The influence of oxygen flow during deposition on the structural, mechanical and tribological properties of titanium oxide magnetron sputtered thin films

D. G. CONSTANTIN, C. MOURA[a] D. MUNTEANU*, L. CUNHA[a]
Dept. of Materials Science and Engineering Transilvania University, 500036 Brasov, Romania
[a]Centro de Física, Universidade do Minho, 4710-057 Braga, Portugal

This work reports on the study of mechanical and tribological properties of titanium oxide films produced by direct current reactive magnetron sputtering. The mechanical and tribological properties of the deposited coatings were analyzed as function of the oxygen flow rate used during the deposition process and were correlated with the structural aspects. The structural characterization results reveal a dependence of the film texture on the oxygen flow rate. The gradual increasing of oxygen flow bring the TiO_x compound first in a crystalline structure variant (TiO_2 - anatase preferential growth) followed further by a significant loss in crystallinity. Considering the same variation of oxygen, the mechanical properties of the films (hardness, Young modulus and adherence) generally become better in the amorphous region while the friction coefficient decreased.

(Received August 14, 2012; accepted October 30, 2012)

Keywords: Titanium oxide, Sputtering, Structure, Hardness, Friction, Wear

1. Introduction

Titanium oxide is one of the most extensively studied transition-metal oxides, and thin films of this material have numerous applications, such as antireflection coating, multilayer optical coatings (used as optical filters), optical wave guides [1], dye-sensitized solar cells, gas sensors [2], heat mirrors on building and automotive glasses, self-cleaning glass, air cleaning lamp, wiper-less windshield environmental applications [3]. Many researchers have focused on this kind of applications due to their high refractive index, high dielectric constant, photo-catalytic and antibacterial, disinfection, antifogging and self-cleaning properties [4].

A large number of processing techniques such as electron-beam evaporation [5], ion beam assisted deposition [6], direct – current (d.c.) or radio – frequency (r.f.) magnetron sputtering [2, 3], sol-gel processes [7], chemical vapour deposition [4] and plasma enhanced chemical vapour deposition processes [8] have been used to deposit titanium oxide thin films.

Among them, the sputtering deposition process has been widely used because of its simplicity, flexibility in the materials combination and tailoring in size distribution [2]. Different studies in the literature are referring to the deposition of titanium oxide films by sputtering [2, 9, 10, 11]. These studies reported structural, morphological or compositional aspects in correlation with different types of properties, especially the optical, photocatalytic and hydrophilic ones. Only few data are available in the literature on the mechanical and tribological properties of titanium oxide films [3, 12, 13]. Haseeb et al. [3] reported that the titanium oxide films possess superior hardness and acceptable wear resistance. Thus, they deposited titanium oxide thin films on microscope glass slide substrates by radio-frequency magnetron sputtering, at different temperatures - room temperature, 200 °C and 300 °C, using a constant oxygen reactive gas-flow of 10 sccm. Their results showed an increase in hardness from 11.5 GPa to 13.6 GPa with increasing temperature. The wear track width decreases from 18.8 to 9.6 μm with increasing of deposition substrate temperature indicating an improved wear resistance with increasing temperature. This improvement of wear properties for the films deposited at higher temperatures is likely to be attributed to the improved of hardness and to a lower grade of crystallinity.

Krishna et al. showed that the thickness of the titanium oxide films has significant influence on the mechanical and tribological properties [12]. According to Krishna, in the case of certain films obtained in this case on AISI 316 L stainless steel substrates by (d.c.) magnetron sputtering of TiO_2 target, with increasing of films thickness (0.16, 0.44 and 0.92 μm) the films hardness increase too (7.9, 8.9 and 8.7 GPa) and the friction coefficient values register a tendency for slowly decreasing, 0.4 to 0.3.

In addition, Lackner et al. [13] observed that generally, for films prepared by pulsed laser deposition, the increasing of oxygen content in composition leads to lower values for hardness and elastic modulus. According to these aspects, if the oxygen flow varies between 10 to 60 sccm, the hardness decreases from 11.16 to 4.25 GPa and the elastic modulus from 208.9 to 154.6 GPa. The friction coefficient values reported by Lackner are between 0.7 and 0.5, the lower values characterizing the coatings with more oxygen. In fact, the tendency of amorphization of the film structure leads to the improving of friction conditions by obtaining smaller surface roughness and friction coefficient values [14].

Taking into account these aspects of state-of-art, the structural phase-ratio, the hardness and the elastic modulus strongly depend on the oxygen gas flow and, of course, on the oxygen content in the film. Moreover, it is important to conclude that, very often, amorphous titanium oxide phases have been found to present superior mechanical properties compared to crystalline ones.

There is a general agreement in the literature that the performance of coated devices and components, in any real application, is mainly determined by the properties of near-surface layers [15]. This implies that the solutions to achieve a coating tailored for a particular application, will essentially depend on the ability to achieve a suitable performance concerning the mechanical properties of the film.

In order to maintain or increase the lifetime of a particular coated object/device/part, certain properties such as hardness as well as the coating adhesion or tribological behaviour have been extensively adopted as fundamental aspects for quality and process control.

The work described in this paper deals with the deposition and characterization of titanium oxides thin films on high speed steel substrates by direct current magnetron sputtering. The main objective of this study was to correlate the deposition conditions with mechanical and tribological properties, namely hardness, Young modulus, friction coefficient and wear rate.

2. Experimental details

Within the frame of the experimental program, the samples were deposited by direct current magnetron sputtering from a high purity Ti target (99.6 at% purity) onto polished high-speed steel (AISI M2) samples (□ 25 x 5 mm) – used for characterization mechanical and tribological properties, single crystalline silicon (100) samples (30 x 20 x 1 mm) – for structural characterization and stainless steel samples (□ 25 x 0.6 mm) – for thickness measurements. Prior to all depositions, the substrates were ultrasonically cleaned and sputter etched for 15 minutes in an argon flow, which was fixed at 100 sccm. Depositions were carried out under an Ar/O_2 atmosphere in an Alcatel SCM-650 apparatus, and the substrates were rotating at 65 mm over the target at a constant speed of 4 rpm. The working pressure was kept approximately constant at $5x10^{-3}$ mbar during the entire coating deposition process. The oxygen (reactive) gas flow varied from 0 to 40 sccm (0, 10, 20, 30, 40 sccm). The working gas flow (argon) was kept constant at 100 sccm. The films have been prepared at room temperature (20 ^{o}C) and the deposition time for each sample was 1 h.

The film’s thickness of as deposited samples was obtained by “Ball Cratering” technique using the CALOTEST method (CSM Instruments). A short summary of all prepared samples, regarding the thickness and the oxygen flows used, is given in Table 1.

The phases-structure aspects of the films were analysed by X-Ray Diffraction (XRD) using a Philips PW 1710 diffractometer in a Bragg-Brentano θ-2θ configuration and a CuK_{α} radiation. From the broadening of diffraction peaks, the grain size was estimated using the Scherrer formula [16].

Table 1. Deposition parameters, thickness and roughness average of the films

Sample	Oxygen flow [sccm]	Thickness [μm]	Error thickness [μm]	Areal roughness average S_a [nm]
Ti(1)	0	0.52	±0.01	52.4
TiO_x(2)	10	0.74	±0.03	7.6
TiO_x(3)	20	0.48	±0.03	13.8
TiO_x(4)	30	0.51	±0.06	11.2
TiO_x(5)	40	0.56	±0.04	10.8

Film’s hardness and Young’s modulus were determined from the loading and unloading curves, carried out with an ultra low load-depth sensing nanoindenter - CSM Instruments type, equipped with a Berkovich diamond indenter (α = 65.3°±0.3°), operating at a constant approach load rate of 1500 nm/min. up to a maximum indentation depth of 74 nm. The maximum load value was 1.3 mN, the holding time at maximum depth 1s and, the unloading rate was 1500 nm/min. For each sample, an average number of 8 indentations were performed.

The tribological characterization of titanium oxide films was conducted on a Universal Micro Materials Tester UMT-2MT type, (CETR Company) using a reciprocating ball-on-flat geometry. Unlubricated tribo-tests at room temperature and relative humidity of 50 ± 5% were performed under macro - testing (0.5 N) conditions. The sliding friction force at the contact was measured by dual beam 2-axis friction/load sensors mounted separately on the UMT-2MT tribometer, having a resolution of 10 μN (FVL model) and 0.25 mN (DFM-0.5 model) respectively, for macro-testing. A Si_3N_4 ball with a diameter d of 5 mm and a surface roughness R_a of about 2 nm was used as the mating material. A schematic arrangement of the tribometer is given in Fig. 1. The wear resistance of the films was evaluated based on the maximum sliding distance till the appearance of the first delamination (SDFD). This first delamination was registered online, both visual (by optical microscope) and acoustic.

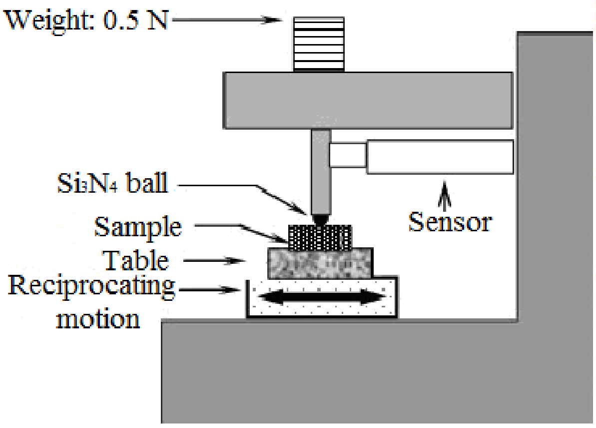

Fig. 1. Schematic arrangement of the Universal Micro Materials Tester UMT-2MT.

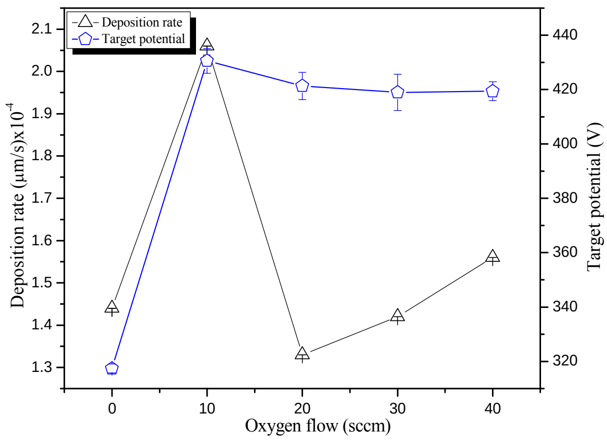

Fig. 2. The variation of the deposition rate and target potential of as produced titanium oxide coatings with reactive gas flow.

The surface topography of the films (surface roughness) was investigated by using Atomic Force Microscopy (AFM-NT-MDT model NTGRA PRIMA EC). The images were taken in semi-contact mode with “GOLDEN" silicon cantilever (NCSG10, force constant 0.15 N/m, tip radius 10 nm). Scanning was conducted on three different places (a certain area of 10 x 10 μm for each section) randomly chosen, at a scanning rate of 1Hz. The resulted values of S_a roughness average (areal roughness according ISO 25178) are presented in Table 1.

3. Results and discussion

3.1 Thickness, deposition rate and target potential

Table 1 presents the films thickness for all the samples as a function of oxygen flow. This parameter varied between 0.48 and 0.74 μm. Fig. 2 presents the variation of deposition rate and target potential as a function of reactive gas flow. It can be seen from this figure a sudden increase of the target potential value with the increase of the oxygen flow to 10 sccm; at the same time, it is important to observe a smooth decrease in the deposition rate from an oxygen flow interval from 10 to 20 sccm. If the first aspect of deposition rate could be explained by the continuous increasing of oxygen flow, the second variation of deposition rate emphasizes the developing of the so-called target poisoning by the reactive gas. This phenomenon is explained by formation of a compound layer on the target surface, which has a different ion-induced secondary electron emission (ISEE) coefficient than the target material. Due to effect of the poising of the target, the deposition rate is affecting [17].

Furthermore, from the same figure, it is observed that the deposition rate of the films increased from roughly $1.33x10^{-4}$ to $1.56x10^{-4}$ μm/s with increasing of the oxygen flow more than 20 sccm (from 20 to 40 sccm). As the oxygen flow increase, the argon bombardment rate increase too on the target, increasing the deposition rate of the films [18].

3.2 Structural features

As a general overview, the structural characterization results reveal a dependence of the film texture on the oxygen flow rate. The samples prepared with a low value of oxygen flow (10 and 20 sccm) reveal a crystalline structure (especially for 20 sccm), which is basically constituted by (112) TiO_2 - anatase preferential growth.

The increase of the oxygen flow is followed by a significant loss in crystallinity, the films prepared with maximum oxygen flows become amorphous. Taking into account similar studies in the bibliography, this structural behaviour can be explained by taking into account the increase of the available oxygen over supersaturating level [19]. These conditions reduce the possibility of crystallization and facilitate the increasing of defects number till the amorphization.

Referring to the XRD - pattern of the sample prepared with 20 sccm oxygen flow, few weak intensity peaks appeared on the diffraction figure, which correspond to (100) and respectively (101) planes of that hexagonal Ti type structure. The development of such kinds of Ti peaks in this case could be explained base on the insufficient oxygen content in the films, which may not be enough to form specific TiO_2 phase.

In detail, the Fig. 3 presents the XRD patterns of the pure titanium (reference sample) as well as for titanium oxide variants. The films exhibit XRD patterns corresponding to the pure titanium (JPCDS card no. 44-1294), anatase phase of titanium oxide (JPCDS card no. 00-021-1272, 00-002-0406) and amorphous state.

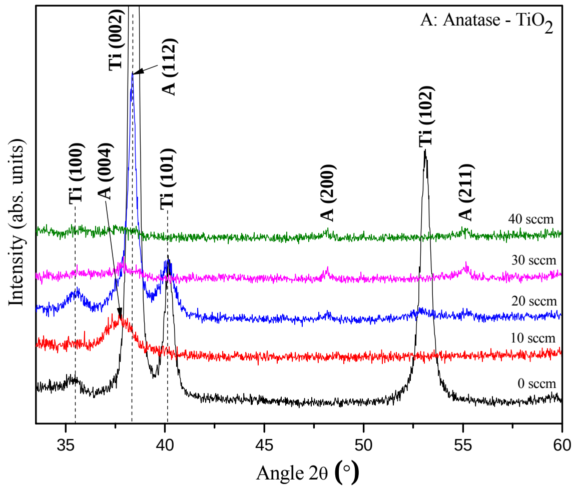

Fig. 3. XRD diffraction patterns of pure titanium and titanium oxide coatings deposited on silicon (100) with different reactive oxygen flows. Vertical line corresponds to the titanium oxide diffraction peak positions. The patterns were vertically shifted for the shake of clarity.

Similarly results have been obtained also by J. M. Chappé, Ab. Benyoucef and V. Tamilselvan in [20, 21, 22].

The mean grain size of crystalline anatase phases were calculated by Scherer's equation. The increase of the oxygen flow rate seems to have a small effect on the grain size; all the grain average dimensions were centred around 18 nm. However, a tendency for a light increasing of this parameter has been observed when the oxygen flow increased too.

3.3 Mechanical and tribological behaviours

3.3.1 Hardness and Elastic modulus

Fig. 4 presents the evolution of the hardness and elastic modulus as a function of the deposition parameters. It can be seen that for pure Ti film was obtained the high value of the hardness which corresponds to 7.38 GPa. This value of hardness sharp decrease when in the deposition chamber has been introduced oxygen. According to P. Baroch et al., this behaviour could be attributed to the significant decreasing of crystallinity and, at the same time, it is possible due to the small amount of sputtered Ti and hence a relatively small amount of oxygen, which is needed to form the titanium oxide films [23].

Moreover, for variation of oxygen between 10-30 sccm, the coatings present almost the same values of hardness, 5.18 to 5.47 GPa, with a slow increasing based probably on the increase of both crystallinity and film's thickness. Similar results for hardness were obtained by Hasan et al. - 5.5 GPa for an oxygen flow of 10 sccm, which deposited TiO_2 films at room temperature by reactive magnetron sputtering [24].

The highest value of the hardness - 7.33 GPa - corresponding to the titanium oxide film prepared with the maximum oxygen flow (40 sccm). This increase in hardness could be explained by looking at the changes of film's thickness and structure. In fact, the increasing of film thickness could contribute to this hardening behaviour; on the other hand, the developing of amorphous structure with increasing the oxygen content is believed also to offer to the film a compacted and dense aspect which leads to a higher value of hardness. Related to these, according to the literature, the Zywitzki et al. [25] reported slightly higher values of hardness (8 GPa) for anatase titanium oxide deposited by reactive pulse magnetron sputtering. This difference can be explained by the use of pulsed mode, which increases density plasma near substrate and thus creates an intensive particle bombardment of substrate. For the maximum value of oxygen, the increasing of hardness could be also generated by a possible of formation poorly crystallised oxide structures.

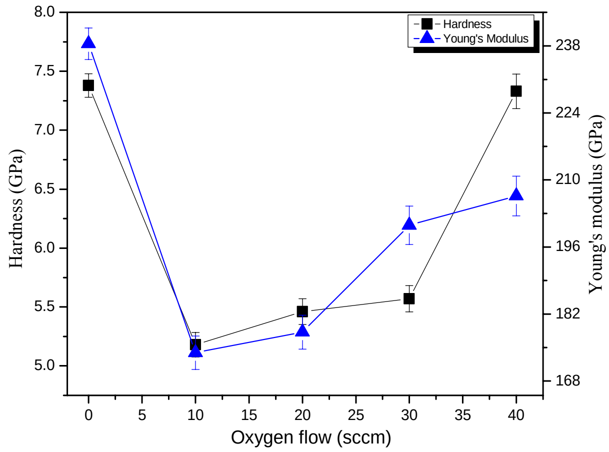

Fig. 4. Evolution of the hardness and elastic modulus as a function of the reactive gas flow..

The hardness evolution can be correlated as well with the elastic modulus values. Also, the Young's modulus (elastic modulus) values are presented in Fig. 4. It is known that, generally, this parameter has a similarly variation with the hardness. In this case, for reference sample (titanium pure) was obtained a highest value of the elastic modulus (238 GPa). Moreover, for the oxygen flow from 10 to 40 sccm, the elastic modulus presents a continuous increasing, varying from 173 up to 206 GPa. In fact, though both parameters (hardness and elastic modulus) have in generally the same variation, in this case, the elastic modulus revealed a sudden increase, earlier that hardness, starting with 20 sccm flow for oxygen. Starting with this value of oxygen flow, the structural characterization revealed the apparition of TiO_2 anatase-phase, under tetragonal crystallographic aspect. This evolution of the compound by increasing the oxygen amount, from amorphous to crystalline in the beginning could explain the small jump of Young's modulus values. This aspect was observed also by Anderson in [26], but for temperatures above 210 ^oC and it could be correlated also with the density of material.

Thus, the apparition of the crystalline state of anatase – TiO_2 is done probably by keeping almost the same density of material. As a result of this evolution, the elastic modulus increases, for the moment, in an accelerate mode in comparison with hardness (Fig. 4, interval of oxygen 20-30 sccm). Furthermore, for more oxygen in the deposition chamber, the amorphous structural aspect becomes more and more intense and the density of material increases. This could explain the increasing in hardness. No clear correlation or influence was observed between hardness and films thickness.

3.3.2 *Friction coefficient, roughness and wear resistance*

Fig. 5 presents the variation of the dynamic friction coefficient of titanium oxide coatings as a function of the oxygen gas flow. The experimental results show a clear influence of oxygen on this parameter. The maximum values of friction coefficient (around of 0.60) was observed for the pure Ti film, and the minimum ones (around of 0.24) for sample prepared with an oxygen flow of 30 sccm. As a general aspect, the friction coefficient value becomes lower with increasing of oxygen. This aspect is in a good correlation with the AFM roughness results (Table 1), which revealed a clear difference between the roughness of pure-Ti film and the Ti-oxygen film variants. The apparition of TiO_2 crystalline state leads to an almost constant value for friction coefficient for an oxygen flow between 10 – 20 sccm. This interval is characteristic also for the lowest values of hardness.

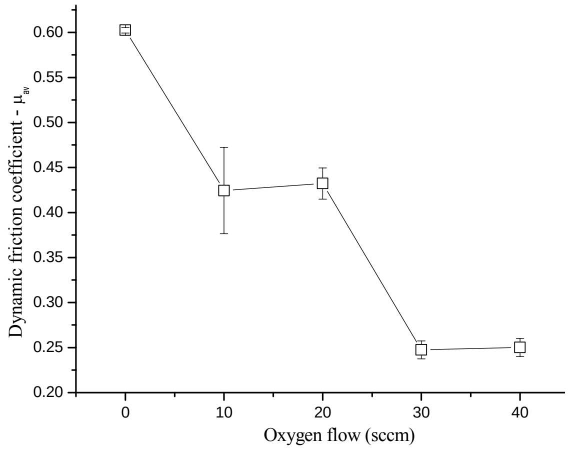

Fig. 5. Variation of the dynamic friction coefficient of titanium oxide, against a Si_3N_4 balls, as a function of the reactive gas flows.

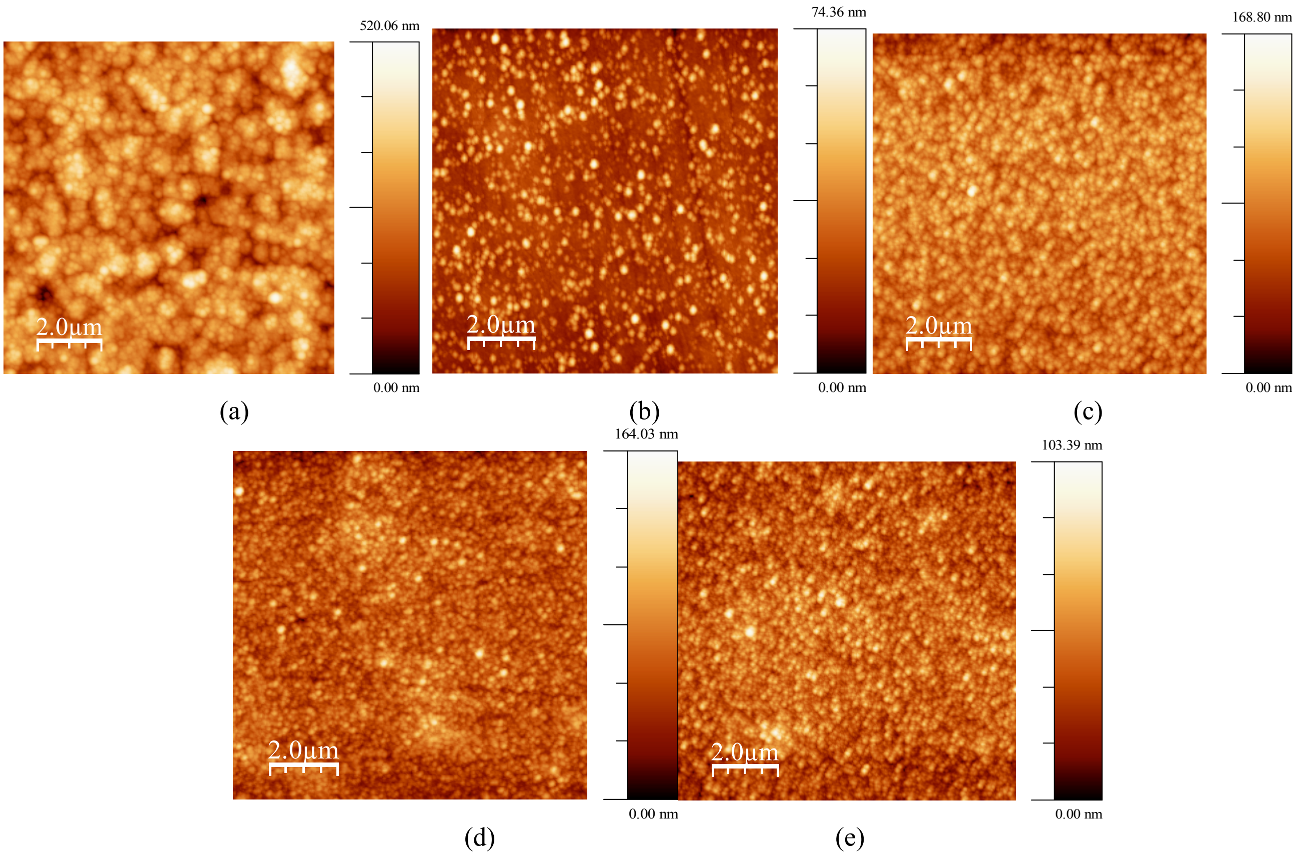

Fig. 6. Surface areal roughness images obtained by AFM: (a) sample 1, S_a = 52.4 nm; (b) sample 2, S_a = 7.6 nm; (c) sample 3, S_a = 13.8 nm; (d) sample 4, S_a = 11.2 nm; (e) sample 5, S_a = 10.8 nm.

It is important to remark in this transient interval from crystalline titanium to crystalline anatase – TiO_2, the minimum value of roughness. Moreover, the roughness value is not very different starting with this point.

Regarding the wear behaviour, for the structural interval from pure-Ti film to anatase – TiO_2 film (the first three samples) the obtained results show the lowest values (Fig. 6).

With the increasing of oxygen flow above 20 sccm, there is a clear tendency for an improvement of the mechanical properties (hardness and Young modulus – Fig. 4) and of tribological parameters (friction coefficient value and wear resistance), Fig. 5 and Fig. 7. Taking into account the XRD results, this region is characteristic to the amorphous structures and, it is known that Ti–O coatings with more oxygen have either the possibility to form magnelis phases, (TiO_{2-x}) types, which is known to have low friction coefficients, or to obtain poorly crystallised oxide structures [27].

We could conclude that these kinds of structures are able to better accommodate the deformations induced by the movement of the ball tip. At the same time, the hardness and elastic modulus values are high enough on this region, revealing a good elasticity in these films.

As can be observed, generally, there is also a good correlation between friction coefficient and wear resistance of the films (Figs. 5, 7). Relating to this aspect, it can be discuss about two important regions: (i) the region of crystallographic - TiO_2 films (10 – 20 sccm for oxygen flow) characterized by a medium value of friction coefficient and a low value of wear resistance and, (ii) the region of amorphous - TiO_2 films (30 – 40 sccm for oxygen flow) characterized by a low friction coefficient, a good wear resistance and an acceptable high value for elastic modulus.

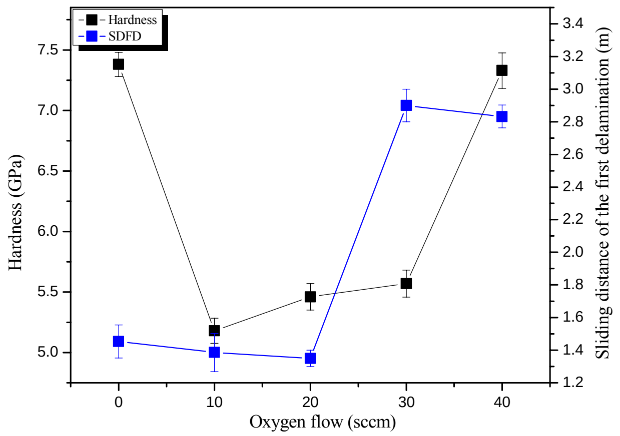

Fig. 7. Variation of the hardness and wear resistance of the coatings as a function of the reactive gas flows.

At the same time, within the frame of these experimental results, the films thickness seams to not have any influence on the tribological parameters.

4. Conclusions

Titanium oxide thin films were produced by direct current magnetron sputtering. The thin films were deposited onto high-speed steel, silicon and stainless steel substrates, from a pure Ti target, varying the flow rate of the reactive gas. The mechanical and tribological properties of the deposited coatings were analyzed as function of the oxygen flow rate during the deposition processes and, these were correlated with the structural aspects.

In terms of mechanical and tribological behaviour, it was found that the most performing TiO_x coatings were those with an amorphous structure, obtained using oxygen gas flows between 30 - 40 sccm. This region corresponds to an amorphous structural one, and is characterized by coatings with a good adherence and low friction coefficient.

Acknowledgement

This paper is supported by the Sectoral Operational Programme Human Resources Development (SOP HRD), financed from the European Social Found and by the Romanian Government under the contract number POSDRU/88/1.5/S/59321.

References

[1] B. Karunagaran, R. T. R. Kumar, D. Mangalaraj, K. Narayandass, G. M. Rao, Cryst. Res. Tech. **37,** 1285 (2002).
[2] B. Karunagaran, K. Kim, D. Mangalaraj, J. Yi, S. Velumani, Sol. Energ. Mat. Sol. C. **88**, 199 (2005).
[3] A. S. M. A. Haseeb, M. M. Hasan, H. H. Masjuki, Surf. Coat. Technol. **205**, 338 (2010).
[4] H. Sun, C. Wang, S. Pang, X. Li, Y. Tao, H. Tang, M. Liu, J. Non-Crystalline Solids **354**, 1440 (2008).
[5] M. H. Habibi, N. Talebian, J. H. Choi, Dyes Pigments **73**, 103 (2007).
[6] S. Miyaki, T. Kobayashi, M. Satou, F. Fijimoto, J. Vac. Sci. Tech. **A9**, 3036 (1991).
[7] Z. Wang, U. Helmersson, P. O. Käll, Thin Solid Films **405**, 50 (2002).
[8] W. Yang, C. A. Wolden, Thin Solid Films **515** 1708 (2006).
[9] A. Karuppasamy, A. Subrahmanyam, J. Appl. Phys. **101**, 1 (2007).
[10] Q. Ye, P. Y. Liu, Z. F. Tang, L. Zhai, Vacuum **81**, 627 (2007).
[11] Y. Zhang, X. Ma, P. Chen, D. Yang, J. Cryst. Growth **300**, 551 (2007).
[12] D. S. R. Krishna, Y. Sun, Z. Chen, Thin Solid Films **519**, 4860 (2011).
[13] J. M. Lackner, W. Waldhauser, R. Ebner, B. Major, T. Schöberl, Surf. Coat. Technol. **180-181**, 585 (2004).
[14] D. Munteanu, C. Gabor, D. G. Constantin, B. Varga, R. Adochite, O. C. Andrei, J. M. Chappe, L. Cunha, C. Moura, F. Vaz, Tribol.Int. **44**, 820 (2011).
[15] Y. Pauleu, P. B. Barna, Protective coatings and thin films, synthesis, characterization and applications, NATO Science Partnership Sub-series: 3, High Tech. 21 ed. Kluwert Academic publishers, Dodrecht, Netherlands (1997).

[16] N. Martin, A. M. E. Santo, R. Sanjinés, F. N. Lévy, Surf. Coat. Technol. **138 (1)**, 77 (2001).
[17] I. Safi, Surf. Coat. Technol. 127, 203 (2000).
[18] A. S. Reddy, H. H. Park, V. S. Reddy, K. V. S. Reddy, N. S. Sarma, S. Kaleemulla, S. Uthanna, P. S. Reddy, Mater. Chem. Phys. **110**, 397 (2008).
[19] F. Vaz, P. Cerqueira, L. Rebouta, S. M. C. Nascimento, E. Alves, Ph. Goudeau, J. P. Riviere, K. Pischow, J. de Rijk, Thin Solid Films **447–448**, 449 (2004).
[20] J. M. Chappé, A. C. Fernandes, C. Moura, E. Alves, N. P. Barradas, N. Martin, J. P. Espinós, F. Vaz, Surf. Coat. Technol. **206**, 2525 (2012).
[21] Ab. Benyoucef, Am. Benyoucef, F. Lapostolle, D. Klein, B. Benyo, Revue des Energies Renouvelables ICRESD-07 Tlemcen, 2007, p. 61.
[22] V. Tamilselvan, D. Yuvaraj, R. Rakesh Kumar, K. Narasimha Rao, Appl. Surf. Sci. **258**(10) 1, 4283 (2012).
[23] P. Baroch, J. Musil,, J. Vlcek, K.H. Nam, J.G. Han, Surf. Coat. Technol. **193,** 107 (2005).
[24] M. M. Hasan, A. S. M. A. Haseeb, H. H. Masjuki, R. Saidur, IJMMME **5 (1)**, 5 (2010).
[25] O. Zywitzki, T. Modes, H. Sahm, P. Frach, K. Goedicke, D. Gloss, Surf. Coat. Technol. **180–181**, 538 (2004).
[26] O. Anderson, C. R. Ottermann, R. Kuschnereit, P. Hess, K. Bange, Fresenius J. Anal. Chem. **358**(1-2), 315 (1997).
[27] A. C. Fernandes, F. Vaz, L. Cunha, N. M. G. Parreira, A. Cavaleiro, Ph. Goudeau, E. Le Bourhis, J. P. Rivière, D. Munteanu, B. Borcea, R. Cozma, Thin Solid Films **515**, 5424 (2007).

*Corresponding author: muntean.d@unitbv.ro