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TiN-based decorative coatings: colour change by addition of C and O

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As a result of technological progress in recent years, a new challenge was passed onto decorative hard coatings. While enhancing the appearance and lending attractive coloration to surfaces, the films are supposed to provide scratch resistance, protection against corrosion and durability. For this work, TiN(O) and TiN(C,O) thin films were prepared. Within the TiN(O) system, film colours varied from the glossy golden type for low oxygen contents to dark blue for higher oxygen contents. In order to reach darker colours (black), TiN(C,O) thin films were deposited, and results revealed the possibility to deposit very dark black films. All these results have been analysed and are presented as a function of both the deposition parameters and the particular composition and crystalline phases present in the films.

1. 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 [1] to diffusion barriers in semiconductor technology [2]. Among several other areas where this successful material has been used, there is one which is simultaneously very popular, but also with a large potential to grow significantly: the decorative field. TiN is known to be capable of fulfilling very restraining requirements of the decorative market – appearance (its attractive golden tone), wear resistant, chemically inert among others. As by joining all the above mentioned valences, TiN is recognized as an important economic "agent", and has experienced a large expansion. Nevertheless, and although the success of this coating material, in the decorative field only golden, greenish, and brownish yellows are normally obtained. Various other shades of grey and black can also be obtained with other ternary nitrides [3,4], as well as blue tones based on borides [4].

Recently, new classes of materials have been gained importance for both decorative and tribological applications, the so-called metal oxynitrides Me(N,O) (Me = early transition metal). Their importance results from the presence of oxygen that allows the tailoring of film properties between those of carbide (or nitride) and the correspondent oxide. Tuning the oxide/nitride ratio allows one to tune the band-gap, bandwidth, and crystallographic order between oxide and nitride and hence the electronic properties of materials and thus the optical ones, including here the colour. The major advantage of this nitride and oxide combination is not only the possibility to have several different colours, but above all the opportunity to have them from the same system: one target (Ti in this case) and the same gas mixture ($N_2 + O_2$).

Despite the huge amount of published scientific works on thin films of metallic nitrides and oxides over 10 years, the area of metal oxynitrides is poorly explored so far and knowledge of the fundamental mechanism that explains the observed behaviour, both structural and mechanical, is yet insufficient. Moreover, the possibility to add another element to the oxynitride matrix, (C will be presented in this work) is also a subject that is gaining increasing importance, but again leading to complex structural arrangements [5,6].Thus, the main motivation was to obtain TiN-based decorative thin films, resulting from O and C additions, TiN(C,O).

2. Experimental

The TiN(C,O) thin films were deposited onto high-speed steel (AISI M2), stainless steel (AISI 316) and single crystal silicon (100) substrates by reactive dc magnetron sputtering in a laboratory-size deposition system. It consisted of two vertically opposed rectangular magnetrons (unbalanced of type 2), in a closed field configuration. The films were prepared with the substrate holder positioned at 70 mm in all runs, using a dc density of 100 $A.m^{-2}$ on the titanium target (99.6 at. %). A gas atmosphere composed of argon (working gas) and nitrogen + oxygen (19:1 ratio) reactive mixture was used for the depositions. The Ar flow was kept constant at 60 sccm and the mixed reactive gas flow rate varied from 4 to 20 sccm. The working pressure was approximately constant at 0.4 Pa and the substrates were biased (V_B = -70 V). The pumping speed was adjusted to 356 L/s. The atomic composition of the as deposited samples was measured by Rutherford Backscattering Spectroscopy (RBS) using a 2 MeV He^+ beam as well as 1.4 and 2 MeV proton beams to increase the accuracy in the oxygen signals. Electron probe microanalysis (EPMA) was also used for the samples prepared with C due to the difficulties of RBS in separating the C, N and O contents. The analyzed area was about 0.5x0.5 mm^2. Ball crater tests were used to measure the thickness of the samples. In order to examine the film structure, X-ray diffraction experiments (XRD) were undertaken in a Philips PW 1710 apparatus, using Cu Kα radiation. The characterization of film's colour was computed using a commercial MINOLTA CM-2600d portable spectrophotometer (wavelength range: 400-700 nm), using diffused illumination at an 8° viewing angle. Colour specification was computed under the standard CIE illuminant D65 and represented in the CIELAB 1976 colour space [7,8].

3. Results

3.1. The TiO_xN_y system

A. Composition

The composition of the samples (by RBS) as a function of the reactive flow rate of reactive gases is presented in Fig. 1.

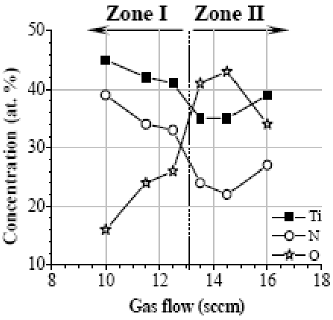

Fig. 1. Atomic composition (RBS) of TiO_xN_y samples as function of gas flow rate.

The stoichiometry of the films was obtained from *R*utherford *B*ackscattering *S*pectroscopy (RBS), by fitting the measured data with the RUMP code simulation [9]. Fig. 1 summarizes the results from all analyzed spectra. From this figure, the first conclusion that might be drawn is that there is significant increase of the oxygen content in the coatings with the increase of the flow rate (except for the highest flow, 16 sccm), in spite of the large amount of nitrogen present in it (one should keep in mind that the flow rate is composed of a mixture of N_2+O_2: 19:1 ratio). Anyway, this result is somewhat expected taking into account the available thermochemistry data for titanium oxides and nitrides [10], which indicates a much higher reactivity of titanium towards oxygen, rather than to nitrogen. A closer look into the results plotted in Fig. 1 also shows the existence of roughly two distinct regions. The first corresponds to the films prepared with gas flow lower than 13 sccm, in which the films reveal slight decreases of both Ti and N contents and a systematic increase of the oxygen content from about 16 at. % to ~26 at. %. The second region incorporates the films prepared with gas flows from 13.5 to 16 sccm. In this region, the films have very few variations in the elemental concentrations, though the 16 sccm samples seem to have a small and unexpected variation (a decrease in the oxygen content and increase in both Ti and N).

This two-zone composition regions can also be evidenced from the plot of the C_O/C_{Ti}, C_N/C_{Ti} and $(C_N+C_O)/C_{Ti}$ atomic ratios (Fig. 2).

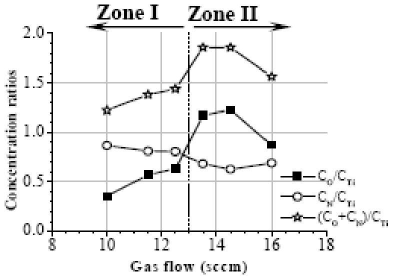

Fig. 2. Atomic ratios of TiO_xN_y samples as function of gas flow rate.

For the films deposited with reactive gas flows below 13 sccm, composition analysis revealed that films within this region have non-metal to titanium atomic ratios, C_O/C_{Ti} and C_N/C_{Ti}, less than one, and values of $(C_N+C_O)/C_{Ti}$ below 1.5. Samples within this zone I have colour appearances from metallic towards bright yellow-pink colour, which gradually shifts to dark golden yellow as the oxygen content increases. In zone II, the C_N/C_{Ti} decreases slightly while C_O/C_{Ti} increases to values around 1. Interesting to note is the values of the $(C_N+C_O)/C_{Ti}$ atomic ratio, which tends to be around 2. This result and the fact that the ratio C_O/C_{Ti} is close to 1 (far from the stoichiometry of TiO_2 compounds) might induce the formation of over-stoichiometric nitride compounds, as well as some mixtures (such as TiO_x and TiN_y). In this second zone, the films tend to develop colour tones that vary from dark brown towards dark blue.

These variations of elemental composition are not easy to anticipate the type of compounds that can be formed, although the fact that the C_N/C_{Ti} in zone I is close to 1 with relatively low values of C_O/C_{Ti} might induce the formation of TiN(O) compounds (oxygen-doped TiN). Regarding zone II, the high amounts of oxygen are expected to have a significant influence in the type of compounds to be formed, and especially in their crystallinity.

B. Structure

In order to understand the mechanisms of chemical reactions occurring within the two different zones and trying to uncover the different compounds that may have been formed, a detailed structural characterization was carried out. Fig. 3 shows the XRD $\theta/2\theta$ diffraction patterns for samples prepared with variation of gas mixture (N_2+O_2) flow, as well as for reference samples: titanium nitride and titanium dioxide. All these samples were prepared under the same conditions of temperature, rotation, polarization of the substrate, target current and working gas flow. Results reveal a strong dependence of film texture on the percentage of oxygen. The sample with lower percentage of this element (16 at. %) reveals a crystalline structure, which is basically constituted by (111) TiN grains.

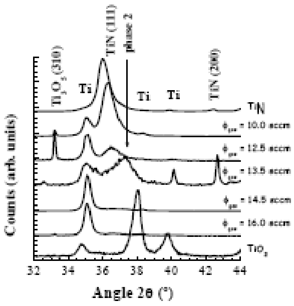

Fig. 3. XRD patterns of TiO_xN_y samples as function of gas flow rate.

This mixture of a pure TiN crystalline lattice and also others with oxygen incorporation, which one might call a phase 2, is even clearer in the diffractograms of the sample prepared with 13.5 sccm, where a mixture of different phases seem to be evidenced by the diffraction signals at 2θ between 35 and 38°. Moreover, this mixture of phases, which may come from the composition features mentioned above (especially the high oxygen amounts present), is already appearing in that sample prepared with 12.5 sccm, where a very broad peak appears on that region.

The increase of the oxygen percentage is followed by a significant loss of crystallinity, being the films with the highest oxygen contents (34 and 43 at. %) practically amorphous. The reason for this increasing amorphization of the films is related to the increase of the oxygen content promoted by the increase in the gas flow (and by the fact that oxygen is much more reactive than nitrogen). The increase of the available oxygen increases the supersaturation, reducing the possibility of crystallization (mostly that of TiN). The extended deformation of the titanium nitride structure, resulting from the incorporation of oxygen, increases the number of defects, facilitating the amorphization. In fact, this oxygen doping explains the broadening of the diffraction peaks, as it can be evidenced for intermediate and highest oxygen contents, where the peak broadening is a clear indication of a mixture of lattice parameters. Although the doping of TiN with other elements has been claimed in different studies, such as those of Ti-Al-Si-N [11], the exact nature of phase 2 is very difficult to evaluate, but it cannot be matched by any known compound formed with Ti and N, or from various phases of titanium oxide.

This fact provides evidence for the possible formation of a titanium, oxygen, nitrogen phase, Ti-O-N, where some of the oxygen atoms are most likely occupying nitrogen positions in the *fcc* TiN lattice. This last assumption has been mentioned in the upper mentioned works [12], but also for recent works concerning (Ta,Si)N coatings [13] in order to explain the XRD results, but no clear experimental evidence was given. Without ion bombardment only that phase 2 was visible [14], leading to the conclusion that phase mixing is most likely a consequence of the ion bombardment. The absence of the ion bombardment and the low deposition temperature do not provide the necessary mobility for the species that will ensure the complete phase segregation, being this the main reason that explains the formation of this Ti-O-N structure - phase 2. This phase could be called a solid solution. Consequently, with increase in surface mobility provided by the increase in temperature and/or ion bombardment, phase segregation is enhanced and thus one can observe the formation of TiN polycrystalline grains, although traces of that Ti-O-N phase are still visible in some samples, such as those prepared with 12.5 and 13.5 sccm. Beyond this main finding of phase mixture, several reflections corresponding to Ti-O structures were also indexed. These structures also tend to disappear with the increase of the oxygen content, which is again a consequence of the difficulty in growing "pure" structures with the gas mixture.

C. Colour

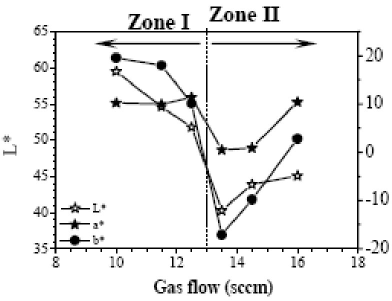

Fig. 4. Colorimetric parameters of TiO_xN_y samples as function of gas flow rate.

The composition and the structure have consequences in the physical and mechanical properties of TiO_xN_y films. Fig. 4 shows the colour coordinates L*, a* and b*, represented in the CIELAB (1976) colour space [7,8]. A relatively large spectrum of intrinsic colours was obtained for gas flows lower than 16 sccm. For flows higher than 16 sccm, only interferential colours are obtained, and thus no references are made in this paper. As can be seen from the figure, with increasing flow rate from 10 to 13 sccm (increasing oxygen content), the value of a* (redness) remains practically constant, while b* (yellowness) and L* (brilliance) values decrease.

For films within zone I, the colour changes from a very bright yellow-pale to dark golden yellow as the oxygen content increases. With further increase of the flow rate, zone II, the film colour changes to dark blue (negative b* values and relatively low a* values) at higher flow rates. A significant decrease of L* was also observed for the films deposited in zone II. For gas flows higher than 16 sccm the colour was dark blue.

3.1. The TiN(C,O) system

It is well-known the growing interest in coating objects with very dark colours for several decorative purposes. The fact that only dark blue colours were obtained in the TiON system, the addition of carbon was carried out in order to try to reach those darker tones. In order to prepare the TiN(C,O) coatings, the deposition system was the same, but the gas atmosphere was composed of argon (working gas), acetylene (C_2H_2) and a reactive mixture nitrogen + oxygen (17:3 ratio). The films were prepared varying the mixed reactive gas flow (acetylene and N_2+O_2).

A. Composition

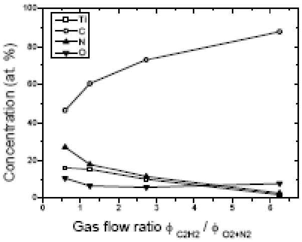

Fig. 5. Atomic composition (RBS) of TiN(C,O) samples as function of gas flow ratio.

Looking to coatings composition it is noticed a high carbon atomic concentration in all the analyzed samples (Fig. 5), which was observed to be the required procedure to obtain the dark coatings (Fig. 6).

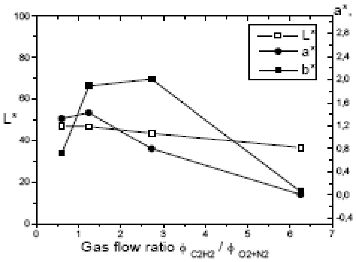

Fig. 6. Colorimetric parameters of TiN(C,O) samples as function of gas flow ratio.

The increase of the gas flow ratio $\Phi(C_2H_2)/\Phi(O_2+N_2)$ influenced mainly the a* and b* colorimetric parameters, which are close to those of very dark tones.

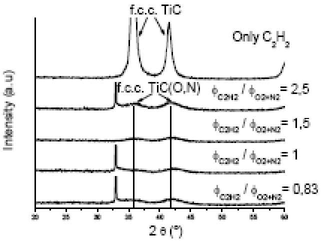

Fig. 7. XRD patterns of TiN(C,O) samples.

Measurements performed in the coating with higher C concentration revealed the highest black tone. In terms of structure, the samples produced only with acetylene and argon flow revealed a TiC-type structure (fcc NaCl type). The decrease of $\Phi(C_2H_2)/\Phi(O_2+N_2)$ induced a significant amorphisation, but keeping a very poorly crystallized TiC-type structure, with possible N and O inclusions, (Fig. 7).

4. Conclusions

Thin films within the Ti-N-O ternary system were prepared by reactive magnetron sputtering. Structural characterization results reveal a strong dependence of the film texture on the percentage of oxygen. The increase of the oxygen percentage is followed by a significant loss in crystallinity, being the films with the highest oxygen contents amorphous. However, for intermediate and higher oxygen contents, the diffraction peaks seem to indicate a mixture of lattice parameters. Regarding colour variations, it was observed that for low oxygen contents a bright yellow-pink colour was obtained, which gradually shifts to dark golden yellow as its contents increases. For larger contents of oxygen the colour produced is a dark blue.

On the other hand, Ti-C-N-O system is only starting to be analyzed. Anyway some preliminary results were presented, mainly concerning composition as function of current ratio applied to the targets, structure and colour.

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