Adhesion of reactive magnetron sputtered TiN$_x$ and TiC$_y$ coatings to AISI H13 tool steel

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Abstract

Reactive Magnetron Sputtered TiN and TiC films were deposited on AISI H13 tool steel and silicon (111) substrates, under nitrogen and argon or methane and argon reactive plasma. Depth sensing techniques were used to assess the mechanical properties of the films, namely hardness and Young modulus using a load of 7.0 mN. TiN and TiC were deposited using a magnetron sputtering technique, the amount of nitrogen in the sputtering gas being changed from 3 to 38 vol.% and the amount of methane from 2 vol.% to 27 vol.%. The $H/E$ ratio (Hardness/Young Modulus) of TiN films increases continuously when the amount of nitrogen in the sputtering gas is increased from 3 to 38 vol.%. For TiC films the ratio $H/E$ reached a maximum for a methane content of 12 vol.% in the sputter gas. The film to substrate adhesion was measured using Rockwell C tests. The adhesion of the film to the substrate was greater when the $H/E$ ratio of the film and of the substrate were similar.

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Keywords: Magnetron sputtering; $H/E$ ratio; Adhesion and coatings

1. Introduction

The deposition of ceramic films on tool steel by vapor deposition techniques is now a common practice. These layers can be produced by different processes, divided basically into two main groups: chemical vapor deposition (CVD) and physical vapor deposition (PVD). Each of these processes has advantages and disadvantages depending mainly on the final application and on the desired properties of the coating.

Controlling the adhesion of the deposited ceramic layer to the substrate constitutes one of the main difficulties and an object of concern of many research groups and of commercial organizations in the area of surface engineering and surface science. Some studies, developed during the 80s, showed that adhesion could be improved through the deposition of a Ti intermediate layer [1–3]. Other pre-treatments like substrate hardening and duplex treatments performed before PVD, CVD, HVOF (high velocity oxygen fuel) and multilayer depositions have led to a significant improvement of the film-substrate adhesion due to an increase of the load bearing capacity of the substrate [4–7]. The first work dealing with TiN coatings deposited on plasma nitrided tool steel surfaces was published in the 80s [8] and the plasma nitriding pre-treatments (low and high pressure) became technologically feasible for industrial applications [8–16]. When performed in a hybrid reactor (inside the same chamber), duplex treatments improve the adhesion of the TiN ceramic film to the substrate [13].

There are three different ways of relating hardness and Young modulus to the mechanical properties of the film. Matthews and Leyland proposed the study of the relationship between the tribological properties of ceramic coatings and the ratio between the hardness ($H$) and the Young Modulus ($E$) of the film. This ratio, according to the authors, is related to the elastic strain to failure of the coating [17]. On the other hand, the $H^3/E^2$ parameter proposed by Johnson [18] was associated to the coating resistance to plastic deformation [17]. This ratio can only be used for a configuration similar to a rigid-ball in contact with an elastic/plastic plate [18], provided that the hardness of
the plate is three times its yield strength [19]. Finally, \((H/E)^{1/2}\) has been related to the fracture toughness of the coating [20,21]. All these ratios are very important when analyzing the adhesion of the coating to the substrate.

The tribological performance of a coated surface strongly depends on the film-substrate adhesion. Several different methods have been used to measure adhesion. Scratch test adhesion measurements are very sensitive to changes in intrinsic (loading rate, scratching speed) and extrinsic factors (substrate and coating properties, surface roughness) [22]. The Rockwell C adhesion (CEN/TS 1071-8 standard) test may be easily carried out on coated specimens, giving qualitative information about the adhesion characteristics of specific coatings and can be used to rank coatings obtained under different processing conditions, being useful for industrial applications. The relationship between \(H/E\) ratios of substrate and coating and the adhesion strength quality determined in Rockwell C tests is not well established in literature.

The objective of this work is to assess the adhesion of magnetron sputtered TiN and TiC coatings to AISI H13 tool steel substrates using the Rockwell C test and to establish a relationship between the results and the \(H/E\) ratios of the substrate and of the deposited films.

2. Experimental procedure

2.1. Deposition of TiN, and TiC\(_y\) coatings

TiN\(_x\) and TiC\(_y\) films were deposited by reactive rf magnetron sputtering, using high purity 99.999% titanium target and (N\(_2\) and CH\(_4\)) reactive gases. The coatings were deposited on two types of substrates: polished quenched and tempered AISI H13 tool steel and (111) single crystal silicon. Tables 1 and 2 show the treatment conditions for obtaining TiN\(_x\) and TiC\(_y\) films, respectively. Substrate temperature was kept at 623 K, bias voltage was grounded and the power applied to the cathode magnetron was 500 W. Before deposition, the sputtering chamber was evacuated to less than 10\(^{-6}\) Torr (4.0 × 10\(^{-4}\) Pa). In all treatments a 200 to 400 nm Ti intermediate layer was deposited to improve adhesion [1–3].

2.2. Hybrid duplex treatment

Hybrid duplex treatments were carried out in a home built hybrid reactor shown schematically in Fig. 1, where pulsed plasma nitriding and unbalanced reactive magnetron sputtering are performed in the same cycle, without exposing the surface of the sample to atmospheric pressure. The treatment conditions are shown in Table 3. A commercially pure Ti target, 160 mm in diameter, was used placed at 120 mm from the substrate. Plasma nitriding was performed in conditions to avoid the formation of a white layer.

2.3. Mechanical properties of the films

Nanohardness and Young modulus of the coatings deposited onto the H13 steel were determined, using loading and unloading curves data, obtained with an instrumented nanoindentation equipment, using a Berkovitch tip (the values presented are the mean of 15 nanoindentation measurements). The measurements were made in a Hysitron Triboscope coupled to a SHIMADZU SPM 9500 J3® atomic force microscope. The Oliver and Pharr [21] method for measuring and calculating mechanical properties of materials using nanoin dentation techniques was used. A Berkovich diamond tip was used with a maximum load of 7.0 mN, a loading rate of 1.4 mN/s and a creep time of 5 s. The maximum nanoindentation depth did not exceed 10% of the film thickness.

Vickers microhardness measurements were made in the diffusion zone of plasma nitrided specimens with an indenter load of 10 g and for a loading time of 15 s. The mean value of 15 measurements made on top of the surface is presented.

2.4. Chemical composition, microstructure, and thickness of the coatings

Microstructure characterization, measurement of the coating thickness and WDS X-ray microanalyses were done on TiN\(_x\) and TiC\(_y\) coated Si wafers.

Chemical microanalyses were performed using a Leica/ Cambridge Stereoscan 440 scanning electron microscope equipped with a Microspec 400 wavelength dispersive spectrometer (WDS). Ti (99.6 wt.%), C (Vitreous) and BN (B=43.55 wt.% and N=56.45 wt.) standards (MAC-Micro Analysis Consultants) were used. Nitrogen quantification was optimized, reducing the influence of the Ti–L\(_1\) line (31.36 Å) on the N–K\(_\alpha\) line (31.60 Å). Si wafers were used as substrate, so that the WDS microanalyses showed lower peak superposition in the obtained spectra when compared to those obtained for a steel sample.

Microstructure and thickness of the coatings were determined with a scanning electron microscope (SEM) through the analysis of the fracture sections of coated Si wafers, which can be easily fractured.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CH(_4) flow (sccm)</th>
<th>Ar flow (sccm)</th>
<th>% vol CH(_4)</th>
<th>Pressure (mTorr)</th>
<th>Time (min)</th>
<th>Deposition rate (10(^{-2}) µm/min)</th>
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<tr>
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<td>6.0</td>
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<td>A4</td>
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<td>38.5</td>
<td>3.3</td>
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<td>19.0</td>
<td>26.9</td>
<td>2.3</td>
<td>120.0</td>
<td>0.47</td>
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<th>% vol CH(_4)</th>
<th>Pressure (mTorr)</th>
<th>Time (min)</th>
<th>Deposition rate (10(^{-2}) µm/min)</th>
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<td>3.3</td>
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<td>0.78</td>
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2.5. Rockwell C adhesion

An Otto Wolpert–Werke indenter was used for the Rockwell C (max. load 1471 N) adhesion tests. Even though the Rockwell C technique does not provide a quantitative evaluation of coating adhesion, it can be used to establish a classification of the quality of the adhesion. This kind of test is strongly dependent on coating thickness and substrate hardness. Loading the Rockwell tip generates damage next to the edge of the indentation mark. DIN CEN/TS 1071-8 standard was used to assess the damage and to rank the adhesion of different coatings, using an optical microscope with 100:1 magnification [24]. Three indentations were done on each sample. The strength adhesion quality varies from HF1 to HF6. HF1 to HF4 define a sufficient adhesion, whereas HF5 and HF6 indicate poor adhesion.

3. Results and discussion

3.1. Microstructure of the coatings deposited on Si

Fig. 2 shows SEM images of the reactively deposited TiN coatings with the Ti intermediate layers for conditions “A” as defined in Table 1. All the microstructures can be described as a dense array of clearly defined fibrous columnar grains, typical of zone-T in the Thornton structure - zone model. Table 1 shows that the increase in the nitrogen content of the reactive gas decreases the deposition rate due to poisoning of the target by the reactive gas [25–27]. Thus, the deposition time was increased to maintain the thickness of the deposited films. Fig. 3 shows microstructures of the samples B1, B2 and B3, which also resemble zone-T in the Thornton structure-zone model. On the other hand, the microstructure of the B4 sample is lamellar and graphite has precipitated on the surface of the sample. However, it is important to notice that no correlation can be predicted between these microstructures and the ones of coatings on steel substrate.

3.2. Nanoindentation and chemical composition

Table 4 shows nanohardness, Young modulus, thickness and chemical composition of the coatings deposited on AISI H13 tool steel.

Reactive magnetron sputtering in the A2, A3 and A4 conditions led to the formation of TiN as shown in Table 4, where the compositions of the films range from 45 to 49 at.% Ti.

<table>
<thead>
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<th>Table 3</th>
<th>Treatment conditions used in the hybrid process</th>
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<td>N2 flow (sccm)</td>
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<tr>
<td>PVD-A2</td>
<td>2.0</td>
</tr>
<tr>
<td>Plasma nitriding</td>
<td>200</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic representation of the hybrid reactor: Triode Magnetron Sputtering [23] and of the pulsed plasma nitriding.
While, reactive magnetron sputtering in the B2 condition led to the formation of TiC as shown in Table 4, from where it is seen that the composition is approximately 57 at.% Ti and 43 at. % C.

Increasing the nitrogen content in the sputter gas increases continuously the hardness of the samples (A2–A4). Grain size, preferred orientation and residual stresses could be responsible for the increase in hardness of these coatings. On the other hand, the increase of the methane content in the sputter gas up to 12% increases the hardness up to 33.6 GPa. The maximum hardness is reached when the Ti/C ratio approaches 1:1. These results were confirmed by X-ray diffractometry.

Fig. 2. SEM of the fracture cross-section of the coatings for reactive deposition Ti+N₂.

Fig. 3. SEM of the fracture cross-section of the coatings for reactive deposition Ti+CH₄.
Table 4
Mechanical properties, thickness and chemical composition of the coatings deposited by reactive magnetron sputtering

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hardness (GPa)</th>
<th>Young modulus (GPa)</th>
<th>Thickness (μm)</th>
<th>at.% C</th>
<th>at.% Ti</th>
<th>at.% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>9.5±0.9</td>
<td>176±10</td>
<td>3.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>20.1±0.5</td>
<td>340±8</td>
<td>2.5</td>
<td>45.01</td>
<td>54.99</td>
<td></td>
</tr>
<tr>
<td>A3</td>
<td>25.6±0.8</td>
<td>332±4</td>
<td>1.8</td>
<td>48.30</td>
<td>51.70</td>
<td></td>
</tr>
<tr>
<td>A4</td>
<td>28.6±1.6</td>
<td>353±8</td>
<td>1.8</td>
<td>48.53</td>
<td>51.47</td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>11.9±0.6</td>
<td>195±4</td>
<td>2.9</td>
<td>39.50</td>
<td>60.50</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>33.6±1.4</td>
<td>324±5</td>
<td>2.1</td>
<td>57.41</td>
<td>42.59</td>
<td></td>
</tr>
<tr>
<td>B3</td>
<td>14.3±1.1</td>
<td>147±5</td>
<td>2.3</td>
<td>76.47</td>
<td>23.53</td>
<td></td>
</tr>
<tr>
<td>B4</td>
<td>–</td>
<td>–</td>
<td>1.0</td>
<td>35.58</td>
<td>64.13</td>
<td></td>
</tr>
</tbody>
</table>

Table 5 shows the H/E ratio of the coatings obtained by reactive deposition of (Ti+N₂) and (Ti+CH₄) coatings deposited on quenched and tempered AISI H13 tool steel. The H/E ratio also increases continuously with the increase of the N₂ amount in the sputtering gas, for the range of nitrogen contents used in this work (from 3.0 to 38% of N₂ in volume). For the (Ti+CH₄) reactive deposition, the H/E ratio reached a maximum level for a methane content of 12 vol.% in the sputter gas.

The A1 to A4 and B1 to B3 conditions of reactive (Ti+CH₄) and (Ti+N₂) magnetron sputtered coatings allows changing the H/E ratio of the coatings between 0.054 and 0.103. This range of H/E ratio allows to compare the effect of the H/E ratio on the coating adhesion properties. On the other hand, the H/E ratio of the substrate can be changed by plasma nitriding. The H/E ratio of the quenched and tempered H13 tool steel is 0.023. After plasma nitriding the H/E ratio rises to 0.053.

In Table 5 it can be seen that TiN deposited in the condition A2 gives a H/E value around 0.05, similar to the one obtained for the nitried layer. Although sample B1 also has an H/E ratio around 0.05, its hardness is too low and this coating was considered useless for practical applications.

Fig. 4 shows an optical micrograph of the diffusion layer and of the TiN film after the hybrid duplex treatment. The thicknesses of the diffusion zone and of the TiNₓ were 20 μm and 2.5 μm respectively. Vickers hardness, measured on top of the diffusion zone layer, was 1250±10 HV₀.01.

Fig. 5 shows some typical results of the adhesion strength quality, obtained during the Rockwell C adhesion test [24] performed on the coatings deposited on AISI H13. Table 5 shows these results based on the observation of crack patterns on top of the specimens.

Samples A2, A3, B1, B2 and B3 show HF5 and HF6 adhesion strength qualities, indicating a poor adhesion to the substrate. Failure of the coating occurs with delamination due to the growth of radial cracks and to pile-up formation in the substrate. The A1 and A4 coatings show HF4 adhesion strength quality and failure of the coating also occurs by delamination due to the same mechanisms mentioned above, although in a smaller extent. HF4 adhesion strength quality may be interpreted as a transition between good adhesion and poor adhesion. None of the specimens showed circular cracks in the neighborhood of the indentation.

Plasma nitriding the H13 tool steel resulted in a 20 μm diffusion layer without the formation of a white layer; the adhesion strength quality of the coating deposited on the plasma nitrided steel was HF1. Although radial cracks and substrate pile-up could be seen near the indentation mark, they did not lead to failure of the coating by delamination, indicating a very good adhesion of the coating. The significant improvement of the adhesion strength quality can be associated to the hardening of the substrate due to plasma nitriding, increasing the load bearing capacity of the substrate.

The H/E values of the plasma nitrided substrate and of the TiN (A2) coating, deposited in the hybrid process, are very similar (~0.05), leading to a gentle transition of mechanical properties. It is worth noticing that the thickness of the TiN coating obtained in the hybrid treatment is also 2.5 μm.

According to Mathews et al. H²/E² is an indicator of the coating resistance to plastic deformation. The H²/E² values for the TiN (A2) film (H=20 GPa and E=340 GPa), for the plasma nitrided H13 steel (H=12 GPa and E=210 GPa) and for the non-nitrided H13 steel (H=6 GPa and E=210 GPa) are 0.04, 0.07 and 0.005 respectively. The H²/E² values for the TiN (A2) coating and for the plasma nitrided steel are quite similar, in contrast with the value for the non-nitrided steel which is one order of magnitude lower. This great difference accounts for the poor adhesion properties of the TiN coating to the non-nitrided quenched and tempered H13 tool steel.

4. Conclusions

Changing the amount of reactive gas in the rf magnetron sputtering process using (Ti+N₂) and (Ti+CH₄) gases, allows...
to obtain $H/E$ ratios of the Ti$_N$ and Ti$_C$ coatings from 0.054 to 0.103.

A Ti$_N$ coating, with 20 GPa hardness and an $H/E$ ratio near 0.053, deposited on plasma nitrided H13 tool steel gave the best results of adhesion in the Rockwell C adhesion test.

The hybrid duplex treatment of tool steels allows to obtain substrates and coatings with similar $H/E$ ratios, improving the adhesion of the ceramic coating to the substrate.

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