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TRIBOLOGICAL MECHANISMS IN DRY SLIDING CONTACT ON CERAMIC COATINGS [1]

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Abstract
The wear and friction of hard coatings in dry sliding conditions has been experimentally studied. In particular, the formation of transfer layers along the wear track and on the ceramic ball counterpart has been considered. The experiments have been done on Titanium Nitride hard coatings obtained by two industrial procedures: Chemical Vapor Deposition, CVD, and Cathodic Arc Physical Vapor Deposition, PVD. We show that the different metallic titanium content of the two sort of coatings determine an important difference in the transfer layer formation during sliding tests. Also, we demonstrate experimentally, that by impeding the formation of transfer layers during the sliding tests, the wear track and friction coefficient records turn to be very stable and reproducible, but the measured values of wear rate and friction coefficient can greatly differ from those obtained when the sliding test generates transfer layers.
Key words: Transfer layer; Wear; Friction; Pin-on-disc; Hard coating; Ceramic wear.

Resumo
Temos estudado experimentalmente o atrito eo desgaste de revestimentos duros em condições de deslizamento seca. Em particular, nós investigamos a formação da camada de transferência ao longo da pista de desgaste e nas bolas de cerâmica contraparte. Os experimentos foram realizados em revestimentos de nitreto de titânio obtidos por dois processos industriais: por Chemical Vapor Deposition, CVD, e de Arco Catódico Physical Vapor Deposition, PVD. É mostrado que os diferentes teores de metal de titânio nos dois tipos de revestimentos determinan uma diferença significativa na formação da camada de transferência durante os ensaios de deslizamento. Além disso, é mostrado experimentalmente que, impedindo a formação de camadas de transferência durante o test de deslizamento, os sulcos de desgaste formados e os coeficientes registrados, são muito estáveis e reproduzíveis, mas os valores medidos da taxa de desgaste e coeficiente atrito podem ser muito diferentes daqueles obtidos quando o teste de deslizamento gera camadas de transferência.
Palavras-chave: Camada de transferencia; Desgaste; Fricção; Pino-sobre-disco; Revestimento duro; Desgaste da cerâmica.

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1 INTRODUCTION

Dry frictional sliding between two engineering materials has been hardly employed in the past because of the massive wear that it causes in most cases. Instead, lubricated friction has been always preferred in the engineering solutions. Nowadays, the modern hard coatings, CVD and PVD, have alleviated the wear problems and in numerous specific applications hard coatings are used without any lubrication.[1] Therefore, now it is necessary to characterize the wear and friction mechanisms in dry sliding conditions for a variety of materials, particularly coatings.[2,3] The dry wear and friction tests are generally conducted in pin-on-disc apparatus in reciprocating or in turning arrangement. These procedures consist in a repetitive multiple pass test for the friction in a localized area of the sample surface and once completed, they measure the wear track produced during a very high number of passes. Sample and pin can be the same material o can be different materials; in the last case, pin material is generally chosen to be the harder material. Wear can occur in both, the sample and the pin; wear in the sample appears as a worn track with certain volume of disappeared material and in the pin wear appears as a volume diminution at the contact area. The mechanisms involved in dry wear can be various, being the most fundamental: adhesive wear and tribo-chemical wear.[1] Adhesive wear implies some plastic or elastic asperity deformation to create intimate contact areas with atomic spacing contact between pin and sample materials, and some atomic inter-diffusion in these contact areas, the material worn form a very fine particle debris that is deposited around the wear track and has similar chemical composition as the worn material. Tribo-chemical wear implies the formation of some compound molecules by chemical reaction at the surface of contact areas; in general it produces metal oxides, because of the oxygen absorbed molecules from the air. Abrasive wear can occasionally occur, caused by relatively big hard particles being pluck from the track and they can keep on the abrasive process, abrasive wear goes often catastrophic. Molecules and debris produced during the wear process can be swept away or can form a compact an relatively thick film that keeps adhered to the pin or to the wear track surfaces and can be very stable, this are called transfer layers and they deeply modify the friction coefficient values and the wear mechanisms, once formed. Transfer layers are ubiquitous in the dry friction between metal surfaces,[4] in these cases they are formed by a transferred metal layer or by a metal oxide layer. Dry friction on bulk ceramic materials mostly produces abrasive wear, because of the brittleness of the ceramic material and then the transfer layer does not form. But in dry friction on CVD or PVD hard coatings, transfer layers can form and moreover they tend to be not stable, causing instabilities in the friction test records. CVD and PVD hard coatings are considered ceramic materials, they are very tough and less brittle and they can contain microscopic metallic inclusions, as a consequence of their industrial fabrication process. Our work consisted on exploring the formation of transfer layers during the pin-on-disc test of alumina balls against one of the most popular hard coatings: Titanium Nitride, TiN, prepared by two different industrial processes: by high temperature CVD and by cathodic arc PVD deposition, on flat steel coupons.

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2 MATERIALS AND METHODS

Titanium Nitride, TiN, have been deposited on AISI M6 steel coupons 25mm diameter and 8 mm thick. The steel surface has been polished to a metallographic specular finish and degreased. Deposition of CVD TiN has been conducted in an industrial CVD system at a temperature of 850ºC with slow cool-down in nitrogen atmosphere. The composition and thickness of the coatings have been determined by Glow Discharge Optical Spectroscopy, GDOS. The thicknesses of these CVD coatings range from 9 to 12 microns. As seen in the optical microscope these coatings are flat, mirror-like, and show some surface roughness in form of scattered pimples and pinholes. After deposition, the coatings surface has been polished once more with 1 micron silicon carbide polishing pad. Deposition of PVD TiN has been conducted in an industrial cathodic arc evaporation reactor in nitrogen atmosphere. The deposition temperature has been 500ºC and deposition time has been calculated to obtain a 3 microns thick TiN layer. Previous to the TiN deposition, a thin intermediate layer of pure titanium metal has been deposited, at -500 V sample bias, in order to obtain a very good adhesion of the coating to the steel substrate. The surface of the PVD samples showed a mirror-like finish and, under optical microscope, showed scattered pimples of different sizes, most of them very small, typical of the liquid titanium metal micro-droplets ejected from the PVD Ti cathode during arc evaporation of titanium. After deposition, PVD coatings have been slightly polished with 1 micron silicon carbide pad, in order to eliminate the bigger metal droplets protruding from the coating surface.

The pin-on-disc system turns the sample at a speed of 0,5 turns/second and it has a support arm to keep the alumina ball on the sample with a force perpendicular to the sample surface determined by the weight placed on the ball support. Tests have been conducted with an applied normal force of 2 Newtons, previous tests have been done with forces ranging from 1 N to 10 N without appreciate any difference in the observed behaviour and measurements. The ball describes a circular path on the turning sample with a diameter that can vary between 1,2 and 1,8 mm depending on the sample fixture. The friction force is transmitted to the arm that keeps the ball and is measured with a sensitivity of 0,001 N, the absolute value of the measurement is calibrated before every run by applying a load of 10 grams on the arm. The friction force values are divided by the applied normal force value and the resulting friction coefficient numerical values are registered at a rate of 3 measurements per second. Typical test last 180 minutes, this means that the sample does 5400 cycles during a full wear test.

Alumina balls are commercial 6 mm diameter balls, with a nominal hardness of 16.5 GPa (HV10 = 16,500N/mm^2) and a nominal surface roughness of Ra = 10 nm. Balls are observed at the optical microscope after fixing to the ball holder in order to be sure that no local micro-defect exists at the contact area. Alumina balls show some residual surface roughness because of their polycrystalline structure. Sapphire balls of the same size, but with lower surface roughness, Ra = 2 nm, have also been used, in the same test conditions, in order to check the possible effect of the residual surface roughness. But after a short sliding time, sapphire balls show, under high power optical microscope, a scratched contact area with some increase in roughness, and than, their behaviour related to the friction coefficient records and related to transfer layer formation does not differ of those of alumina balls.

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3 RESULTS AND DISCUSSION

3.1 Friction Coefficient Records and Transfer Layers

Friction coefficient records, along the test time, are good guides to asses the formation of a transfer layer either on the ball or in the wear track, once the transfer layer forms, the friction coefficient changes, in general by increasing its initial state value and besides it becomes very unstable. All the TiN samples we have studied generate a transfer layer, at least on the ball, some time after the ball-on-disc test starts. In CVD TiN coatings, the transfer layer formation is delayed for a short period, some minutes, and is deposited exclusively on the ball contact area, rarely on the wear track. These facts, about friction coefficient affected by the transfer layer formation, can be observed in a representative example shown in in Figure 1 (a) that shows the friction coefficient record of alumina ball on CVD TiN. Besides, in PVD TiN coatings, the transfer layer appears very soon and it coats the ball contact area and quickly the wear track bottom coats with a thick, irregular shape, transfer layer. Also the differences between CVD and PVD coatings can be appreciated by comparing micrographs (a) in Figure 2 and (a) in Figure 3: wear tracks have been imaged in the optical microscope with Nomarski Interference Contrast (NIC), CVD TiN in Figure 2 (a) shows a rather deep track, with irregular worn bottom, but no transfer layer can be appreciated in the tack. On the contrary PVD TIN in Figure 3 (a) shows a track with a thick continuous transfer layer adhered to its bottom; this transfer layer cannot be detached by rubbing it with a cotton cloth nor scratching it with a sharp steel cutter tip, does it disappear after consistent rubbing with a silicon carbide polishing pad; after that the remaining track is much less deep that the track in CVD TiN. Transfer layers on the alumina ball forms, in both examples, and they have the form of a patch with irregular contours and with the approximate size of the contact area. Transfer layer produced when sliding on CVD TiN can be seen in the optical micrograph in Figure 4(a) and also in the Scanning Electron Microscope (SEM) micrograph of Figure 4(b). The patch on the ball is thick, compact and stable and it is rather flat, with some undulations that reproduce the channelled undulated form found in the CVD track in Figure 2(a). These transfer layer patches on the alumina balls, cannot be detached by scratching with a sharp steel cutter tip; but they can be totally removed after consistent rubbing with an aluminium oxide polishing pad. The EDS-SEM mapping analysis for the Ti element, Figure 4 (b) shows that the patch contains titanium and no other metal has been found in the patch. Mapping for aluminium shows the patch area totally darkened, as compared to the surrounding alumina ball area that shows a high aluminium signal. Most likely the transfer layer patch on the ball is made of titanium oxide because in the optical microscope image it shows as a transparent layer with interference rainbow fringes.

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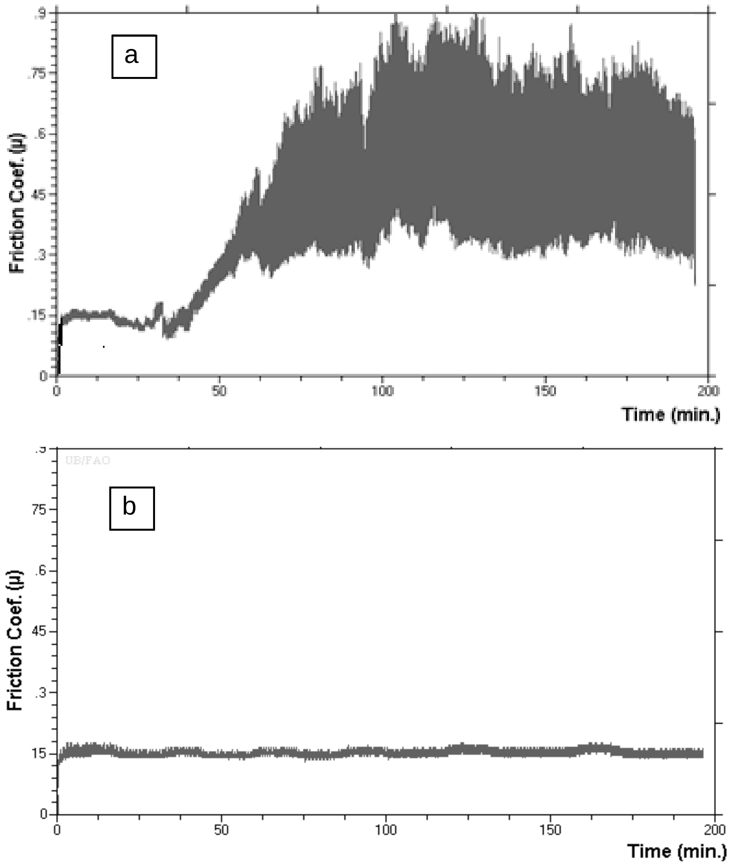

Figure 1. Friction coefficient records of CVD TiN with transfer layers on the ball and on the track (graph a) and with no transfer layers (graph b).

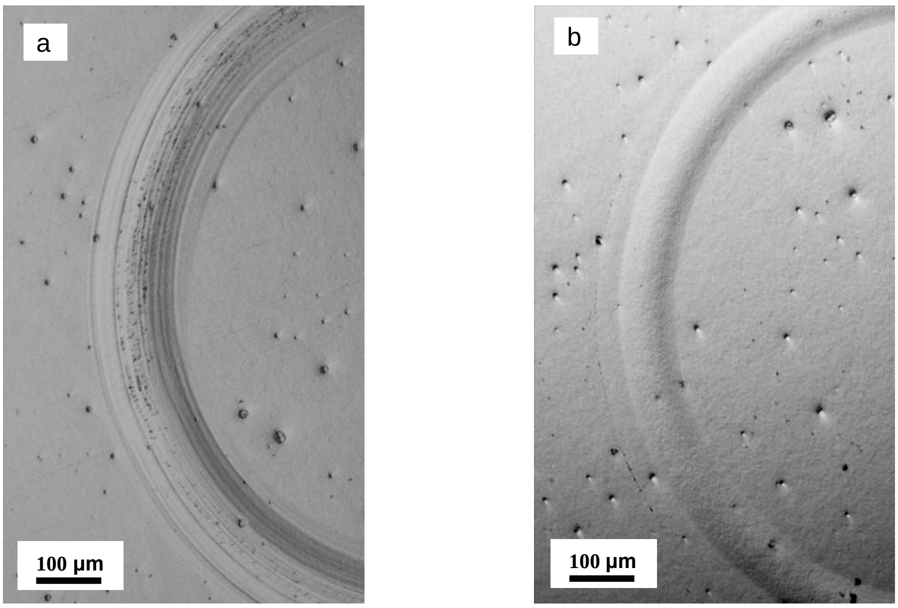

Figure 2. Optical microscope (NIC) of wear tracks on CVD TiN. With transfer layer on the ball (a). With no transfer layer (b).

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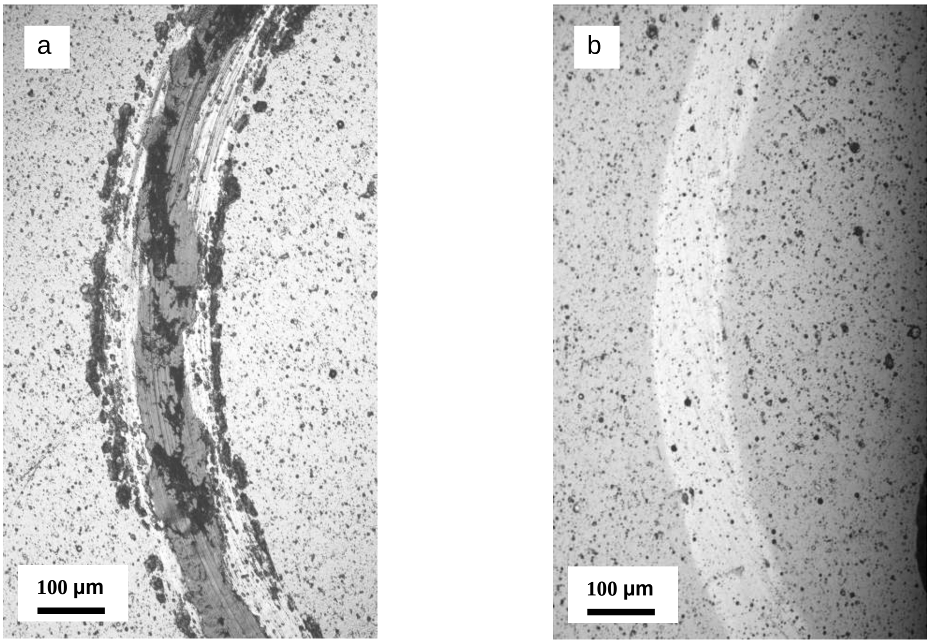

Figure 3. Optical microscope (NIC) of wear tracks on PVD TiN. With transfer layers on the track and on the ball (a) and with no transfer layers (b).

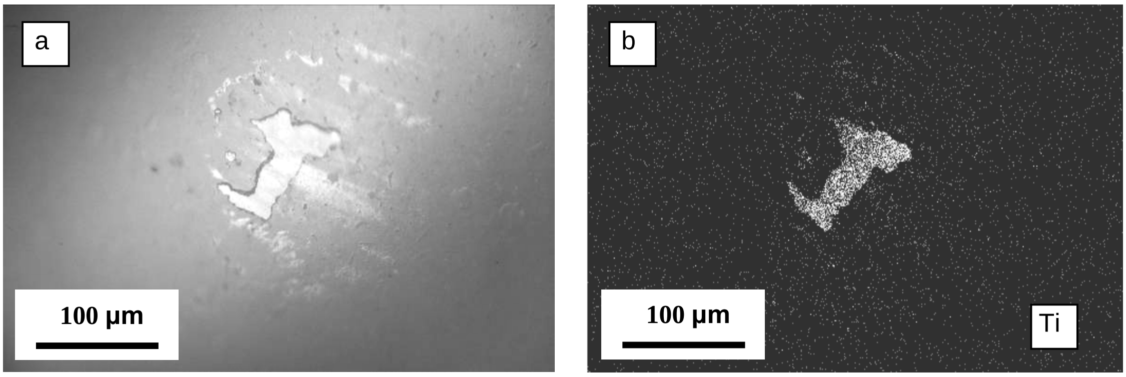

Figure 4. Optical microscope (NIC) of the transfer layer on the alumina ball (a). The same transfer layer image obtained with a SEM with EDS mapping analysis for the Ti element (b).

3.2 Wear tracks without transfer layers

In order to avoid the formation of transfer layers, we conducted the ball-on-disc tests with repeated and careful cleaning of any transfer layer that could appear on the alumina ball, this clean up routine has been carried on by rubbing the alumina ball surface with an aluminium oxide polishing pad of 1 microns grain size. With this precaution, the transfer layer is impeded to form on the alumina ball and then no transfer layer forms on the wear track, in no case. These results can be observed in the optical micrographs in Figures 2 (b) and 3 (b). They show very clean wear tracks on the CVD TiN and PVD TiN coatings, respectively, and they can be compared to wear tracks in Figures 2 (a) and 3 (a) created when transfer layer build ups had not been impeded.

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Without transfer layers on the ball and on the track, wear tracks produced on CVD and PVD TiN coatings show a smooth cylindrical shape that reproduces well the sphericity of the test ball. The shape and depth of the wear tracks can be obtained from the interferential microscope micrographs, Figures 5(a) and 5(b). In these figures the depth and shape of wear tracks on CVD TiN, can be compared. Figures 5(a) and 5(b) show the depth profile of the wear tracks, on CVD TiN, previously shown in Figures 2(a) and 2(b), respectively. With the “no transfer” condition, the depths of the wear tracks are very reproducible from one test to the next, in track depth and in track volume, and consequently the measured wear rate values are consistent.

In the same way, friction coefficient records are very stable along the test and, after an initial setting time, as a general rule very short. The friction coefficient value is very constant along the test, shows only very small oscillations that can be proved to be of the same period as the sample rotation period. This can be appreciated, for example, in the friction coefficient record in Figure 1 (b), which is totally different, and much smoother, than the record in Figure 1 (a) obtained on the same CVD sample, but with the transfer layer formed on the alumina ball.

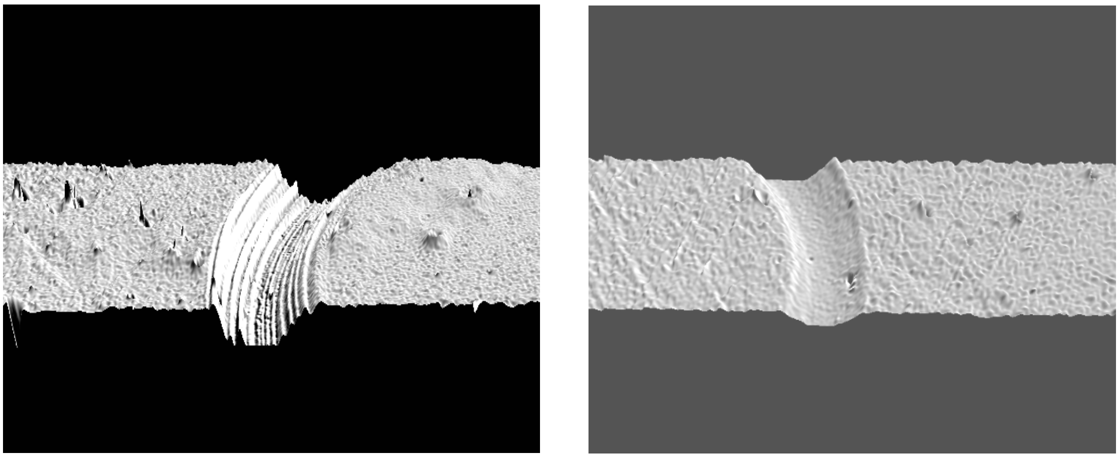

Figure 5. Interferential microscope micrographs of wear tracks on CVD TiN. With transfer layer on the ball (a). With no transfer layer (b).

3.3 Discussion

The formation of a transfer layer on the alumina ball counterpart happens in all the studied cases, this transfer layer cannot be a metal film because it shows a higher hardness than metals and because it appears very often transparent or partially transparent under optical microscopy observation. We have tested TiN coatings, and by EDS analysis, the only metal that we found in the transfer layer is titanium, we can consider that the titanium metal worn from the TiN coating reacts with the oxygen and forms titanium oxide that grows as a thin film very well adhered to the alumina ball. The residual roughness of the alumina balls does not play a role, because very similar results have been obtained when using sapphire balls with lower roughness than alumina balls. In the Cathodic Arc PVD TiN, the coatings contain small droplets of non nitrided titanium metal, and we can suppose that this metal in excess can facilitate, as well, the formation of thick transfer layers at the bottom of the wear tracks in the coating.

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The transfer layer adhered to the ball counterpart cause a pronounced wear and high friction, specially in CVD TiN coatings, this can be avoided by repeatedly cleaning the transfer layer on the ball, this procedure is very useful to obtain good wear test and friction results, but in practice it will not be applicable to real industrial mechanisms working continuously in dry conditions. Transfer layers deposited in the wear track in PVD TiN coatings can also be avoided during the wear tests, by applying the same procedure, but if allowed to form, they have an even worse annoying effect on the wear and friction tests results. In some applications they could be useful because they reduce the wear rate of the coating if they are long-standing.[5,6]

4 CONCLUSIONS

Transfer layer formation plays a crucial role in the mechanisms and in the results of dry friction and wear tests on hard coatings. Transfer layer formation can be avoided by a careful removal procedure during the test, than the wear tracks and the friction values are very reproducible, but they differ of those obtained in the more usual wear test practice.

Acknowledgements

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REFERENCES

1 HOLMBERG, K; RONKAINEN, H; MATTHEWS, A. Tribology of Thin Coatings. *Ceramics International* v. 26 – 7, p. 787-795, 2000.
2 OUYANG, JH; SASAKI, S, The friction and wear characteristics of cathodic arc ion-plated (V,Ti)N coatings in sliding against alumina ball, *Wear,* v. 257, p. 708-720, 2004.
3 CHENG YH, BROWNE T, HECKERMAN B, MELETIS EI, Mechanical and tribological properties of nanocomposite TiSiN coatings, *Surf. & Coat. Tech.,* v. 204 – 14, p. 2123-2129, 2010.
4 KATO H, JYOKO Y, SASASE M, et al. Characteristics and Wear Properties of Metal Transfer Layers Produced by Friction, *Journal Of Japanese Society of Tribologists,* 55 – 3, p. 200-207, 2010.
5 ZHOU Z, RAINFORTH WM, TAN CC, ET AL., The Role Of The Tribofilm And Roll-Like Debris In The Wear Of Nanoscale Nitride PVD Coatings, *Wear*, v.263, p.1328-1334, 2007.
6 WU PQ, TANG B, CELIS JP., Effect of material transfer on the counterbody on friction and wear of TiN coatings in oscillating contacts, *Surf. & Coat. Tech.,* v. 201-1-2, p. 413 -417, 2006.