THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^{0}. 2 – 2014, ISSN 1453 – 083X

RESIDUAL STRESS AND TRIBOLOGY BEHAVIOUR OF TiCx COATING DEPOSITED BY NPCVD METHOD

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ABSTRACT

In this paper, thin TiCx films were coated by chemical vapour deposition method, and various duty cycles were carried out in order to observe the influence of this parameter on residual stress and tribology behaviours. The duty cycles were 35, 43 and 50% at 500 ^{o}C operating temperature. Therefore, wear behaviour, hardness and chemical analyses of TiCx coating were characterised, and it was found that the residual stresses in the coating were compressive, which were-1.14189 - 0.12985 and -0.1749 MPa at three different duty cycles, i.e. 35, 43 and 50% respectively. According to the results, the coating that was applied at 43% exhibited superior wear resistance and possessed the lowest friction coefficient of ~ 0.059 in a pin-on-disc test.

KEYWORDS: wear, residual stress, TiCx coating, NPCVD, duty cycle

1. Introduction

Titanium carbide (TiCx) coatings are well known for combining a number of special properties, which have made them of particular interest for a broad range of applications. They are used as wear resistant coating for cutting tools and inserts and diffusion barriers in semiconductor technology [1–3]. It has been established that the properties of TiCx microstructure coating strongly depend on the deposition conditions and elaboration methods [3]. There are a lot of methods to apply hard alloys coating, including chemical vapour deposition at low pressure (LPCVD), plasma assisted CVD (PACVD) and chemical vapour deposition at normal pressure (NPCVD); however, it is an appropriate method for the deposition of wear resistant coatings on temperature sensitive materials [4]. Normal presure CVD has the major advantage that coatings of uniform thickness and composition can be produced even on substrates with a complex shape at high temperature [3–8]. Further study has indicated that the properties of titanium carbide are related to its chemical composition and texture and are a result of low adhesion or residual stresses in the thin film [3–11]. The residual stress in thin film deposited by NPCVD may be either compressive or tensile, depending on the deposition conditions. However, applying TiCx microstructure coating on metals is so difficult, since this compound is metastable, and the reaction between atoms in the NPCVD method is complicated. Among several parameters with important effect on the properties of the TiCx microstructure coating, duty cycle plays an essential role as a thermodynamic and kinetic parameter.

More study showed that the duty ratio and pulse frequency affect the chemical deposition and that the processing rate can be improved [12–14].

Therefore, in the present paper, we studied the influence of duty cycle on the structure, morphology, chemical composition and tribological behaviour of TiCx.

2. Materials and methods

The alloy WC – Co was used as substrate material. Table 1 illustrates the results of chemical analysis accomplished by spark emission spectroscopy test. The samples of substrate with the dimension 18 x 18 x 5 mm were quenched and tempered to a hardness of 17 000 MPa. After being polished to a Ra of 2 μm using Al_2O_3 slurry, the samples were first cleaned with acetone and then cleaned in ethanol and a chemical process in Ar and H_2 before deposition.

3. TiCx coating deposition

The TiCx microstructure coating was deposited by NPCVD in a reactor using a $HCl–CH_4–H_2–Ar$ gas mixture. The pressure in the reaction chamber amounted to 1 at. For more details concerning the deposition conditions, see Table 2. The substrate temperature was achieved by auxiliary heating system. Three kinds of duty cycles including 35, 43 and 50% were selected for investigating the influence of duty cycle on residual stress and tribology behaviour of TiCx microstructure coating.

4. Characterisation of TiC microstructure coating

The surface morphology, uniformity and homogeneity of the coated samples were examined by (Philips) scanning electron microscopy (SEM) and atomic force microscopy (AFM), and also the coating thickness was measured by cross-section SEM analyses.

Micromechanical properties such as Young’s modulus E and hardness HV of the TiCx microstructure coatings were evaluated by microindentation technique (TriboScope). The AFM was a MicroScope III, and the indentation time was set to 10 s. The sensor of the transducer recorded the values of normal force and depth. From the analysed load–displacement curves, the Young’s modulus of the measured films can be calculated as follows.

$$1/E_r=2\beta/S(A_c/\pi)^{1/2} = (1-\upsilon^2{}_m)/E_m+(1-\upsilon^2{}_i)/E_i \quad (1)$$

where: Ac, Er, S and β denote the actual contact area, the reduced elastic modulus for each indenter/specimen combination, the measured stiffness and a shape constant of 1 for the Berkovich tip respectively.

The subscripts m and i denote the film and the indenter tip respectively, E is the Young’s modulus, and υ is Poisson’s ratio. The indenter properties used in this study’s calculations are E_i = 1140 GPa and υ_i = 0.07, and the assumed Poisson’s ratio of TiCx is υ_m = 0.17[8].

The crystalline structure of the coating was determined by X-ray diffraction (XRD) (using a Dron diffractometer in continuous scanning mode and using Mo, K_α radiation λ = 154056 µm).

Table 1. *Chemical analysis of widia achieved by spectroscopy test*

Composition	WC	Co
Weight per cent	0.94	0.06

The first part of this study is concentrated on using XRD for the purpose of characterising the TiCx microstructure coating with special emphasis on residual stress measurements, in which the stresses are measured using the conventional $\sin^2 \psi$ method [12, 13]; the second part of this study is devoted to investigate the effect of duty cycle on the tribology behaviour of the TiCx microstructure coating. The film composition was determined by X-ray photoelectron spectroscopy (XPS) using monochromatic Al K_α radiation. The adhesion of the TiCx microstructure coatings on hot working widia was analysed with a microscratch tester with a diamond tip (radius of 10 µm). The sliding speed was fixed at 15 µm s^{-1}. The critical load Lc was defined as the lowest load at which the TiCx microstructure coatings started to delaminate. The delamination of the coatings was confirmed through observation with an optical microscope. A pin on disc apparatus was carried out on the TiC microstructure coating under loading conditions of maximum 1 GPa pressure with Ø6 mm ball; this is the Hertzian pressure so close to the working condition, such as cutting and forming tools, [15–17]. The load was 5 N, and the sliding speed was 0.1 m s^{-1}. All the tests were performed for 1500 cycles. The temperature and relative humidity were 30 °C and 36% respectively. Before the tests, the samples were cleaned with ethanol and dried in hot air.

5. Results and discussion

The geometry of the test samples for each of the factor series summarised in Table 2 was kept the same, and also the positions in the process chamber were kept alike.

Table 2. *Process parameters for deposition of TiCx*

Parameter	**Value**
Temperature [°C]	≤ 1050
Process time [h]	4
Ar +H_2 [L/h]	2.8
H_2 + CH_4 + HCl [L/h]	0.8
Duty cycle [%]	35, 43 and 50

In this work, titanium tetrachloride is obtained directly in the working chamber of the ferrotitanium and concentrated hydrochloric acid at elevated temperature (over 1000 °C) according to the reaction:

$$Ti_{(s)} + 4HCl \rightarrow TiCl_4 + 2H_2$$
$$TiCl_4 + CH_4 + H_2 \rightarrow TiC + 4HCl + H_2$$

It is noteworthy that the originality of the paper consists in direct titanium tetrachloride working inside, avoiding the import of this tetrachloride which shows a high toxicity.

Figure 1 demonstrates the XRD diffraction patterns for the deposited samples with three different duty cycles, i.e. 35, 43 and 50%. X ray diffraction is a well established technique for the measurement of residual stress in coatings [12].

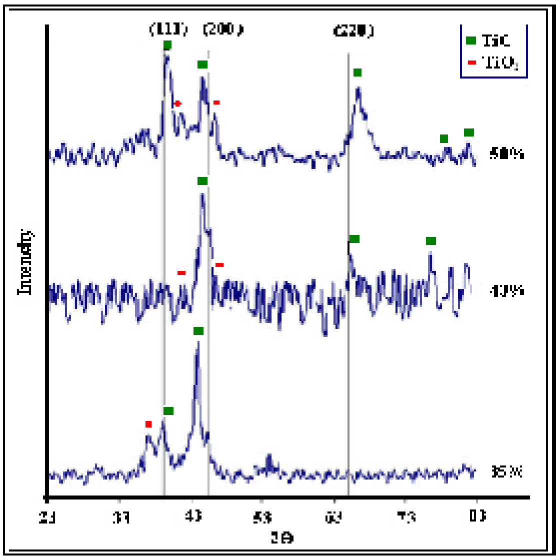


***Fig. 1.** X-ray diffraction patterns for TiCx microstructure coating at three different duty cycles of 35, 43 and 50%*

As Fig. 1 shows, the (200) plane is the preferred structure; therefore, this result implies that the TiCx coating was deposited under a thermodynamically stable condition since the (111) structure (or texture) is the common structure of TiC that is observed.

The lowest energy surface for the TiCx crystal is the (200) plane and this is the structure that is expected for coatings deposited under thermodynamic equilibrium [14, 18]. In order to clarify the effects of duty cycle on the chemical composition of TiCx microstructure coatings.

Figure 2 displays the C 1s and Ti 2p XPS spectra of the TiCx microstructure coatings deposited at three different duty cycles. The Ti 2p XPS signal is composed of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ doublets with binding energies of 455 • 2 and 460 • 8 eV respectively. These two doublets are separated by 6.0 eV. The C 1s spectrum shows a peak at 281.6 eV, and TiO_2 is represented by the Ti $2p_{3/2}$ peak at 458.4 eV. The existence of the Ti 2p and C 1s peaks indicates that the coating obtained under the deposition conditions (Table 2) is TiC.

Moreover, no significant variation of the surface chemical composition (C/Ti ratio) was observed with the increase in duty cycles.

As it was mentioned previously, the stresses in the TiC microstructure coatings were measured in the present paper using the conventional $\sin^2 \Psi$ technique [12].

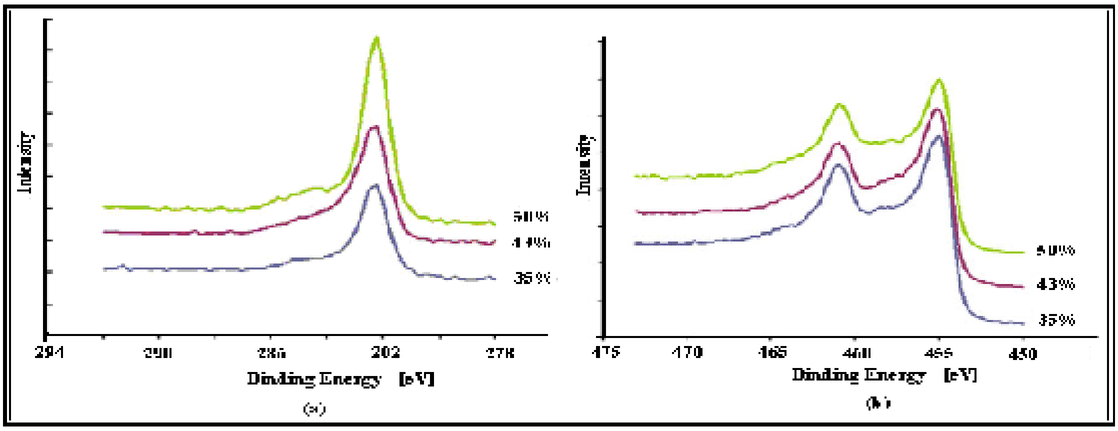


***Fig. 2.** X-ray photoelectron spectroscopy spectra for surface of TiCx microstructure coatings deposited at three different duty cycles of 35, 43 and 50%: a) C 1s spectra peaks; b) Ti 2p spectra peaks*

It is supposed that the TiC microstructure coating under investigation can be considered homogeneous (in principle, preferential orientation free) and in a biaxial stress state. The residual stress can be deduced from the following relation (equation (2)):

$$\varepsilon = \sigma\ [(1+\upsilon)/E \bullet \sin^2 \Psi] - 2\upsilon/E] \qquad (2)$$

The critical load L_c was measured with a microscratch tester, and it is related to the adhesion strength of the TiC microstructure coating on hot working widia sample. The L_c values explained here were averaged for five times.

The results of residual stress in the TiC microstructure coating versus three different duty cycles are shown in Fig. 3.

The TiC microstructure coating deposited at 35% duty cycle has a relatively low adhesion strength compared to other duty cycle and increases the duty cycles from 35 to 43%, enhancing the adhesion strength from 18 to 36 mN, but following the increasing duty cycle led to a decrease in adhesion strength from 36 to 27 mN. However, the adhesion strength was enhanced by increasing duty cycle. The low adhesion strength of the TiC microstructure coating at low duty cycle can be explained as a result of the internal stress with a high atomic density or the structural difference between films and substrates, its inherent brittle properties and chemical composition.

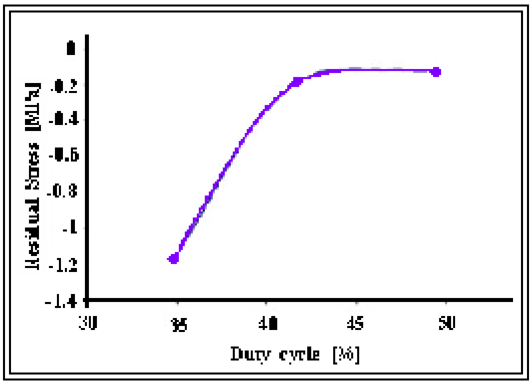


Fig. 3. *Residual stress of TiC microstructure coating as function of duty cycle*

5.1. Effect of duty cycle on residual stress

In Fig. 1, it can be observed that the increasing duty cycle from 35 to 43% has caused the (200) plane to be the preferred structure, and the TiO_2 phase was detected. It is clear that the detected peak was increased by rising duty cycles from 43 to 50%; moreover, the (200) and (111) planes are then the preferred structures. Actually, the various compounds between Ti–C and residual stress in the TiC microstructure coating cause a shift of peaks towards higher angles with increasing duty cycles from 35 to 50% [14, 18–20].

It should be mentioned that the residual stress in the TiC microstructure coating has an important role in forming the preferred orientation, and the latter is governed by the lowest overall energy conditions.

However, the best duty cycle to grow the (200) plane as a preferred orientation is 43%, the crystallite size of the TiC microstructure coating (which was calculated using the Scherrer formula) is 7 µm.

An evident change in grain size is observed for changing duty cycle.

Actually, the grain size of the TiC was decreased by rising the duty cycle from 35 to 50%, as raising the duty cycle leads to an increase in number of nucleation and cluster on the substrate. Finally, the grain size of the TiC microparticles is decreased accordingly.

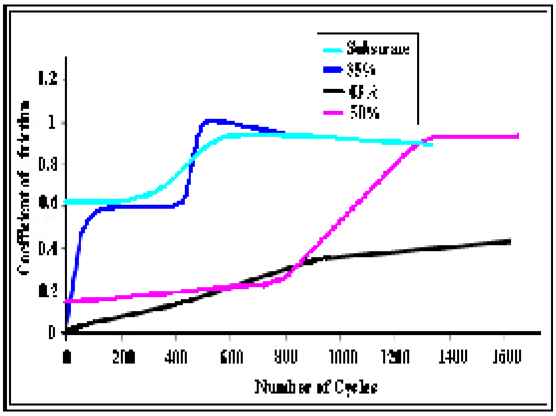


Fig. 4. *Friction coefficient of TiCx nanostructure coating versus number of cycles at three different duty cycles*

A sign of the preferred orientation has been achieved from measurements of the (111) and (200) reflections. As shown in Fig. 1, for all the coatings except for 50% duty cycle, the (200) direction is the preferred one with variations in the (111):(200) ratio ranging from 0 to 0.2.

Figure 2 illustrates that the residual stress in the TiCx microstructure coating is compressive, and the increasing duty cycle from 35 to 50% causes the compressive stress to drop from -1.14189 to -0.12985 MPa. It is usually believed that the residual stresses in a TiC microstructure coating are composed of the thermal stress component due to the difference in thermal expansion coefficients between the thin film and the substrate, which is created in the cooling stage from high temperature down to room temperature, as well as an intrinsic stress component depending on non-thermal origins.

Table 3. *Properties of TiC microstructure coating at three different duty cycles*

Duty cycle [%]	**Grain size** [µm]	**Thickness** [µm]	**Critical load** [mN]	**Hardness** [GPa]	**Residual stress** [MPa]
35	8.7	1.8	18	29.09	-1.14189
43	5.6	2.5	36	12.63	-0.12985
50	4.97	2.5	27	21.07	-0.1749

Fundamentally, the residual stress of the former origin in the TiC microstructure coating is an intrinsic stress component and is considered to depend strongly on the process parameters, such as duty cycle, reactor pressure and operating temperature. This is speculated to be due to the more gradual crystal growth of the TiCx microstructure coating at 43 and 50% in comparison with the 35%, which may generate some intrinsic origins of the stress. In addition, it is believed that oxygen impurities lead to an increase in compressive stress in the TiC microstructure coating.

Figures 1 and 3 show the TiO_2 phase with TiC phase at 35%, and this impurity causes a rise in compressive stress rather than 43 and 50% duty cycle.

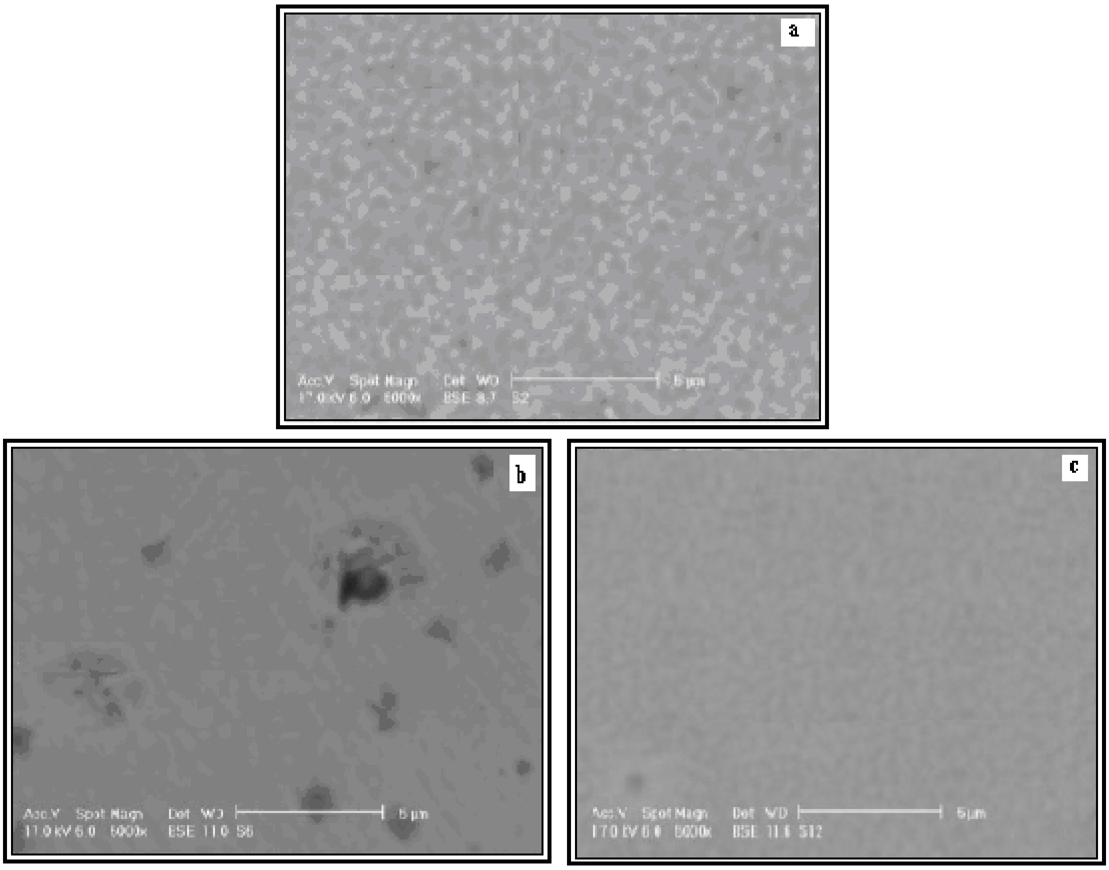


Fig. 5. *Images (SEM) of TiCx microstructure coating deposited at three different duty cycles: a) 35%; b) 43%; c) 50%*

Therefore, impurities play an important role in generating the residual stress in the coating. Indeed, deposition of the TiC microstructure coating at middle duty cycle (43%) may relieve the residual stress of the thin film, and the dependence between residual stress and preferred orientation in the TiC microstructure coating reveals that the preferred orientation is (200) [21]. Small areas of (111) textured TiC were also observed in this paper, while the general texture was predominantly (200).

5. 2. Effect of duty cycle on tribological behaviour

Figure 4 shows the variation of friction coefficient in the TiC microstructure coating as a function of the number of cycles for three different duty cycles, namely 35, 43 and 50%. For the coating, the friction coefficient in the initial stage is 0.13, 0.06 and 0.15 for 35, 43 and 50% duty cycle respectively. The friction coefficient of the TiC microstructure coating deposited at 35% duty cycle presents a drastic change from 0.13 to 0.6 and, after 200 and 400 cycles, presents a drastic change from 0.6 to 1.1 for both TiC microstructure coatings deposited at 35% duty cycle and substrate [22].

For the TiC microstructure coatings deposited at 43 and 50% duty cycles, the friction coefficients were constant with an average value of, 0.08 and 0.19 respectively and fluctuate slightly with changes in the number of cycles. Especially at the initial wear stage, the friction coefficient of the TiC microstructure coatings deposited at 35% duty cycle drastically fluctuated with changes in the number of cycle, indicating that wear mainly takes place at some protruding portions of the pin and discs. This behaviour was seen for the final wear stage of the TiC microstructure coatings.

***Table 4**. TiCx microstructure coating at three different duty cycles*

Duty cycles	35%	43%	50%
Ra [µm]	8.992	10.509	14.057
Rrms [µm]	11.668	13.429	18.034

Table 3 shows the properties of TiC microstructure coating at three different duty cycles. It can be seen that the wear mass loss for both the widia substrate and the TiC microstructure coatings increases with the increase in number of cycles. Compared with the substrate, the TiC microstructure coatings have smaller mass loss, especially for coatings deposited at 43 and 50% duty cycles.

In addition, the mass loss of the W–Co pins drastically increases with the increase in number of cycles. It is mentioned that the W–Co pin as the counter body of the TiC microstructure coatings presents less wear mass loss compared to widia substrate. However, it was found that the friction coefficient decreased with the increase in duty cycle from 35 to 43% and then increased with the rise in duty cycle from 43 to 50%. However, the TiC microstructure coating, which was applied at 43%, exhibited the lowest friction coefficient of ~0.06, as shown in Figure 4.

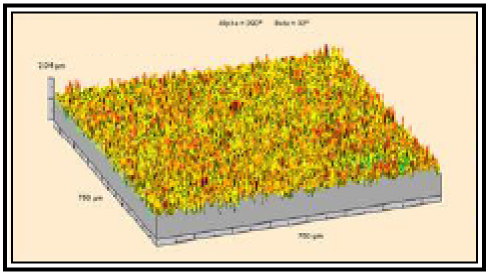
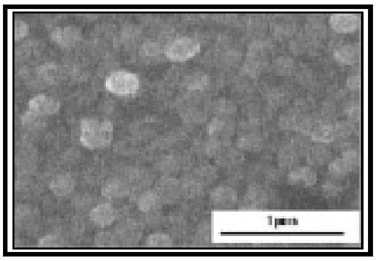
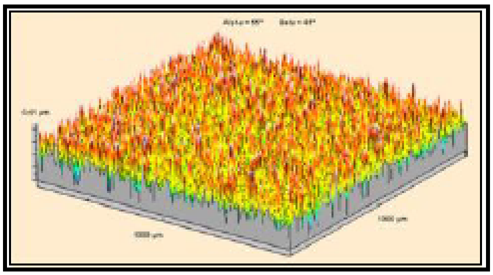
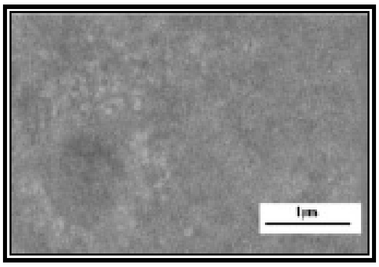
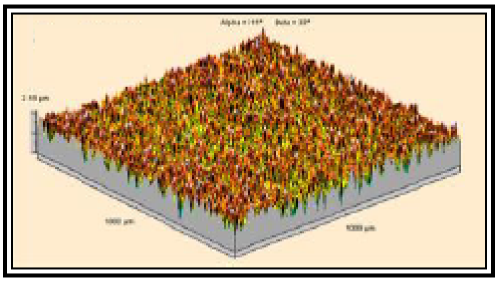
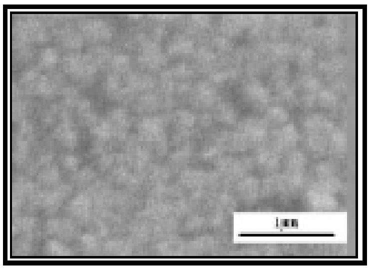
Duty cycles	Images AFM 3D Dimension 1x1 µm	Images AFM 2D Dimension 1x1 µm
35%		
43%		
50%		

***Fig. 6.** Images (AFM) and roughness plot of TiCx microstructure at three different duty cycles: a 35%; b 43%; c 50%*

According to Fig. 4, the coating deposited at lower duty cycle showed a much higher friction coefficient than that of the higher duty cycle. It should be considered that the high friction coefficient is probably due to the coarsening of particles in the depositing process. Actually, the increase in particle size may decrease the convergence of particles. Figure 5 demonstrates the SEM images of the TiC microstructure coating in three kinds of duty cycles, i.e. 35, 43 and 50%. Surface morphology plays an important role in the tribology behaviour of the TiC microstructure coating. It can be seen that the surfaces of the two coatings, which were deposited at 35 and 50%, show similar microstructures (rough surfaces) containing 0.1–0.2 µm aggregates of 4–10 µm TiC grains, and increasing the duty cycle from 35 to 43% produces relatively smooth and dense surfaces. The surface topographies and roughness plot of the TiC microstructure coating at three different duty cycles, including 35, 43 and 50%, are shown in Fig. 6. This Figure depicts that asperities are distributed over a broader range of heights for 50% compared to 35 and 43%.

The results of surface roughness are presented in Table 4. It can be seen from Table 4 that Ra is defined as the mean value of the surface height relative to the centre plane, and Rrms is the root mean square roughness profile of the surface height within the scanned area, and both have been used to explain the surface morphology [23].

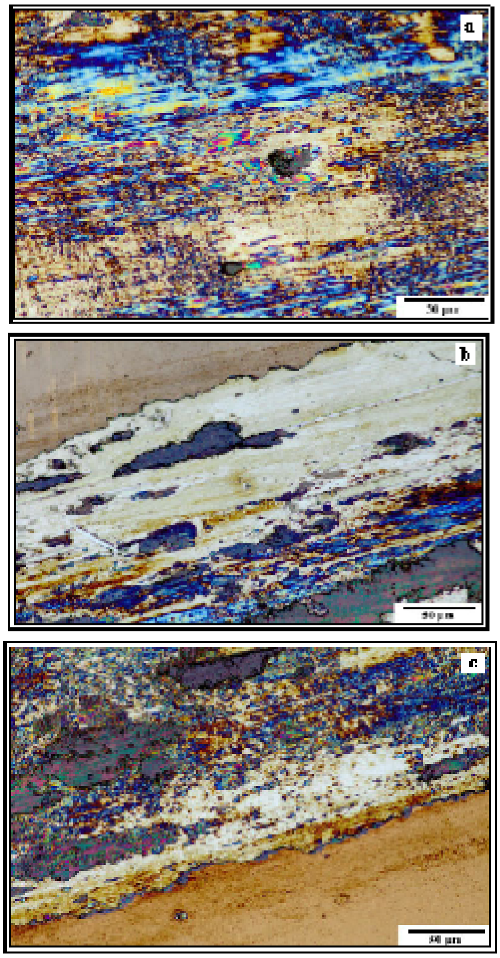


***Fig. 7.** Optical microscopy images of TiCx microstructure coating wear track at three different duty cycles: a) 33%; b) 40%; c) 50%*

This is confirmed by roughness values Rrms of 11.668, 13.429 and 18.034 µm at three different duty cycles, including 35, 43 and 50% respectively.

Both the AFM images and the Rrms values prove that increasing duty cycles from 35 to 43 and 50% causes a reduction in overall roughness of the coating. Therefore, the SEM and AFM images of the TiC microstructure coating (Figs. 5 and 6) indicated that the growth mechanism of coatings at 35 and 50% are island-like growths, while at 43%, there is a layer growth. Therefore, the relatively smooth and dense surfaces (at 43%) lead to the lowest friction coefficient of ~0.06, as shown in Fig. 3. Nevertheless, the deposition parameters are responsible for the layer growth, and it can be concluded for the NPCVD process that the chemical deposition conditions, during deposition, such as duty cycles, determine the nucleation and growth of the layer.

It is noteworthy that increasing the hardness of the TiC microstructure coating is determined by decreases the friction coefficient. In addition, the gradual increase in friction coefficient at 43 and 50% is probably due to the decrease in hardness steadily. The failure of the TiC microstructure coating was determined by the increase in friction coefficient to 1.

The related optical microscope results are presented in Fig. 7.

Figure 7a–c reveals that a peeling of the TiC microstructure coating from the substrate has occurred on the surface. This Figure indicates that the TiC microstructure coatings were worn off to different degrees and islands of broken coatings, where coating was delaminated and substrate was exposed, were formed on the wear tracks. Increasing duty cycles from 35 to 43 or 50% causes to find a few TiC particles in the wear track of the TiC microstructure coating, and according to Fig. 7a, it can be found that the tribology behaviour of TiC microstructure coating for lower duty cycle (35%) may be due to oxide formations during the wear test.

The main wear mechanism of the TiC microstructure coating is the pull-out of particles for fatigue. This is because the extrusive particles bear the load during the process of wear.

After the long term action of the load, the bond will be slacked, and finally, the particles will be pulled out. Therefore, the TiC microstructure coating, which was deposited at 43%, has good wear resistance for its good plasticity (elasticity and microhardness) and compact fine grain microstructure. In addition, the lowest friction may be attributed to the formation of carbon compounds, such as CO_2 and amorphous carbon, and graphitization in the coating wear track, as shown in Fig. 7b. It should be noted that the main wear mechanisms of 50% duty cycle are the pull-out of particles for fatigue (such as oxide formations) and the formation of carbon compounds in the coating wear track, as can be observed in Fig. 7c.

6. Conclusion

Among several parameters, duty cycle plays an essential role as a thermodynamic and kinetic parameter.

The main conclusions are the following.

1. The (200) plane is the preferred structure at lower duty cycle (35%), and an increasing duty cycle from 35 to 50% causes the formation of other planes of TiC, such as (111) and (220) planes.
2. These peaks move to higher angles with increasing duty cycles from 35 to 50%.
3. The grain size of the TiC microstructure coating (~7 μm) was decreased by raising the duty cycle, since the number of nucleation was increased by rising the duty cycle.
4. The residual stress in the TiC microstructure coating is compressive, and the increasing duty cycle from 35 to 50% causes to drop the compressive stress.
5. The highest compressive residual stress was obtained at the lowest duty cycle (35%), and the lowest compressive residual stress was attained at middle duty cycle (43%).
6. The friction coefficient decreases with the increase in duty cycle from 35 to 43% and then increases with the rise in the duty cycle from 43 to 50%.
7. The lowest friction coefficient is ~0.06, and the TiC microstructure coating (which was applied at 43%) with the lowest residual stress (-0.12985 MPa) gives the best wear resistance under loading experiment.

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