pulse–pause ratio, if the pulse period is in the range 10–40 µs.

3.3. Structure and properties

Metallographic grinding (Fig. 6) revealed a homogeneous TiN_x layer without intermetallic phases in the layer and interface range. This indicates a possible way of avoiding the interaction processes between the gas phase and the binder metal of the cermet which have been observed in thermal CVD processes and which lead to brittle intermetallic inclusions, so decreasing the quality and wear resistance of the layers and of the layer–substrate composites.

Normally, a columnar structure with a ⟨2 0 0⟩ preferred orientation was observed independently of the

Figure 4 The dependence of the N- and O-content of the TiN_x layers on the $TiCl_4$ flow rate at a substrate temperature of 500 °C and a partial-pressure ratio in the input gas of $(p_{H_2}/p_{N_2})_0 = 9.5$ (the Ti made up the balance to 100 at %: (●) N, (▲) Ti, and (■) O.

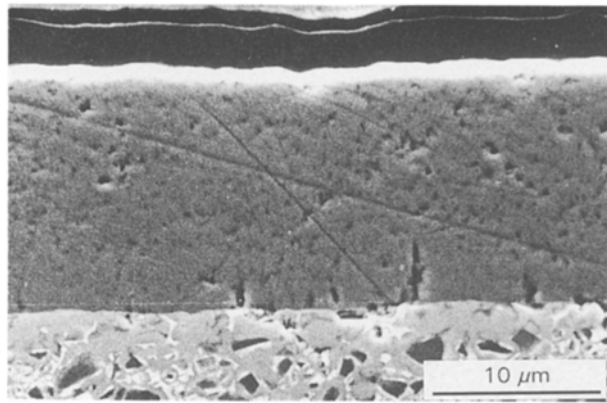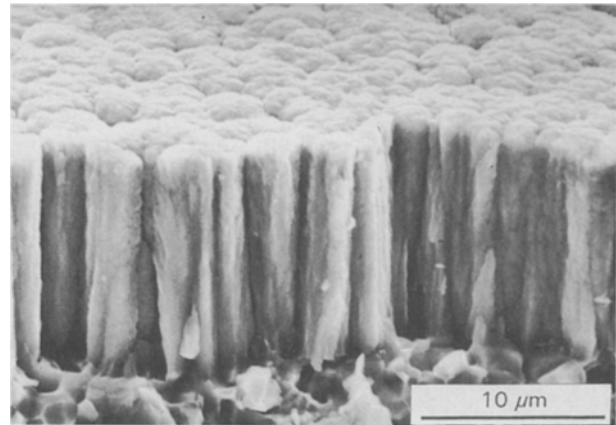*Figure 6* Metallographic grinding of a TiN$_x$ layer deposited at 500 °C.

Figure 7 A SEM fractograph of a TiN$_x$-coated cermet with columnar growth of the layer (with a substrate temperature of 700 °C, and a total pressure of 330 Pa).

initial gas composition and independently of the substrate temperature in the range 500–700 °C (Fig. 7). Investigations of PECVD and PVD processes have shown that the texture depends on the hydrogen and nitrogen partial pressures [13] and on the energy of the bombarding particles [14]. Usually, a $\langle 1\,1\,1\rangle$ preferred orientation was detected for PVD and a $\langle 2\,0\,0\rangle$ orientation was detected for PECVD. A change from a columnar to a granular, equiaxed structure (Fig. 8) can be achieved if the TiCl$_4$ partial pressure is higher than 1.6 Pa at 700 °C. It is well-known that a granular structure reduces the crack extension and improves the wear resistance.

Lattice-constant determinations by conventional X-ray analysis of the PECVD TiN$_x$ layers with low oxygen impurities resulted in values between 0.425 and 0.427 nm, these values are generally higher than the literature data for stoichiometric TiN$_x$ ($a = 0.424$ nm [15]) deposited by conventional CVD.

Oxygen impurities lead to lower lattice constants, chlorine and hydrogen as well as superstoichiometrically solved nitrogen and compressive stress to higher values [16, 17]. Because of the low chlorine and hydrogen contents (< 2 at %) in optimized coatings, stress and additional solved nitrogen are probably responsible for the higher lattice constants.

Laser surface-roughness measurements were carried out to investigate the layer topography. Textured, columnar grown layers were associated with an increase in the roughness value R_a, over the value in the substrate, this increase was about 100% for a layer thickness of 2–4 µm and it was 200% for a layer thickness of 7–10 µm. For granular, equiaxed layers no substantial increase in the surface roughness was observed up to a layer thickness of 10 µm.

The adhesion was estimated by scratch-test investigations. An apparatus was used with a continuously increasing load and with automatic recording. The scratch trace was investigated microscopically. The results are given in Tables III and IV. The adhesion strength clearly increased as the temperature, the deposition rate ($(p_{H_2}/p_{N_2})_0$, TiCl$_4$ flow rate) and the plasma power density increased. The temperature influence is due to enhancement of diffusion processes in

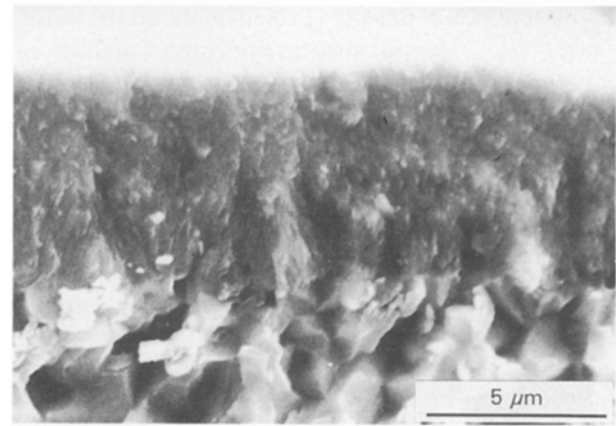*Figure 8* A SEM fractograph of a TiN$_x$-coated cermet with a granular, equiaxed layer structure (with a substrate temperature of 700 °C and a total pressure of 450 Pa).

TABLE III The dependence of the critical load measured by the scratch test on the TiCl$_4$ flow rate and the partial-pressure ratio $(p_{H_2}/p_{N_2})_0$ for TiN$_x$-coated cermets prepared at various substrate temperatures (for a TiN$_x$ layer thickness of 4–8 µm)

Substrate temperature (°C)	$(p_{H_2}/p_{N_2})_0$	TiCl$_4$ flow rate ($\times 10^{-3}$ mol h^{-1})	Critical load (N)
500	9.5	5	1
	9.5	7.5	2–9
	3.4	10	0
	9.5	10	18–75
	12.7	10	31–54
600	9.2	7.5	8–16
	3.7	10	21–49
	9.5	10	33–100
	9.5	15	33–66
700	9.5	10	24–36
	4.2	15	32–90
	9.5	15	85–113
	10	20	87–114
	9.1	26	94–110

the interface range, whereas the increase in the adhesion strength with increasing deposition rate and plasma power density should be caused by decreasing oxygen and chlorine concentrations in the layers and

by stronger interaction between activated gas-phase species and solid atoms (see Figs 4 and 5, and Table II). Furthermore, a suitable plasma pretreatment of the substrate directly before the start of the deposition process can also improve the adhesion. As a result, a remarkable increase in the critical loads to values between 40 and 75 N was observed for the TiN_x layers deposited at 500 °C.

The microhardness of the TiN_x layers was measured by means of a Vickers indenter with a load of 0.5 N (Table V and Fig. 9). An elevated oxygen level in the layers led to a lower microhardness than in the stoichiometric TiN_x. The influence of the substrate temperature on the microhardness of nearly stoichiometric and oxygen-poor coatings is shown in Table V.

The PVD layers prepared at low temperatures also had relatively high microhardness values. After a tempering procedure at 700 °C, the microhardness of these layers was reduced to values nearly equal to $2500H_v$ according to our microhardness at 700 °C [16]. One explanation is that the higher microhardness was caused by layer stresses and lattice imperfections, but the effect of the grain-boundary hardening cannot be excluded.

Friction wear investigations were carried out with a modified pin–disk–tribometer, where the coated cermet edge was placed in contact with a rotating

silicon-nitride ring. Correlations were found between the process parameters and the results of the layer characterization (scratch test, microhardness, oxygen content). The TiN_x layers with low oxygen contents and the highest microhardnesses had the lowest friction wear (Fig. 9).

3.4. Wear behaviour

The wear behaviour of the TiN_x-coated cermets was investigated by continuous and interrupted turning tests with steel and cast iron. The coating of cermets with titanium nitride by PECVD caused a substantially higher cutting performance in continuous (Figs 10–13) and interrupted turning.

The influence of the layer thickness and the substrate temperature on the tool life in continuous turning of the unalloyed steel C60N is presented in Figs 10 and 11. The longest edge life was observed for a layer thickness of 3–6 μm. The influence of the substrate temperature was relatively low. The coatings deposited at 700 °C had a higher wear resistance for a cutting speed of 200 m min^{-1}, but the coatings depos-

TABLE IV The dependence of the critical load of TiN_x layers measured by the scratch test on the plasma power density at a substrate temperature of 500 °C (for a TiN_x layer thickness of 4–8 μm)

Power density (W cm^{-2})	0.4	0.5	0.6
Critical load (N)	4 ± 3	22 ± 4	45 ± 16

TABLE V The dependence of the microhardness of the TiN_x layers on the substrate temperature

Substrate temperature (°C)	Microhardness, H_V [0.05]
500	3320
600	2880
700	2330

Figure 10 Continuous turning of the steel C60N plotting the dependence of the tool-life increase of PECVD-TiN_x-coated cermets (with a substrate temperature of T_s = 500 °C) on the layer thickness (uncoated cermet = 100%) at a constant flank wear of 0.3 mm.

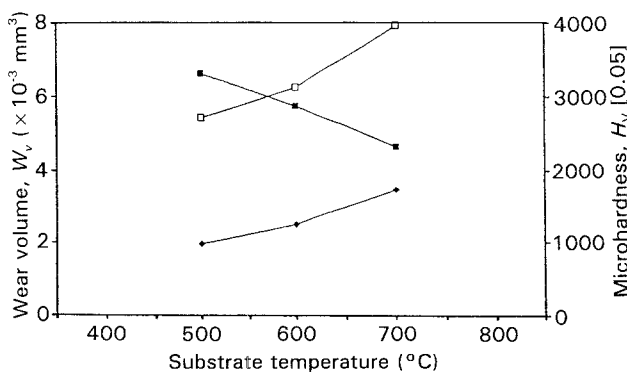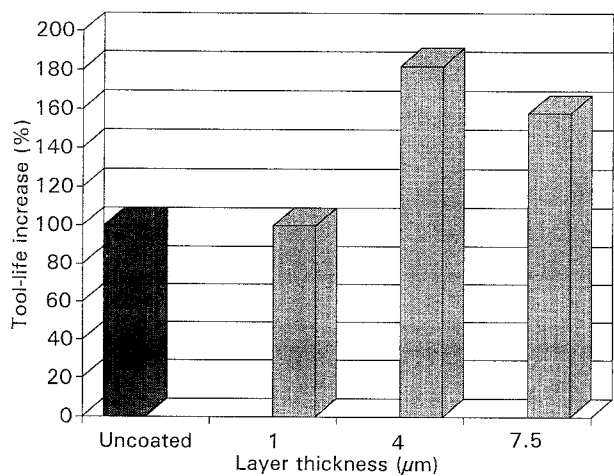Figure 9 ($\square$, $\blacklozenge$) The erosion volume of coated cermets and ($\blacksquare$) the TiN_x microhardness as a function of the substrate temperature (for a normal load of 5 N, and a friction length of 300 m). For TiN thicknesses of: ($\blacksquare$, $\square$) 3 μm, and ($\blacklozenge$) 7 μm.
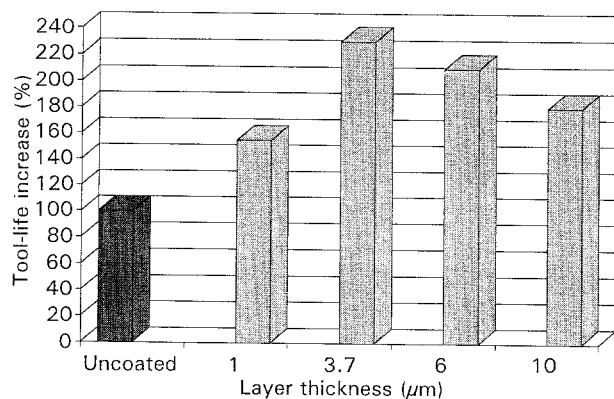
Figure 11 Continuous turning of the steel C60N plotting the dependence of the tool-life increase of PECVD-TiN_x-coated cermets (for a substrate temperature of T_s = 700 °C) on the layer thickness (uncoated cermet = 100%) at a constant flank wear of 0.3 mm.

Figure 12 Continuous turning of the cast iron GGL 25 plotting the dependence of the tool-life increase of PECVD-TiN$_x$-coated cermets (with a substrate temperature of $T_s = 500\,°C$) on the layer thickness (uncoated cermet = 100%) at a constant flank wear of 0.3 mm.
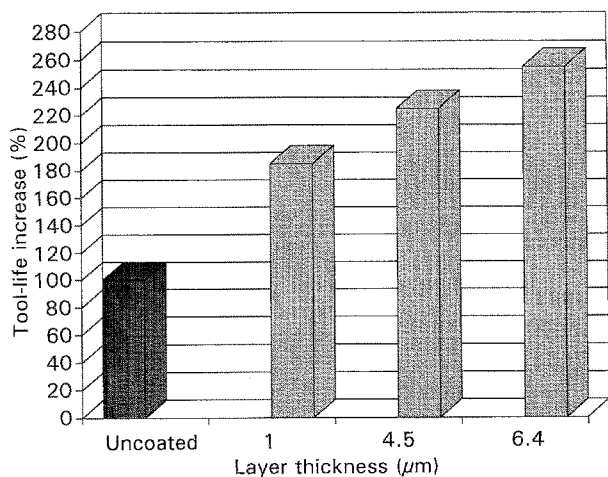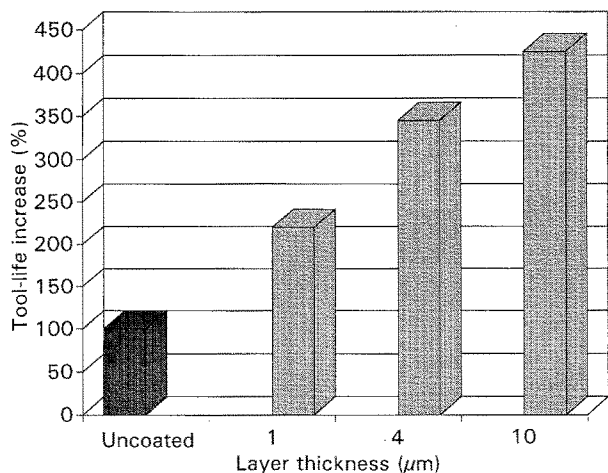

Figure 13 Continuous turning of the cast iron GGL 25 plotting the dependence of the tool-life increase of PECVD-TiN$_x$-coated cermets (with a substrate temperature of $T_s = 700\,°C$) on the layer thickness (uncoated cermet = 100%) at a constant flank wear of 0.3 mm.

ited at 500 °C had better results at lower cutting speeds.

As mentioned earlier, for applications in the interrupted cutting of steel, only binder metal-rich substrates with sufficient toughness was used. The interrupted turning test was carried out in the cutting speed range 80–300 m min^{-1} for two cutting depths, 1.0 and 2.5 mm. The coated cermets with a 4–7 μm TiN$_x$ layer had a twofold to threefold longer tool life than the uncoated cermets. The coating procedure at 500 °C, in comparison with that at 700 °C, resulted in a higher edge life, especially for a cutting depth of 2.5 mm. For the lower cutting depth, 1.0 mm, the cermets prepared at the two temperatures had comparable lifetimes. Kato *et al.* [5] also found higher lifetimes for TiN$_x$-coated cermets in the continuous turning test with steel, but higher lifetimes were not found in the interrupted cutting test. Kato *et al.*'s PVD coating process at 700 °C with long deposition times,

145–450 min, led to a considerable lowering of the transverse rupture strength (TRS). We also measured the TRS of our PECVD-coated cermets, and only a weak decrease, below 5% was found for substrate temperatures up to 600 °C and a value of nearly 10% was found, at 700 °C. The reason for this is the shorter deposition time of 30–120 min, and we believe this shorter time is an advantage of the PECVD process. The lower edge life of our cermet prepared at 700 °C, for a cutting depth of 2.5 mm, is correlated with this lowering of the TRS.

For the first time we have reported wear investigations of coated cermets for the cutting of cast iron. Another behaviour can be stated there. So far, the relative unimportance in industrial applications of uncoated cermets is caused by their progressive flank wear, their crater wear and their partial formation of a buildup edge. A high initial wear for cutting speeds higher than 180 m min^{-1} was also observed. Coating of cermets with TiN$_x$ by PECVD remarkably improves the wear resistance. The lifetime increases as the layer thickness increases (Figs 12 and 13) up to a fourfold increase over the value in the uncoated cermet. These PECVD coatings have excellent adhesion, especially in the layers deposited at 700 °C, in spite of their high thicknesses.

4. Conclusions

TiN$_x$ layers were deposited on cermets using pulsed, d.c., PECVD in a hot-wall reactor system. The most important process parameters influencing the deposition rate, the layer composition, the structure, the properties and the wear behaviour were the TiCl$_4$ flow rate, the hydrogen/nitrogen partial-pressure ratio, $(p_{H_2}/p_{N_2})_0$, the substrate temperature and the power density of the pulsed d.c. glow discharge. The following results were obtained.

1. Nearly stoichiometric TiN$_x$ layers with low oxygen and chlorine impurities can be prepared at high deposition rates, which are characterized by a sufficiently high TiCl$_4$ flow rate of $(p_{H_2}/p_{N_2}) > 9$, a plasma power density in the range 0.4–0.8 W cm^{-2} and substrate temperatures of 500–700 °C.

2. The formation of brittle intermetallic phases can be avoided, up to a substrate temperature 700 °C.

3. The TiN$_x$ layers usually had a columnar structure with a $\langle 2\,0\,0 \rangle$ texture, a granular, equiaxed structure was obtainable for higher TiCl$_4$ partial pressures.

4. The highest microhardness values, above 3000 H_v, were observed for the layers prepared at 500 °C. The tendency of the microhardness values correlates with the results of the friction wear investigations: the higher the microhardness is, the lower will the friction wear be.

5. The adhesion strength of the TiN$_x$ layers was best for coatings with low oxygen and chlorine contents, and it therefore depends on the initial gas phase and on the plasma parameters. The adhesion strength can be improved with an increase in the substrate temperature and with a suitable plasma pretreatment.

6. The wear resistance of the cermets was remarkably increased by coating with TiN$_x$. This was found

for the continuous turning of steel and cast iron and for the interrupted turning of steel. The lifetime increased by a factor of two for the continuous turning of unalloyed steel and by a factor of four for the turning of cast iron.

Acknowledgements

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