JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 8, No. 2, April 2006, p. 712 - 715

The influence of oxygen flow on the tribological behaviour and residual stress of TiCO thin - films

D. MUNTEANU[*], R. COZMA[a], B. BORCEA, F. VAZ[b]
Dept. of Technological Equipment and Materials Science, Transilvania University, 29 Eroilor Blvd., 500036 Brasov, Romania
[a]*Dept. of Product Design and Robotics, Transilvania University, 29 Eroilor Blvd., 500036 Brasov, Romania*
[b]*Dept. of Physics, Minho University, 4800 – 058 Guimarães, Portugal*

Within the frame of this work TiCO d.c. reactive magnetron sputtered films were prepared on (AISI M2) steel samples at 200°C. The depositions were carried out from a TiC solid target 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. Static friction coefficient, wear and residual stresses are characterized and discussed as a function of both process parameters (oxygen flow and time). 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. At the same time, for an oxygen flow rate higher than 2 sccm and a high compressive residual stress level, the deposited films presented good wear behaviour.

(Received January 18, 2006; accepted March 23, 2006)

Keywords: Titanium, Oxycarbide, 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.

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 = 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 - $\Phi 25\times 5$ mm) were used from the tribological tests and the second ones (manufactured from AISI 316 - Φ25×0.5 mm) for establishing the thickness and residual stresses.

The depositions were carried out in "home-made" equipment 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 of the order of 10^{-4} Pa and increases to values around 3×10^{-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 determined 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.

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]:

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

where $E_s/(1\text{-}\nu_s)$ 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.

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

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:

$$tg\alpha_l = \mu_s \tag{2}$$

The static friction coefficient values were determined, 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 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

Referring to the static friction coefficient, for each sample, a small increase in roughness of plane fixed half-couple leads to a small decreasing of friction coefficient. This aspect could be explained taking into account the number of micro-contact bonds, which decreasing if the roughness of plane fixed half-couple increase.

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 and the static friction coefficient. 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.

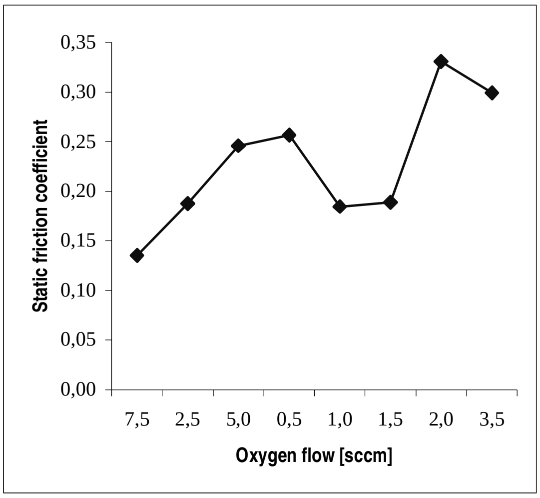

Fig. 1. Evolution of the static coefficient of friction (μ_s) of the deposited films as a function of the oxygen flows used for preparing coatings.

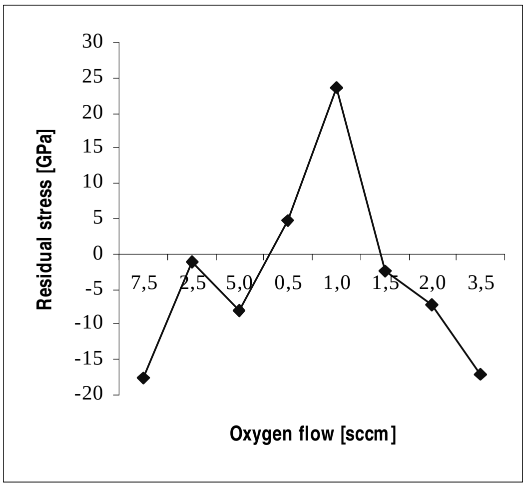

Fig. 2. Variation of the residual stress level of the deposited films as a function of the oxygen flows used for preparing coatings.

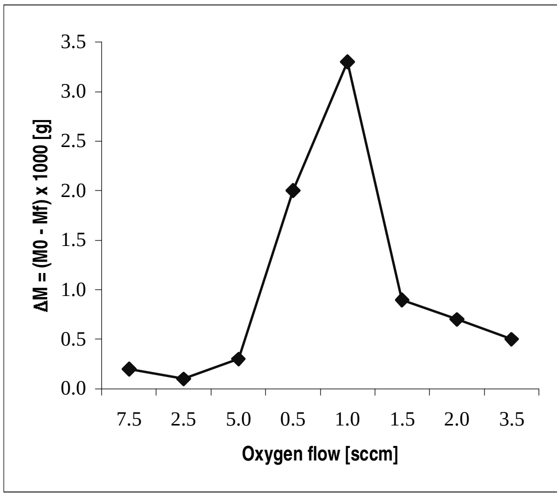

Fig. 3. The total mass loss of the deposited films after wear tests as a function of the oxygen flows used for preparing coatings.

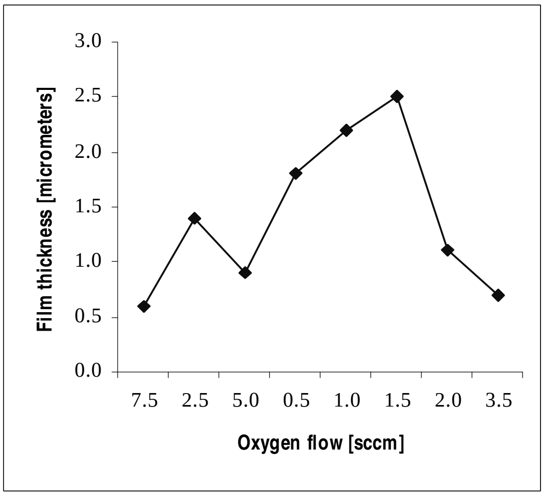

Fig. 4. The thickness of the films as a function of the oxygen flow.

The evolution of residual stress levels as a function of the oxygen flows is illustrated in Fig. 2. Generally, for an oxygen flow belongs to the interval 0.5 – 1 sccm, residual tensile stresses were registered in the films. It is clear that a developing of compressive residual stress level in the films (recommended for good wear behaviour) follows an increase in oxygen content.

Fig. 3 summarizes the wear behaviours of the coatings after the pin-on-disk wear tests, under the applied load of 10 N. There is a good correlation between the wear strength and the residual stress level; thus the developing of compressive residual stresses in the films leads to very good wear behaviour of these. In terms of total mass loss during wear tests, very good results (the minimum mass loss) were obtained in the case of films which have been prepared with an oxygen flow beteween 2.5 and 7.5 sccm (TiCO2, TiCO3, TiCO1). No good results are registered for TiCO 4 and TiCO 5 samples characterized by tensile residual stresses. 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.

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. At the same time, there is no linear correlation between oxygen flow and thickness. From the above experimental results the maximum thickness values were registered for oxygen flows between 0.5 and 1.5 sccm. For all these cases, the deposition time was the same, 5400 s.

Some recent structural investigations showed that the evolution of the different film's properties is related three different growth regimes that were developed. These different regimes were directly correlated with the composition, evolution of the films and the particular ratio of the different elements. Structure characterization results showed that for oxygen flow less than 2.5 sccm the films crystallize in a TiC B1-NaCl-type crystal structure in the carbide regime. Then, if the oxygen flow increase, a special transition regime is developed, and the films show a clear tendency towards amorphization. For flow values bigger than 5 sccm, in the predominant oxide zone, the films show a mixture of both poorly crystallizes anatase and rutile phases. This special kind of structure seems to confer to the films good friction-wear behaviour.

4. Conclusions

Thin films within Ti-C-O ternary system were prepared by reactive dc magnetron sputtering. Friction characterization results reveal a non-linear dependence between the oxygen flow and the static friction coefficient. The minimum value (μ_s = 0.1355) is registered for maximum oxygen flow used (7.5 sccm).

Residual stresses measurements revealed that the compressive level (recommended) for a good wear behaviour, is reached if the oxygen flow increase over of 1 sccm. Generally, an increase of oxygen flow is followed by an increase in the residual (compressive) stress level.

Regarding the wear behaviour, it is essential, however, to point out that 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.

The results showed that the evolution of the different film's properties is related 3 different growth regimes that were developed (carbide, transition, oxide).

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**, 11 (2004).
[2] E. Budke, J. Krempel-Hesse, H. Maidhof, Surf. Coat. Technol. **112**, 108 (1999).
[3] B. Zega, Surf. Coat. Technol. **39 – 40**, 507 (1989).
[4] C. Mitterer, J. Komenda – Stallmaier, P. Losbichler, P. Schmolz, Vacuum **46**, 1281 (1995).
[5] R. Fraunchy, Surf. Sci. Rep. **38**, 195 (2000).
[6] H. Hitermann, Vapour Deposited Wear Protective Coatings, Miltenberg – Germany, ed. CEI – Europe, Finspang, Sweden, **109 – 129**, (1986).
[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**, 493 (2002).

*Corresponding author: muntean.d@unitbv.ro