Hard and wear-resistant titanium nitride coatings for cemented carbide cutting tools by pulsed high energy density plasma

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Abstract

Hard and wear-resistant titanium nitride coatings were deposited by pulsed high energy density plasma technique on cemented carbide cutting tools at ambient temperature. The coating thickness was measured by an optical profiler and surface Auger microprobe. The elemental and phase compositions and distribution of the coatings were determined by Auger microprobe, x-photon electron spectroscope, and X-ray diffractometer. The microstructures of the coatings were observed by scanning electron microscope and the roughness of the sample surface was measured by an optical profiler. The mechanical properties of the coatings were determined by nanoindentation and nanoscratch tests. The tribological properties were evaluated by the cutting performances of the coated tools applied in turning hardened CrWMn steel under industrial conditions. The structural and mechanical properties of the coatings were found to depend strongly on deposition conditions. Under optimized deposition conditions, the adhesive strength of TiN film to the substrate was satisfactory with the highest critical load up to more than 90 mN. The TiN films possess very high values of nanohardness and Young’s modulus, which are near to 27 GPa and 450 GPa, respectively. The wear resistance and edge life of the cemented carbide tools were improved dramatically because of the deposition of titanium nitride coatings.

Keywords: Pulsed plasma; TiN film; Cemented carbide; Cutting tool

1. Introduction

Thin films are widely used as coatings in a variety of applications, either as structural overcoats or as functional coatings. Various hard coatings have been shown to improve the tribological properties of tools in an ideal way and widely used to improve the performance and extend the life of cutting tools, dies and moulds, etc. In many cases, titanium nitride is one of the best coating materials because it can satisfy most of the coating requirements. However, sometimes traditional hard coatings of titanium nitride (TiN) cannot meet the
requirements in many applications, especially under extreme conditions, because of its relatively low hardness (~2000 Hv), high friction coefficient (>0.4), inadequate thermal stability and insufficient corrosion resistance [1–3]. Much attention has been paid to date to the deposition techniques. The most frequently employed synthetic approaches to hard and wear-resistant coatings are chemical vapor deposition (CVD) and physical vapor deposition (PVD) processes. Both partly competing deposition techniques, permit the deposition of thin hard coatings (approximately 3–15 µm) on tools, but differ regarding process temperature and process flexibility [4].

Mainly for coating cemented carbides, the CVD hard coating processes usually operate at higher temperatures (750–1000 °C) and permit lower reaction temperatures by the use of special precursors. They are, however, limited by the requirements of environment protection and by thermodynamic reasons for the synthesis of complex metastable coatings. Being more environmentally friendly and more thermodynamically suitable for the deposition of ternary and quaternary multi-component superhard coatings as compared to the CVD processes, PVD processes operate at a lower deposition temperature between 180–500 °C and permit the coating of heat treated tool steels without loss of hardness in the substrate material. The coating of high speed steel tools, drills, end mills, plain milling cutters, broaches, reamers, forming tools and others represent a wide range of applications [2–5]. However, there are still problems of low adhesive strength between the substrate and coatings, and low deposition rate [3,5].

In this investigation, a new technique, pulsed high energy density plasma, is introduced to the processing of coatings.

2. Experimental

2.1. Some fundamentals of the pulsed high energy density plasma

The experimental equipment for coating is schematically illustrated in Fig. 1. It consists of three sections: the fast pulsed magnetic-valve characterized by the pressure of working gas ($P_{N2}$) and the working voltage ($V_{puff}$), the pulsed plasma gun characterized by the discharging voltage between the outer and inner electrodes ($V_{gun}$), and the vacuum reaction chamber, where the sample temperature, the distance ($d$) between the sample and the coaxial pulsed plasma gun, and the chamber pressure are the most important parameters that influence the properties of the coatings. More detailed descriptions are presented in Refs [5–8].

During coating, when the base pressure in the reaction chamber was below $10^{-3}$ Pa, a voltage of a few kVs was loaded between inner and outer electrodes of the pulsed plasma gun. The discharge was initiated after the working gases were pumped into the chamber at certain values of pressures (approximately 0.1–0.2 Pa) by the fast pulsed magnetic-valve ($P_{N2} \sim 2 \times 10^5$ Pa). The discharge would cause the working gases and the electrode materials to be ionized into plasma with the percentage of un-ionized atoms being lower than 5%.

The plasma was then accelerated to a high translational speed of 10–50 km/s under the action of the Lorentz-force $J \times B$. The speed of the plasma mainly depends on the discharging voltages. At the end of acceleration, there were almost no un-ionized atoms in the plasma. Then the plasma spurts from the coaxial plasma gun and bombards the sample surface where some special reactions between materials of the substrate and the plasma might occur [5–8].

The plasma was detected and analyzed by a double Langmuir probe and GE-100 optical grating spectroscopy. The plasma parameters are summarized in Table 1 [5–8]. Just because of the high electron temperature and high energy density of the plasma, its thermal effect, which varies with the thermal diffusivities of different substrate materials, will spread theoretically to a depth of approximately 20–30 µm in the cemented carbide substrates. The amount of implantation of process gases will be at least $10^{17}$ particles/cm².

Experiences with a variety of coatings, including TiN, Ti(CN) and cubic BN coatings on metallic substrates [6–8], and TiN coatings on silicon nitride ceramic substrate [5], have shown that the coatings fabricated by this technique have strong...
adhesion to the substrate, relatively high deposition rate, high efficiency of using energy, easy control of the chemical composition and thickness of the coatings, and the capability to form compound coatings at low temperature. The pulse plasma technique has three combined effects: deposition, ion implantation and quenching. One of them may play a more important role than others in surface treatment depending on experimental conditions [8–10]. In this paper, the preparation and properties of TiN coating on cemented carbide tools were reported. The influences of (shot) number of the pulsed plasma ($N_{\text{pulse}}$) and discharging voltage of the pulsed plasma gun on the microstructures and properties of the coatings onto cemented carbide substrates were investigated.

2.2. Deposition of TiN coatings

As substrates, cemented carbide cutting tools with an international standard shape of SNGN 1204 08 0.3 × 30° (12.7 × 12.7 × 4.76 mm) were used. The surfaces of partial samples were polished using diamond paste to an average surface roughness (Ra) of 0.02 μm in order to carry on nano-hardness and nanoscratch tests after coating. The main properties of the substrate material are listed in Table 2. The tools were cleaned ultrasonically before coating.

TiN was selected as the coating material and deposited by pulsed high energy density plasma. In this study, titanium was used for both the outer and inner electrodes. Nitrogen with a purity of more than 99.9 vol.% was used as working gas. The deposition process parameters are specified in Table 3. $N_{\text{pulse}}$ and $V_{\text{gun}}$ were changed in the range of 1–40 times and 1.5–3.5 kV, respectively, in order to investigate their influences on the properties of the coatings.

2.3. Characterization of the coatings

The microstructures of the specimen surface and cross-section were observed using a JSM-6301F scanning electron microscope (SEM). Typical results are shown in Fig. 2.

The coating thickness and surface roughness were measured with a Wyko optical profiler MHT-III. Typical results are illustrated in Fig. 3.

The elemental distributions of the coatings were recorded by a PHI-610/SAM surface Auger microprobe (AES), and the elemental bonding
Table 2
The main parameters of the substrate materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Density</th>
<th>Microhardness</th>
<th>$K_{IC}$</th>
<th>$\sigma_{RT}$</th>
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<tbody>
<tr>
<td>Cemented carbide</td>
<td>14.6–14.9 g/cm³</td>
<td>13–16 GPa</td>
<td>&gt;10 MPa·m¹/²</td>
<td>&gt;1670 MPa</td>
</tr>
</tbody>
</table>

Table 3
Experimental conditions for the deposition TiN thin films

<table>
<thead>
<tr>
<th>Discharging voltage</th>
<th>$V_{puff}$</th>
<th>$P_{N2}$</th>
<th>Gun-to-sample distance</th>
<th>Chamber pressure</th>
<th>Sample temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0–3.5 kV</td>
<td>1.5 kV</td>
<td>~2.0×10⁵ Pa</td>
<td>30 mm</td>
<td>10⁻³ Pa</td>
<td>Room temperature</td>
</tr>
</tbody>
</table>

Fig. 2. The SEM images of typical sample: (a) surface, second electron; (b) cross-section, fracture, second electron; (c) cross-section, fracture surface, backscattering; (d) cross-section, polished, backscattering. Synthesis conditions: $V_{gun} = 3.0$ kV, $N_{pulse} = 2$. 
states were determined by a PHI-5300/ESCA X-ray photon-electron spectroscope (XPS). The phase composition of the samples was determined by X-ray diffraction (XRD) using a D/max-RB diffractometer with a Cu Kα radiation of 1.541 Å at 40 kV and 120 mA. A continuous-scan method was used with 6° per min. Some of the results are illustrated in Figs 4–6.

The nanoscratch (NST) and nanoindentation tests (NHT) of the coatings were carried out under a mode of dynamic loads using an XP nanoindenter (Nanoinstruments Innovation Center, MTS systems, TN, USA). During the nanoindentation tests, the main test inputs were listed below: the maximum load 300 mN, the depth limit 500 nm, and the allowable drift rate 0.1 nm/s. Figs 7–9 illustrate the influences of \( N_{\text{pulse}} \) and \( V_{\text{gun}} \) on the
nanohardness and Young’s modulus, and the critical loads of the coatings during nanoscratch tests. The coated cutting tools were also used in turning hardened CrWMn steel (HRC 58-62) to evaluate the wear performance of the coatings. The cutting performances of the tools are shown by flank wear and edge life as illustrated in Figs 10 and 11.

3. Results and discussion

3.1. Structure

The microstructures of the coatings strongly depend on the deposition conditions, especially \(N_{\text{pulse}}\) and \(V_{\text{gun}}\). In terms of hardness and adhesion, \(N_{\text{pulse}}\) and \(V_{\text{gun}}\) for TiN coating onto cemented carbide substrates were optimized to more than 5 pulses and 3.0 kV, respectively. Fig. 2 shows the SEM images of a typical sample surface and cross-section of TiN coating on cemented carbide substrate. The cross-section microstructure (Fig. 2b–d) shows that the coating has a densified structure compared to the substrate structure, although there may be some porosity in the coating. As can be seen, the size of porosity in the coating was not more than 250 nm, and the grains of coating (approximately 100 nm) are fine as compared to those of the substrate (approximately 1–1.5 µm). It can also be
seen from Fig. 2c–d that the grains of the substrate became finer after coating, due to the radiation effect of the high energy density plasma. No apparent columnar grain structure as presented predominantly in typical vapor deposited TiN coatings was observed, and it is suggested that the coatings may at least partly have to do with an equiaxed structure. The main reason for the equiaxed structure is that the bombardment of the plasma in pulsed mode restricts the growth of TiN grains and forces TiN to renucleate although the instant temperature increasing in substrate (in fact, the substrate temperatures were only slightly higher than room temperature) during plasma bombardments may also play an important role in the TiN growth. And further research has been carried on. The dense and equiaxed structures with fine grains provide the base for the high hardness of the coated tools and the excellent wear performance as presented in sections 3.3 and 3.5. The surface SEM image (Fig. 2a) also indicates that the coatings exhibit fine grains and smooth surface. Although the coated tool surface was a little rougher than that of the cemented carbide tool substrate, the average roughness (Ra) of the coating surface observed by an optical profiler was not more than 100 nm. The smooth tool surface means that the coatings are promising candidates for cutting tools of high precision.

The film thickness is related to the electrode material, the substrate material, \( N_{\text{pulse}} \), \( V_{\text{gun}} \), and the distance \( d \) between the gun and the substrate. According to the results from the Wyko optical profiler, the relationship between the thickness of the deposited coatings and \( N_{\text{pulse}} \) were illustrated in Fig. 3. From this figure, it can be seen that the deposition rates of titanium nitride films were approximately 1.2–1.5 \( \mu \text{m} \) per pulse (one shot of the pulsed plasma) with a small decrease in deposition rate along with the increase in \( N_{\text{pulse}} \) under the deposition conditions as listed in Table 3, which is generally consistent with the results of AES analysis as showed in Fig. 5. Compared with TiN coatings deposited onto a ceramic substrate under the same conditions where the grain size of TiN is not more than 80 nm, the interfaces between the coatings and substrates are approximately 300 nm, and the deposition rate is measured to be 60–80 nm/pulse [5], this coating has a slightly larger grain size and much higher deposition rate per pulse, but somewhat thinner interfaces between the substrate and the coatings, which may be attributed to the different thermal diffusivities of both substrate materials, in other words, different temperature effects from the pulsed plasma. With increasing \( V_{\text{gun}} \), the coating exhibits a thicker interface, due to the increasing implantation effect of the pulsed plasma. The thickness of the coating and interface decreases with the increase in \( d \), due to the decrease in energy or speed of the plasma.

Fig. 4 shows the XRD spectra of typical samples. The coating exhibits a polycrystalline structure with (111)/(200) preferential growth. Roughly estimated from the XRD peak width, the grain size is no more than 80 nm, which is consistent with the SEM observations, and the lattice constant is about 4.24 Å, which is consistent with the value calculated theoretically.

3.2. Composition

The elemental compositions and distributions in depth of the typical sample shown in Fig. 5 were calculated from its Auger results. Here the sputtering rate by \( \text{Ar}^+ \) etching was 25 nm/min. From Fig. 5, it can be seen that the total thickness of the coating was about 2.5 \( \mu \text{m} \), which is consistent with the results of SEM observation and optical measurement, and the interface between the coating and substrate was approximately 250 nm and basically comparable to the results of SEM observation, which means that the coatings and the substrates mix with each other closely. The long tails and gradual/or graded coating-substrate interface transition, which promise a strong adhesive strength between the coating and the substrate, are due to the implantation effect of the plasma into the cemented carbide substrate. The compositions of the coatings were also determined by XPS. A typical result is illustrated in Fig. 6. The XPS analysis shows that titanium and nitrogen are the main elements in the sub-surface region with a certain amount of oxygen atoms as contaminants and some carbon atoms due to the sputtering effect of plasma. The ratio of titanium to nitrogen is about 1.1:1, which is consistent with the results of AES.
and XRD analysis. It should also be mentioned that, due to the sputtering effect, there were sometimes, some W and Co atoms in the sub-surface region in certain cases. The XPS results are basically consistent with the XRD patterns as illustrated in Fig. 4.

All the results presented above proved that TiN coatings were successfully deposited onto the cemented carbide substrates. Why can the titanium nitride be formed at ambient temperature onto the substrates? This indeed is one of the advantages of plasma synthesis of compounds. In the plasma process using the coaxial plasma gun, the working gases are ionized, causing atoms to lose or gain one or more electrons. So, the reaction of ionized gases requires much less energy, and can occur at a low temperature. The pulsed plasma can also cause a fast heating and cooling process on the sample surface, which will render the surface structure microcrystalline, amorphous and ceramic depending on the experimental conditions [6].

3.3. Hardness and Young’s modulus

Fig. 7 shows the relationship between the changes of nanohardness and Young’s modulus of the coated tools, and shot number of the pulsed plasma \((N_{\text{pulse}})\). Fig. 8 shows the nanohardness and Young’s modulus of the coated tools as functions of the discharge voltage \((V_{\text{gun}})\). Three features should be stressed here:

1. The coated tools show large increases in nanohardness and Young’s modulus as compared with the cemented carbide cutting tool substrate, and the maximum increases in nanohardness and Young’s modulus are approximately 48% and 54%, respectively. The possible mechanisms for the enhancements in hardness and Young’s modulus include radiation hardening during the implantation of plasma, the formation of metastable super-saturated solid solution, and solid solution hardening. The vapor deposition at a relatively lower temperature significantly increases the super-saturation of the sputtered particles on the growing surface which favors the formation of solid-solutions and even metallic glasses [11,12]. These are reasonable considering the discussion in sections 3.1 and 3.2.

2. The nanohardness and Young’s modulus of the coated tools increase with the increase in \(N_{\text{pulse}}\), and gradually become constants. Besides the effects mentioned in the upper section, with the increase in \(N_{\text{pulse}}\), the thickness of the coatings increased as illustrated in Fig. 3, and the effect of the cemented carbide tool substrates with lower hardness and Young’s modulus decreased. So, the hardness and Young’s modulus of the coatings increased with increasing \(N_{\text{pulse}}\). Because the coatings possessed the same composition and structure, their values of hardness and Young’s modulus would be near to constants (the real values of the TiN coatings deposited), although their thickness may be somewhat different.

3. As discussed before, the proper \(V_{\text{gun}}\) also plays an important role in the formation of dense alloyed phase solid solution with fine grain size. This mechanism enhanced the coating’s hardness. The nanohardness and Young’s modulus almost increase linearly with the \(V_{\text{gun}}\), due to the increasing implantation effect of the pulsed plasma. Because of the increase in \(V_{\text{gun}}\), there are increases in the energy, the density, the temperature and the speed of the pulsed plasma, the hardening effect on the coatings and the substrates enhanced. The following factors may also have contributions to some extent to the strengthening of the surface hardness: the fast heating and cooling process may induce compressive stresses in the surface layer; the fine grains may increase the potential to prevent movement of the dislocation; the pulse plasma may induce a high density of tangled dislocations, which can also restrict the motion of the dislocation [5,8].

3.4. Adhesion strength

Micro/nanomechanical and tribological characterization of the coatings deposited have been conducted using a nanoindenter with a nanoscratch attachment by many researchers [13–16]. A well-defined critical load \((L_c)\) for each film was determined by the nanoscratch techniques. In this investigation, the coatings were scratched by a face-forward Berkovich diamond indenter with a
continuous depth sensing nanoscratch system like
the method used by these researchers. Experimental results indicate that the nanoscratch system has very good sensitivity for detecting the coating cracking, delamination, and brittle fracture caused by scratching. The adhesion strength of thin films to substrates is characterized by the critical load at which any of the coating failures occurred. Fig. 9 illustrates the critical loads of TiN films onto cemented carbide substrate as a function of $N_{\text{pulse}}$ and $V_{\text{gun}}$. Three points should be highlighted here:

1. All the samples exhibit rather high critical loads, and the penetration depths at critical loads are in the range of 0.3–6.0 µm, indicating that this process can effectively improve the adhesion strength of the alloyed coating on the cemented carbide cutting tool substrate. The maximum critical load could be higher than 90 mN, by which the maximum penetration depth is not more than 2.0 µm, indicating that the film was very well adhered to the cemented carbide substrate. The implantation of the plasma ions was responsible for it. From this, one can see from the wide graded interface between the deposited film and the substrate from the elemental distributions as shown in Fig. 5. The wide graded interfacial layers as transitional layers strengthened the adhesion of TiN films to the cemented carbide substrates.

2. With an increase in $N_{\text{pulse}}$, the $L_c$ gradually increases and eventually become a constant, which is similar to changes of hardness and Young’s modulus with an increase in $N_{\text{pulse}}$. The reason for this change is that an increasing film thickness tends, usually, to decrease the shear stress transmitted to the interface, which results in a good adhesion of the films to the substrate [5,8]. The reason that the $L_c$ approached to a constant with increasing $N_{\text{pulse}}$ may be due to the same effects resulting in the changes in nanohardness and Young’s modulus.

3. The adhesion strength increases linearly with $V_{\text{gun}}$, which is similar to changes of hardness and Young’s modulus. The reason should be the same as that of the change in nanohardness, that is, it is due to the increases in speeds, density and temperature of the plasma with an increase in $V_{\text{gun}}$ [5,8].

3.5. Wear

The wear performance was evaluated by the turning of steel with the coated cemented carbide cutting tools. Usually, the uncoated cemented carbide tools cannot be used in the turning of hardened CrWMn steel. To our knowledge, there is as yet no literature on the turning of hardened CrWMn steel using cemented carbide tools with TiN coatings. And traditional TiN coated tools cannot be used in turning such steel. However, the tools with TiN films prepared by high energy density pulse plasma technique were successfully used in the turning of such steel, and showed rather low flank wear and long tool life. The wear performances of the coated cutting tools are shown in Figs 10 and 11.

Many effects may influence the wear performance of a coated tool, including the film thickness, the adhesive strength of films to tool substrates, the cutting speed, and so on. Usually, under the same cutting conditions, with increasing cutting speed, the flank wear will increase; a coating surface with higher nanohardness may have a better cutting performance; increasing the thickness of film will extend the tool life; and a stronger adhesion of TiN films to the tool substrate will cause samples to have a better wear resistance [5]. For the coated tools presented in this investigation, the high hardness, excellent adhesion strength and perhaps the equiaxed grain structure of TiN coatings may play a positive role in the cutting performance.

4. Conclusions

Titanium nitride films have been successfully deposited at ambient temperature on cemented carbide tools using high energy density pulse plasma techniques. It was found that the structure and the mechanical properties of the coatings strongly depended on the deposition conditions, especially the shot number of pulsed plasma and the discharge voltage. Under optimized deposition conditions, the TiN coatings showed very high nano-
hardness and Young’s modulus, which were near to 27 GPa and 450 GPa, respectively. The adhesion strength of the TiN film to the cemented carbide tool substrate was also significantly improved. The maximum critical load by nanoscratch test was more than 90 mN. The tools with TiN coatings prepared by the technique can be used in turning hardened CrWMn steel under industrial conditions. The wear performance of the tool was improved dramatically by the deposited TiN coating, which means that such TiN coating is a good candidate for cutting tools for hardened steel.

References

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