Effect of the inert/reactive gases ratio and bias voltage on the tribological properties of VN coatings

S Rabadzhiyska1, M Ormanova, N Ivanov and P Petrov

Acad. Emil Djakov Institute of Electronics, Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee, 1784 Sofia, Bulgaria
E-mail: s_rabadjiiska@ie.bas.bg

Abstract. Vanadium nitride (VN) thin films were deposited on 304L high-speed stainless steel (HSS) specimens using a DC reactive magnetron sputtering system. The experiments were carried out with a varying ratio of reactive/inert gases of 1.7, 2.3 and 3 and a negative substrate bias of −30 V, −40 V and −50 V. Grazing incidence X-ray diffraction was used to characterize the structure of the layers produced. The coatings’ roughness and tribological behavior was evaluated.

1. Introduction

In recent years, transition metal nitrides have been used widely as protective hard coatings in view of increasing the lifetime and performance of cutting and forming tools. Because of their outstanding mechanical, optical, electrical and magnetic properties, the nitride coatings have been successfully explored in the last few decades for many industrial and lightweight applications [1-3].

Vanadium nitride (VN) has received increasing attention in recent years due to its typical properties, including extreme hardness, high melting point, wear and corrosion resistance, good electrical and heat conductivity, stability at high-temperatures, as well as good catalytic activity [4,5]. Owing to these properties, VN have found a wide-range of technological applications as field emitters, superconductors and buffer layers in microelectronics. The frequent application of VN as an important steel additive can be ascribed to its beneficial effect on fine grain and precipitation strengthening, which can improve the overall performance of the steel and reduce the cost of the smelting process by using nitrogen to decrease the vanadium content in the steel [6-8]. Reactive magnetron sputtering is among the most commonly applied methods for production of dense, high-quality VN films with excellent adhesion of the coatings to the substrate.

The microstructure characteristics of VN coatings are generally influenced by the processing parameters, including the applied bias voltage, current, deposition time, substrate materials, heat treatment and pressure of the working and inert gases. The substrate bias voltage and target current play an important role in determining the mechanical properties of the coatings, while the combination of appropriately selected technological parameters enhances the morphological, tribological and corrosion properties of the coatings.

The aim of the present work is to characterize VN coatings deposited at various bias voltages and reactive/inert gas ratios. For this purpose, experiments were performed using magnetron sputtering and 304L stainless-steel substrates, because this steel is widely used in industrial and medical applications.
applications. The morphological characteristics of the layers prepared were assessed, together with the variation of the tribological properties with the bias voltage.

2. Materials and methods

Samples of 304 L stainless steel containing: 0.029 wt% C; 0.3 wt% Si; 1.6 wt% Mn; 0.026 wt% P; 0.001 wt% S; 0.065 wt% N; 18.06 wt% Cr and 8.0 wt% Ni, were used as substrates for deposition of ceramic VN coatings by DC reactive magnetron sputtering. The diameter of the sputtered target was 100 mm; the purity of V was 99.8%. Before the deposition, the substrate surface was etched by Ar⁺ plasma for 10 min to eliminate any oxide layers.

Two sets of experiments were carried out at different technological parameters. The first set of coatings was produced to assess the influence of the bias voltage on their mechanical properties. For this purpose, three samples were prepared at −30 V, −40 V and −50 V. The second series of coatings was prepared to evaluate the effect of the ratio of reactive/inert gas on the coatings’ hardness and tribological properties; reactive/inert gas ratios of 1.7, 2.3, and 3 were used. The deposition temperature was kept constant (350 °C).

The crystalline structure of the coatings was characterized by grazing incidence X-ray diffraction. An X-ray diffractometer equipped with a parabolic X-ray mirror, a parallel plate collimator and a scintillation detector with Cu Kα radiation at an angle of 3° was employed. The experiments were carried out at 2θ from 30° to 40° with a step of 0.05° and scan step time of 1.5 s. The phase identification was performed using the International Center for Diffraction Data (ICDD) database. An AFM Universal Nanomechanical Tester (UNMT) with a 10-nm curvature radius of the silicon tip (Bruker Surface Analysis, USA) was used to characterize the nano-surface topography. The studies were realized in a non-contact mode, each surface being scanned at different locations with a scanning area of 80×80 μm. The tribological behavior of the samples was investigated by ball-on-flat dry slide examination on a UMT-2M (Bruker-CETR) tribotester with a hardened steel ball (Cr coating) at a loading force of 2 N for 5 and 10 min at room temperature (~25 °C) and relative air humidity 30 – 40%.

3. Results and discussion

Figure 1a) shows XRD patterns of the VN coatings deposited at three different bias voltages. A high-intensity Bragg peak at 2θ = 43.67° is seen corresponding to reflections from (200) planes, which indicates a high degree of crystallinity along this orientation; the other Bragg peaks of lower intensity at 2θ = 37.08° and 2θ = 64.2° are associated with reflections from the (111) and (220) planes, respectively [11-13]. The phase identification indicated the presence of VN and V₂N crystal phases. Thus, the aforementioned orientations correspond to a face-centered cubic (fcc) NaCl-type Fm3m structure related to the δ-VN phase. This is in agreement with JCPDS PDF #35-0768 for VN and #33-1439 for V₂N from the ICDD card [14-16]. As can be seen in the figure, increasing the bias voltage to −50 V leads to the V₂N phase peak almost disappearing due to the instability of this phase. Figure 1b) displays XRD patterns of thin VN films formed at different inert/reactive gases ratios. The patterns show the presence of an fcc VN phase with space group Fm3m (225) and reflections corresponding to the (111), (200) and (220) crystallographic planes [13]. Apparently, the grains oriented in the (200) direction predominate, as (200) becomes more pronounced at the higher P_N/P_Ar = 2.3.

Table 1 summarizes the results for the lattice parameters and microstrain of the VN films prepared at different bias voltages (−30 V, −40 V, −50 V) and P_N/P_Ar (1.7, 2.3, 3). The experimentally determined lattice parameters for all crystallographic directions are in agreement with those in the database, which is evidence for the low degree of microstrain of the VN coatings deposited by us under the technological conditions quoted above.

The surface morphology of the VN coatings deposited at different bias voltage and inert/reactive gases ratio was assessed by atomic force microscopy. Figure 2 presents three-dimensional AFM images of the VN ceramic coatings produced at the three different bias voltages. Except the average roughness Sₐ, the heights distribution can also be evaluated to determine the asymmetry parameter Sₐₖ.
Complete symmetry of the heights distribution is observed when $S_{ik} = 0$. Values exceeding 0 correspond to an asymmetric distribution.

![XRD pattern of VN coatings deposited at different: a) bias voltage; b) ratio of reactive/inert gases.](image)

**Figure 1.** XRD pattern of VN coatings deposited at different: a) bias voltage; b) ratio of reactive/inert gases.

| Lattice parameters (nm) | Microstrain |
|-------------------------|-------------|
|                         | 111         | 200 | 220 | 111 | 200 | 220 |
| 30V                     | 0.4197 | 0.4141 | 0.409 | 0.0138 | 0.0005 | -0.0118 |
| 40V                     | 0.4179 | 0.4137 | 0.4085 | 0.0097 | -0.0005 | -0.0131 |
| 50V                     | 0.4169 | 0.4146 | 0.4116 | 0.0072 | 0.0016 | -0.0057 |
| 1.7                     | 0.4137 | 0.4146 | 0.4078 | -0.0006 | 0.0015 | -0.0146 |
| 2.3                     | 0.4169 | 0.4146 | 0.4116 | 0.0072 | 0.0016 | -0.0057 |
| 3                       | 0.4153 | 0.4141 | 0.4073 | 0.0033 | 0.0005 | -0.0158 |

**Table 1.** Lattice parameters and microstrains along the (111), (200) and (220) orientations for different bias voltage and ratio of reactive/inert gas.
The values obtained are shown in Table 2. As seen, the bias voltage affects strongly the surface roughness of the VN films (Figure 2). In fact, as the bias voltage is raised from $-30$ V to $-40$ V, the average roughness reaches 324.2 nm, compared to 151.6 nm at $-50$ V. Also, the substrate bias voltage affects the crystallites size, but not the texture of the coatings. Higher values of the bias voltage (up to $-100$ V) lead to a decrease of the crystallites size forming the coating. A lower bias voltage corresponds to a bigger size of the crystallites in the coating [17-20]. The $S_h$ values correspond to asymmetrical heights distributions for all bias voltages applied. The same tendency is observed for this parameter for the VN coatings obtained at different ratios of inert/reactive gases, namely, the highest surface roughness value of 308.6 nm is seen at the lowest ratio of 1.7. Increasing this ratio in the magnetron system, the average roughness drops drastically to 151.6 nm, which is more than twice.

The friction coefficients measured by ball-on-flat tests of the VN coatings formed under various technological conditions, namely, bias voltage and ratio of inert/reactive gases, at room temperature...
are shown in Table 2. The results demonstrate that for a friction time of 5 minutes, the lowest friction coefficient (COF, 0.4579) is measured for the VN film prepared at a bias voltage of −50 V, while the highest COF is exhibited by the film deposited at −30 V (0.5809). Raising the friction time to 10 minutes results in similar COF values of the films formed at −30 V and −50 V, while the friction coefficient of the VN film deposited at −40 V is slightly higher. A weak increase is noticed in the COF for all coatings, except for one obtained at −30 V, where there is a small drop. The highest friction coefficient is obtained at a 1.7 ratio of gases for a friction time of 5 minutes. The same trend is noticed for the friction time of 10 minutes, when the COF continues rising. However, the VN layer produced at a ratio of 2.3 shows a higher friction coefficient for a friction time of 5 minutes.

**Table 2.** Statistical parameters of the average surface roughness Sa, the asymmetry parameter Sas, and friction coefficient (under different loading and friction time) of VN coatings deposited at different bias voltage and ratio of reactive/inert gases.

| Voltage | Sa, nm | Sas, nm | COF time 5 min | COF time 10 min |
|---------|--------|--------|---------------|----------------|
| VN -30V | 193.8  | 0.250  | 0.5809        | 0.5446         |
| VN -40V | 324.2  | 0.256  | 0.4787        | 0.5593         |
| VN 50V  | 151.6  | 0.560  | 0.4579        | 0.5226         |
| VN 1.7  | 308.6  | 0.118  | 0.5801        | 0.6187         |
| VN 2.3  | 151.6  | 0.560  | 0.4579        | 0.5226         |
| VN 3    | 128.1  | 0.465  | 0.5442        | 0.5571         |

To summarize, the thin VN film grown at a bias voltage of −50 V and an inert/reactive gas ratio of 2.3 demonstrated the best combination of tribological and morphological properties, namely, low COF and roughness. Raising or lowering the gas ratio leads to the deposition of coatings with high values of the COF and the roughness, which is an undesired effect for VN films intended for modern applications. The XRD patterns indicate the presence of VN and the unstable V2N crystal phase. The peak of highest intensity at 2θ = 43.67° corresponds to reflections from the (200) planes for different bias voltages and gas ratios.

**4. Conclusions**

Thin VN coatings were deposited on 304 L stainless steel at a bias voltage of −30 V, −40 V, −50 V and inert/reactive gas ratio of 1.7, 2.3, 3 by DC magnetron sputtering with the aim to study these parameters’ effect on the structural, morphological and tribological properties of the coatings. The XRD results showed the presence of a face-centered cubic (fcc) VN phase with space group Fm3m (225) and reflections corresponding to the (111), (200) and (220) crystallographic planes. Increasing the bias voltage and the gases ratio resulted in the growth of VN layers with a lower surface roughness and low microstrain values. These results were confirmed by the estimated lattice parameters values, which were close to the ones cited in the ICDD database. The lowest COF (0.45) was exhibited by the VN film fabricated at −50 V and a 2.3 gas ratio. The low surface roughness value and the small friction coefficient of the deposited VN coatings are evidence for the films’ high wear resistance.

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