TRIBOLOGICAL PROPERTIES MODIFICATION OF TITANIUM BY PLASMA CARBONITRIDING

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Abstract. *Titanium and its interstitials compounds are been largely studied due to it high sensibility when atoms such as C, N, O and H are inserted into its lattice. Particularly about carbonitriding, it is known which those elements have strong influence on tribomechanical properties of the titanium. In this work the titanium was carbonitrided in Ar-N2-CH4 plasma mixture at 500 °C along to 1 hour. The modified surface was measured by a pine on disk tribometer before and after the treatment in order to know the friction coefficient and wear parameters. The results were compared to chemical and microstructural characteristics of the surface obtained by the GIXRD, NRA and Profilometry analysis in order to describe the influence between interstitial elements and tribomechanical properties of the titanium. It has been seen which the friction coefficient of titanium decreased when the carbon atoms were present into its structure.*

Keywords: *plasma, titanium, carbonitriding, tribology.*

1. INTRODUCTION

Titanium and its alloys have several properties which make them interesting materials in order to be utilized in a large number of industrial applications. Some of its advantages are: low density, excellent corrosion, erosion and wear resistance and high rate E/m (module of elasticity/mass) allowing structures lighters and more resistant; capacity of work in high temperatures and, in some cases, cryogenic properties. However, they present some limitations which reduce its spectrum of applications, especially those which require good tribological properties (for example, application in engineering like gears and bearings). That problem may be solved utilizing technologies in surface modification with covering, thin film deposition, thermal and thermochemical treatments (Fang *et al*, 2004; Zhecheva *et al*, 2005). In different contributions, it has already demonstrated which the ionic nitriding treatment may increase the superficial hardness and/or tribological properties (Berberich *et al*, 2001; Chen and Juang, 1997). Carbides and nitrides of transition metals promotes much interest due to their properties such as high hardness and Young's module, high electrical conductivity, considerable temperatures resistance, high corrosion and decomposition resistance (Toth, 1971). TiCN layers present a low friction coefficient and better wear resistance than TiN layers, independent of the associated material. (Knotek *et al*, 1992). The multiple phases of TiCN thin films combines the advantages of high hardness of TiC and high ductility and adhesion force of TiN having better mechanical properties than only one phase of TiC or TiN (Randhawa 1987; Huber *et al*, 2003). The morphology, structure and composition of TiCN are investigated in several studies (Schneider *et al*, 1995; Bull *et al*, 2003). In order to that it has been shown TiCN layer consists in a solid solution of TiN and TiC which acquires the advantages and characteristics of both. Especially in tribological applicatios, where abrasion is the dominant wear mechanism. It is due to the hardness difference between TiN and TiC and the presence of C which acts like a lubricant decreasing the wear and friction coefficient (Wei *et al*, 2001). The tribological comportment of TiCN films is varied due to the changing of covering factors which include the substrate, deposition parameters, stoichiometry, wear mechanism, etc. (Berberich *et al*, 2001; Chen *et al*, 1997). Carbonitrided titanium also presents good wear resistance due to its low friction coefficient (Polcar *et al*, 2005). In this work is studied the influence of concentration of C and N in TiCN layers produced by thermochemical treatment by plasma.

2. MATERIALS AND METHODS

Titanium disc with 15 mm in diameter and 1 mm in thickness were obtained by stamping technique from titanium (grade 2) plates. They had a metallographic preparation (the pieces were sanded until the granulometry 2000 and polished with colloidal silica of 0,06 µm) and then thy were thermochemically treated by plasma of N_2 – Ar – CH_4 gas mixture. The N_2 – Ar gas flow were maintained constant in 4 SCCM and CH_4 gas flow has values of 2, 3 and 4 SCCM.

In order to subserve the understanding about different gas concentration into the plasma, it was created a formalism in order to characterize that gas combination. The nomenclature is z N_2 – y Ar – x CH_4 where “x”, “y” and “z” represent the flow (SCCM) of the respective gases. For the carbonitriding of Ti samples, it was utilized a plasma reactor with the characteristics presented in the figure 1.

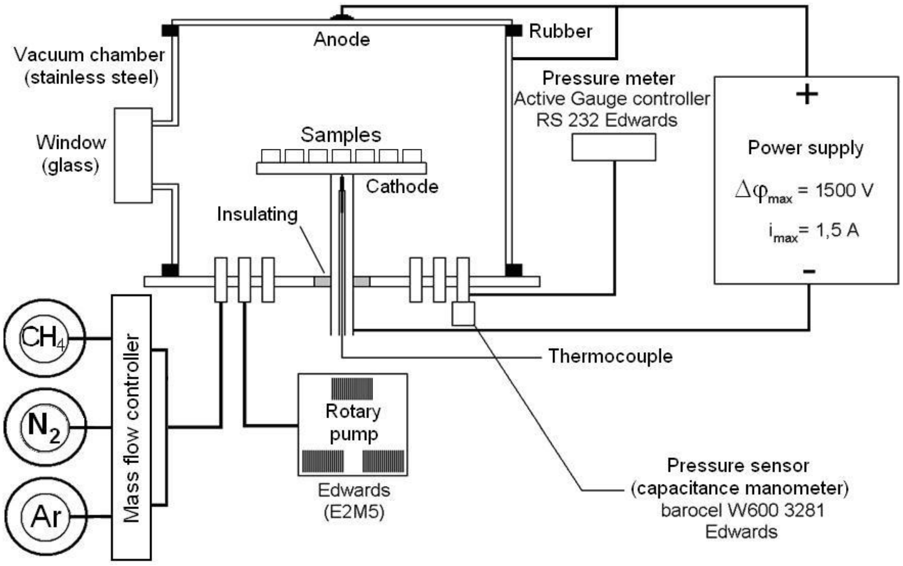


Figure 1. Plasma reactor schematic representation, including gas inner and evacuation system.

The system utilized in order to active the plasma process consists of a high voltage DC source (maximum output 1500 V, 1,5 A), a vertically mounted cylindrical vacuum chamber (300 mm in diameter and 300 mm in height, made of stainless steel). In the main cylinder there is a window made of glass (borosilicate). The plasma was generated due to a electrical potential difference between negatively polarized electrode (cathode and worktable with 100 mm in diameter) and the rest of the chamber (anode), held at ground potential. Inserted into the cathode axis there is a thermocouple. In the inferior flange, there are several connections for the pressure measurement by a sensor, gas inlet and outlet. The superior and inferior extremities of the main cylinder are closed utilizing L gaskets and the flanges.

The samples were grouped in three lots for each CH_4 gas flow with 20 unities and placed on the cathode. The residual pressure obtained was 0,3 mbar. The pre-sputtering process was carried out utilizing 50% Ar – H_2 (4 SCCM) during 30 min, 100 Pa and 200 ºC. The carbonitriding treatment was performed during 1 h, 2,2 mbar and 500 ºC in different plasma concentration (4 N_2 – 4 Ar – 2 CH_4, 4 N_2 – 4 Ar – 3 CH_4, 4 N_2 – 4 Ar – 4 CH_4).

Friction coefficient analysis was performed utilizing a pin on disc tribometer. The load and rotation were maintained constant, 2 N and 150 rpm, respectively. In order to identify the phases on the surface of the material, it was utilized the Greasing Incidence X-Ray Diffraction technique (GIXRD). The C and N concentration profile was determined utilizing the Nuclear Reaction Analysis (NRA). After wearing the surfaces were analyzed through a mechanical profilometer (Ambios Technology XPII).

3. RESULTS AND DISCUSSION

GIXRD technique was utilized in order to determine the phases on the surface of the treated titanium. The figure 2 exhibits the diffractogram for analysis in incident angle of 0,5º on samples treated in different concentration of carbonitriding plasma. That angle was chosen because of the minor depth which the X-ray beam penetrates, avoiding the important contribution of Tiα phases of the substrate. TiN peaks are more evident than TiCN peaks in samples which present lesser CH_4 gas flow. Tiα peaks are related with the substrate which due to the thinness film grown (about 250 nm) they are detected relatively easy by the instrument. TiN and TiCN peaks are rounded because of the increasing of these amorphous phases. The Ti peaks shift in the plane (002) on the sample treated by 4 Ar – 4 N_2 – 3 CH_4 plasma mixture is related to the larger quantity of defect into the crystalline lattice due to the insertion of interstitial elements.

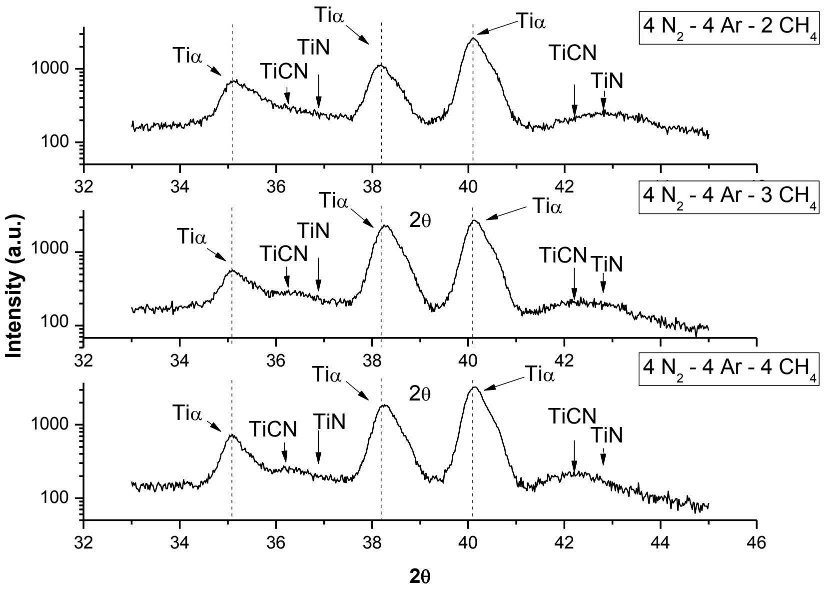
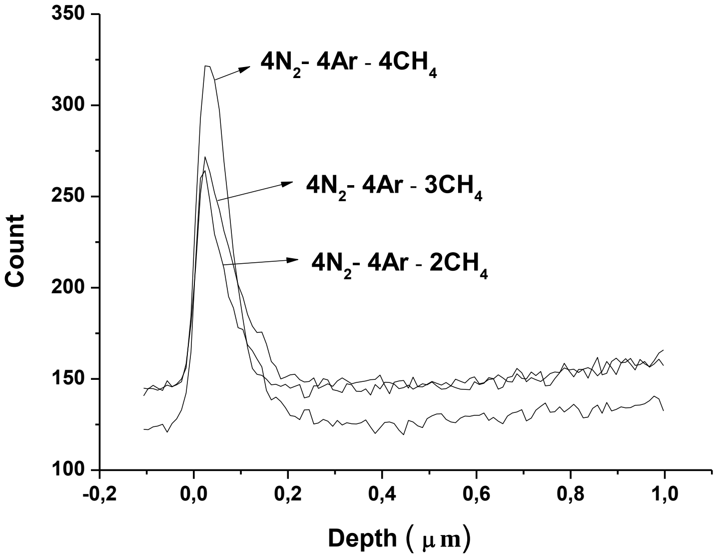
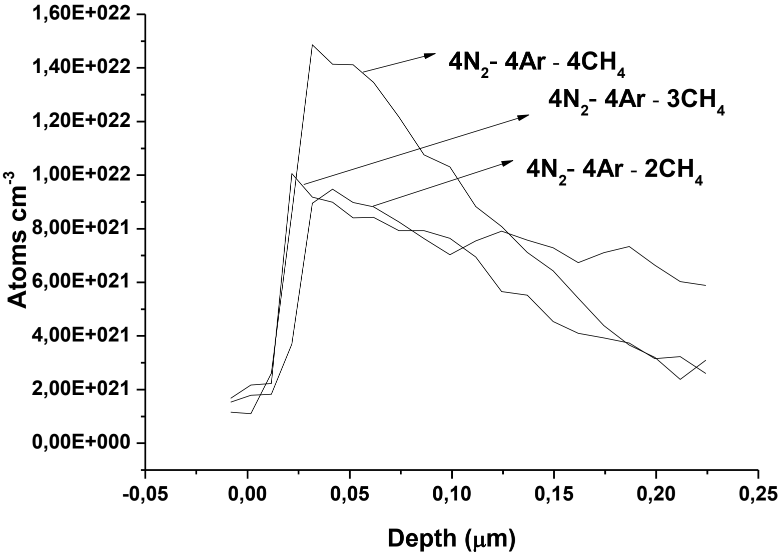


Figure 2. GIXRD technique utilizing 0,5° for samples tretaed in 4 N_2 – 4 Ar – x CH_4. The index “x” has values 2, 3 and 4 with SCCM dimension.

The $^{12}C(\alpha,\alpha)^{12}C$ reaction in order to detection of C was performed according to the experiment carried out by (Driemeier and Baumvol, 2008). The count quantity of particles α is referent to the quantity of C difused into the sample. It was impossible to obtain a result related to the atomic concentration of C similarly which was made for N atoms because a pattern was not found. The figure 3(a) and 3(b) displays C and N concentration profile for three plasma conditions utilized. The condition 4 N_2 – 4 Ar – 4 CH_4 presents higher peak of concentration on the surface acquiring saturation, differently of other conditions which were equals. However, in the conditions which the peaks of concentration were lesser (4 N_2 – 4 Ar – 2 CH_4 and 4 N_2 – 4 Ar – 3 CH_4), there was more diffusion of C and N, due to the higher reactivity.



(a)



(b)

Figure 3. C and N concentration in depth profile. (a) Nuclear reaction for $^{12}C(\alpha,\alpha)^{12}C$ and (b) Nuclear reaction $^{15}N(\rho,\alpha\gamma)^{12}C$.

The pin on disc experimental results are presented in the figure 4.

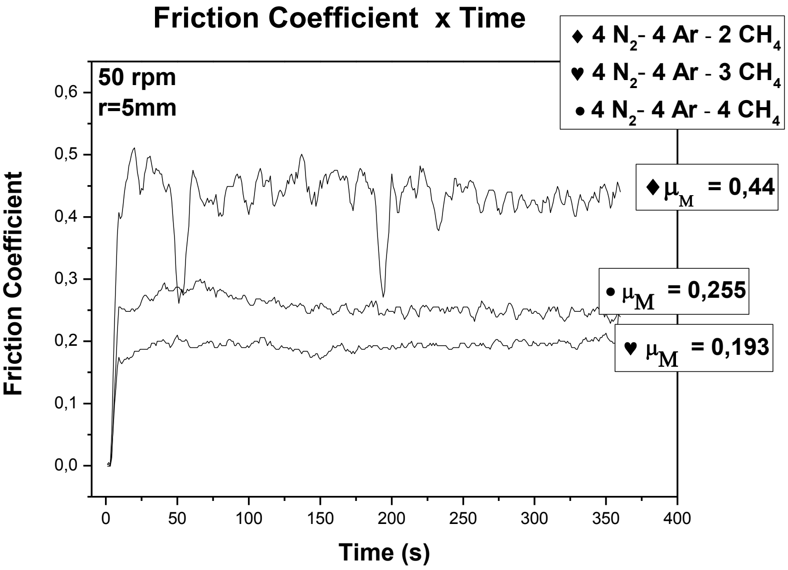


Figure 4. Friction coefficient x time graph for samples treated in different plasma conditions at a rotation of 50 rpm and 360 seconds in duration.

The samples treated in lesser CH_4 gas flow presented higher friction coefficient in the assays which lasted 360 s in a rotation of 50 rpm. The graphic also shows which when the TiCN layer is completely thinned out, automatically the friction coefficient increases until the same numeric value of the Ti surface. That characteristic was observed on the non treated titanium. The oscillations presented in the experiments in the 4 N_2 – 4 Ar – 2 CH_4 plasma atmosphere are related with the local plastic deformation and the film adhesion. Those adhered materials make a kind of peaks where the pin collides resulting in variance in the friction coefficient. The wear profiles of samples treated in different plasma conditions are presented in the figure 5.

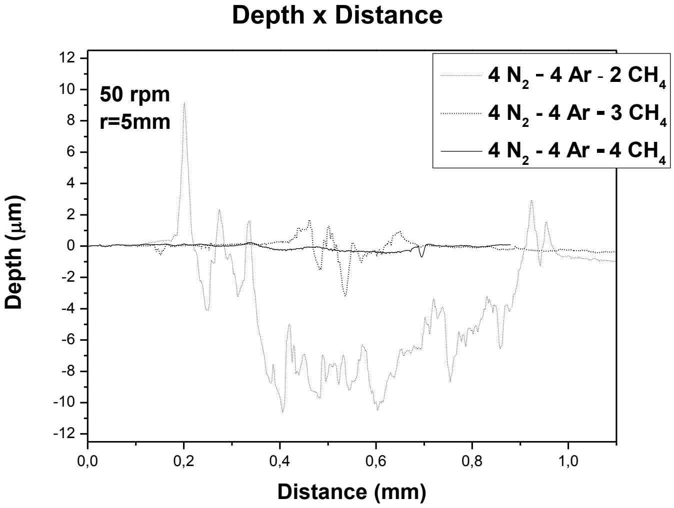


Figure 5. Wear profile of samples with different plasma treatment.

The figure revels that the samples presented a wear profile characteristic in order to each treatment condition. Also it possible to see which the screech formed is inversely proportional to the CH_4 gas flow. In other hand, methane in this situation is a reducer agent of friction coefficient and the wear rate is directly proportional to that coefficient. The significant wear profile of 4 N_2 – 4 Ar – 2 CH_4, is due to the plastic deforming of film, promoting the adhesion of the film on the pin making it to slip on the same material and causing serious damages.

4. CONCLUSIONS

- The treated samples with different concentrations of carbonitriding plasma result in variations of tribological comportment;
- DRX analysis shows the introduction of CH_4 have influence in the intensity TiN phase on the sample. In the other hand, this phase decreases when CH_4 gas flow is higher;
- All samples present simultaneously the formation of layer composed by TiN and TiCN phases after treatments in condition of 4 N_2 – 4 Ar – x CH_4. The Tiα peaks are related to the substrate because of the thinness of the film;
- NRA shows that the insertion of elements N and C is not directly proportional to the gas concentration;
- The wear rate is directly proportional to the friction coefficient value, ie, the film with low friction coefficient present elastic comportment, guarantying higher durability than the film with higher friction coefficient, which is the most of the time it has a plastic comportment, allowing a rupture.

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The following text, properly adapted to the number of authors, must be included in the last section of the paper:
The authors Ricardo Rocha (physicist), Julio Barbosa (physicist), Danilo Braz (chemist), Antonio Nunez Filho (material engineer), Thiago Medeiros (material engineer), Saulo Jacobsen (physicist), Custodio Gerra Neto (dentist) and Clodomiro Alves Junior (physicist) are the only responsible for the printed material included in this paper.