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Tribological characterisation of magnetron sputtered Ti(C, O, N) thin films

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Abstract:

Ti(C, O, N) thin films were prepared by magnetron sputtering and analysed in terms of their tribological properties. Surface and tribological parameters were analysed and discussed as a function of the films composition and structural features, as well as their thickness. The evolution of friction coefficient values was in concordance with the wear behaviour of the films. According to the atomic composition of the films, an increasing of the carbon percentage and a compound chemical formula closed to the stoichiometric TiC lead to a very good wear behaviour. This aspect is also directly correlated with the friction behaviour.

Keywords: thin film; wear behaviour; friction; roughness; composition.

1 Introduction

Several modifications on thin films have been tried and the addition of, for example, nitrogen, has shown to reduce the inner stress, electrical resistivity and friction coefficient (Polcar et al., 2003). In the same way, 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.

With the technological progress, decorative hard coatings are expected to accomplish a double purpose: while enhancing the appearance and lending attractive colouration to surfaces, the films are supposed to provide scratch and wear resistance and protection against corrosion (Munteanu et al., 2006).

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 (Hsieh et al., 2003). Because of their low friction, the coating is durable at slow cutting speeds especially (Baravian et al., 1995). 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 (Knotek et al., 1993).

Adding oxygen to the film is a possibility to improve the coating's characteristics. It is expected that the Ti(C, O, N) films will exhibit good resistance to friction wear and corrosion due to the small atomic size of oxygen, which creates high hardness and a compressive stress state (Hsieh et al., 2003; Shi et al., 1998; Stanishevsky and Lappalainen, 2000).

Among a large variety of deposition techniques, 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.

In the present paper the Ti(C, O, N) thin films, with various compositions, were deposited in a closed field unbalanced reactive d.c. magnetron sputtering system, varying the gas flow ratio, $\Phi(C_2H_2)/\Phi(O_2 + N_2)$. In terms of research program, the purpose of this work is to present experimental results on the deposition conditions, composition and tribological aspects of Ti(C, O, N) films; at the same time, a qualitative explanation relating to the correlation between the mentioned aspects from above is given.

2 Experimental details

Ti(C, O, N) thin films were deposited (at 200°C) onto high-speed steel (AISI M2) substrates by reactive d.c. 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 d.c. 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. During deposition, the working pressure was kept approximately constant at 0.4 Pa and the substrate bias voltage was – 70 V. In all the cases the deposition time was 1 h.

The atomic composition of the as deposited films was measured by Electron Probe Microanalysis (EPMA) in a Cameca SX-50 apparatus. Before the tribological tests, the samples were first degaussed and then alkaline cleaned and wiped. Thin film's roughness was estimated using a TR110 type roughness-meter. For each sample was performed a number of four measurements. In order to establish the static friction coefficients (at start) for all the samples, a typical method such as the inclined plane slope was used. According to this method, 20 friction tests were performed for each sample, as follows: ten in one direction and ten abeam, such as the one-way roughness would not influence the moving of the samples. The average roughness values of the fixed half-couple were $R_z = 2.09$ µm, for the longitudinal direction of friction tests, and $R_z = 3.12$ µm in the cross direction.

The dynamic friction coefficient and wear rate values (abrasion wear) were estimated using a pin-on-disk tribosystem (CSM instruments), that is schematically shown in Figure 1.

Figure 1 The pin-on-disk tribosystem (schematic arrangement)

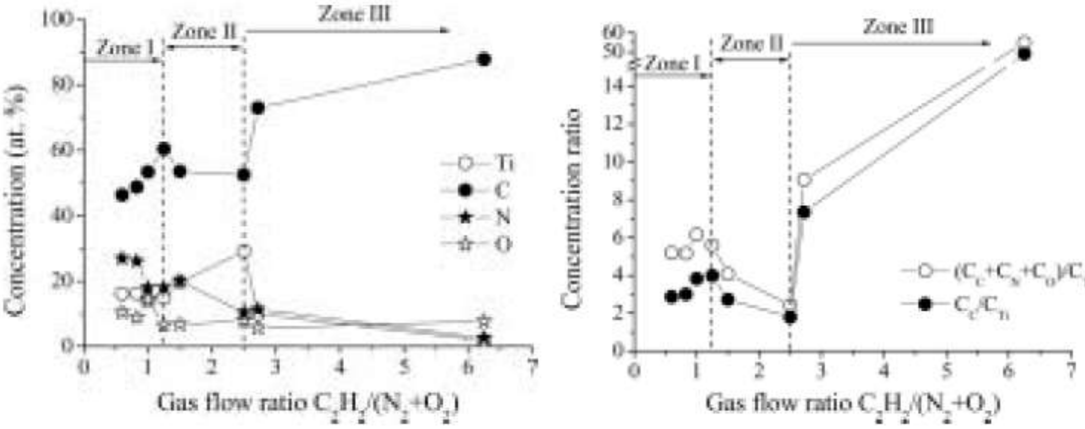
A sphere shaped static partner is loaded on to the test sample with a precisely known force. The static partner, a 6 mm diameter steel ball (AISI 100Cr6), was mounted on a stiff lever, designed as a frictionless force transducer. The sample rotates on the sample holder. As the sample is rotating, resulting frictional forces acting between the ball and sample are measured by very small deflections of the lever using an LVDT sensor; (in this case, the acquisition rate was 5 Hz). Thus, the LVDT sensor measures the tangential force F_t and provides then the friction coefficient measurement (dynamic friction coefficient).

Wear rates for both the ball and sample are calculated from the volume of material lost during a specific friction run. This simple method facilitates the determination and study of friction and wear behaviour of the samples. The calculation of the worn track section for each sample was also done using a profilometer, Taylor Hobson type. For all wear tests, the annular type wear surface was characterised by a radius of 9.01 mm. The linear speed of the rotating plateau was 4.8 cm · s^{-1}. The maximum number of laps was 450. The normal load applied by the ball on the sample surface was 5 N. Before all the wear tests, the samples, the sliding half-couples and the balls were cleaned with isopropanol. The environmental conditions for all tribological tests were: T = 24°C and 30% humidity.

3 Results and discussion

In order to prepare films with various compositions, the $C_2H_2/(O_2 + N_2)$ gas flows ratio varied between 0.6 and 6.25.

Figure 2 (a) Atomic concentration as a function of the gas flows ratio and (b) concentration ratio as a function of the gas flows ratio

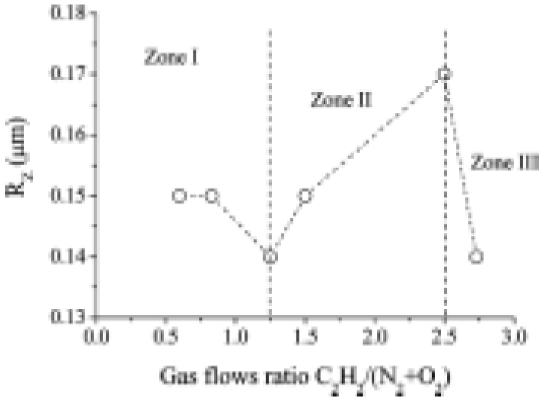


(a) (b)

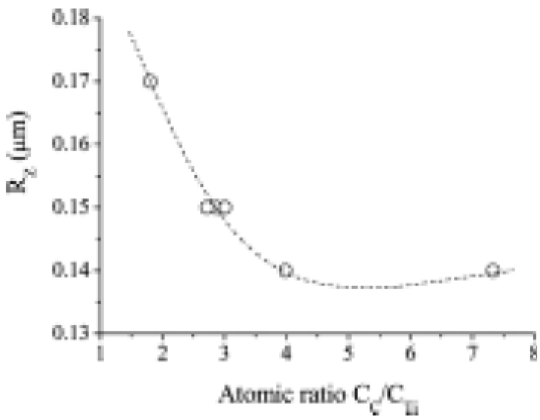
Figure 2 shows the evolution of atomic compositions and the atomic ratios of the deposited films as a function of the used gas flow ratios. In terms of the chemical composition, the results (Figure 2) show that using gas flows ratios up to ~1.3, the films present an almost constant value of both Ti (around 15–16 at. %) and O (within 6–10 at. %), with a slight increase of C (from about 46 at. % to 60 at. %) and a decrease, also small, of N (from 27 at. % to 18 at. %), Figure 2(a). These small variations can also be seen by the evolution of the concentration ratios depicted in Figure 2(b), where both C_C/C_{Ti} and $(C_C + C_N + C_O)/C_{Ti}$ present slight increases from about ~2.9 to 4 and from about 5.2 to 6.2, respectively. The films prepared within these conditions will be referred as belonging to a zone I throughout the entire text. For gas flows ratios varying from 1.3 up to about 2.5, the C content decreases slightly (from ~60 at. % down to about 53 at. %), while Ti increases from about 15 at. % to 29 at. % (Figure 2(a)). Nitrogen and oxygen showed only small variations. The films prepared within these conditions (gas flows ratios) will be known as belonging to zone II. At gas flows ratios above 2.5, an abrupt increase of the carbon content (from 53 at. % to 88 at. %) and a decrease of titanium (from 29 at. % to 2 at. %) are registered. The other elements keep an approximately constant value of concentration, roughly below 10 at. %. This will be referred throughout the text as zone III, whose films, due to their significantly high C content, are roughly C-doped type ones.

Regarding the tribological characterisation, the first parameter evaluated was roughness (R_z). This parameter represents the surface asperity measured in ten points and it is known in tribology as "ten tops height" parameter; in fact, it represents the difference between the average of the first five highest asperity tops and the one of the first five deepest hollows of the surface profile. The measured values of roughness ranged from 0.14 μm to a maximum of 0.17 μm, values which are small for this kind of roughness. Moreover, these low values of R_z and, at the same time, the small variation of 0.03 μm, reveal a moderate topography of surfaces, which means a high uniformity of the external zone of the films. The results showed only small variations, with some dependence with the gas flows ratio, and thus the coatings particular composition. In fact, a closer look to the plot of Figure 3(a) shows that the evolution of roughness has an inverse trend of that one of the composition ratios, illustrated in Figure 3(b). It seems that the higher the C content, the lower is the film's surface roughness. Figure 3(b) shows the evolution of this parameter as a function of the C/Ti atomic ratio. The plot clearly shows the decrease trend of roughness with the decrease of Ti content and the increase of C content, which was somehow expected. In fact, although there are no many conclusive investigations on the dependence between film's composition and roughness, Zhang et al. (2005) showed that, increasing of Ti content in the titanium carbides leads generally to an increase of film's roughness; at the same time, the film structure becomes more and more compact (also on the surface) as the carbon content in coating increases (Kwasny et al., 2004).

Figure 3 The influence of (a) gas flows ratio and (b) atomic ratio C_C/C_{Ti} on the evolution of the films roughness (R_z)



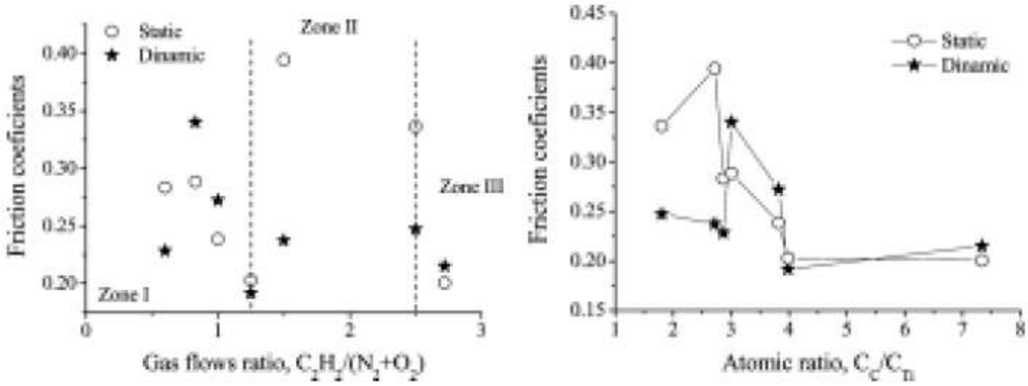
(a)



(b)

Figure 4 shows the dependence of film's friction coefficients (both static and dynamic) on gas flow ratio (Figure 4(a)) and on the atomic ratio C_C/C_{Ti} (Figure 4(b)).

Figure 4 Static and dynamic friction coefficients as a function of (a) the gas flows ratio and (b) the atomic ratio C_C/C_{Ti}



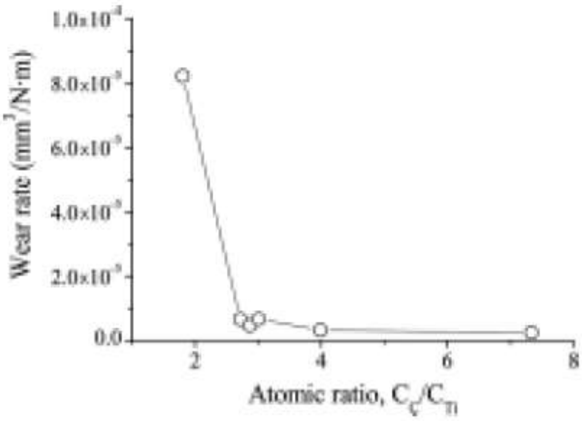
(a) (b)

This figure shows that, again, different behaviours are observed in the different zones of films. First of all, it seems that similarly to what was observed for roughness, the films from zone II have higher static friction coefficients, while those from zones I and III present relatively lower ones, especially those from zone III. Moreover, the plot from Figure 4(b) shows that there is also a tendency to the decrease of the static friction coefficient with the increase of the C content (and decrease of Ti), as in fact observed for the roughness evolution. A more complex behaviour is that one revealed by the evolution of the dynamic friction coefficient, which shows a two-fold behaviour. The films from zone I and III have relatively lower dynamic friction coefficients, while those from zone II have the highest ones. This behaviour shows that, although important, composition seems to affect this parameter differently from the previous ones.

From the experience of other works, it can be observed that generally, for the same roughness, increasing hardening of materials (in this case of the coating) leads to lower friction coefficient values. Bergmann and Vogel (1986) have shown that the metal/carbon coatings have a coefficient of friction lower than pure metal coatings. This is due to a higher value of hardness and, of course, to a lower roughness.

Figure 5 shows the evolution of the wear rate of the films as a function of the atomic ratio C_C/C_{Ti}.

Figure 5 Wear rate as a function of the atomic ratio C_C/C_{Ti}

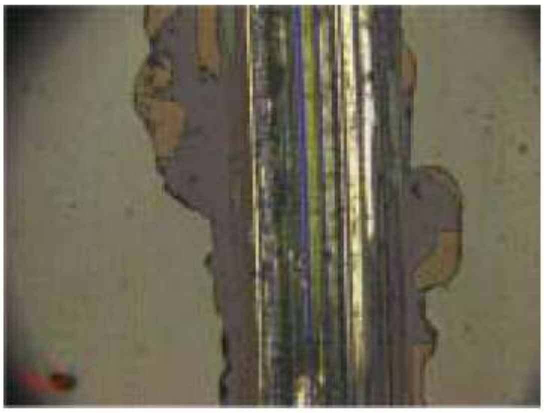


Similarly to roughness and friction coefficients, the wear depends on the C content, and the sample with the lowest C content shows the highest wear rate. In fact, it is not surprising to observe that the sample with the highest roughness corresponds to that one with the highest friction coefficient (static one) and thus the sample with the highest wear rate. For instance, in a closer manner, Machet et al. (1986) showed that multilayer coating TiN/TiCN/C is harder than TiN alone by a factor of ~1.5, and its wear resistance is 3–9 times higher, but the friction coefficient is lower. Besides, a higher contribution of C related to Ti in the composition confers to the film a uniform nucleation and growth, and finally, a better uniformity. Besides, a higher C content leads to a higher hardness (a higher compressive state level) and a lower friction coefficient (especially the dynamic one).

These facts can also be observed in Figure 6, where the wear tracks for two different samples are presented. The first micrograph corresponds to the sample with the highest carbon percentage (73 at. %). This sample ($TiC_{7.3}O_{0.56}N_{1.14}$) presented a good wear behaviour, having the smallest wear rate, namely 2.47×10^{-6} mm^3/N · m. In the second micrograph, we have a sample ($TiC_{1.8}O_{0.27}N_{0.36}$) with one of the lowest carbon content (52.5 at. %), and as it can be seen from the results, with a much higher wear rate, namely 8.22×10^{-5} mm^3/N · m. It can be easily observed that in this case the coating was broken.

Figure 6 Micrographs of the wear tracks for the films with (a) the highest C content ($TiC_{7.3}O_{0.56}N_{1.14}$) and (b) the lowest C content ($TiC_{1.8}O_{0.27}N_{0.36}$) (see online version for colours)

(a)



(b)

4 Conclusions

Ti(C, O, N) 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 R_z roughness of as deposited films seem to have the same behaviour with the increasing of carbon percentage. The maximum values for friction coefficient (both static and dynamic) were registered at about a value of 2.5 for $C_2H_2/(O_2 + N_2)$ flows ratio, zone where there is the possibility that the TiC cubic lattice should begin to dezorganise. In terms of concentrations, this point (2.5) marks a tendency for keeping almost constant the C and N concentrations in the films with the increasing of $C_2H_2/(O_2 + N_2)$ flows ratio.

The friction coefficient evolutions, both for static and dynamic parameters, are in concordance with the wear behaviour of the films. The smaller values and the constant evolutions of the dynamic friction coefficients during the wear tests are typically for the samples with the best wear behaviours.

The wear strength depends on the carbon concentration. Thus, an increasing of the carbon percentage in the films gives a good durability.

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