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Structural, mechanical and electrochemical comparison of TiN and TiCN coatings on XC48 steel substrates in NaCl 3.5% water solution

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ABSTRACT

Titanium carbonitride (TiCN) and titanium nitride (TiN) were deposited on steel substrates XC48 using magnetron sputtering technique. The hardness of both films increases with the substrate bias voltage and that of TiCN is always greater. The electrochemical behaviors of the deposited films in NaCl 3.5% water solution were studied by using potentiodynamic polarization and optical microscope. The results unambiguously show that the coated XC48 steel displays a better resistance to uniform and pitting corrosion than the bare material and that coating with TiCN enhances furthermore this performance.

1. Introduction

Progress in industry requires the improvement of relevant materials properties (e.g., the wear and corrosion resistance) which can be achieved by coating using PVD methods [1,2]. Recently, coating compounds containing Ti (in TiN, TiCN, TiC etc.) have been investigated as they provide high wear resistance, excellent biocompatibility, high hardness and good chemical stability [1–3]. In addition, due to their variable colours they have been frequently used for decorative applications such as in jewellery, watch cases and eyeglass frames [4]. It is recognized that TiCN and TiN are very effective in enhancing the corrosion resistance [5,6].

In our previous works [7,8], magnetron sputtering was used to deposit TiN, TiC and TiCN on XC48 steel at ambient temperature and low pressure in order to study the effects of the deposition parameters on the physical and mechanical properties of the coatings. The purpose of this work is to investigate the corrosion behavior of the TiN and TiCN coatings on XC48 steel in a NaCl 3.5% solution. The results will be analyzed in the light of the effects of the sputtering parameters (in particular the substrate bias voltage) on their entailed properties. To this end, the potentiodynamic polarization technique and the optical microscopy observations will be used.

2. Experimental details

Titanium nitride (TiN) and titanium carbonitride (TiCN) were deposited onto steel substrates XC48 (samples of 10 mm diameter) by Reactive Magnetron Sputtering technique excited by radio frequency (13.56 MHz) from a pure titanium target (99.999%). The deposition chamber consists of a cylindrical stainless steel reactor of 230 mm diameter and 250 mm height. The substrates were mounted at the midpoint of a circle planetary substrate holder (100 mm in diameter). The distance between the Ti target and the substrate holder was about 30 mm. The pressure control device consisted of a penning and baratron gauges. Argon with high purity (99.99%) was used as the sputtering gas. The reactive gases were nitrogen with high purity (for the TiN) and a mixture of nitrogen and methane (for TiCN). In all the runs, the substrates were not heated. However, the ion bombardment induced a heating of the substrate up to a final temperature that did not exceed 200 °C.

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Table 1
Sputtering conditions for the deposition of TiN and TiCN coatings.

Target	Pure Ti metal
Target–substrate distance	5 cm
Sputtering gas	Ar
Reactive sputtering gases (TiN)	N_2
Reactive sputtering gases (TiCN)	CH_4, N_2
Sputtering gas pressure	10 mTorr
Sputtering parameters	150 W
Bias substrate	0 to −100 V
Deposition time	60 min
Substrate temperature	Not heated

The deposition rates were obtained from the ratio of the coating thickness to the deposition time as described in our previous work [9]. The thickness of the coatings was measured with a stylus profilometer. In order to create a thickness gradient between coated surface and base material, a small glass cover slip was placed on the surface so that the coating thickness could be measured at ±0.1 μm accuracy.

The hardness was evaluated by nanoindentation using a nanoindenter (CSM) system with a Berkovich-diamond indenter. The instrument was operated in the continuous stiffness mode with a maximum load of 100 mN. Hence, the indentation depths are expected to be less than about 150 nm (less than15% of the coating thickness) allowing minimizing the interference of the substrate hardness. In order to avoid the effect of non-uniformity of the coating, a series of 10 indents was performed and the results were averaged. The indents were separated by about 10 μm for preventing overlapping effects.

The surfaces of the samples (before and after the electrochemical tests) were characterized by optical microscope. The sputtering parameters are given in Table 1. Supplementary details of the experimental procedures can be found in our previous works [7–11].

The electrochemical behavior of the TiN and TiCN coatings on XC48 steel in a NaCl 3.5% solution was studied using an EG&G 273A potentiostat controlled by the Softcorr M352. Prior to each measurement, the sample was exposed to corrosion test at open circuit potential in the corrosion test solution for 3 h to ensure the stabilization potential. All the experiments were conducted at constant temperature 25 °C. The polarization curves were plotted by scanning the electrode potentials at 1 mV/s. A saturated calomel electrode (SCE) was used as reference (to measure the potential across the electrochemical interface) and a platinum sheet as counter electrode. Data were automatically collected and analysed using Softcorr M352 and CView2 Soft. The corrosion current density of each sample was determined by extrapolating the linear parts of the anodic and cathodic branches of the polarization curves following Tafel plot method principle. The corrosion potential (E_{corr}), the corrosion current (i_{corr}), the anodic Tafel slope (B_a) and the cathodic Tafel slope (B_c) were measured.

3. Results and discussion

3.1. Deposition rate

Fig. 1 shows the deposition rates of TiN and TiCN as a function of the substrate bias voltage (V_{SB}). For both components, the deposition rate decreases as V_{SB} increases. The reduction of deposition rate can be ascribed to the re-sputtering effects provoked by the bias voltage (i.e., kicking off the added atoms or growing surface by the incoming ions [12]).

3.2. Hardness

The variations of the hardness of the deposited TiCN and TiN as a function of the substrate bias voltage V_{SB} are shown in Fig. 2. It can be seen that the hardness of TiCN is always higher than that of TiN. Indeed, when V_{SB} changes from 0 to −100 V, the hardness of TiCN increases from 16 GPa to a maximum of about 39 GPa. In the case of TiN, it increases from 4.9 GPa to a maximum value of 34.1 GPa and then decreases to 30 GPa. The measured maximum values of the hardness of the coatings are achieved at about the same substrate bias (−75 V). These results are in agreement with those suggested elsewhere [13,14]. The increasing hardness of TiCN and TiN with the applied negative substrate bias voltage can be assigned to the induced microcrystalline structure in the nanocomposite coating [15].

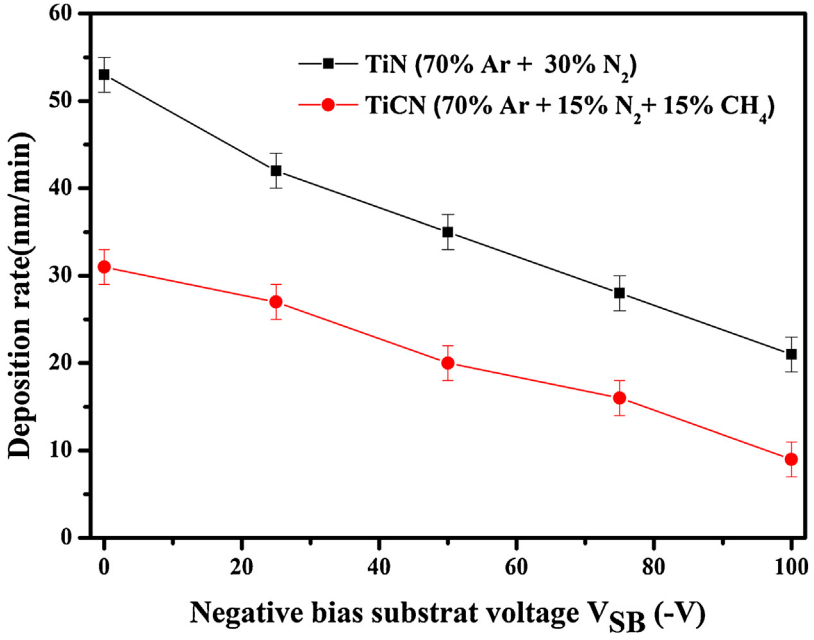

Fig. 1. Deposition rate of TiN and TiCN versus the negative substrate bias voltage V_{SB}. The total pressure is 10 mTorr and the power 150 W.

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