Microstructure, Mechanical and Tribological Properties of Reactive Magnetron Sputtered Titanium Carbide Coatings

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Abstract

This study describes the correlation between the microstructure, mechanical and tribological properties of Ti₁₋ₓCₓ coatings (with x being in the range of 0-1), deposited by reactive magnetron sputtering from a Ti target in Ar/C₂H₂ mixtures at ~200 °C. The mechanical and tribological properties were found to strongly depend on the chemical composition and the microstructure present. Very dense structures and high hardness and elastic modulus values, combined with low wear rates, were observed for films with chemical composition close to TiC. X-ray diffraction studies showed that the coating deposited at high C₂H₂ flow rates composed of randomly oriented TiC crystallites. Morphological investigations by scanning electron microscopy indicate that the morphology is strongly dependent on the carbon content of the coating. Coatings overall composition, and relative phase fraction are investigated using X-ray photoelectron spectroscopy. The presence of free amorphous carbon as DLC was found in the case of the coatings deposited at 43 and 50 sccm of C₂H₂, where this is not the case for coatings deposited at lower C₂H₂ flow rates. Both the mechanical properties and tribological
...performance of the coatings were found to be dependent on carbon content and the optimum performance was that of the coating deposited at 43 sccm where a nanocomposite dual system is formed.

**Keywords:** carbides, nanocrystalline, sputtering, tribology.

**Introduction**

Hard and low-friction carbon-based tribological (solid lubricant) thin films and coatings, the subject of a large amount of research over the last approximately 25 years [1] cover a wide range of industrial applications such as automotive, forming, punching, plastic moulding, biocompatible implants, and computer hard drives. Hard carbon based coatings have previously been shown to substantially increase contact fatigue life when applied to steel substrates [2]. Metal-free and metal-containing hard carbon based coatings have been intensively studied. Metal-containing coatings are reported to possess better adhesion to steel substrates than metal free hard carbon based coatings [3].

Transition metal carbides, such as TiC, characterized by short bonds, high hardness, high strength and high thermal and chemical stability, are widely used as wear resistant materials in, for example, carbide cutting tools [4]. One class of metal containing hard carbon based coatings are deposited by sputtering pure metal cathodes in inert/hydrocarbon gas mixtures, where coating deposition results from the reaction, at the substrate surface, of sputtered metal atom flux with gas phase ionic and radical hydrocarbon species generated from the glow discharge plasma [5]. In the last few years, advances in coating deposition technologies have resulted in the development of supertough wear-resistant coatings, based on nanocrystalline carbides (TiC, WC) in an amorphous diamond-like carbon matrix [6]. Another approach has been based on metal–metal nanocomposite coatings, promising considerable scope to provide a low coating elastic modulus, while allowing ceramic values of hardness to be achieved. Various studies have shown that physical vapor deposited (PVD) metallic coatings doped with nitrogen, carbon or boron (primarily in supersaturated interstitial solid solution) can provide ceramic or near-ceramic hardness, while retaining a low elastic modulus similar to that of the metal substrate component [7, 8]. These coatings
performed better in laboratory tribological tests compared to (often much harder) ceramic nitride, carbide or boride equivalents, with a correspondingly higher elastic modulus [7, 8].

In this study, we report the synthesis of TiC coatings by sputtering pure Ti cathode in the presence of different Ar/C₂H₂ flow ratios. Experimental results for the influence of various amounts of carbon on the structure, mechanical and tribological properties of PVD deposited Ti₁₋ₓCₓ films are presented. The overall result of this investigation can be summarized by stating that coatings deposited at intermediate C₂H₂ flow rates presented a denser structure and in turn possessed improved mechanical properties and better tribological performance.

**Experimental**

**Coating Synthesis**

Ti-C coatings were deposited onto polished 100Cr6 substrates by reactive magnetron sputtering from a segmented Ti target (5.7 W/cm²) of 1000 mm x 175 mm x 11 mm in argon/acetylene (Ar/C₂H₂) mixtures, using an industrial magnetron sputtering PVD unit with a base pressure of < 10⁻⁵ mbar and deposition pressure of 3-3.5 x 10⁻³ mbar, depending on the acetylene flow rate (varied from 0 to 63 sccm). Substrate temperature and target to substrate distance were kept constant at ~ 200 °C and 200 mm, respectively, and no substrate bias voltage was applied. Prior to deposition, the 100Cr6 stainless steel substrates were ultrasonically cleaned in acetone and then in ethanol, then placed in the chamber on the substrate table. Coatings for mechanical tests were then deposited to a thickness of 2 to 3.0 µm.

**Coating Analysis**

The crystallographic structure and texture of the films were analysed by glancing-angle X-ray diffraction (GAXRD), using CuKα radiation at an incident angle of 5.0°. Chemical composition of the Ti-C coatings was determined by X-ray photoelectron spectroscopy (XPS), using a VG-Scientific Sigma Probe spectrometer employing a monochromated Al-Kα source and a hemispherical analyser. Etching was performed at 3kV on a main chamber pressure of 1x10⁻⁷ mbar giving ~0.75 µA of etch current and using the x10 magnification
setting (~5mm etch area). The microstructure was investigated using Transmission electron microscopy (TEM). Fracture cross-sections of coated samples were prepared for SEM morphology and topography studies. Film thickness was measured using a Calotester from CSM (and verified by SEM cross-sectional measurements). The ball-crater method was applied using the Calotester to determine the thickness of different layers. The procedure was performed using a 20 mm diameter ball with 1000 l/min and 60 s of grinding period. Coating adhesion was evaluated according to the Rockwell C hardness test [9], where a coated sample is placed under the Rockwell indenter and a pilot load is applied before the main load is introduced. Coating cracks and/or delamination is compared against a defined adhesion strength quality, with a classification from HF1 to HF6, where HF1 indicates good adhesion, with only radial cracks around the indent and HF6 indicates poor adhesion. Hardness and elastic modulus values were determined using a Fischerscope H100 and a Clark Digital Microhardness Tester, both equipped with a Vickers indenter, and a Hysitron TriboScope, equipped with a Berkovich indenter. Loads were varied between 10 to 50 mN (Fischerscope and Clark Digital Microhardness Tester) and 3 to 6 mN (TriboScope), with a sequence of ten indents at each load.

Ball-on-disc dry sliding experiments were conducted at room temperature (22°C) at a controlled humidity 20% using a Standard Tribometer, shown in Figure 1. The sliding velocity was 0.1 m/s and a track radius of 11 mm. For better control of the experimental conditions Ruby balls were used so the only contribution to wear is from the coating. Ruby balls of 0.6 mm diameter were chosen as counterpart. The abrasive conditions of the Ruby counterpart were simulated using a load of 10 N corresponding to an initial Hertzian pressure of ….MPa. The resulting wear marks were analysed by optical microscopy and the coating wear volumes were in turn evaluated by stylus profilometry (TENCOR P-15).

Results and Discussion

Microstructure

Figure 2 shows the X-ray diffraction (XRD) patterns of the Ti-C coatings as deposited on 100Cr6 substrate at different C2H2/Ar flow rates. The standard 2θ positions for fcc (cubic) TiC (JCPDS # 32-1383) is added to the figure. The coating deposited at zero C2H2 flow rate the main crystalline phase was, as expected, metallic Ti (101) as indicated by reflection
which corresponds to Ti at 39.5°. Ti-C coatings deposited at low C\textsubscript{2}H\textsubscript{2} flow rates (25 and 37 sccm) present reflections which correspond to understoichiometric TiC\textsubscript{0.2} and TiC\textsubscript{0.7}, phases (as shown from XPS studies), respectively. The peaks now presented to be shifted from 39.5 (pure Ti) to 36.9° (25 sccm) and 36.1° (37 sccm), respectively. The coatings deposited at high C\textsubscript{2}H\textsubscript{2} flow rates (43 and 50 sccm) exhibited reflections which correspond to randomly oriented TiC crystallites. As the flow rate of C\textsubscript{2}H\textsubscript{2} increased the diffraction peak appeared at a lower angle. This is in agreement with an increase in the TiC lattice parameters as more carbon is incorporated in the lattice leading to the formation of stoichiometric and overstoichiometric TiC crystallites. In all cases no graphitic carbon peak or amorphous carbon was observed. To determine the crystallinity grade of the produced coatings, the grain size was determined from the Full Width Half Maximum (FWHM) of the X-ray peaks throughout the equation [10]:

\[
\text{grain size} = \frac{0.9\lambda}{\lambda \cos \theta \text{FWHM}}
\]

where, \(\lambda\) is the wavelength of the incident radiation and \(\theta\) is the Bragg’s angle. FWHM analysis indicated that the TiC-crystallite size is in the range of 7-18 nm. However, this particle size is different from that estimated from TEM studies. This suggests that the microstructure consists of stressed nanometer-sized metal carbide crystallites embedded in a matrix of amorphous carbon. This is in agreement with other similar systems in the published literature [11-13].

Laser Raman Spectroscopy was performed to clarify the binding state of the amorphous carbon and the results are shown in Figure 3. Raman bands of about 1550 cm\textsuperscript{-1} which appeared in the TiC (43 sccm) are attributed to the amorphous carbon with high hardness, i.e., i-carbon or diamond like carbon probably with the bond of sp\textsuperscript{3} hybrid orbital [14]. However, Raman bands of about 1380 and 1600 cm\textsuperscript{-1} which appeared in the case of TiC (deposited at 100 sccm) indicate that disordered graphite exists in this coating [14].

**SEM**

Figure 4 shows representative scanning electron microphotographs obtained over the cross-sections of two different coatings. As it is clearly seen in Fig. 4(a), the coating deposited at zero C\textsubscript{2}H\textsubscript{2} flow rate exhibits columnar microstructure which is typical for a
microcrystalline coating, whereas Ti-C coating deposited at 43 sccm C$_2$H$_2$ (Fig. 4(b)) exhibits a featureless “glassy” structure which is typical for a nanocrystalline growth mode. From SEM studies performed on all the coatings under study it was found that coatings deposited at C$_2$H$_2$ flow rates lower than 43 sccm presented a columnar microstructure where the size of the columns appears to depend on the metal and carbon content of the coating. The observed gradual change from a columnar towards to a non-columnar morphology at higher C$_2$H$_2$ flow rates is probably due to increasingly concurrent growth conditions of two different phases, amorphous carbon and TiC.

**TEM**

Figure 5 presents dark field transmission electron microscopy images obtained over TiC coatings deposited at 25 (Fig. 5a) and 43 (Fig. 5b) sccm flow rate of C$_2$H$_2$, respectively. From these images the average grain size is estimated to be approximately 6 nm and 4 nm for the first and the second coating, respectively. This difference in average grain size can be rationalized from the fact that in coating deposited at 25, there is only the TiC$_x$ phase, whilst for coating deposited at 43, both TiC$_x$ and DLC are present, so competitive grain growth leads to smaller grain sizes.

**XPS**

The chemical bonding structure of the near surface region of the coatings was studied by XPS. Error! Reference source not found. shows the respective Ti 2p (Fig. 6a) and C 1s (Fig. 6b) core-level spectra of the coatings deposited at different C$_2$H$_2$ flow rates. XPS analysis was performed, after sputter cleaning of the surface with an Ar ion rastered beam. The photoelectron peak Ti2p3/2 of a binding energy close to 454 eV corresponds to the carbide [15]. As the C concentration is increased, the Ti 2p peak shifts to higher binding energy, whereas the C 1s carbide peak remains at the same energy. This is consistent with a progressive change in the TiC$_x$ stoichiometry. As x increases (from sub-stoichiometric towards stoichiometric and over-stoichiometric), then the nearest neighbour environment of C atoms within TiC$_x$ will remain almost unchanged, but for the Ti atoms, there is an increasing number of nearest neighbour C atoms, hence the Ti 2p3/2 peak shifts to higher binding energies.
XPS results obtained on samples deposited at different C$_2$H$_2$ flow rates clearly revealed that C 1s presents more than one component, as clearly seen in Fig. 7. The fitted peak areas are a qualitative measure for the abundance of the individual bonds in the near surface region of each sample. The peak fitting of C 1s region was based on the binding energies of different C species, such as: bulk TiC at 282.1±0.2 eV, C atoms at the edge of the TiC nanocrystallites at 283.1±0.2 eV, sp$^2$ C at 284.5±0.2eV and sp$^3$ C at 285.2±0.2eV [15, 16, 17]. Figure 7 presents the peak fitting of C 1s region for the coatings deposited at 25 and 43 sccm, respectively. It can be observed that the C 1s region of coating deposited at 25 sccm C$_2$H$_2$ presents contributions only from bulk TiC (282 eV) and Ti at the edge of TiC grains (283 eV). On the other case presented, coating deposited at 43 sccm C$_2$H$_2$, contributions from bulk Ti, Ti at the edge of TiC grains, sp$^2$ C, and sp$^3$ C can be seen. Results of the overall TiC$_x$ stoichiometry and relative phase fraction are given in Table 1. Relative phase fraction was based on the assumption that a simple two phase system is present (TiC and DLC). According to the literature peaks at 282.1 and 283.1 eV give the carbide content and peaks at 284.4 and 285.2 eV give the DLC content [18].

**Hardness and Elastic Modulus**

Hardness and elastic modulus values, determined using a Fischerscope H100, as a function of C$_2$H$_2$ flow rate are plotted in Figure 8. Evaluation of these measurements was done using a Hysitron Triboscope instrument. For pure Ti coating (0 sccm C$_2$H$_2$), hardness values of approximately 6 GPa were observed (similar to bulk values). This low hardness value can be attributed to the soft metallic character of the coating according to XRD studies presented. With increasing C$_2$H$_2$ flow rate, the amount of carbon in solid solution in the titanium lattice increased. This is also in agreement with the 2 theta shift of XRD peaks at lower angles, as previously discussed. Hence, the hardness increase can be explained in terms of solid solution strengthening of the Ti coating with C-atoms. Another reason for hardness increase is the changing of carbon binding state from graphite to amorphous. A further increase in carbon led to an increase in hardness for coatings consisting of the TiC phase (43 sccm C$_2$H$_2$). For this coating, XPS studies revealed the presence of nanocrystalline TiC and 13 at.% of amorphous DLC phase. The amount of amorphous phase coincides with a monolayer surrounding the nanocrystallites leading in
this way to hardness improvement [19]. This structure generates increased hardness because the mobility of dislocations is hindered and the grain boundary sliding is suppressed at the decreased grain size.

Also, from Error! Reference source not found. it is clear that increasing the C$_2$H$_2$ flow rate (from 0 to 43 sccm) causes a rather significant increase in the elastic modulus values (from 131±7 to 249±12 GPa). On the other hand, for coatings deposited at high C$_2$H$_2$ flow rates a decrease in elastic modulus is observed. For coatings deposited at 43, 50, and 100 C$_2$H$_2$ flow rate the crystallite size of TiC$_x$, as estimated using Scherrer equation Error! Reference source not found., was found to be smaller than the one of the coatings deposited at low C$_2$H$_2$ flow rate due to competitive grain growth in these cases. Strong correlations between the variations of the elastic properties and the variations in the film thickness, grain size, has been previously reported 0.

According to the literature [21] the Ti dissolution limit in an a-C matrix is 4 - 8 at.%. As the Ti composition increases beyond the dissolution limit, the volume fraction of TiC nanometer sized crystallites embedded within the a-C matrix increases. With increasing TiC nanocluster volume fraction, the average coating modulus and hardness increase significantly. Increasing C$_2$H$_2$ flow rate in values higher than 43 sccm, a decrease in hardness and elastic modulus values was observed. The exact physical mechanism responsible for such decreases are unclear, but are likely to be related to the change in bonding configurations in the near region of TiC crystallites. Also, this decrease could be attributed to the change from a uniform to a non-uniform lattice expansion as more C in incorporated into the TiC lattice leading to the formation of overstoichiometric nanocrystallites [22].

An important parameter describing the plasticity of the material is H/E ratio. For the coatings studied here this ratio was found to increase in the 0.05-0.15 range as C$_2$H$_2$ flow rate increases. Highest H/E values ratio (elastic behaviour 0) was found for coatings deposited at C$_2$H$_2$ flow rates in the 43-100 sccm range. The coatings deposited at a lower C$_2$H$_2$ flow rates, exhibit the lowest H/E values corroborating their more plastic behaviour.

*Tribological Performance*
Figure 9(a) shows a photograph of a representative Ti-C coated specimen and the corresponding wear track diameter after 5,000 passes in ball-on-disc tests at room temperature (Ruby balls counterparts, 10 N load), and Figure 9(b) the corresponding wear track depth. The wear scans for all specimens started and finished outside the wear track as shown in Fig. 9(b). The profilometric scan shown in this figure was 1.5 mm long while the wear depth was approximately 1.5 µm as shown in Fig. 9(b). For all measurements, the same scan length was used, while the wear depth varied between 0.5-40 µm (Table 2).

The wear rate for all the coatings is presented in Figure 10. It is observed that the coatings deposited at 43 and 50 sccm of C₂H₂ flow rates exhibited the minimum wear rates. At the same time, the coefficient of friction was found to be in the 0.3-1 range. Coatings deposited at 0, 37, 43 and 100 sccm C₂H₂ presented a friction coefficient value of 1, 0.5, 0.35 and 0.7, respectively. Coatings deposited at low C₂H₂ flow rate, which consist of soft metallic Ti and understoichiometric titanium carbides (according to XRD and XPS studies) exhibited the worst performance in tribological tests (Figure 10). According to these results it is seen that the coating deposited at 43 sccm C₂H₂ presented the lowest value of friction coefficient, the minimum wear depth and wear rate. On the other hand, coatings deposited at 25 and 37 sccm of C₂H₂ consist only of TiC nanocrystallites, whereas no amorphous tissue phase was found. The coating deposited at 25 and 37 sccm flow rate produced a wear depth of 45 and 12 µm, respectively. On the other hand, the coating deposited at 43 and 50 sccm C₂H₂ flow rate exhibited the best performance (minimum wear depth, ~0.4 µm and 1.3 µm) during tribological performance. This can be attributed to the following: (1) according to the XRD studies, this coating consists of randomly oriented TiC crystallites (not understoichiometric phases), (2) XPS results after peak fitting showed that this coating consists of TiC nanocrystallites (4 nm) embedded in 13 at.% and 20 at.% of amorphous tissue C-phase (nanocomposite dual system), respectively. This nanocomposite dual system (nc-TiC/a-DLC) improves the hardness and leads to low wear rate, (3) the coating deposited at 43 sccm presented the highest hardness value due to its nanostructure and (4) according to Raman studies, the carbon state in this coating is amorphous carbon with high hardness. The coating deposited at 63 sccm C₂H₂ flow rate exhibited lower resistance during these tests. This could be attributed to change of binding state of incorporated
carbon in TiC coatings. These states could be graphite-like, diamond like or interstitial carbon [14].

Conclusions
In summary, we report results on the influence of the structure and chemistry on mechanical and tribological properties of magnetron sputtered Ti$_{1-x}$C$_x$ coatings. We showed that the coatings structure gradually changes from understoichiometric titanium carbide towards stoichiometric and overstoichiometric TiC with increasing C$_2$H$_2$ flow rates, while an additional amorphous DLC phase can be formed at intermediate C$_2$H$_2$ flow rates changing the whole system from one phase (TiC$_x$) to two phase (nc-TiC$_x$/a-DLC) nanocomposite system. These structural changes are accompanied by very dense coating growth modes which lead to with highest hardness and elastic modulus, combined with low wear rates and friction coefficient values.

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References

[17] ............
[18] ............
Table Captions:

**Table 1:** Stoichiometry and Relative phase fraction for TiC coatings deposited at different C₂H₂ flow rates, as obtained from XPS studies

**Table 2:** Effect of C₂H₂ flow rate on wear depth and friction coefficient for TiC coatings
Figure Captions:

Figure 1: High Temperature Tribometer (HTT) for friction coefficient and wear depth evaluation of Ti-C coatings.

Figure 2: XRD patterns of Ti-C coatings deposited at different C\textsubscript{2}H\textsubscript{2} flow rates.

Figure 3: Raman spectra obtained over the Ti-C coatings deposited at (a) 43 sccm and (b) 100 sccm, flow rates of C\textsubscript{2}H\textsubscript{2}.

Figure 4: Scanning electron microphotographs obtained over Ti-C coatings deposited at (a) 0 and (b) 43 sccm of C\textsubscript{2}H\textsubscript{2}, respectively.

Figure 5: Dark Field transmission electron microphotographs of TiC coatings deposited at (a) 25 and (b) 43 sccm of C\textsubscript{2}H\textsubscript{2}.

Figure 6: (a) Ti 2p and (b) C 1s XPS core level spectra for the Ti-C coating deposited at variable C\textsubscript{2}H\textsubscript{2} flow rate.

Figure 7: C 1s peak fitting for the TiC coatings deposited at 25 and 43 sccm C\textsubscript{2}H\textsubscript{2}.

Figure 8: Hardness and elastic modulus of Ti-C coatings.

Figure 9: (a) Ball-on-disc wear track of coated specimen after tribological test at 10N (5,000 passes) against Ruby ball counterpart and (b) corresponding wear track depth.

Figure 10: Effect of C\textsubscript{2}H\textsubscript{2} flow rate on the wear rate for TiC coatings different deposited at C\textsubscript{2}H\textsubscript{2} flow rates in the 0-100 range.
Table 1: Polychronopoulou et al.

<table>
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<th>C$_2$H$_2$ flow rate</th>
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<td>TiC$_{0.7}$</td>
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<td>87</td>
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<tr>
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<td>DLC</td>
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Table 1: Polychronopoulou *et al.*

<table>
<thead>
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<th>43</th>
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<td>45.6</td>
<td>12</td>
<td>1.05, 0.6, 1.8</td>
<td>1.53, 1.25</td>
<td>40</td>
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<td>0.5+</td>
<td>0.38, 0.4, 0.35</td>
<td>0.35</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Figure 1: Polychronopoulou et al.
Figure 2: Polychronopoulou et al.
Figure 3: Polychronopoulou et al.

(a) Raman Shift (cm$^{-1}$) vs. Intensity (a.u.)

(b) Raman Shift (cm$^{-1}$) vs. Intensity (a.u.)
Figure 4: Polychronopoulou et al.

(a) 0 sccm C$_2$H$_2$  
(b) 43 sccm C$_2$H$_2$
Figure 5: Polychronopoulou et al.

25 sccm (a)

20 nm

43 sccm (b)

20 nm
Figure 6: Polychronopoulou et al.

Figure 7: Polychronopoulou et al.
25 sccm $C_2H_2$ (a)

43 sccm $C_2H_2$ (b)
Figure 8: Polychronopoulou et al.
Figure 9: Polychronopoulou et al.
Figure 10: Polychronopoulou et al.