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STRUCTURAL AND TRIBOLOGICAL ASPECTS ON Ti(C,O,N) MAGNETRON REACTIVE SPUTTERED THIN-FILMS

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ABSTRACT

Magnetron sputtering is a flexible technique and allows producing a significant amount of types of coatings. Within the frame of present work, Ti-C-O-N thin films were deposited onto high-speed steel (AISI M2), substrates by reactive dc magnetron sputtering in a laboratory-size deposition system. It consisted of two vertically opposed rectangular magnetrons, in a closed field configuration. The films were prepared using dc power source on a titanium target (99.6 at.%). A gas atmosphere composed of argon (working gas), acetylene and nitrogen/oxygen (17:3) reactive mixture was used for the depositions. In terms of structure, the samples produced only with ethylene and argon flow reveal a TiC structure (NaCl type). The decrease of $\Phi(C_2H_2)/\Phi(O_2+N_2)$ induces amorphisation, but TiC structure, with possible N and O inclusions, is still detected. In terms of tribological aspects, the static friction coefficient and roughness (R_z) were analyzed and discussed depending of composition and structure.

KEYWORDS: magnetron, sputtering, roughness, friction

1. Introduction

During the last years, there have been several attempts to improve the properties of diamond-like carbon (DLC) films by the addition of other elements, such as silicon, nitrogen and varios metals. Many modifications have been tried and the addition of, for example, nitrogen, has shown to reduce the inner stress, electrical resistivity and friction coefficient [1]. In the same manner, oxygen has always been looked upon as an interesting element in thin film materials, not only because of its high reactivity with most metals, but also due to the changes that induces in chemical bonding states, and in the material’s electrical, optical, and mechanical characteristics.

Titanium carbonitride coatings Ti(C,N), are used mostly to improve tool life by combining the properties of TiN and TiC. The advantages of these coatings over other coatings material, stem from its superior friction behaviour in contact with steel, high hardness and residual stress [2]. Because of their low friction, the coating is durable at slow cutting speeds especially [3]. The combined effect of low friction behaviour and high residual stress help preventing cutting-edge deformation for high speed steels, and on carbides reduces the cutting-edge chipping. Moreover, it provides excellent resistance to wear due to the coating high hardness [4]. Adding oxygen to the film is a possibility to improve the coating’s characteristics. The presence of oxygen allows the tailoring of films properties between those of metallic-like carbides and those of the corresponding ion oxides, and from these a wide range of applications. It is expected that the Ti(C,N,O) films will exhibit good resistance to friction wear and corrosion due to the small atomic size of oxygen, witch creates high hardness and a compressive stress state [2,5,6].

In the present paper the Ti(C,N,O) thin films, with various compositions, were deposited in a closed field unbalanced reactive d.c. magnetron sputtering system, varying the $\Phi(C_2H_2)/\Phi(O_2+N_2)$ flow.

Sputtering is one of the most commonly used methods for the deposition of thin films. Its popularity stems from simplicity of the physical processes involved, versatility of the technique, and flexibility for alteration and customisation. It is widely used in the semiconductor, photovoltaic, recording and automotive industries. In addition, specialised applications of sputtering in the manufacturing of sensors, decorative glasses, optical devices, etc, are also very common.

High melting point materials like ceramics and refractory metals, which are hard to deposit by evaporative techniques, are easily deposited using sputtering. Sputtering techniques range from a simple dc glow discharge, which is limited to the sputtering of conductive targets, to RF sputtering where any target regardless its conductivity can be sputtered, to a more sophisticated ion beam sputtering (IBS) in which very controlled deposition of material is possible.

In terms of deposition rates, there are sputtering techniques now available, which rival evaporation or other higher deposition rate techniques. The purpose of using a magnetic field in a sputtering system is to make efficient use of the electrons and cause them to produce more ionisation [7].

Taking into account the fact that unbalanced magnetron (the magnetic field lines does not all close on the cathode surface) sputtering was used in this paper, an image is presented in figure 1.

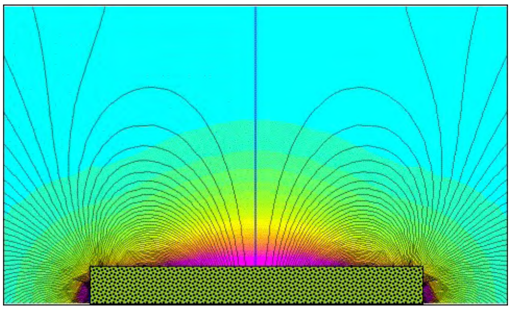

Fig. 1. *Unbalanced magnetron [8].*

2. Experimental details

Within the frame of present work, Ti-C-O-N thin films were deposited onto high-speed steel (AISI M2), substrates by reactive dc magnetron sputtering in a laboratory-size deposition system. It consisted of two vertically opposed rectangular magnetrons, in a closed field configuration.

The films were prepared using dc power source on a titanium target (99.6 at.%). A gas atmosphere composed of argon (working gas), acetylene and nitrogen/oxygen (17:3) reactive mixture was used for the depositions (as shown in table 1).

The deposition was carried out using a laboratory-size deposition system. During deposition the working pressure was approximately constant at 0.4 Pa and the bias voltage was -70V. In all the cases the deposition time was kept at 3600s.

Table 1. *Gas flows (experimental variants)*

Samples	Gas flow [%]		
	C_2H_2	O+N	Ar
TiCON 1	3	11	12
TiCON 2	5	8	12
TiCON 3	2	16	12
TiCON 4	2	8	15
TiCON 5	2	20	15
TiCON 6	1.5	6	15
TiCON 7	1.5	10	15
TiCON 8	1.5	18	15
TiCON 9	1.5	25	12
TiCON 10	1.5	0	15

The atomic composition of the as deposited samples was measured by electron probe microanalysis (EPMA) in a Cameca SX-50 apparatus. The crystallographic structure was investigated by X-ray diffraction (XRD) in the Bragg-Bretano configuration, using monochromatic Cu Kα radiation. Atomic Force Microscopy (AFM) - 5x5□μm line scans was used for roughness characterization. The static friction coefficient values were established, for each sample, in different-friction condition, using a plane fixed half-couple manufactured by heat treatable steel (AISI B7), in annealing heat-treatment conditions. The friction plane fixed half-couple had a lot of roughness R_z values, comprised between 0.4 and 2.5 μm. The work with different roughness values of fixed plane half-couple is important in order to could take into consideration the possible influence of sliding – plane 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 environmental conditions of tribological tests were: T = 23.5^{o}C and 63% humidity.

3. Results and discussion

The measured values of the friction coefficient vary between 0.2 and 0.39, while the roughness values range from 0.13μm to a maximum of 0.21μm. The results showed a correlation between the friction coefficient and roughness evolution with the growth of the C_2H_2/(O+N) flows ratio (figure 2).

A simultaneous growth of the friction coefficient and roughness can be observed up to a 0.25 value of the $C_2H_2/(O+N)$ ratio, then the parameters register an abrupt decrease on the flow value interval from 0.25 to 0.3. After this critical value of the $C_2H_2/(O+N)$ flows ratio, the two parameters evolution is stable.

As a conclusion we could underline the existing dependence between static friction coefficient (μ) and roughness (R_z); these parameters are both increasing or decreasing on a certain interval of flow values.

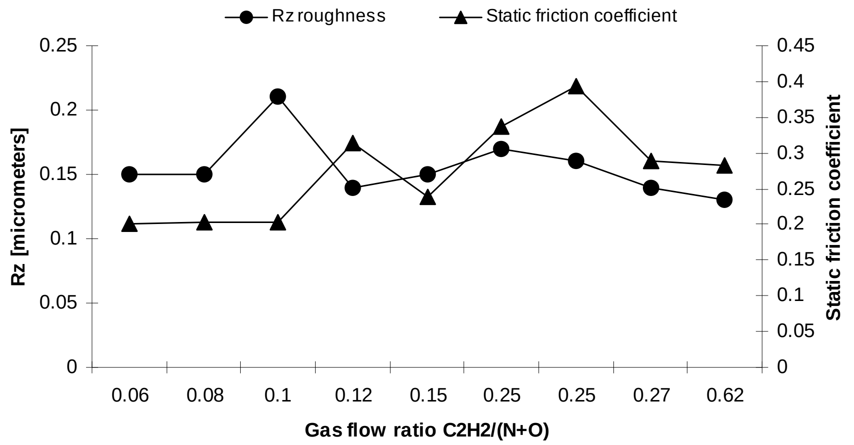

***Fig. 2.** Influence of gas flow ratio on friction coefficient and roughness.*

In terms of the chemical composition, the results showed that, at 0.25 gas flow ratio the carbon percentage moves from an abrupt growth to a slower growth. The amount of titanium present an emphatically decrease around 0.25 gas flows ratio, while the oxygen starts growing and the nitrogen percentage is changeless (steady) for a short interval and starts a slow decrease around 0.3 gas flow ratio (figure 3).

From a tribological point of view, we can say that the growth of the oxygen percentage it is linked to the decrease of the roughness and friction coefficient values. Also, a decrease in the titanium percentage leads to a decrease of roughness and friction coefficient.

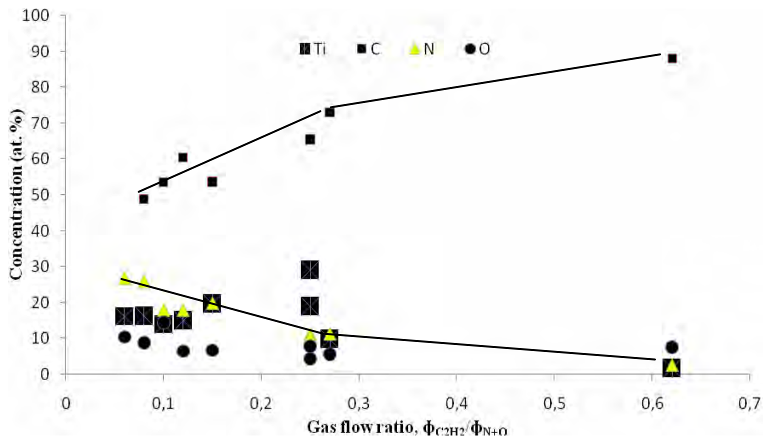

***Fig. 3.** Corelation between concentration and gas flow ratio.*

4. Conclusions

TiCON thin-films were prepared by reactive magnetron sputtering on high-speed steel (AISI M2) substrate, using a mixture of C_2H_2 and (N_2+O_2) as reactive gases. The static friction coefficient and Rz roughness seams to have the same behaviour with the increasing of carbon percentage in the film. The maximum values for friction coefficient were registered at about a value of 0.25 for $C_2H_2/(O+N)$

flows ratio, zone where is supose that the TiC cubic lattice begins to dezorganize. In terms of concentrations, this point (0.25) marks a tendency for keeping almost constant the C and N concentrations in the films with the increasing of C_2H_2/(O+N) flows ratio.

References

[1] **Fernandes A., Carvalho P., Vaz F., S. Lanceros-Méndez A.V. Machado, N.M.G. Parreira , J.F. Pierson , N. Martin**, *Property change in multifunctional TiCxOy thin films: Effect of the O/Ti ratio,* Thin Solid Films 515 (2006) 866–871, www.sciencedirect.com, 2006;

[2] **J.H. Hsieh , W. Wu , C. Li , C.H. Yu , B.H. Tan**, *Deposition and characterization of Ti(C,N,O) coatings by unbalanced magnetron sputtering*, Surface and Coatings Technology 163 –164 (2003) 233–237, www.elsevier.com/locate/surfcoat, 2003;

[3] **Baravian G., Sultan G., Damond E., Detour H**., Surf. Coat.Technol. 76/77 (1995) 687.

[4] **Knotek O., Loffler F., Kramer G**., Surf. Coat. Technol. 61(1993) 320.

[5] **Y. Shi, H. Peng, Y. Xie, G. Xie, C. Zhao**, Surf. Coat. Technol.132 (1998) 26.

[6] **Stanishevsky A., Lappalainen R**., Surf. Coat. Technol. 123(2000) 101.

[7] **Munteanu D., Vaz F.,.Munteanu A, Schreiner A.,.Ionescu C,.Olteanu C,.Borcea B,** *Straturi subţiri de tip Ti-Si-C şi Ti-O-C obţinute prin pulverizare reactivă în sistem magnetron,* Editura Universităţii Transilvania, Brasov, 2007;

[8] www.pvd-coatings.co.uk