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Characterisation of TiC_xO_y thin films produced by PVD techniques

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Properties

ABSTRACT

Purpose: The purpose of this work consists in the characterisation of TiC_xO_y thin films produced by dc reactive magnetron sputtering. The main goal consists in studying the influence of the reactive gas flow in the atomic composition, structure, colour and electrical and mechanical properties of the films.

Design/methodology/approach: All the deposition parameters were maintained constant except the reactive gas flow. After deposition, the properties of the coatings were measured and were related with variation of reactive gas flow.

Findings: The results show that the films properties subsist into 3 different regimes – i) carbide, ii) a transition zone and iii) an oxide one. The colour results indicate a strong dependence on the O/Ti ratio. A progressive reduction of hardness and residual stresses with increasing of the O/Ti ratio was observed. The residual stresses, as well as the film structure, seem to play an important role on the adhesion of the coatings.

Research limitations/implications: The main limitation of this work is linked to the deposition technique itself. It is difficult to avoid surface defects and pinholes that strongly influence the tribological results.

Practical implications: TiC_xO_y thin films are multifunctional due to present good electrical and optical properties but also good mechanical properties which allow them to be used in several applications; from decorative to electronic applications.

Originality/value: There is a new class of coatings where the research of TiC_xO_y thin films is included: the multifunctional coatings. This class of coatings should be easy to prepare and to tune the properties as function of particular applications. This characteristic may be extremely important to advanced coatings industry.

Keywords: Mechanical properties; Multifunctional materials; Ti-C-O; Structure

1. Introduction

Transition metal carbides, such as TiC, belong to a class of very hard materials and often crystallize in the rock salt structure. This class of material is a serious candidate for a vast range of high-technology applications because they exhibit a rare combination of metallic, but also covalent and ionic properties [1-3]. Technological applications can range from metallurgy, aeronautics, electronics and medicine, to protect and to decrease wear in a variety of components.

Carbide films may be produced by chemical vapour deposition (CVD) and physical vapour deposition (PVD) techniques [4-8].

Table 1.
Oxygen flow during deposition, composition, O/Ti ratio and thickness of the analysed samples

Sample	Oxygen flow (sccm)	Ti (at. %)	C (at. %)	O (at. %)	O/Ti	Thickness (μm)
$TiC_{1.3}O_{0.8}$	0.5	32.1	41.4	26.5	0.8	0.9±0.1
$TiC_{1.3}O_{1.1}$	1.0	28.8	38.2	33.0	1.1	1.5±0.1
$TiC_{0.9}O_{1.6}$	1.5	28.2	25.9	45.9	1.6	1.4±0.1
$TiC_{0.2}O_{1.8}$	2.0	33.2	6.8	60.0	1.8	1.2±0.1
$TiC_{0.1}O_{2.6}$	2.5	27.3	2.5	70.2	2.6	1.0±0.1
$TiC_{0.1}O_{3.4}$	3.5	22.6	1.6	75.8	3.4	0.6±0.1

Most of CVD methods are limited owing not only to environmental problems, but also to the high temperatures involved during processing. The increasing needs to produce multifunctional materials, with properties that become suitable for a certain application, have provoked a fast development of the investigations in this field of materials science. The addition of a third element is often seen a successful approaches. The addition of O to the Ti-C matrix is one of the possibilities that can be seen as generating a wide spread of properties. The presence of oxygen on TiC films allows the tailoring of film properties between those of metal carbides and those of the ionic oxides, with the consequent variation of the properties between those two extremes. The main purpose of this work is to present experimental results on the influence of oxygen additions to Ti-C films and to advance a qualitative explanation for the development of the different structural arrangements. Special attention will be given to the formulation of a simple model, which explains the revealed behaviour concerning the growth modes and the evolution of film's mechanical and tribological properties.

2. Experimental

TiC_xO_y films were deposited by reactive dc magnetron sputtering, from a TiC target onto (100) crystalline Si wafers, high-speed steel (AISI M2) and stainless steel (AISI 316) substrates. The films were prepared using a current density of 25 A.m^{-2}. The working atmosphere was composed of argon (60 sccm) and oxygen (0.5 to 3.5 sccm). The substrates were grounded in a static mode.

The atomic composition of the samples was measured by electron probe microanalysis (EPMA). The crystallographic structure was investigated by X-ray diffraction (XRD). Atomic Force Microscopy (AFM) was used for roughness characterization. The colour of the films was obtained with a spectrophotometer, using visible region of electromagnetic spectrum. Colour specification was computed under the standard CIE illuminant D65 and represented in the CIELAB 1976 colour space [9]. The residual stresses of the coatings were obtained from the substrates curvature, using Stoney's equation [10]. The hardness and Young's modulus of the deposited films were determined from the loading and unloading curves, performed with an ultra low load-depth sensing Berkovich nanoindenter. The maximum load used was 30 mN, with a loading time of 30 s, a holding time of 30 s and an unloading time of 30 s, obtaining an average number of 15 indentations per sample. The adhesion/cohesion of the coatings was evaluated by scratch-test. The load was linearly increased from 0 to 50 N, using a Rockwell C 200 μm radius indenter tip. The tests parameters were: loading speed of 10N/min, and scratch speed of 1 mm/min. The critical load values, L_c, corresponding to the adhesive failure mechanisms were measured by analyzing the failures events in the scratch track by optical microscopy.

3. Discussion of achieved results

3.1. Composition, structure and colour

In table I it is shown a summary of all films. From the table results, it is clear that as the oxygen flow increases, the atomic concentration of C decreases, the atomic concentration of O increases and the atomic concentration of Ti suffers only slight variations. O/Ti atomic ratio increases almost linearly with the increase of the oxygen flow, which might be an indication of Ti target poisoning. Taking into account the different elements compositions, the films may be divided into 3 multiphase regions: i) a region I - where the films were prepared in the carbide regime (O/Ti < 1.6); ii) a transition regime - Region T (1.6 < O/Ti < 2.6), and iii) Region II - Oxide zone (O/Ti > 2.6).

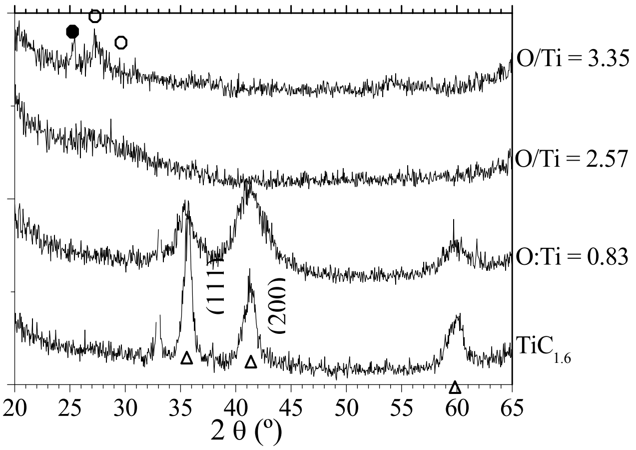

Fig. 1. X-Ray diffraction patterns of Ti-C-O films for different O/Ti ratio. △ TiC ● a - TiO_2 ○ r - TiO_2

XRD patterns reveal that each of the different growth modes resulted in different structural arrangements. Region I, developed a crystalline structure indexed to a fcc type, typical for TiC. The same type of structure can also be observed for the TiC film, $TiC_{1.6}$, which is an interesting result since the carbon content is relatively high. This relatively high carbon content induces that this particular TiC film might have also an amorphous carbon phase in the grain boundaries of the TiC grains, forming a composite of the type nc-TiC/a-C, as claimed by several authors [4]. Moreover, a closer look to the diffraction patterns reveals that there is some tendency for the increase of the peak intensity ratio I(200)/[I(111)+I(200)] towards values typical of randomly oriented films, with the increase of the O/Ti ratio. Also, some tendency to the decrease of grain size with increasing of the O/Ti ratio is evidenced by the significant peak broadening revealed by the film prepared with 0.5 sccm oxygen flow, when compared to the $TiC_{1.6}$ film. This growth of an amorphous oxide phase would, in fact, be consistent with this grain size reduction.

The results obtained for the T zone reveal an extensive tendency to amorphization of the films. In this region, the carbon content is significantly reduced and the amount of oxygen is already relatively high, which might be a sign of some difficulties to form carbide phases and thus enhancing the tendency to prepare amorphous films.

For higher O/Ti ratios, the obtained structures consist in oxide phases (a mixture of anatase and rutile phases).

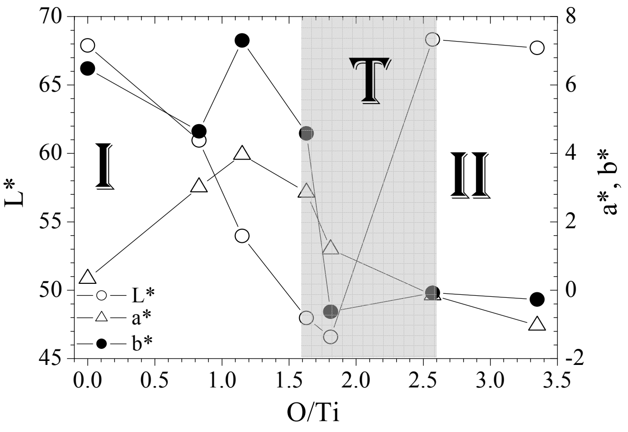

Fig. 2. Average colour coordinates as a function of O/Ti ratio

The three distinct behaviours occurring within the different zones can also be correlated with the film's colour characterization, Fig. 2. This figure shows the colour coordinates L*, a* and b*. It can be observed that with increasing O/Ti atomic ratio (up to ~1.2), the value of a* (redness) increases as well as the b* value (yellowness), reaching its maximum value. The L* values (brilliance) show a significant decrease for the Ti-C-O films with the increase of O/Ti ratio up to O/Ti ~1.8. The colour changes from a metallic tone for the lowest O/Ti ratios (also for the $TiC_{1.6}$ film) to a very bright grey tone at O/Ti ~1.2. Further increases of the O/Ti ratio induced the change of film's colour towards very dark grey tones, as revealed by the film with an atomic ratio O/Ti ~1.8, where in fact the results indicate a transition form the metallic to a transition mode.

In the transition zone, there is an inversion of the tendency for L* to decrease. The plot shows a significant increase of this colorimetric coordinate, whose value increase from ~45 to 70. Slight increase in b* and decrease in a* where also observed. In the oxide zone (O/Ti ratios higher than ~2.6), there was a clear tendency for the films to reveal interference colours, with very high values of L* and very low values of both a* and b*. The overall behaviour can be explained by the decreasing metallic character of the films with increasing O/Ti ratio and the transition towards a more insulating type represented by the oxide-type films prepared at the highest oxygen flows, see Fig. 1. The electron charge transfer from Ti atoms to metalloid (O and C) atoms increases with increasing metalloid content in Ti-C-O.

3.2. Mechanical properties

The evolution of hardness, residual stress and critical load as a function of the O/Ti ratio is shown in Fig. 3. Once again, the different structural changes have some effects on hardness evolution, where a significant reduction of hardness values is observed with the increase of the O/Ti ratio. The hardness ranges from typical values of TiC films for the lowest O/Ti ratio, to those of TiO_2 films for the highest O/Ti ratio [11-12]. The possibility of having a nanocomposite structure of the form nc-TiC(O)/a-C is consistence with the high hardness values obtained in the films located in zone I, as observed by the authors of recently published works [13-14]. The structural changes induced by the oxygen incorporation in the films, seems to be the major responsible to this decrease in hardness, as well as the continuous amorphization tendency that the films revealed with increasing of the O/Ti ratio as seen in the structural results (Fig. 1) [15]. For the highest O/Ti ratios, there is a slight improvement of hardness, which might be related with the formation of poorly crystallized oxide phases (anatase and rutile).

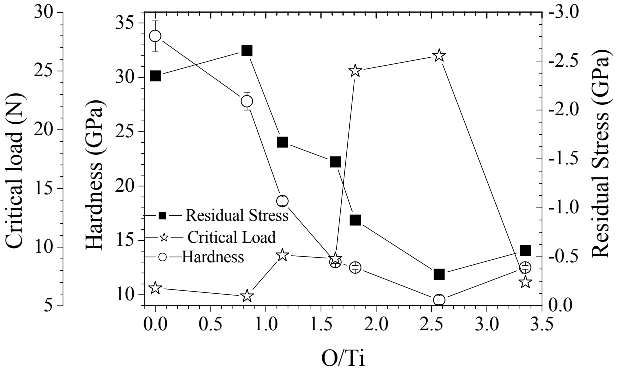

Fig. 3. Evolution of hardness, residual stresses and critical load of sputtered TiC_xO_y films as a function of the O/Ti ratio

It is worth mention the evolution of the residual stresses as a function of the O/Ti ratio, Fig. 3. The plot shows that there is a significant reduction of stresses with the increase of the O/Ti ratio, indicating that the strain energy parameter is probably becoming less importance than the surface free energy that starts to prevail. For the $TiC_{1.6}$, the high compressive stresses can be a result of the insertion of the C atoms in the interstitial octahedral spaces of the host TiC matrix. The insertion of oxygen atoms in the TiC lattice can occur with the increase of the O/Ti ratio and might explain the almost amorphous nature of the existing TiC grains detected in XRD (see Fig. 1). Residual stresses can be correlated as well with the hardness values. From Fig. 3, it is clear that as the residual stresses decreases, the hardness suffers also a decrease, which means that beyond the different structures arrangements, the level of the compressive residual stresses is also acting as a hardening factor.

Regarding the evolution of the adhesive critical loads (first appearance of the substrate) as a function of the O/Ti ratio, it seems that once again the different structural changes occurring in the films are inducing different adhesion behaviours. In fact, the highest critical loads occurred for films that the XRD results revealed amorphous structures, region T, which is understandable since these kinds of structures are able to better accommodate the deformations induced by the movement of the scratch tip. Another point is related with the residual stresses states in the films. In fact, and taking into account the result obtained in region I and T, there seems to be some correlation between stresses and adhesion, since lower compressive stresses correspond to higher critical adhesion loads. Nevertheless, these residual stress states are not able to alone explain all the behaviours since in the oxide region the stress levels are lower, but the critical adhesion loads are also significantly lower. If one keeps in mind that in this oxide region there is already some tendency to obtain poorly crystallized oxide structures, this means that the structural features are playing a decisive role for the adhesion behaviour.

4. Conclusions

TiC_xO_y thin films were deposited by dc reactive magnetron sputtering from a TiC target. The results showed that the evolution of the different film's properties is related to 3 different zones: a carbide zone; a transition zone, and an oxide one. There is a straight correlation between these regions and the film's composition evolution and the particular ratio of the elements.

The structural characterization showed that in the carbide regime the films crystallize in a TiC B1-NaCl-type crystal structure. In the transition regime, the films show a clear tendency towards amorphization, while a mixture of both poorly crystallize anatase and rutile phases are observed in the films within the oxide zone.

A progressive reduction of hardness with increasing of the O/Ti ratio was observed, which was interpreted as the result of continuous amorphization of the films, with a slight increase in the oxide zone due to the formation of poorly crystallized oxide structures. The residual stresses also presents a decrease with increasing of O/Ti ratio. The relation between those properties means that the level of the compressive residual stresses is acting as a hardening factor. The residual stresses are also playing an important role in the adhesion as well as the film structure. Adhesion is enhanced with the decrease of the residual stresses, till the oxide region where a changing of this behaviour is observed.

The colour results indicate a strong influence of the O/Ti ratio on this property, which is directly related with the structural changes.

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