

## Study on the Thermal Stability of Ti(C,O,N) Decorative Coatings

C. Moura<sup>1</sup>, L. Cunha<sup>1</sup>, J.-M. Chappé<sup>2</sup>, F. Vaz<sup>2</sup>

<sup>1</sup>Centro de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

<sup>2</sup>Centro de Física, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal

### Abstract

This work reports on the study of thermal stability of dark decorative Ti(C,O,N) thin films produced by reactive magnetron sputtering, from a pure titanium target, using acetylene and an oxygen and nitrogen mixture as reactive gases. The thermal resistance and evolution of structural and physical properties were studied by performing annealing experiments at three different temperatures: 800, 900 and 1000 °C. In order to study the effect of the thermal treatments on the properties of the films, mainly the physical ones (where surface colourations will deserve particular importance), X-ray diffraction (XRD) and Raman spectroscopy (RS) were used. The optical properties of the films were obtained by reflectance experiments, in visible region, and the colour of the films is expressed in the CIE 1976 L\*a\*b\* colour space.

### Introduction

Stoichiometric titanium nitride (TiN) is actually one of the most important technological coating materials, not only because of its excellent tribological properties but also due to a good chemical stability. It is certainly, in tribological terms, the most explored hard thin film material and most extensively used in industry. It is used in a wide range of applications, which range from protective material for machine parts and cutting tools<sup>[1]</sup> to diffusion barriers in semiconductor technology.<sup>[2]</sup> Titanium carbide thin films (TiC) have found wide application in various tribological engineering devices owing to its excellent hardness and therefore wear resistance. Titanium carbonitride thin films (Ti(C,N)) are generally used to improve tool life by combining the properties of tough TiN and hard TiC.

Adding oxygen to Ti(C,N) coatings is expected to allow obtaining a good resistance to oxidation and corrosion. Few publications were done on this Ti–C–O–N quaternary system<sup>[3–5]</sup> and mainly on tribological properties. Apart from them, two studies about decorative applications of

Ti(C,O,N) coatings have been led by the authors.<sup>[6,8]</sup> Until now, the studies were restricted to descriptive works on some specific properties. Therefore, the goal of this paper is to better understand the structural properties of Ti(C,O,N) thin films deposited by magnetron reactive sputtering, by studying their thermal stability. For the deposition of the films, a simple process using only two reactive gases, a pure gas and a gas mixture, was used. Then some annealing experiments were done and the influence of the oxygen + nitrogen flow rate on the composition, structure and colour is detailed, as a function of the annealing temperature. Different techniques were used such as electron probe microanalysis (EPMA), X-ray diffraction (XRD) or Raman spectroscopy (RS).

### Experimental Part

The depositions of titanium oxycarbonitride thin films were performed in a laboratory-size unbalanced (type II) direct current (DC) magnetron sputtering system. The films were prepared with the substrate holder positioned at 70 mm from the target in all runs, applying a discharge current density of 100 A m<sup>-2</sup> on the titanium target. The substrates (silicon wafers with (100) orientation and mechanically polished high speed steel AISI M2) were grounded and kept at a constant temperature  $T = 473$  K. For this, an external heating resistance positioned at 80 mm from the substrate holder was used to heat the samples. A thermocouple was placed close to the surface of the 'substrate holder' on plasma side (not in direct

C. Moura, L. Cunha  
Physics Department, University of Minho, Campus de Gualtar,  
4710-057 Braga, Portugal  
Fax: +(351) 253 678981; E-mail: cmoura@fisica.uminho.pt  
J. M. Chappé, F. Vaz  
Physics Department, University of Minho, Campus de Azurém,  
4800-058 Guimarães, Portugal

contact, since depositions were done in rotation mode), and the temperature was measured immediately after stopping the discharge. A deposition time of 1 h was used in all experiments. The base pressure was below  $2 \times 10^{-4}$  Pa. The titanium target (99.96% purity and a size of  $20 \times 10 \text{ cm}^2$ ) was sputtered in an argon (working gas) + gas mixture (oxygen and nitrogen source:  $\text{N}_2:\text{O}_2$  ratio of 17:3) + acetylene (carbon source) atmosphere. Following a previous study,<sup>[6]</sup> the argon, acetylene and gas mixture flow rates were systematically changed from 55 to 60 sccm, from 1 to 5 sccm and from 2 to 35 sccm, respectively, to obtain three samples with different compositions, which would represent the overall behaviour observed in this Ti(C,O,N) thin film system. The annealing treatment was done in a vacuum furnace (base pressure below  $5 \times 10^{-4}$  Pa) and at three temperatures: 800, 900 and  $1\,000^\circ\text{C}$ . Annealing conditions were performed in a three-step process. First step was a heating ramp of 1 h till the desired temperature, while the second step consisted in maintaining of the films at this selected annealing temperature during 1 h. Finally (third step), the samples were left in high vacuum for a non-forced cooling process.

The elemental composition of the coatings was investigated with a Cameca SX-50 EPMA, operating at 15 keV as acceleration voltage. XRD experiments were performed in a conventional Philips PW 1710 diffractometer, using  $\text{Cu K}\alpha$  radiation in Bragg-Brentano configuration. Raman measurements were performed at room temperature with a Jobin-Yvon (T64000) triple monochromator, equipped with a liquid nitrogen cooled charge couple device (CCD) detector, with a resolution better than  $1 \text{ cm}^{-1}$ . The excitation line, 488 nm, of an argon ion laser was focused onto the sample using a  $100\times$  MS Plan objective of an Olympus Microscope BHSM, in a backscattering geometry. The spectra were obtained with a measured power of about 0.5 mW on the sample, to avoid heating.

The film's colour was represented in the CIEL\*a\*b\* 1976 colour space by using a commercial Minolta CM-2600d portable spectrophotometer (wavelength range: 400–700 nm), with diffused illumination (D65 light source) at an  $8^\circ$  viewing angle (specular component excluded).

## Results and Discussion

For this study, only three samples were selected from a large set of dark-toned decorative Ti(C,O,N) thin films that have been previously prepared.<sup>[6]</sup> This selection has been carried out according to the overall behaviours that have been observed. Thus, one of the samples was selected according to its relatively higher crystallinity and the more metallic-like appearance (higher reflectivity and luminescence). This sample was produced with a gas mixture flow of 2 sccm, presenting a stoichiometry of the type  $\text{TiC}_{1.18}\text{O}_{0.38}\text{N}_{0.14}$ .

On the other 'extreme', a second sample,  $\text{TiC}_{0.21}\text{O}_{2.30}\text{N}_{0.24}$ , produced with a gas mixture flow of 35 sccm, was selected according to its significantly higher oxygen content, and thus with a roughly oxide-like appearance (an interference like tone and a wavy-like reflectivity behaviour). In the transition between these two samples, a third one has been selected, which revealed for all properties a transition between the two previously

mentioned ones. This sample presents a stoichiometry of  $\text{TiC}_{2.71}\text{O}_{0.73}\text{N}_{1.22}$ , and it was prepared with a gas mixture flow rate of 10 sccm. Details on all these samples can be found elsewhere.<sup>[6]</sup>

For the sake of clarity and by analysing the composition results and structural data of the as-deposited Ti(C,O,N) samples,<sup>[6]</sup> and the subsequent behaviour with variation of the annealing temperature, the three selected samples may be divided in two basic categories:

- (i) face centered cubic (fcc)-type samples — resulting from the comparison of their XRD patterns with those of a 'pure' TiC-(TiN- or TiO-) type structure. The presence of fcc phases is evident, even if sometimes small, but that became clearer when the annealing temperature was increased. When compared to the composition of a 'pure' TiC-(or TiN or TiO), the NM/Ti atomic ratio, where NM stands for 'Non Metal' (C, N and O), one of the samples,  $\text{TiC}_{1.18}\text{O}_{0.38}\text{N}_{0.14}$  is slightly over-stoichiometric and it will be referred in the text as  $\text{Ti}(\text{C},\text{O},\text{N})_{1.6}$ . To note that the stoichiometry of this sample varies only slightly with the annealing temperature, as it will be shown later in the text, and thus the decision to put this fixed index. The second sample in this category,  $\text{TiC}_{2.71}\text{O}_{0.73}\text{N}_{1.22}$ , if compared to the composition of a 'pure' TiC-(or TiN or TiO) has a NM/Ti atomic ratio highly overstoichiometric and thus it will be noted in the text as  $\text{Ti}(\text{C},\text{O},\text{N})_{4.7-3}$ . The arrow in the index means that, contrarily to the previous sample, the stoichiometry will vary significantly between these two values with the annealing temperature, as it will be shown later.
- (ii) oxide-type sample,  $\text{TiC}_{0.21}\text{O}_{2.30}\text{N}_{0.24}$ , — because of the NM/Ti atomic ratio is slightly overstoichiometric ( $\text{Ti}(\text{C},\text{O},\text{N})_{2.6}$ ) when compared to the composition of  $\text{TiO}_2$  and the amount of oxygen is significantly higher than that one the other metalloids. Similarly, to the first of the fcc-type sample, the annealing temperature will not affect significantly the stoichiometry of this sample and thus its representation is done with a fixed index.

In terms of basic characterization, experimental results revealed that the evolution of the samples properties with the temperature of the thermal annealing is highly dependant of their initial composition and structure. Figure 1 shows the variation of the NM/Ti atomic ratio, as function of the temperature.

The first observation that has to be taken into account is the strong decrease of the NM/Ti ratio, for the annealing temperature of  $900^\circ\text{C}$ , in the highly overstoichiometric sample,  $\text{Ti}(\text{C},\text{O},\text{N})_{4.7-3}$ . In comparison, the variation of the atomic ratio of samples  $\text{Ti}(\text{C},\text{O},\text{N})_{1.6}$  and  $\text{Ti}(\text{C},\text{O},\text{N})_{2.6}$  is almost insignificant, as previously mentioned. This behaviour may be understood if a close look is taken into the

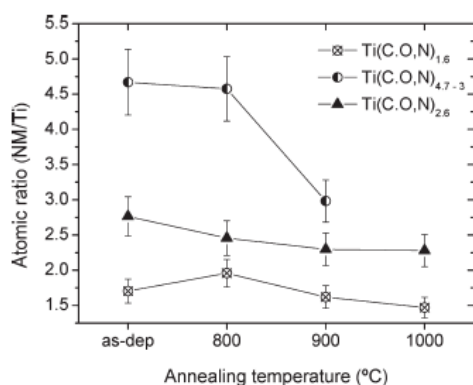


Figure 1. Atomic ratio between non-metallic elements over the atomic ratio of titanium, as function of annealing temperature.

stoichiometry of the samples. There is a clear excess of metalloid elements, in sample  $\text{Ti}(\text{C},\text{O},\text{N})_{4.7-3}$ , when compared to what happens with sample  $\text{Ti}(\text{C},\text{O},\text{N})_{1.6}$  related with stoichiometric TiC (TiN or TiO), or with sample  $\text{Ti}(\text{C},\text{O},\text{N})_{2.6}$  related to  $\text{TiO}_2$ . The increase of the atomic mobility, due to the increase of the annealing temperature, promotes atomic rearrangements and thus, in consequence, some possible losses of NM elements. This atomic rearrangement is clearly observed in the structural analysis done by XRD (Figure 2).

The structural evolution of the  $\text{Ti}(\text{C},\text{O},\text{N})$  coatings as a function of temperature, was analysed on the basis of XRD. It is important to note that TiC, TiN and TiO present the same crystallographic structure with close lattice parameters:  $a_{\text{TiC}} = 0.4328 \text{ nm}$  (JCPDS04-004-2919),  $a_{\text{TiN}} = 0.4241 \text{ nm}$  (JCPDS04-001-2272) and  $a_{\text{TiO}} = 0.4177 \text{ nm}$  (JCPDS04-001-6834). Therefore, XRD is not a suitable method to distinguish between these three compounds, especially in an over-stoichiometric condition such as the one possible in this case, or a solid solution-type compound,

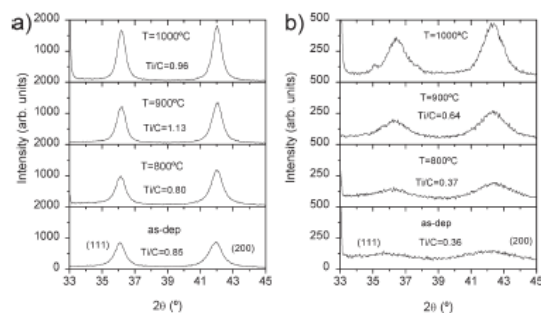


Figure 2. X-ray diffraction patterns of titanium oxycarbonitrides (a)  $\text{Ti}(\text{C},\text{O},\text{N})_{1.6}$  (b)  $\text{Ti}(\text{C},\text{O},\text{N})_{4.7-3}$ , as function of annealing temperature.

where all or some of C, O and N atoms may be within the same cubic lattice, and thus a lattice parameters distribution would be expected (significant peak broadening such as those in the as-deposited samples and mainly in that from the  $\text{Ti}(\text{C},\text{O},\text{N})_{4.7-3}$ ). Anyway, for the as-deposited  $\text{Ti}(\text{C},\text{O},\text{N})_{2.6}$  sample, XRD results show that the sample presents low crystallinity, as usually observed in as-deposited  $\text{TiO}_2$ -type compounds.<sup>[7]</sup> With annealing, the XRD patterns show the expected evolution of grain refinement, and the characteristic signature of a mixture of oxide-phases,<sup>[8]</sup> rutile and anatase mainly.

For the samples  $\text{Ti}(\text{C},\text{O},\text{N})_{1.6}$  and  $\text{Ti}(\text{C},\text{O},\text{N})_{4.7-3}$ , the diffraction patterns, observed for angular positions between  $33$  and  $45^\circ$ , are displayed in Figure 2a and b, respectively. The XRD diffraction patterns of both samples reveal the presence of (111) and (200) diffraction peaks that may be assigned to the TiC fcc structure with probable inclusions of oxygen and/or nitrogen atoms ( $\text{TiC}_x(\text{O},\text{N})$ ), as already pointed out in previous work.<sup>[6]</sup> The as-deposited slightly over-stoichiometric sample ( $\text{Ti}(\text{C},\text{O},\text{N})_{1.6}$ , fcc-type) exhibits no preferential orientation. The thermal annealing treatment leads to the increase of the intensity of the previously detected diffraction peaks, revealing some refinement of grain size. The crystallite size calculated according to the Scherrer's method, from the full width at half maximum of the (111) diffraction peak, shows that the grain size of the  $\text{Ti}(\text{C},\text{O},\text{N})_{1.6}$  sample increases from about 7 to 12 nm, with the increase of annealing temperature.

On the other hand, the as-deposited highly over-stoichiometric sample ( $\text{Ti}(\text{C},\text{O},\text{N})_{4.7-3}$ , fcc-type) presents a roughly amorphous structure. The fact that this sample presents a NM/Ti ratio of about 4.7 imposes a great deal of difficulties to form periodic structural arrangements. One possibility is that the former cubic lattice, being significantly Ti deficient, with many (N, O or C) interstitials/substitutions, induces significant lattice distortions. With the thermal treatment, the loss of NM elements allows the rearrangement of the structure and thus, the formation of small grains of a nanoscaled type, where nanograins (cubic lattice type, with Ti vacancies and mixed O+N) are dispersed in a carbon amorphous matrix. The crystallite size calculated by the Scherrer's method from the full width at half maximum of the (111) diffraction, although with a significant degree of uncertainty, shows that it varies from 2 up to 4 nm, in the  $\text{Ti}(\text{C},\text{O},\text{N})_{4.7-3}$  sample.

In order to have some elucidation about the carbon matrix, Raman experiments were done in all samples. Figure 3a and b shows the Raman spectra, between 800 and  $2000 \text{ cm}^{-1}$  range, for  $\text{Ti}(\text{C},\text{O},\text{N})_{1.6}$  and  $\text{Ti}(\text{C},\text{O},\text{N})_{4.7-3}$  samples, respectively, as function of annealing temperature.

For both samples, the characteristic signatures of carbon were detected: the higher frequency band ( $\approx 1580 \text{ cm}^{-1}$ ) and the lower frequency band ( $\approx 1390 \text{ cm}^{-1}$ ) are generally

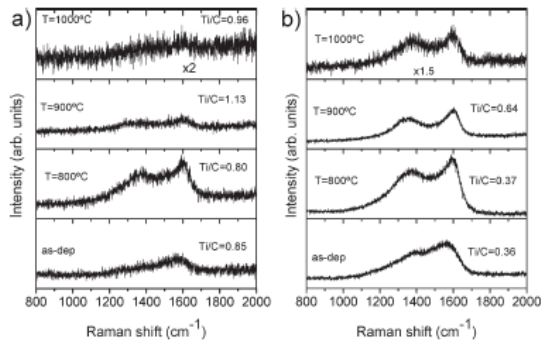


Figure 3. Raman spectra of oxycarbonitrides (a)  $\text{Ti}(\text{C},\text{O},\text{N})_{1.6}$  (b)  $\text{Ti}(\text{C},\text{O},\text{N})_{4.7-3}$ , as function of annealing temperature.

recognized as G- and D-band, respectively, for carbon materials. The former originates from a Raman allowed  $I'$  point vibration in the graphite planes, corresponding to the optical phonon modes of  $E_{2g}$  symmetry and the latter is disorder-induced and associated with optical phonons close to the  $K$  point of the Brillouin zone in graphite. The D-band becomes Raman active due to the lack of long range order in amorphous carbon-based materials and arises from limitation in the graphite domain size, induced by grain boundaries or imperfections. This observation is consistent with the presence of a carbon amorphous matrix.

For the slightly over-stoichiometric sample (Figure 3a), the bands present lower intensity (almost half of the intensity) and are less resolved than those observed in the highly overstoichiometric sample (Figure 3b). This is an indication that the amount of free carbon in the sample  $\text{Ti}(\text{C},\text{O},\text{N})_{1.6}$  is lower than the one present in the sample  $\text{Ti}(\text{C},\text{O},\text{N})_{4.7-3}$ . For the slightly over-stoichiometric sample, as the size of  $\text{Ti}(\text{C},\text{N},\text{O})$  crystallites increases due to the annealing, the fraction of free carbon decreases and the correspondent Raman signal decreases. This result is consistent with the observed behaviour of the composition and XRD patterns evolution, where the variation in the NM/Ti atomic ratio and the intensity due to diffraction peaks related to Ti compounds increases in intensity, with the increase of the annealing temperature. In the case of the highly overstoichiometric sample, the intensity of the Raman signal shows a significant increase and the two bands are more clearly distinguished, than in the previous sample. This behaviour is due to the fact that the amount of free carbon is higher, when compared to sample  $\text{Ti}(\text{C},\text{O},\text{N})_{1.6}$ . In fact, for this sample, the C:Ti ratio is higher than 2.5. In consequence, it is expected that the intensity of Raman carbon bands is higher than the previous ones. With the increase of the annealing temperature, the decrease in the intensity of the Raman signal is expected. The increase of

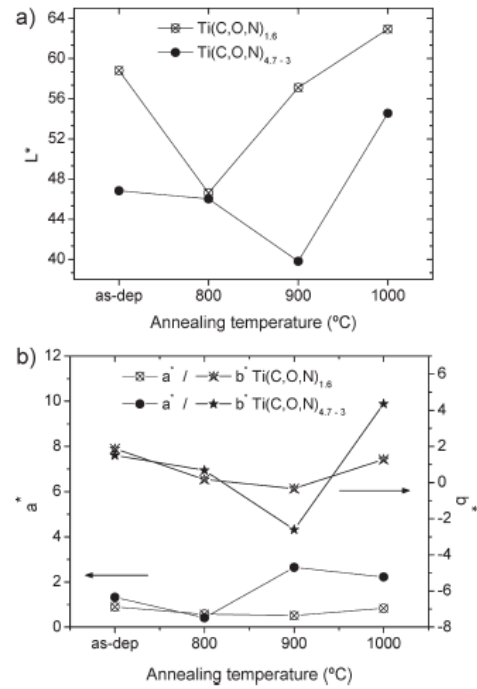


Figure 4. Average colour coordinates [(a)  $L^*$ , (b)  $a^*$  and  $b^*$ ] of  $\text{Ti}(\text{C},\text{O},\text{N})$  films in the CIE Lab colour space function of annealing temperature.

the atomic mobility, due to the increase of the annealing temperature, promotes atomic rearrangements and, in consequence, some losses of NM elements as previously mentioned.

On the other hand the as-deposited sample presents a broad band, due to the superposition of the D- and G-bands characteristic of the carbon amorphous materials. With the increase of the annealing temperature, the separation between the two bands increases: the D-band shifts to lower wave numbers and the G-band shifts to higher values. This effect is an indication of the increase of order in graphite crystalline domains and an increase of the size of microcrystals due to the increase of the temperature suggesting an increase in the graphitic order in the carbon matrix.<sup>[9]</sup>

Being of decorative nature (dark black coatings), one of the most interesting points concerns the thermal stability of the material, namely its colour. Macroscopically and taking into account the human perception of colours, it was not detected any change in the colour of the samples caused by the annealing treatment. Colour measurements using the CIE  $L^*a^*b^*$  1976 colour space system, allows a quantitative comparison of the colour evolution as function of the temperature of the thermal treatment. This analysis was

not carried out in the oxide-type sample,  $(\text{Ti}(\text{C},\text{O},\text{N})_{2.6})$  due to its characteristic transparency to visible radiation and in consequence, its colour is not intrinsic, but resultant of interference effects. The behaviour of the other two samples is represented in Figure 4a and b, showing the variation of the chromaticity parameters ( $a^*$  and  $b^*$ ) and lightness factor ( $L^*$ ), respectively.

The results show only small variations of the chromaticity parameters ( $a^*$  and  $b^*$ ), not detectable by a healthy human eye, as expected. The thermal treatment promotes an increase of surface roughness. This increase of roughness produces variations of the  $L^*$  factor that does not allow to draw any significant conclusion nor present a suitable comparison between the behaviour of samples.

## Conclusion

For this study, three samples were selected from a large set of dark-toned decorative  $\text{Ti}(\text{C},\text{O},\text{N})$  thin films: fcc-type samples slightly over-stoichiometric and a highly over-stoichiometric, and an oxide-type sample. In terms of basic characterization, experimental results revealed that the evolution of the samples properties with the temperature of the thermal annealing is highly dependant of their initial composition and structure. For the fcc-type samples, it was shown that with the thermal treatment, the loss of NM elements allows the rearrangement of the structure and thus, the formation of small grains of a nanoscaled type, where nanograins (cubic lattice type, with Ti vacancies and mixed O + N) are dispersed in a carbon amorphous matrix. The presence of this amorphous matrix was confirmed by Raman measurements.

Colour measurements using the CIEL\*a\*b\* 1976 colour space system, allows a quantitative comparison of the colour evolution as function of the temperature of the

thermal treatment. The results show only small variations of the chromaticity parameters ( $a^*$  and  $b^*$ ), not detectable by a healthy human eye, evidencing a high stability.

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