ASSESSMENT OF THE WEAR RESISTANCE AND ADHESION OF PVD TiN AND TiCN-COATED AISI 316L STAINLESS

Renato Altobelli Antunes, renato.antunes@ufabc.edu.br
Universidade Federal do ABC (UFABC)
Rua Santa Adélia, 166 – Bairro Bangu – Santo Adré – SP CEP: 09210-170
Isolda Costa, icosta@ipen.br
Instituto de Pesquisas Energéticas e Nucleares (IPEN)
Av. Prof. Lineu Prestes 2242, Cidade Universitária, São Paulo – SP CEP: 05508-900

Abstract. *High hardness ceramic coatings like titanium nitride (TiN) and titanium carbonitride (TiCN) have been considered as alternatives to increase fatigue and wear strength of metallic materials used as orthopaedic implant devices. These films are mechanically suitable and intrinsically biocompatible, highly desirable features when a biomedical application is envisaged. The aim of this work was to evaluate the wear resistance of PVD TiN and TiCN-coated AISI 316L stainless steel using sphere-on-disc test. The adhesion of the coatings was determined through a scratch test. The results were evaluated through optical micrographs of the scratched region identifying the failure mode typical of each coating (adhesive or coesive failure). Vickers nanoindentation measurements have also been made and the results have been correlated with those of the wear test. TiCN-coated 316L specimens presented lower coefficient of friction and higher hardness in comparison with TiN-coated ones. These properties clearly point towards a good wear resistance of TiCN layer and poorer performance of TiN films. It should be emphasized, tough, that TiN-coated specimens performed better in the scratch test, showing adhesive rather than cohesive failure mode. From a mechanical point of view TiCN films, regardless its lower adhesive strength, presented interesting properties to be considered as candidate materials to increase stainless steel implant devices wear resistance.*

Keywords*: PVD films; TiN; TiCN; wear; adhesion*

1. INTRODUCTION

In physical vapor deposition (PVD) processes atoms or molecules are vaporized from a solid or liquid source, transported in vapor form through a plasma environment and condensed over a substrate (Mattox 2000).

Titanium nitride (TiN) is a representative member of metal transition refractory nitrides. It exhibits properties of both covalent and metallic compounds. It is used as a barrier diffusion layer between silicon substrates and aluminum metallization due to its good electrical conductivity and adhesion. TiN presents high hardness, wear and corrosion resistance being suitable for producing coatings on machine tooling (Purushotham et al. 2003). TiN is also beneficial to increase fatigue resistance of metallic substrates (Teoh 2000). Additionally it is biocompatible and may be used as coating of implant devices such hip prostheses.

TiCN presents many similarities with TiN properties. It is also produced from PVD processes and may be considered for biomedical applications. Its structure is composed of multilayers with different ratios between carbon and nitrogen which increases the fracture toughness of the film (Mattox 1995). When compared to titanium nitride, TiCN coatings present higher hardness as shown by nanoindentation measurements. Consequently it has a positive influence on fatigue and wear resistance of the metallic substrate (Fang et al. 2004). Nevertheless, the information about TiCN coatings for orthopaedic devices is scarce in the literature (Hollstein and Louda 1999).

Adhesion is one of the main properties demanded from any deposited layer on a metallic substrate. The adhesion quality determines the performance and life of the coated device. Lack of adhesion may lead to premature failure as a consequence of interfacial fractures (Zaidi et al. 2006). The scratch test is widely used to evaluate adhesion of PVD films (Sui and Cai 2007). The test is conducted as follows: a Rockwell C indenter is put in contact with the surface of the coated specimen. A normal force is applied to the coating and progressively increased. At the same that the normal force is applied the specimen moves with a constant linear velocity until a maximum pre-determined load is reached. Then, the surface of the PVD film is observed through an optical microscope in order to identify the failure mode of the coating. The failure mode may be classified in two different ways: cohesive or adhesive failure. The first case is typical of a good adhesion at the interface film/substrate; the substrate is not exposed, i.e., the film remains along the entire wear track. The second one is typical of a poor adhesion at the interface film/substrate; the substrate is exposed, i.e., the film is delaminated in the surroundings of the risk.

In this work, the wear resistance of PVD TiN and TiCN coatings deposited on AISI 316L stainless steel specimens was evaluated through a sphere-on-disc test. The results have been correlated with Vickers nanoindentation measurements. Additionally, the scracth test was used to evaluated the quality of the interface film/substrate.

2. EXPERIMENTAL

2.1. Materials

The metallic substrate used in this work was AISI 316L stainless steel whose composition is shown in Tab. 1.

Table 1. Composition of AISI 316L substrate.

	C	Si	P	Cr	Mn	Cu	Ni	Mo	N	Fe
Mass (%)	0,01	0,04	0,01	17,4	1,78	0,03	13,5	2,12	0,01	Bal.

Cathodic arc evaporation PVD method was used to produce TiN and TiCN coatings The layer thickness for all the coated specimens was 2 μm for both films. The deposition parameters are shown in Table 2.

Table 2. Main process parameters of the PVD method used to produce the TiN and TiCN films.

Parameter	Typical Value
Pressure	10^{-2} mbar
Voltage in the specimens	200 V
Current in the evaporators	50 A
Substrate temperature	450 - 500 ºC
Time to reach a 2-μm layer	1,5 hora
Cooling time	2 horas

2.2. Adhesion test

The scratch test was used to evaluate the adhesion of TiN and TiCN to the AISI 316L substrate. The test was performed using CSEM-REVETEST equipment in the Metallurgical Center of Bodycote-Brasimet Enterprise in São Paulo. The maximum load applied was 70 N and 100 N for TiN and TiCN films, respectively with 5 risks per specimen. Each risk was 5 mm long. Film adhesion was qualitatively evaluated from the observation of the coating failure mode after the scratch test using an optical microscope.

2.3. Nanoindentation measurements

Nanoindentation measurements of TiN and TiCN layers have been performed using a Fischerscope nanoduremeter model H100V. Computer software registers the penetration depth as a function of the applied load. The parameters used for the measurements are shown in Tab. 3. Hardness (H) is determined from the following equation:

$$H = P_{max}/A \quad (1)$$

Table 3. Parameters used for nanoindentation measurements.

Number of measurements	15
Spacing between measurements (μ)	10
Maximum load (mN)	10
Time at maximum load (s)	20

In equation (1), A is the area of the impression mark and P_{max} is the maximum load during the test.
The Young Modulus of TiN and TiCN coatings was also determined by means of equation (2), known as the Hertz equation:

$$(1-\nu^2)/E = (1-\nu_i^2)/E_i - 1/E_r \quad (2)$$

In this equation, ν is the Poisson's ratio of the coating material (TiN or TiCN), E is the Young Modulus of the coating, ν_i is the Poisson's ratio of diamond (Vickers indenter used in the hardness measurement), E_i is the Young Modulus of diamond and E_r is the reduced Young Modulus related to the pair coating/diamond.

The values of Poisson's ratio of each kind of film were found in the literature: ν_{TiN} = 0,19 (Franco 2003; Fang et al. 2004) and ν_{TiCN} = 0,18 (Fang et al. 2004). The values for diamond were ν_i = 0,07 and E_i = 1029 GPa (Franco 2003).

E_r was determined using a calibration procedure developed by Oliver and Phar (1992). This parameter depends on the kind of the indenter, the real contact area and the contact stiffness.

The values of nanohardness (H) and Young Modulus (E) were used to determine the H/E ratio of each coating. This ratio is a qualitative indication of the material's wear resistance (Leyland and Matthews 2000). The higher the H/E ratio the higher is the elastic recovery of the material and the load necessary to cause plastic deformation, i.e., the higher wear resistance of the material.

2.4 Wear test (sphere-on-disc)

The wear resistance of uncoated, TiN and TiCN coated AISI 316L specimens was evaluated using a tribometer Plint model TE66. The specimens were in the form of discs with 5 mm thickness and 100 mm diameter. The test is based on the sphere-on-disc geometry. The disc is fixed at the gyratory tribometer support. The sphere was a 6,35 mm silicon nitride ball which applied a 10 N load against the disc. The disc presented a 50 rpm speed of rotation with a radius of 25 mm. The total period of test was 30 minutes. After the tests, the discs have been observed in an optical microscope to evaluate the damages made by the sphere on their surfaces.

3. RESULTS AND DISCUSSION

3.1 Adhesion test

Figure 1 presents an optical micrograph of a TiCN-coated specimen after the scratch test with a 70 N maximum load. This load caused the coating to failure in the cohesive mode. As shown in Figure 1 the substrate was not exposed. However, there are clear signs of fracture in the adjacent areas around the risk. Some fractured regions are pointed out in the figure. With a maximum load of 100 N the failure mode was also cohesive and the surface of the specimen was very similar to that shown in Fig. 1. Figure 2 shows an optical micrograph of a TiN-coated specimen after scratch test with a maximum load of 100 N.

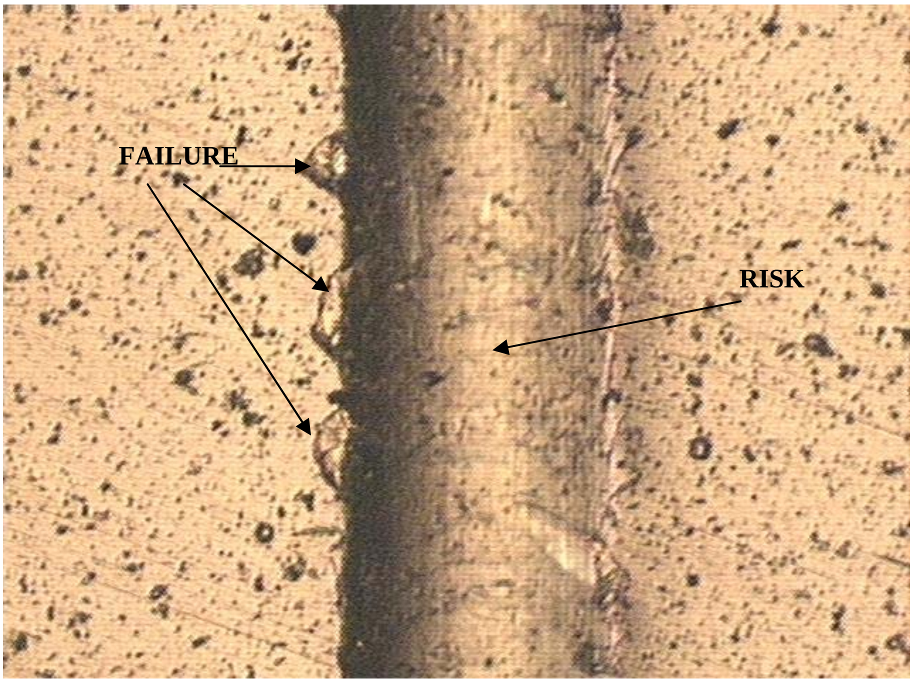

Figure 1. Optical micrograph of TiCN film after scratch test. Maximum load of 70N.

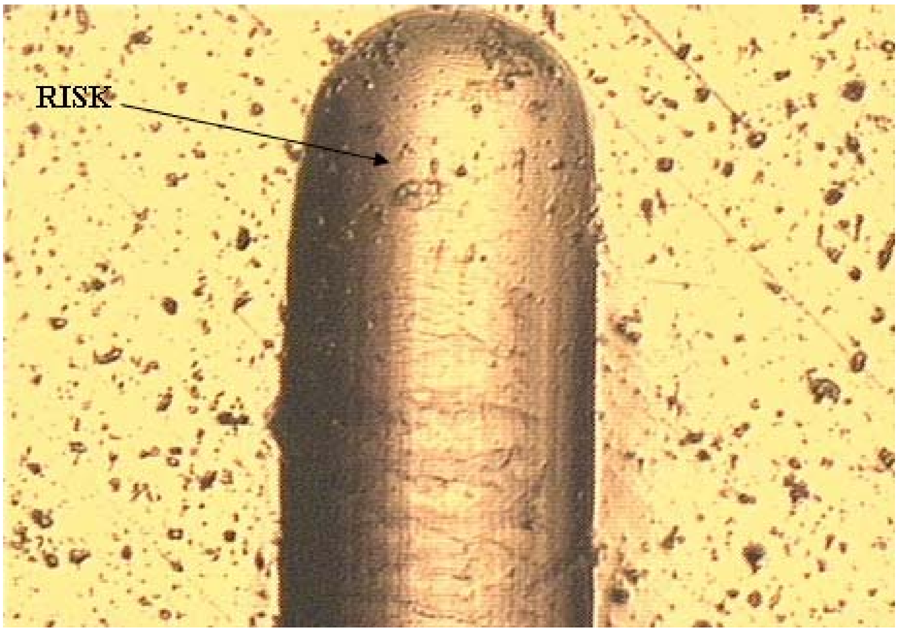

Figure 2. Optical micrograph of TiN film after scratch test. Maximum load of 100 N.

TiN film did not present adhesion failure either with a maximum load of 70 N or 100 N. Heinke et al. (1995) have found that PVD TiN films showed good adhesion to SAE 52100 chromium steel. They ascribed a ductile character to the TiN layer and observed only little delamination with a maximum load of 100 N.

According to Bull et al. (2003) the main features that affect the critical load in which the adhesion failure of a film undergoing scratch test occurs are the type of substrate, coating thickness and residual stresses originated from the friction between the diamond indenter used in the test and the film. Both PVD layers used in this work have roughly the same thickness of 2 μm and the metallic substrate was the same. It is most probable, then, that the major contribution to the different adhesion behavior observed for TiN and TiCN films should be due to a distinct residual stress level of the coatings.

3.2 Nanoindentation

The results of nanoindentation measurements of TiN and TiCN films are shown in Tab. 4.

Table 4. Nanoindentation measurements of TiN and TiCN films.

	Vickers Nanohardness (H) (GPa)	Young Modulus (E) (GPa)	H/E ratio
TiN	19,50	432,9	0,045
TiCN	18,58	332,3	0,059

Hardness (H) and Young modulus (E) values are related to the stifness and resistance to plastic deformation of the coatings. However, the ratio between these two properties is a qualitative indication of the materials' wear resistance (Leyland and Matthews 2000). Thus, if one considers each property separately an important feature of PVD films, that is their wear resistance, does not become evident. So, taking into account the H/E ratio values shown in Tab. 4, the best wear performance should be ascribed the film with the higher H/E ratio. It is expected, then, that the TiCN layer should be more resistant to wear that the TiN layer. Wear tests based on the sphere-on-disc geometry have been performed to confirm these results.

3.3 Wear test (sphere-on-disc)

The variation of the coefficient of friction of uncoated 316L, TiN and TiCN-coated 316L with the sliding distance is shown in Fig. 3. It is worth noting that uncoated 316L presented a continuous increase of the coefficient of friction. The test was prematurely interrupted when the sliding distance reached 6 m which was equivalent to a period of 2 minutes.

This interruption was intentionally done due to an excessive vibration of the test device during the experiment. The vibration was originated from the intense friction between the silicon nitride sphere and uncoated 316L disc.

For the TiN-coated 316L the test was interrupted when the sliding distance was 55 m which was equivalent to a period of approximately 6 minutes. The coefficient of friction of the TiN film presented a significant oscillation with peak values between 0,6 and 0,7. The interruption was done for the same reasons pointed out for the uncoated 316L specimens.

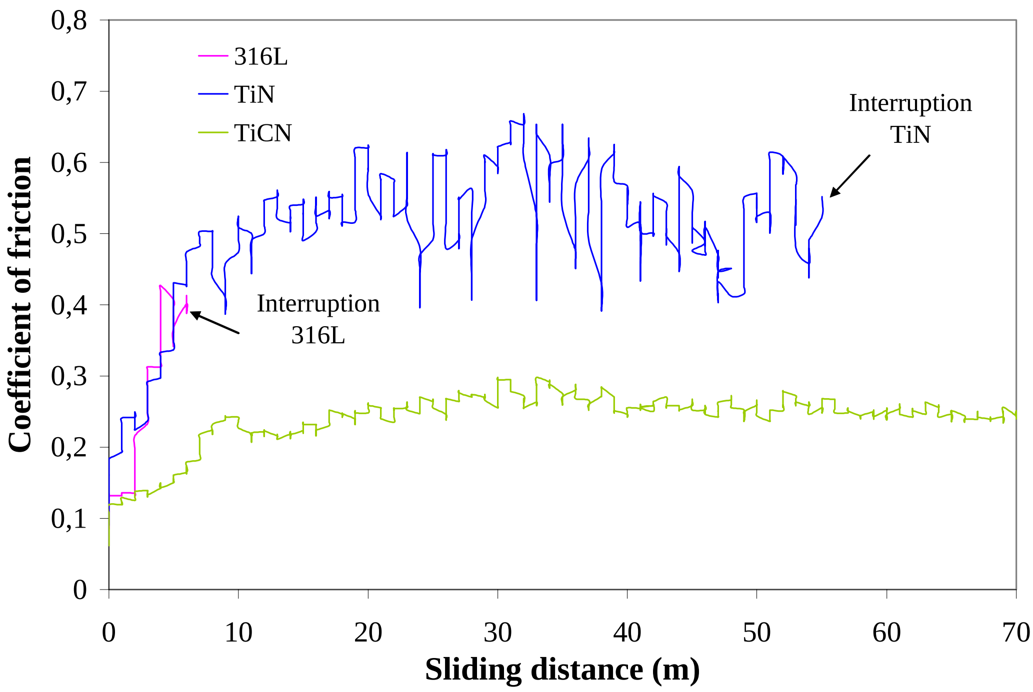

Figure 3. Variation of the coefficient of friction of uncoated 316L, TiN and TiCN-coated 316L with sliding distance.

The variation of the coefficient of friction of the TiCN-coated 316L disc was much softer during the experiment when compared to uncoated and TiN-coated discs. It is evident that the values of the coefficient are much lower than those of the TiN-coated specimen. The experiment was not interrupted for the TiCN-coated disc, reaching a sliding distance of 289 at the end of the test, after 30 minutes.

According to the literature the higher the H/E ratio of a material the higher its wear resistance (Leyland and Matthews 2000; Batista et al. 2003). TiCN coating presented lower values of coefficient of friction than TiN layer. This result points towards a better wear resistance of the TiCN film. The H/E ratio values shown in Tab. 4 confirm the literature findings, i.e., the PVD layer with the lowest H/E ratio (TiN) presented the highest coefficient of friction.

After the sphere-on-disc tests the surface of each disc was observed using an optical microscope. The wear track of the TiCN-coated disc presented fewer signs of degradation when compared to that of the TiN-coated disc. It is important to emphasize that the experiment was much shorter for the TiN-coated specimen, as mentioned above, due to the excessive friction between the silicon nitride sphere and the TiN film. Takadoum et al. (1996) have also found that TiN presented lower wear resistance than TiCN. The superior behavior of TiCN was ascribed to the presence of carbon in the film. This element acts as a lubricant, diminishing the coefficient of friction of the material (Vancoille et al. 1993; Bergmann et al. 1990). The optical micrographs of uncoated 316L, TiN and TiCNcoated 316L discs after the sphere-on-disc tests are shown in Figs. 4-6

It has to be outlined that the uncoated 316L disc presented a wear behavior much inferior to either TiN or TiCN-coated discs. The degradation observed in the wear track of this material after the test (Fig. 4) was significantly sharper when compared to the PVD coated discs. So, it is clear that both PVD films evaluated in this work were efficient to increase the wear resistance of 316L stainless steel. Even the titanium nitride layer, which presented lower resistance than the TiCN film showed less variation of the coefficient of friction, allowing a longer experiment period than the uncoated 316L disc. Thus, the TiN layer increases the wear resistance of 316L stainless which is an essential property for implant devices.

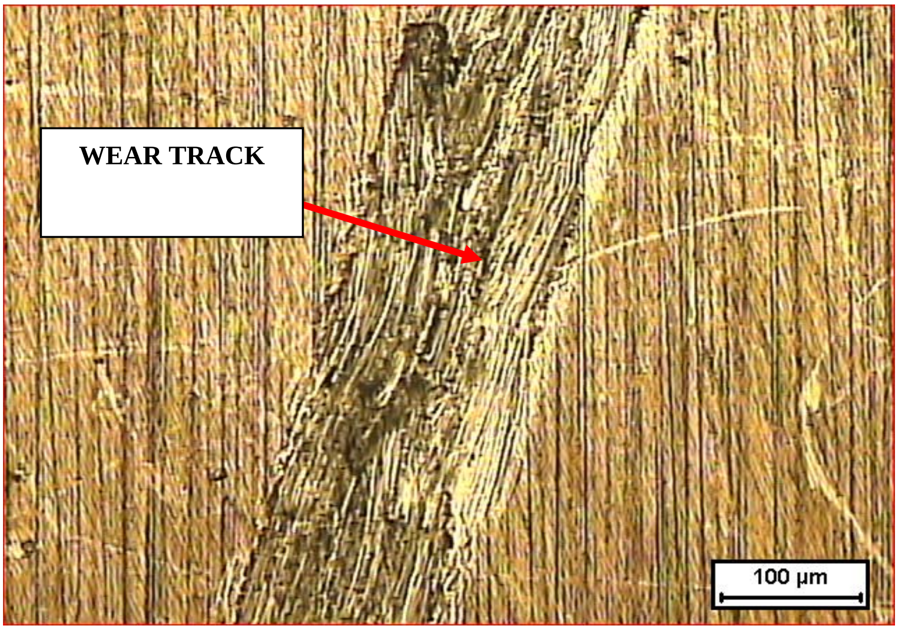

Figure 4. Optical micrograph showing the wear track on the surface of na uncoated 316L disc after the sphere-on-disc test.

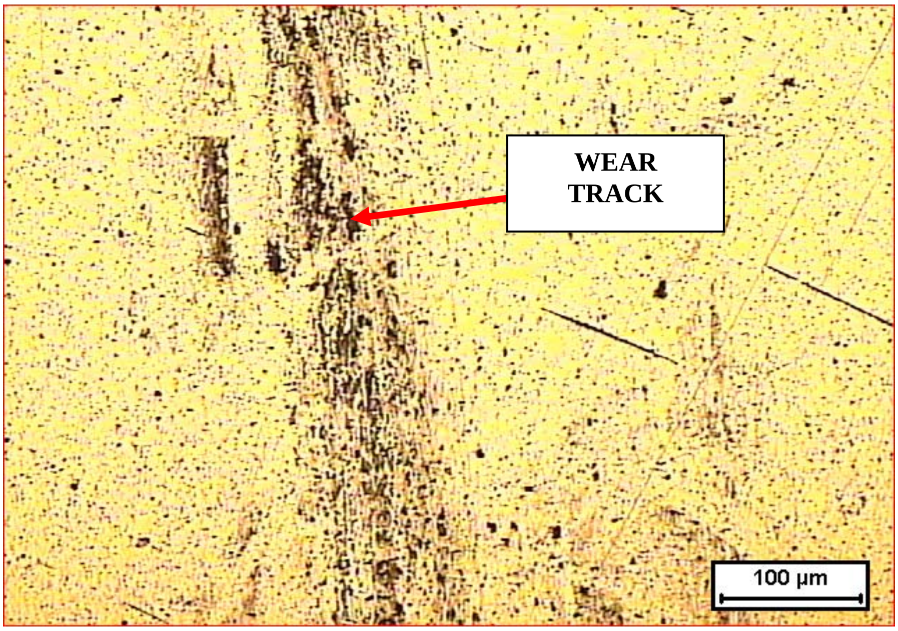

Figure 5. Optical micrograph showing the wear track of the PVD TiN coated 316L disc after the sphere-on-disc test.

4. CONCLUSIONS

The results of the sphere-on-discs experiments showed that the PVD films were efficient to increase the wear resistance of 316L stainless steel. The best performance was ascribed to the TiCN film probably due to the presence of carbon in its structure, acting as a lubricant, lowering the coefficient of friction of the material. It is suggested, from the mechanical findings of this work, that PVD TiCN films may be considered as coating materials for implant devices. However, biocompatibility tests are due to confirm this possibility from a biological point of view.

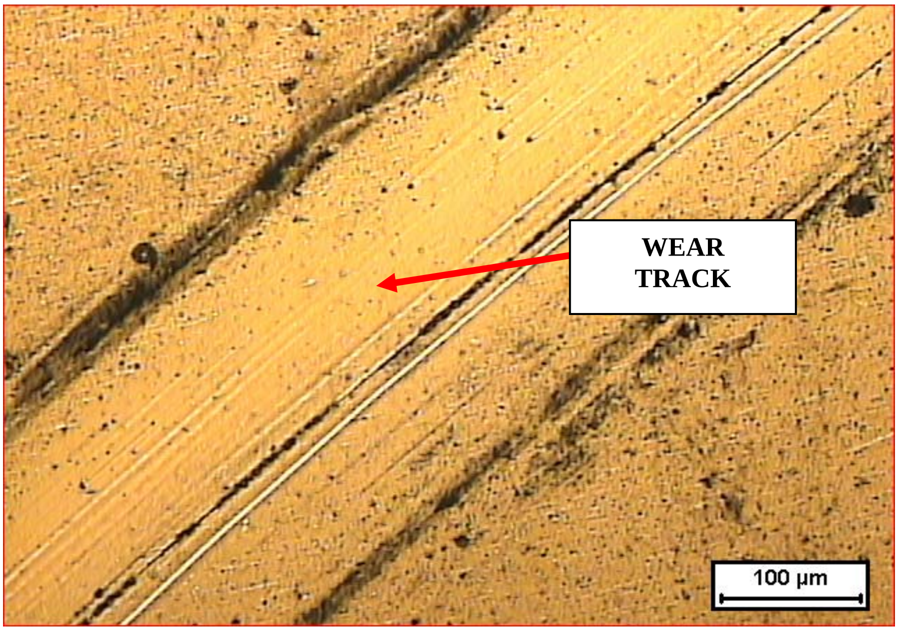

Figure 6. Optical micrograph showing the wear track of the PVD TiCN coated 316L disc after the sphere-on-disc test.

5. ACKNOWLEDGEMENTS

Many thanks are due to Dr. Ronaldo Ruas of Bodycote-Brasimet for providing the PVD films and for the use of the Metallurgical Center to perform the adhesion tests. Dr. Maria Cristina Moré Farias of LFS (Mechanical Engineering Department of University of São Paulo) is acknowledged for her help with the analysis of the sphere-on-disc tests. Mr. Leandro Justino de Paulo of LFS is acknowledged for the nanoindentation measurements and sphere-on-disc experiments.

6. REFERENCES

Batista, J. C. A., Godoy, C., Pintaúde, G., Sinatora, A., Matthews, A., 2003, "An approach to elucidate the different response of PVD in different tribological tests", Surface and Coatings Technology, Vol. 174-175, pp. 891-898.

Bergmann, E., Kaufmann, H., Schmid, R., Vogel, J., 1990, "Ion-plated titanium carbonitride films", Surface and Coatings Technology, Vol. 42, pp. 237-251.

Bull, S. J., Bhat, D. G., Staia, M. H., 2003, "Properties and performance of commercial TiCN coatings. Part 2: tribological performance", Surface and Coatings Technology, Vol. 163-164, pp. 507-514.

Fang, T.-H., Jian, S.-H., Chuu, D.-R., 2004, "Nanomechanical properties of TiC, TiN and TiCN thin films using scan probe microscopy and nanoindentation", Applied Surface Science, Vol. 228, pp. 365-372.

Fang, T.-H., Jian, S.-H., Chuu, D.-R., 2004, "Nanomechanical properties of TiC, TiN and TiCN thin films using scan probe microscopy and nanoindentation", Applied Surface Science, Vol. 228, pp. 365-372.

Franco, Jr., A. R., 2003, "Obtenção de revestimentos duplex por nitretação a plasma e PVD-TiN em aços ferramenta AISI D2 e AISI H13", Thesis, University of São Paulo.

Heinke, W., Leyland, A., Matthews, A., Berg, G., Friedrich, C., Broszeit, E., 1995, "Evaluation of PVD nitride coatings using impact, scrach and Rockwell-C adhesion tests", Thin Solid Films, Vol. 270, pp. 431-438.

Hollstein, F., Louda, P., 1999, "Bio-compatible low reflective coatings for surgical tools using reactive dc-magnetron sputtering and arc evaporation – a comparison regarding steam sterilization resistance and nickel diffusion", Surface and Coatings Technology, Vol. 120-121, pp. 672-681.

Leyland, A., Matthews, A., 2000, "On the significance of the H/E ratio in wear control: a nanocomposite coating approach to optimised tribological behavior", Wear, Vol. 246, pp. 1-11.

Mattox, D., 1995, "Hard Coatings by PVD", Plating and Surface Finishing, Vol. 82, No. 1, pp. 48-49.

Mattox, D., 2002, "Physical vapor deposition (PVD) processes", Metal Finishing, Vol. 100, pp. 396-408.

Oliver, W. C., Pharr, G. M., 1992, "A new improved technique for determining hardness and elastic modulus using and sensing indentation experiments", Journal of Materials Research, Vol. 7, No. 6, pp. 1564-1582.

Purushotham, K. P., Ward, L. P., Brack, N., Pigram, P. J., Evans, P., Noorman, H., Manory, R. R., 2003, "Tribological studies of Zr-implanted PVD TiN coatings deposited on stainless steel substrates", Wear, Vol. 254, pp. 589-596.

Sui, J.H., Cai, W., 2007, "Mechanical and corrosion study of diamond-like carbon coating on NiTI alloys", Surface and Coatings Technology, Vol. 201, pp. 5121-5123.

Takadoum, J., Bennani, H. H., Allouard, M., 1996, "Friction and wear characteristics of TiN, TiCN and diamond-like carbon films", Surface and Coatings Technology, Vol. 88, pp. 232-238.

Teoh, S. H., 2000, "Fatigue of biomaterials: a review", International Journal of Fatigue, Vol. 22, pp. 825-837.

Vancoille, E., Celis, J. P., Roos, J. R., 1993, "Dry sliding wear of TiN based ternary PVD coatings", Wear, Vol. 165, pp. 41-49.

Zaidi, H., Djamai, A., Chin, K. J., Mathia, T., 2006, "Characterisation of DLC coating adherence by scratch testing", Tribology International, Vol. 39, pp. 124-128.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.