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MECHANICAL AND TRIBOLOGICAL PROPERTIES OF TiC_xO_y THIN FILMS

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ABSTRACT

The main purpose of this work consists on the preparation of single layered titanium oxycarbide, TiC_xO_y, thin films, deposited by d.c. reactive magnetron sputtering. The depositions were carried out from a TiC solid target, on (AISI M2) steel substrates at 200^oC, under the variation of two process parameters, such us time deposition and flow rate of reactive gas O_2. The O_2 flow varied between 0.5 and 7.5 sccm and the deposition time between 3600 and 6000 s. In terms of film colours, the most interesting colour tones have been observed if the oxygen flow increased. Static friction coefficient, wear and residual stresses are characterized and discussed as a function of both process parameters (oxygen flow and time). The results reveled a good correlation between compressive residual stress level in the films and the oxygen flow. A compressive residual stress state has been observed if the O_2 flow is bigger than 1 sccm. Generally, the addition of oxygen till 7.5 sccm leads to an increasing of this compressive stress level to -17.7 GPa. For an oxygen flow rate higher than 2 sccm and a high compressive residual stress level, the deposited films presented a good wear behaviour. However, the best wear results were registered for a moderate value of the residual stress (-1.18 GPa) and an oxygen flow rate of 2.5 sccm.

KEYWORDS: TiCO, Sputtering, Friction, Residual stress, Wear

1. Introduction

The increasing importance and use of surface coatings for improving component performance brought an increasing need for fundamental understanding of their properties if the optimum coating for a particular purpose is to be selected. The solutions to achieve a coating tailored for a particular task will essentially depend on the ability to establish knowledge of the interrelationship between their physical, structural and mechanical properties. In modern science, a new field is emerging with increasing application possibilities – the so-called decorative thin films.

Decorative hard coatings were first introduced on small consumer products such watches, writing instruments, eyeglass frames, pens, wristwatches, kitchen and bathroom equipment, as well as jewelry parts. While enhancing the appearance and lending attractive coloration to surfaces, the films are supposed to provide scratch resistance, protection against corrosion and durability.

As a result of technological progress in recent years, a new challenge was passed onto decorative hard coatings. The growing demand for low-cost products and reduced material resources imply that the continuous change in target materials and basic PVD deposition procedures to obtain different coloured films is clearly unsuitable [1,2]. At the same time, from the decorative aspect point of view, the attainable colour tones are largely restricted to some golden yellows, various shades of grey and black tones [3,4], although some attempts have been made to obtain other colours [2,4].

Taking these restrictions into consideration, recently two new classes of materials has been gaining importance for both decorative and tribological applications, the so-called metal oxynitrides Me(N,O) and metal oxycarbides Me(C,O) (Me = early transition metal). Their importance results from the presence of oxygen that allows the tailoring of film properties between those of nitride or carbide and the correspondent oxides.

Despite the huge amount of published scientific works on thin films of metallic nitrides and oxides over 10 years, the area of metal oxynitrides and, especially of metal oxycarbides is poorly explored so far and knowledge of the fundamental mechanism that explains the observed behaviour, both structural and mechanical, is yet insufficient [5]. In fact, a basic understanding of the gase-phase and thin-film oxygen and carbon (or nitrogen) incorporation chemistries facilities the processing of oxycarbides (oxynitrides) nanostructures with desirable properties.

Taking into account these features, the aim of the present research is to establish a general basis allowing the interpretation and the prediction of reactively d.c. sputtered TiCO coatings as a function of different preparation conditions, such as those of oxygen flow and deposition time. The sets of deposited samples allowed studying the evolution of the mechanical and tribological properties (thickness, residual stress, static friction coefficient) as a function of the different deposition parameters. The correlation with the wear characteristics is also an important parameter in this work.

2. Experimental details

The TiCO thin-films were deposited by reactive dc magnetron sputtering, onto polished high-speed steel (AISI M2) and stainless steel (AISI 316) (samples) substrates. The first samples (manufactured from AISI M2 - Φ25x5mm) were used from the tribological tests and the second ones (manufactured from AISI 316 - Φ25x0.5 mm) for establishing the thickness and residual stresses.

The depositions were carried out in a "home-made" apparatus under Ar/O_2 atmosphere. The system consists of two vertically opposed rectangular magnetrons (unbalanced) in a closed field configuration. Prior to depositions, the substrates were *ex situ* ultrasonically cleaned and *in situ* sputter etched for 15 min. in a pure Ar atmosphere, using a pulsed power supply: I ≈ 0.35 A; V ≈ 300 V; *f* = 200 kHz.

A turbo molecular pump was used to achieve a base pressure of 2E-4 Pa (before introducing the gas mixture). The substrate temperature during deposition was approximately 200°C, while the substrate bias voltage was kept at the ground state.

The base pressure in the deposition chamber was typically in the order of 10^{-4} Pa and rose to values around 3 x 10^{-1} Pa during depositions.

The experiments were carried out with the TiC target coupled to a dc power supply: I = 0.5 A/cm^2; V ≈ 480 V and the oxygen flow rate varied from 0.5 up to 7.5 sccm. The argon flow was kept at 12 sccm. Table 1 presents, first the oxygen flows used for depositions and second the deposition time.

Film thickness was obtained by "Ball Cratering" technique. This technique, ex-situ, consists, basically, in the erosion of the coating by rotating sphere. A typical mathematical model allows calculating the coating thickness based on dimensions of gotten crater [6]. An average number of five "Ball Cratering" experiments were carried out in each sample to determine its thickness.

Table 1. *The oxygen flows and time deposition values typically of the studied coating conditions*

Sample	Oxygen flow [sccm]	Deposition time [s]
TiCO 1	7.5	3600
TiCO 2	2.5	3600
TiCO 3	5	6000
TiCO 4	0.5	5400
TiCO 5	1	5400
TiCO 6	1.5	5400
TiCO 7	2	5400
TiCO 8	3.5	5400

The technique used for residual stress measurements is based on the curvature or deflection of the substrate. The major advantage of the thin film approximation is the possibility of calculating the coating residual stress using Stoney's equation [7]:

$$\sigma_{res} = -\left[\frac{E_s}{6(1-\nu_s)} \cdot \frac{t_s^2}{t_c}\right] \cdot \left(r_a^{-1} - r_b^{-1}\right) \qquad (1)$$

where $E_s/(1-\nu_s)$ is the biaxial modulus of the substrate's material (in this case, stainless steel, E_s=215 GPa, ν_s=0.3), t_s and t_c are, respectively, the thickness of the steel substrate and coating, r_b and r_a represent the radius of the curvatures of the substrate before and after deposition. The curvature of the samples was analyzed with a laser displacement meter (Keyence LC-2100). The thickness of the substrate was measured using a digital micrometer.

In order to establish the static friction coefficients for all the coatings, a typical method such as the inclined plane slope was used [8]. This system can estimate the static friction coefficient value based on typical linear size measurements, involving the correlation between the friction angles α, and the static friction coefficients μ_s.

Within the frame of this method, the friction couple, which is in a rest position, is inclined by the aid of a plane with variable vertical adjustment, until the sliding phenomenon appears in the couple. The angular value α_l for which the sliding occurs, is in direct correlation with the static friction coefficient μ_s according with:

$$tg\alpha_l = \mu_s \qquad (2)$$

The static friction coefficient values were established, for each sample, in three-friction condition, using a plane fixed half-couple made by heat treatable steel (AISI B7), in normalizing heat-treatment conditions. In the first case the friction plane fixed half-couple had an average roughness R_z = 0.4 μm, in the second 2.25 μm and in the last 2.5 μm. The work with the three roughness values of fixed plane half-couples is important in order to could take into consideration the possible influence of roughness on friction process and to have finally an average value of static friction coefficient.

Before the tribological tests, the samples were first degaussed and then alkaline cleaned and wiped. The fixed half-couple was also degaussed and periodically alkaline cleaned and wiped. According to the method description, 10 friction tests were performed for each sample on each half-couple: 5 in one direction and 5 abeam, such as the one-way roughness would not influence the moving of the samples. In each case, the utmost values were eliminated.

The wear behavior of the coatings (abrasion wear) has been estimated using a custom made pin-on-disk tribosystem [8].

For all wear tests, the annular type wear surface was characterized by an average diameter of approximately 13 mm. According to the technical arrangements, the friction distance length was estimated as 40.82 mm / one rotation cycle. The normal load applied by the pin on the sample surface was 10 N. For each sample, the wear test consisted in 5 minutes of holding load.

The wear distance length created in each sample was calculated as 17.55 m, with a plateau rotating speed of 86 rpm. Before the tests and after each rotation cycle, the samples were gravimetrically measured using an analytical balance Sartorius Master U11206-30 type. The environmental conditions of tribological tests were: T = 23.5 °C and 63% humidity.

3. Results and discussion

Table 2 presents the thickness values of deposited films and the static friction coefficients. Generally, referring to the second parameter, for each sample a small increase in roughness of plane fixed half-couple generally leads to a small decreasing of friction coefficient. Nevertheless, the last column of table 2 presents a general average value of this friction parameter that covers these small variations.

Table 3 shows the results of wear tests and the residual stress levels.

Fig. 1 presents the values of static friction coefficients for different oxygen flows used for preparing films.

This graph shows that, there is no a clear dependence between the oxygen flow (which is a deposition technological parameter) and friction coefficient.

Table 2. *Thickness and static friction coefficients of deposited films.*

Sample	Thickness [μm]	R_z [μm]	μ_s	μ_s (general average value)
TiCO1	0,6	0,4	0,1632	0,1355
		2,25	0,1242	
		2,5	0,1192	
TiCO2	1,4	0,4	0,2233	0,1876
		2,25	0,1825	
		2,5	0,1570	
TiCO3	0,9	0,4	0,2714	0,246
		2,25	0,2096	
		2,5	0,2572	
TiCO4	1,8	0,4	0,2585	0,2565
		2,25	0,2558	
		2,5	0,2552	
TiCO5	2,2	0,4	0,1882	0,1847
		2,25	0,1964	
		2,5	0,1697	
TiCO6	2,5	0,4	0,1844	0,1891
		2,25	0,1833	
		2,5	0,1996	
TiCO7	1,1	0,4	0,3491	0,3308
		2,25	0,3786	
		2,5	0,2648	
TiCO8	0,7	0,4	0,3774	0,2994
		2,25	0,3537	
		2,5	0,1671	

Table 3 shows the results of wear tests and the residual stress levels.

Fig. 1 presents the values of static friction coefficients for different oxygen flows used for preparing films.

This graph shows that, there is no a clear dependence between the oxygen flow (which is a deposition technological parameter) and friction coefficient.

Table 3. *The wear test results and the residual stress levels.*

Sample	Initial mass M_0 [g]	Final mass M_f [g]	$\Delta M = M_0 - M_f$ [g]	Residual stress [GPa]
TiCO1	19.7186	19.7184	0.0002	- 17,703
TiCO2	19.5474	19.5473	0.0001	- 1,188
TiCO3	19.6133	19.6130	0.0003	- 8,105
TiCO4	19.4422	19.4402	0.0020	+ 4,692
TiCO5	19.7143	19.7110	0.0033	+ 23,616
TiCO6	19.7070	19.7061	0.0009	- 2,472
TiCO7	19.7537	19.7530	0.0007	- 7,364
TiCO8	19.4957	19.4952	0.0005	- 17,057

The minimum values of friction coefficient were observed for the films prepared with an oxygen flow of 7.5 sccm and the maximum ones for 2 sccm.

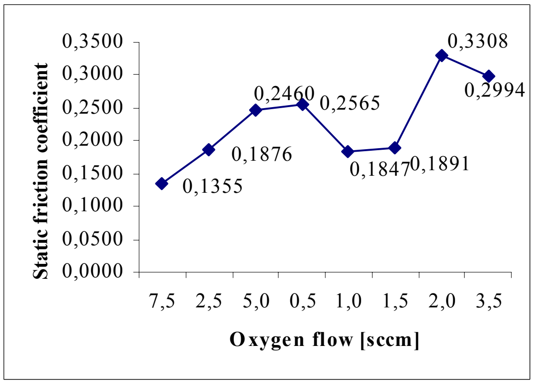

Fig.1. *Evolution of the static coefficient of friction (μ_s) of the deposited films as a function of the oxygen flows used for preparing coatings.*

The evolution of residual stress levels as a function of the oxygen flows is illustrated in Fig. 2.

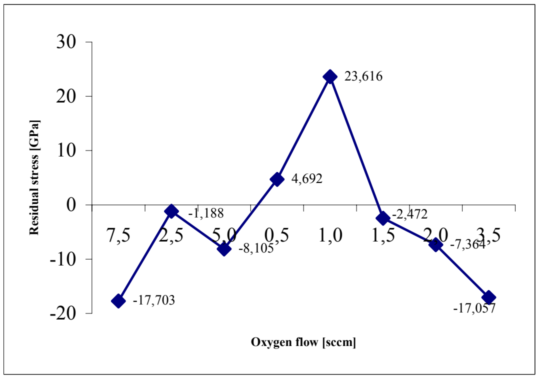

Fig.2. *Variation of the residual stress level of the deposited films as a function of the oxygen flows used for preparing coatings.*

The maximum value of these residual tensile stresses was observed for an oxygen flow of 1 sccm, but also for 0.5 sccm the tensile level of residual stresses is active yet in the films. Generally, it is clear that a developing of compressive residual stress level in the films follows an increase in oxygen content.

The first conclusion that can be drawn from these results shows that the using of oxygen flows lower than 1 sccm leads to the inducing in the films of important residual tensile stresses.

Fig. 3 summarizes the wear behaviours of the coatings after the pin-on-disk wear tests under the applied load of 10 N.

In terms of total mass loss during wear tests, the best results (the minimum mass loss) were obtained in the case of films which have been prepared with an oxygen flow of 2.5 sccm. However, acceptable wear strength was observed for the films prepared with oxygen flows higher than 2.5 sccm. In all these cases, especially for TiCO 2 and TiCO 1 samples, the films presented a very good adherence to the substrate.

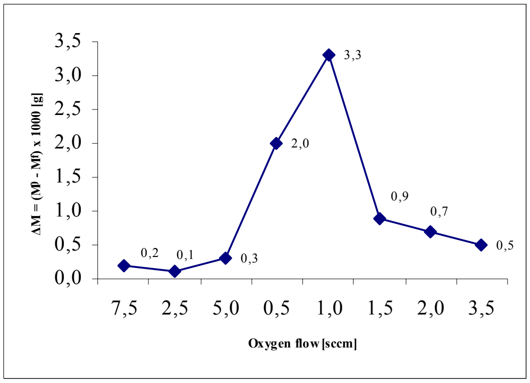

Fig.3. *The total mass loss of the deposited films after wear tests as a function of the oxygen*

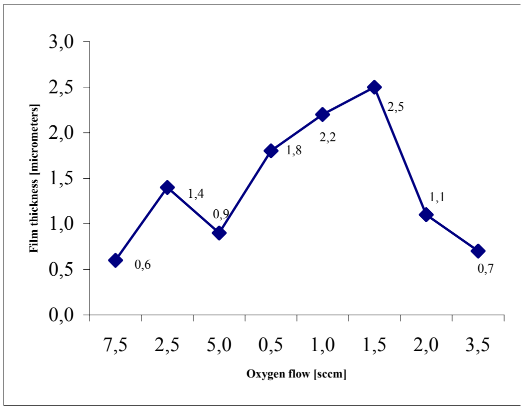

Fig.4. *The thickness of the films as a function of the oxygen flow.*

According with fig. 1, these samples were characterized by a small friction coefficient, which could be a possible explanation of their good wear behaviour. No good results are registered for TiCO 4 and TiCO 5 samples.

These films presented a brittle behaviour during the wear tests, which led to the generation of wear debris on the friction contact surface and also to the direct metal-to-metal contact. It is clear that this wear behaviour is in correlation with the residual tensile stress state registered in both two cases of TiCO 4 and TiCO 5 samples.

According with the results of thickness measurements (fig. 4), it is clear that there is no a real dependence between the films thickness and the deposition time so long as the oxygen flows varied. But the graphic dependence between oxygen flow and thickness leads to the conclusion that doesn’t exist a linear correlation between these two parameters. From the above experimental results the maximum thickness values were registered for oxygen flows between 0.5 and 1.5 sccm. For all these three cases, the deposition time was the same, 5400 s.

Taking into consideration the graphics from fig. 3 and 4, an interesting conclusion could be drawn: the good results of wear strength are associated with an increased presence of oxygen. At the same time in these cases the films thickness presented moderate values, maximum 1.4 μm for the best results.

Referring to the colour tones of the films, it has been observed that an increase of oxygen flow leads to a strong colour changing (apparition), as follows: for small oxygen flow values (0.5, 1 sccm) the films present a silver metallic colour (mirror aspect); for oxygen flow values between 1.5 and 2 sccm the coatings become silver blue towards dark blue. For 2.5 sccm oxygen the film colour goes to a non-pronounced mixture between golden-green and pink. The both colour tones (golden-green and pink) are equal in area for an oxygen flow of 3.5 sccm and, if the oxygen flow increased to 5 sccm this colour aspect is kept but the pink tone become prevalent.

An interesting change in colour was observed for an oxygen flow of 7.5 sccm. Thus, the general prevalent tone of colour is yellow-green but the pink reflection disappeared and is replaced with a brightness-blue tone.

A final worthwhile observation is the possible influence of the residual stresses in the colour tone aspects. In fact, there is a remarkable difference in the colour of the sample prepared with an oxygen flow of 7.5 sccm (which develop in the films the highest compressive levels of residual stresses) than the other samples for which are used lower oxygen flows and the level of residual stresses has lower compressive values or tensile values. High compressive stresses are known to affect the microstructure of a material and thus influence all the properties depending of them.

4. Conclusions

Thin films within Ti-C-O ternary system were prepared by reactive dc magnetron sputtering.

Friction characterization results generally reveal a good dependence between the oxygen flow used for films preparation and the static friction coefficient. Generally, the films prepared with more oxygen reveled a smaller static friction coefficient value (μ_s = 0.1355 for maximum oxygen flow used - 7.5 sccm) than the film, which contain less oxygen.

Residual stresses measurements revealed a good correlation between oxygen flow rate and the level of residual stresses. Generally, an increase of oxygen flow is followed by an increase in the residual (compressive) stress level. If the oxygen flow rate is under 1 sccm the residual stress level become a tensile stress level.

Regarding the wear behaviour, it is essential, however, to point out that an acceptable wear strength is influenced by the presence in the film of a residual compressive stress level. A moderate compressive stress level and confer to the films prepared with more than 2 sccm flow of oxygen a small wear rate and a good adhesion to the substrate. In contrast, the presence of the residual tensile stresses in the films leads to a brittle behaviour of these during the wear tests and increase clearly the wear rate.

Referring to the colour aspect, with the increase in the flow rate of the oxygen reactive gas from 0.5 to 7.5 sccm, the film colour rises slowly from silver-metallic colour to a pronounced mixture tone of yellow-green and blue.

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References

[1]. **F. Vaz, P. Carvalho, L. Cunha, L. Rebouta, C. Moura, E. Alvez, A.R. Ramos, A. Cavaleiro, Ph. Goudeau, J.P. Riviere**, *Thin Solid Films* 469 - 470 (2004), p. 11.

[2]. **E. Budke, J. Krempel-Hesse, H. Maidhof, H. Schussler**, *Surf. Coat. Technol.* 112 (1999), p. 108.

[3]. **B. Zega**, *Surf. Coat. Technol.* 39 - 40 (1989), p. 507.

[4]. **C. Mitterer, J. Komenda – Stallmaier, P. Losbichler, P. Schmolz, W.S.M. Werner, H. Stori**, *Vacuum* 46 (1995), p. 1281.

[5]. **R. Fraunchy**, *Surf. Sci. Rep.*, 38 (2000), p. 195.

[7]. **G.G. Stoney**, *Proc. R. Soc.*, London A82, 172, (1909).

[8]. **D. Munteanu, A. Munteanu**, *Proc. of 3rd Conference “THE” Coatings*, section “Tribology”, Thessaloniki – Greece, 28 – 29, (2002), p. 493.