Original Article

Thickness dependent chemical and microstructural properties of DC reactive magnetron sputtered titanium nitride thin films on low carbon steel cross-section

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Abstract
Polished samples of low carbon steel (LCS) rod cross-sections were sputtered with different thicknesses of TiN thin film using DC reactive magnetron sputtering technique. While other process parameters such as target power (200 W), substrate position (150 mm) and sputtering pressure (1.33 Pa) were kept constant during the deposition, the deposition time was varied from 5 to 20 min. Physical and chemical characterizations of the samples were done using Rutherford backscattering spectroscopy (RBS), X-ray diffraction (XRD) spectroscopy, scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy and optical microscopy. Vickers micro-hardness tester was used for the hardness test. The optimum value of the Vickers hardness was found to be 267.9 for the film deposited at 20 min. The inter-planar spacing was found to be from 2.0362 Å to 2.0890 Å, while corresponding lattice parameter was calculated to be from 4.0724 Å to 4.1780 Å. Scanning electron microscopy observation of the films gave an indication of fine-grained microstructure, which confirms the good adhesion and hardness properties of titanium nitride layer on the LCS substrate. The XRD spectra show that the multiphase reflections TiO\textsubscript{2} (110) and TiN (111) for thinner film samples which shift to a preferred orientation (200) for thicker films, indicating a largely TiN\textsubscript{p} phase. This strongly suggest remarkable changes in crystal orientations of the TiN films with deposition time. Ion beam (RBS) results showed increase in amount of nitrogen contents (47-64\%) in TiN films with thickness and deposition time.

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2238-7654 © 2018 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
1. Introduction

Among different steels types, those produced in the greatest quantities fall within the low-carbon classification. They mostly contain less than about 0.25 wt.% carbon and hardly respond to heat treatments intended to form martensite; therefore, strengthening is achieved by cold work [1]. They are applied in automobile industries, constructions such as pipelines, bridges, etc. When they are protected at the surface, they are applied in energy generation infrastructures, because of its low cost and lowest lifecycle cost. The yield strength of LCS is about 275 MPa and tensile strength varies between 415 and 550 MPa. Since low carbon steel are very crucial for everyday applications, which might not really require the use of expensive superalloys. It is important, therefore, that service life span of this common alloy is improved and also usage failure is prevented by all reasonable means. This can either be achieved by systematic alloying or by protecting the surface by coating using materials with better thermal and mechanical properties [2,3]. The lifespan of tools mostly made of metals such as router bits, micro-drill bits, moulds and general mechanical parts has increased thanks to coating technologies [4,5]. Mostly, solid ceramic thin films, for instance, TiN, TiCN, CrN, and TiAlN made from transition metal nitrides or carbides have been widely used as thin hard coatings on different mechanical parts [6–10]. Among others, TiN films are extensively used for tribological and diffusion barrier applications due to their superior hardness and chemical stability [11,12] and numerous studies have been carried out on TiN related to their applications in mechanical and optoelectronic technologies [7,13–15]. Patsalas [16] observed that nanocrystalline TiN thin films possess enhanced hardness and strength compared to the bulk microcrystalline thin film-form due to the nano-scale size and interface effects, therefore, control of microstructural characteristics such as grain size, shape, textures, porosity, density, and packing factor are vital for ensuring the reliability of TiN thin films in structural and functional applications [17]. Physical vapour deposition (PVD) techniques such as magnetron sputtering, filtered cathodic arc, ion-plating, and plasma-based ion-implantation remains the best and popular technique to deposit TiN thin films [18,19]. For example, in magnetron sputtering, the deposition parameters such as substrate temperature, pressure, target power, substrate bias, and energy flux of bombarding particles utilized for growing the films are known to influence grain growth and crystallographic orientation, which affect the resulting microstructure and properties of the films [20–22,18]. Structure zone model [23,24] provides a qualitative picture of the expected microstructure of the films with respect to temperature, for instance, at low deposition temperatures, the films show an open columnar structure with extended voids along column boundaries [25]. The columns are observed to be composed of smaller equiaxed grains, whereas the voids become filled with an increase in film growth temperature and form a true columnar structure. Sputtering is believed to be the only deposition method that does not depend on melting points and vapour pressures of refractory compounds such as carbides, nitrides, silicides, and borides [5,3,10]. As a result, films of these materials can be sputtered directly onto surfaces without altering substrate properties. The influence of the ion bombardment allows very thin films of TiN, to be obtained with a low electrical resistivity, which is lower than that of titanium metal [26]. Magnetron sputtering is the process of choice for the deposition of wide range of important coatings for wear resistance, corrosion resistance, decorative, and coating with specific optical and electrical properties [27]. The objective of this work is to study the structure and chemical properties of different thicknesses of titanium nitride thin films reactively sputtered on polished commercial low carbon steel rod sections at varied deposition time.

2. Materials and methods

2.1. Deposition procedure

The low carbon steel rod sample (0.2 wt.%, h = 10 mm) was obtained from Nigerian Machine Tools (NMT), Osogbo, Nigeria. The sample was cut into five different smaller sections, and the surfaces were prepared via thorough grinding with emery papers (400 and 500 grit). The surfaces were then finely polished with a mettallurgical polishing powder to give a clean finish. Hence, titanium nitride thin films were deposited on finished LCS surfaces using DC Magnetron equipment (ONYX 2) at different deposition times (5–20 min). The sputtering target was 99.99% pure Ti disc (h = 2 in., 5 mm thick). The sputtering was carried out in an Ar+N₂ atmosphere, after the chamber was purged with argon and evacuated to the pressure of 1.7E–3 Pa. With the shutter positioned between the target and the substrate, the target and substrate were pre-sputtered for 10 min to clean their surfaces by removing the oxide layer or fine layer of solvents that could remain. Pre-sputtering process also enhanced the thermal stability of the deposition chamber. Deposition parameters such as target-to-substrate distance, sputtering power and sputtering pressure were kept fixed at 150 mm, 200 W and 1.33 Pa, respectively. Fig. 1(a) and (b) shows the RBS spectra and optical microscopy micrograph for etched plain polished steel surface. The 3-D projection using Image J software is shown as inset of Fig. 1b. The backscattering spectrum for the low carbon steel substrate is shown in Fig. 1(a) with iron as the main constituent with other constituents light element barely reflected at the background. Other constituents are not quite visible due to fact that most of them are light elements. The nominal composition of the LCS rod is given in Table 1.

2.2. Characterization details

Rutherford backscattering analysis of the samples was done using NEC 5SDH 1.7MeV pelletron tandem accelerator, equipped with an RF charge exchange ion source to provide proton and helium ions. The data obtained was for the determination of the thickness and compositional depth profile of the films. The diffraction analysis was done with MD-10 Precision Mini X-ray Diffractometer with 2 theta angle between 16° and 72° and using CuKα radiation. Scanning electron microscopy instrument, equipped with EDX facility (Carl Zeiss MA-10 SEM) was used to study the surface morphology and the microstructure of the films. High magnification
optical microscope was used to obtain the micrographs also for surface phase microstructures. Micro hardness investigations of the surfaces were done using Vickers’ microhardness tester.

3. Results and discussions

3.1. Thickness and elemental characterizations

The SIMNRA code was used to fit the simulation over experimental data and give information regarding the stoichiometric compositions and thickness of the samples. Both the heavy element Ti, and the light elements (N and O) were detected via the backscattering process, and it is observed that the samples deposited at low sputtering pressure contained noticeable amount of oxygen thus forming metal oxynitride, TiN$_x$O$_y$ at lower thickness and deposition time. The presence of oxygen in the film was first visually observed from the dark blue colour reminiscent of titanium oxynitride, before being analyzed using the ion beam technique. Most probably based on the condition of the chamber, it is observed that the films deposited at lower deposition time contained relatively higher amount of oxygen in the TiN$_x$ deposited, while the film deposited at highest deposition time did not contain oxygen. The emission spectra for the films with different thicknesses are shown in Fig. 2(a-d). The chemical composition results from the deposited TiN$_x$ films on the substrate are presented in Table 2. The depositions were activated after the chamber has been stabilized and cleared of extraneous impurities. Based on earlier studies [28,14], it is observed that the main active material at very low sputtering pressure is usually the ionized Ti atoms in the presence of relatively lower pressure flow of nitrogen, however as the sputtering pressure is increased with the attendant increase in nitrogen partial pressure, the fractional flow of nitrogen increases, which causes a decrease in titanium emission. This increase in sputtering pressure condition usually results in the lowering of the deposition rate [14]. Recent studies on other types of films prepared via sputtering technique have shown similar behaviour based on the optimization of the sputtering pressure [29–33]. Considering the sputtering pressure (1.33 Pa) parameter adopted for the present deposition experiment, which is intermediate between low and high sputtering pressure, it is found that nitrogen ions are more active in the chamber during depositions as shown from the chemical compositions of the samples. Recent observations [34,35] have shown that the degree of filling of the non-metallic sub lattice of the nitride increases linearly as the nitrogen content rises, and that is reason parameters, specifically, temperature, time, and partial nitrogen pressure, which affect the nitrogen content, determine the stoichiometry of the titanium nitride formed. Meanwhile, as the sputtering deposition time increases beyond 5 min, the flow of N$_2$ improve further, and the intensity of N$_2$ emission increases in the chamber. This effect accounted for progressive increase in nitrogen concentrations in samples TiN-S2, TiN-S3 and TiN-S4. Studies [36,14] have shown that variation of the plasma parameters also induce changes to the particle fluxes impacting on the substrate surface and it affect the chemical composition of the films. In the present study, as the deposition time increases, there is a corresponding increase in N$_2$ emission in the plasma at the expense of Ti ions. The depth profile indicating the relationship between the elemental constituents of the film as the thickness increases is presented in Fig. 3. As nitrogen ion flux dominates with sputtering time, the deposition chamber environment attained nitriding mode, which further diminish reactive Ti ions emission. Nitriding mode is usually caused by the surface poisoning of the sputtering target, which caused it to be covered with titanium nitride film, and this condition also resulted in low emission of pure Ti ions from targets. It can be seen that as sputtering time increases, the extraneous oxygen in the chamber became exhausted. Hence, no oxygen was detected in films deposited at 20 min with the highest thickness. It is shown that time as crucial parameter can be optimized to obtained thickness dependent stoichiometric compositions. The evolution of the film constituents in
3.2. Microstructural analysis

Scanning electron micrographs with representative surface plot for each film sample at different thicknesses are shown in Fig. 5(a)–(d). The images for samples deposited at time 5 and 10 min (TiN-S1 and TiN-S2) showed homogeneous and smooth background. However, observations of 3-D plots from optical microscopy micrographs indicated the presence of pores distributed on the surface of the films. The observed “pores” present on the films surface are more or less film surface depressions that appeared based on the initial surface topography of the polished steel substrate as shown in Fig. 1. Hence, at low deposition times (5–10 min), the initial films deposited followed the micro-topography of the substrate surface with intermittent depressions, however, at higher deposition time with corresponding higher film thickness, most of the depressions are filled which resulted in the disappearance of most of the “pores”. Meanwhile, for thicker films deposited at longer time (15 and 20 min), the microstructures appeared denser.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RBS (10¹¹ atoms/cm²)</th>
<th>Elemental compositions (100%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN-S1</td>
<td>917.118</td>
<td>Ti 0.3419 N 0.4724 O 0.1857</td>
</tr>
<tr>
<td>TiN-S2</td>
<td>1099.826</td>
<td>Ti 0.2592 N 0.5577 O 0.1831</td>
</tr>
<tr>
<td>TiN-S3</td>
<td>2041.003</td>
<td>Ti 0.3421 N 0.5269 O 0.1310</td>
</tr>
<tr>
<td>TiN-S4</td>
<td>2941.446</td>
<td>Ti 0.3580 N 0.6420 O ND</td>
</tr>
</tbody>
</table>
and smoother compared to 3-D optical image of the bare substrate. In the obtained photomicrographs of the samples, black streaks of graphite phases situated at the grain boundaries and interspersed within the main α-phases are shown. It is observed that the volume fraction of dark grain boundary phases reduces with thickness and time of depositions of TiNₓ film on the surface of the polished low carbon steel sections. The 3-D plots of the samples TiN-S3 and TiN-S4 are shown in Fig. 5(a) and (b), with the formation of microstructured granular shaped crystallites on the dense and smooth background morphology. Compared with thinner films, smaller amounts of pores are present on the surface. In all samples, it is evident that there was an initial formation of the first relatively smooth layer and then gradual accumulation of the granular crystallites. The main discrepancies identified between the films based on their thickness are in term of the appearance of granular particles and surface uniformity. From SEM images, it is observed that the grains appearing on thinner films are smoother, however for thicker samples, microscopic aggregated tetrahedral shaped crystallites well distributed on the substrate can be observed, with a dense morphology. Typical formation of TiN is a crystal structure of NaCl type with a rough 1:1 stoichiometry, meanwhile, in some cases [37–39] unusual effects of superstructure formation, gas bubbles and partial crystallization have been observed on TiNₓ films and these have been attributed to nitrogen oversaturation at higher N₂ concentrations. In this study, the crystallites, which are evenly distributed on surface morphology of higher thickness samples (TiN-S3 and TiN-S4) could be attributed to the presence of superstructure formations. The porosity of coatings is one of the factors that often affect the corrosion resistance, and it is associated with the microstructure of the coating. The denser the film, the higher the packing factor. Thus, the presence of pores is detrimental to coatings such as nitrides used in severe corrosion applications. Meanwhile, as observed from this study as shown in the micrographs (Fig. 5), the formation of pores was drastically suppressed with increase in the thickness of the films.

3.3. X-ray diffraction analysis

The structural details of the TiN thin films sputtered on four different samples of well-polished low carbon steel at varying times of deposition, and in mixture of both argon and nitrogen are shown in Fig. 6. The thinner TiNₓ films deposited at 5 and 10 min show the formation of crystalline phases of mixed orientations of (111), (200) and (110), which are attributed to TiNₓ (JCPDS card no: 38-1420) and rutile TiO₂ (JCPDS Card no. 21-1272), respectively. However, there is a dramatic change from the mixed TiNₓ phases (111) and (200) to a preferred orientation (200), probably with other
undetectable phases as time of deposition increased. The films thickness and composition changed from TiO\(_2\)N\(_2\) to TiN with the increase in the plasma emission of nitrogen which favoured the formation TiN\(_x\). Pelleg et al. [40] proposed that preferred orientation in films lies on the minimization of surface energy and strain energy. In TiN films, orientation (200) has the lowest surface energy, while (111) has the lowest strain energy. It is reported in studies [41,42] that there are no preferred orientations for thinner TiN films due to the randomly oriented grains. Thus, in the early stage of our experiment, the equivalent intensities of (111) and (200) diffraction peaks are related to the nucleation and growth in random orientations. However, with increasing film thickness, thicker samples TiN-S3 and TiN-S4 films adopted a (200) texture to lower surface energy. The spectrum produced by each of the samples shows the relative variations between the film thickness and orientation angle; inter-planar spacing; lattice parameter and crystal size (Table 3). The orientation intensities of the films vary significantly from film to film (Fig. 6). For a TiN specimen with randomly oriented crystallites, the diffraction peaks are expected in the range of 2\(\theta\) = 30–50° are the (111) and (200) peaks as shown in studies [41–43]. The samples show prominent peaks with a strong (200) crystal orientation with increased intensity and slight relative shift in the angle orientation. The grain size in the sputtered nanocrystalline thin films is influenced by a complex interplay of a number of factors. The most important growth parameters influencing the grain size are the substrate temperature, ion bombardment rate and energy flux [44]. In this study, the controllable parameters were kept constant except the deposition time, which expectedly influenced the films thickness, with the resultant effect on the microstructural orientations. In addition, the sputtering pressure usually influence the sputtering rate from the Ti target [14,15]. In this work, the high deposition time remarkably influence the plasma pressure, and thus the ion impingement on the substrate, which favours nitrogen-rich TiN\(_x\) formation. However, previous studies [13,14] indicated that the use of Ar and N\(_2\) mixtures at low sputtering pressure resulted in a metallic mode of sputtering. The lattice parameter (a) and inter-planar spacing (d) were obtained from the XRD analyses, while the crystal size of the samples are estimated using Debye Scherer’s formula [45,46]. The values obtained are in strong agreement with recent studies [21,47,22,35].

\[
D = \frac{K\lambda}{\beta\cos\theta}
\]

where D is the grain size, \(\lambda\) is the wavelength (1.5406 Å for CuK radiation), \(\beta\) is the full width at half maximum (FWHM), and \(K=0.94\) is the shape factor approximately equal to unity. From

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**Fig. 5** – SEM and optical micrographs of the TiN\(_x\) films on samples (a) TiN-S1, (b) TiN-S2, (c) TiN-S3 and (d) TiN-S4.

**Fig. 6** – XRD spectra for the TiN\(_x\) films on low carbon steel at different deposition time.
observation of Fig. 6, it can be inferred that TiN_x films on the low carbon steel become more crystalline with the deposition time.

3.4. Surface micro-hardness properties

The micro-hardness of the TiN coatings was measured at a load of 49.3 mN to avoid the substrate effect. Hardness values were obtained from the average of five measurements on each sample. The variation of micro-hardness with the time of deposition is shown in Table 4. The Vickers hardness for the control sample (LCS) was determined to be 187.3 HV, and it shows the effect of the TiN_x layer on the low carbon steel. It is observed that the Vickers’s micro-hardness values increases linearly with increasing time of deposition. This is largely due to the increasing amount of TiN_x thin film and its grain geometry sputtered on the substrates. It is also observed that hardness averagely increased with the grain size. Similar observation was reported [42], which indicated a slight increase in grain size with thickness of TiN thin films deposited on silicon wafer. Generally, it can be concluded that the TiN films become more crystalline as the time of deposition increases, hence, from the results and observation of the samples, the more crystalline, the harder it becomes. This is not unexpected, because the crystalline phase is ordered and with high cohesion, contrary to the amorphous phase which is less cohesive (Table 4).

4. Conclusions

Polycrystalline TiN_x thin films with RBS thickness ranging from 917.118 to 2941.446 \times 10^{15} \text{ atoms/cm}^2 were deposited on substrates prepared from polished commercial low carbon steel rod sections by DC reactive magnetron sputtering. Using ion beam and EDX analysis, the influence of deposition time and thickness on the film stoichiometry was shown. From the X-ray diffraction analysis, the grain size and preferred crystal orientations were observed to change with thickness and time. Meanwhile, the evolution of the microstructural phases was observed to be in two steps. For relatively thin samples deposited at 5 and 10 min, other crystal phases were detected with the main TiN_x phase with TiO_2 (110) and TiN_x (111) orientations. The next step evolved as the film thickness increases, with increase in reflection intensity of plane (200), which indicate a change of microstructure with single prefered orientation in the film growth process with time. The change in chemical and microstructural depth profile with thickness shows the effect of time variation and optimization on the other sputtering parameters, which influence not only the thickness but also the grain orientations and film stoichiometry. In this study, at 20 min sputtering time, low carbon steel sample with hard nitrogen-rich titanium nitride surface were obtained with Vickers’ hardness value of 267.9 HV.

### Table 3 – Time of deposition, interplanar spacing and crystal size of TiN on low carbon steel.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inter-planar spacing, d ((\text{Å}))</th>
<th>Lattice parameter ((\text{Å}))</th>
<th>Orientation angle ((2\theta))</th>
<th>Grain/crystal size, (l (\text{nm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN-S1</td>
<td>2.0640</td>
<td>4.1280</td>
<td>43.86</td>
<td>0.26</td>
</tr>
<tr>
<td>TiN-S2</td>
<td>2.0890</td>
<td>4.1780</td>
<td>43.31</td>
<td>0.24</td>
</tr>
<tr>
<td>TiN-S3</td>
<td>2.0575</td>
<td>4.1114</td>
<td>44.05</td>
<td>0.38</td>
</tr>
<tr>
<td>TiN-S4</td>
<td>2.0362</td>
<td>4.0724</td>
<td>44.49</td>
<td>0.35</td>
</tr>
</tbody>
</table>

### Table 4 – Vickers’ hardness values for the sputtered low carbon steel surfaces.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition time (min)</th>
<th>Vickers’s hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN-S1</td>
<td>5</td>
<td>230.8</td>
</tr>
<tr>
<td>TiN-S2</td>
<td>10</td>
<td>256.8</td>
</tr>
<tr>
<td>TiN-S3</td>
<td>15</td>
<td>264.9</td>
</tr>
<tr>
<td>TiN-S4</td>
<td>20</td>
<td>267.9</td>
</tr>
</tbody>
</table>

Conclusions

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