Surface & Coatings Technology 205 (2011) S29–S32

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

The structure and properties of VN-VCN-VC coatings deposited by a high energy ion assisted magnetron sputtering method

E. Grigore *, C. Ruset, C. Luculescu

National Institute for Laser, Plasma and Radiation Physics, 409 Atomistilor Street, PO Box MG-36, Magurele-Bucharest, Code 077125, Romania

ARTICLE INFO

Available online 15 March 2011

Keywords:
Magnetron sputtering
Ion implantation
Hard coatings
Vanadium nitride
Vanadium carbide

ABSTRACT

In the last years the scientific interest for transition metal compounds, used for protective and functional coatings, was extended and included, besides Ti, other elements such as Zr, V, and Hf as potential candidates. Due to their promising mechanical properties, and resistance to high temperature, V compounds received an increasing attention from scientists and end-users.

The present work is dedicated to the study of the characteristics and the properties of the vanadium based multilayer hard coatings deposited by a magnetron sputtering process, assisted by a high voltage pulse discharge. Different multilayer coatings (VC/VN, VN/VC, VN/VCN/VC) were obtained and comparatively analyzed relative to vanadium nitride and vanadium carbide monolayers. Coatings with microhardness up to 3700 HV 0.05 and thickness up to 20 μm have been produced.

Elemental and phase composition, as well as tribological characteristics (wear factor and friction coefficient) of the coatings were investigated. The chemical and structural investigations were performed by GDOES (Glow Discharge Optical Emission Spectrometry), EDX (Energy Dispersive X-ray analysis), XRD (X-ray Diffraction) and SEM (Scanning Electron Microscopy), while microhardness measurements and wear test were used to assess the coatings characteristics. The friction coefficient and the wear resistance of the coatings were evaluated by using pin on disc tests in unlubricated conditions.

1. Introduction

Transition metal compounds, such as carbides and nitrides, deposited as thin coatings on metallic substrates have been widely investigated and used in industrial applications due to their remarkable mechanical and functional properties. Starting the early 80's, titanium nitride, obtained by *PVD* (Physical Vapor Deposition) methods, has been used as wear resistant coating for high speed steel cutting tools, since then becoming a benchmark coating for machining operations. Other transitional elements such as Zr, V, or Hf have been often used in combination with Ti, but their potential has not been yet fully exploited. These elements have been used, for many times, as a secondary alloying element in titanium based compounds. However, in this respect, a large number of scientific papers emphasized the beneficial role of vanadium in multiphase systems like Ti-V-N and Ti-Al-V-N [1–3].

As far it concerns vanadium compounds, carbides and nitrides, a survey of the published studies showed that the balance inclines obvious to vanadium nitride. While vanadium nitride layers have been studied and often used as a component layer in superlattice structures [4,5], vanadium carbide coatings received less attention.

Vanadium carbide are usually obtained by *TRD* (thermo reactive diffusion) a treatment performed in salt baths at elevated temperatures (850–1050 °C) [6,7]. This treatment has some disadvantages related to long treatment period (0.5–10 h) necessary to achieve thickness in the range 5–15 μm, and high processing temperature which can induce serious distortions to the mechanical components. *PVD* methods, on the other hand, can be used to produce a large numbers of compounds, from the category of carbides and nitrides, at a relative high deposition rate (1–4 μm/h) and at low substrate temperatures. In these circumstances *PVD* methods can represent a serious competitor for producing vanadium carbide coatings. Up now only few studies reported the synthesis of vanadium carbide by different methods such as: *PLD* (pulsed laser deposition) [8], magnetron sputtering [9,10] or electron beam deposition [11].

CMSII (Combined Magnetron Sputtering and Ion Implantation) is a magnetron sputtering deposition method, assisted by a pulsed high voltage discharge, that proved to be suitable for producing coatings of 10–20 μm with improved characteristics concerning adhesion, microhardness and high thermal flux resistance [12–14].

In this work the results concerning the microstructural, compositional and functional investigations of the vanadium compounds (nitride and carbide) deposited in multilayer structures will be reported.

* Corresponding author. Tel.: +40 21 4574490; fax: +40 21 4574243.
E-mail address: edigrig@infim.ro (E. Grigore).

0257-8972/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2011.03.023

2. Experimental

Two types of materials were used as substrates: samples made of plain carbon steel C15 (wt.%: C 0.12, Mn 0.53, Si 0.09, Cr 0.06, Ni 0.09, and Fe in balance) with a hardness of 186 HV and M2 HSS steel (wt.%: C 0.88, Mn 0.25, Cr 3.82, Mo 4.2, V 1.84, W 6.2, Si 0.25 and Fe in balance) samples with 900 HV hardness. The samples dimensions were: $30\times20\times3$ mm. The C15 samples were mirror polished on silicon carbide papers and then on diamond paste ($R_a = 0.023$ μm), while the HSS samples were polished just on silicon carbide papers ($R_a = 0.132$ μm).

The deposition was performed by using the CMSII method [12,13]. The samples were cleaned ultrasonically in acetone bath for 15 min, and then were dried in warm air. Inside the vacuum chamber the samples were mounted on a rotating substrate holder positioned at a distance of 90 mm above the magnetron target. The magnetron target was a vanadium disc (purity 99.5%) of 74 mm in diameter and 6 mm thickness. The vacuum chamber was pumped down to a limit pressure of 4×10^{-4} Pa and then it was filled up with Ar up to working pressure (6.6×10^{-1} Pa). The general deposition parameters were the following: magnetron discharge current 1.5 A, magnetron voltage 400–500 V, DC substrate bias voltage −100 V, DC bias current 0.6 A . Simultaneously with DC bias, high voltage pulses with amplitude of 40 kV, and duration of 20 μs were applied on the substrate at a frequency of 25 Hz. During the deposition the samples temperature did not exceed 593 K.

The coatings were deposited at reactive volumetric flow rates optimized, in order to obtain the highest microhardness values for each type of coating. A mixture consisting in argon and reactive gas was used as deposition atmosphere. The argon flow rate of 8 sccm was maintained constant for all experiments. Nitrogen (N_2) and butane (C_4H_{10}) were used as reactive gases. The nitrogen volumetric flow rate, used for deposition of vanadium nitride coatings, was 1.5 sccm, while the butane volumetric flow rate, used for deposition of vanadium carbide was 0.9 sccm.

Each type of multilayer structure was deposited sequentially in the same run, starting with a vanadium adhesion interlayer followed by a vanadium nitride and then by a vanadium carbide layer for the VN/VC multilayer. In the case of the VC/VN multilayer, the coating sequence was the following: vanadium interlayer, vanadium carbide and finally vanadium nitride. In this way the multilayer structures presented in Table 1 were produced. For comparison reasons VN and VC monolayer structures were also produced and analyzed. A three layer structure of VN/VCN/VC was deposited and analyzed too. The volumetric flow rates used for deposit the intermediate VCN layer were the following: nitrogen 0.8 sccm and butane 0.5 sccm.

The phase structure was determined by XRD, using a Rigaku MiniFlex II diffractometer. The analysis was performed in Bragg–Bretano geometry using a Cu Kα radiation. A FEI-Inspect scanning electron microscope has been used to investigate the morphologies of the coatings. EDX analysis has been also used to investigate the chemical composition after the wear test.

Table 1

Coating	Volumetric flow rate (sccm)	Thickness (μm)	Microhardness HV 0.05	Friction coefficient	Wear factor (m^3/Nm)$\times10^{-16}$
VN	1.5	8.5 ± 7%	2970 ± 5.7%	0.62	0.89
VN/VC	1.5/0.9	6.1/6.6 (±7%)	3762 ± 7%	0.56	0.052
VN/VCN/VC	1.5/(0.8 + 0.5)/0.9	9.0/6.3/6.6 (±7%)	3380 ± 6.4%	0.50	2.03
VC/VN	0.9/1.5	6.9/5.7 (±7%)	2849 ± 5.5%	0.58	1.63
VC	0.9	11.1 ± 8%	3720 ± 6.9%	0.55	3.07
HSS	–	–	900 ± 1.2%	0.78	173

The microhardness and the thickness of the coatings were measured using an AHOTEC F700 microhardness tester equipped with automatic image acquisition system and measurements software. Measurements were performed with a Vickers indenter at loads of 50 and 100 g respectively.

The wear properties (friction coefficient and wear rate) of the coatings were evaluated using a pin-on-disc tribometer (CSEM-Instruments). During tests, the samples rotate against a stationary sapphire ball of 6 mm diameter. The tests were conducted for a sliding distance of 500 m in un-lubricated conditions and at a contact load of 10 N and at a speed of 0.5 m/s. The results were analyzed taking as a reference a M2 sample. After the tests, the wear loss was evaluated by measuring the profile of the wear track and integrating the wear profile. Five regions have been used for measure the wear track, the results represent average values of the measurements. A Dektak 150 surface profilometer has been used to obtain the wear profile. The wear factor, defined as $k = V/LS$, where V is the wear volume, L is the normal load, and S is the total distance of sliding, was used to rank the wear performance of each coating.

3. Results and discussions

The C15 coated samples were used for GDOES, XRD and SEM investigations, while the M2 coated samples were used for tribological measurements. The chemical composition of the coatings was determined by GDOES investigations. The results are presented as average concentrations in the plateau regions of the GDOES depth profiles. It has been determined that the nitrogen concentrations for the vanadium nitride coatings was 13 at.% (4.1 wt.%), while the carbon concentrations corresponding to vanadium carbide coatings raised up to 30 at.% (9 wt.%).

In Fig. 1 a typical GDOES depth profile for a VC/VN coating is shown. It can be seen that the elemental profiles of the components are relative constant along each layer. On top, a shallow oxide layer is formed due to the air exposure. From the GDOES depth profiles the thickness of each layer can be observed too. The small shoulder in the V profile, at the interface, can be attributed to vanadium adhesion interlayer of 1.5–2 μm. As it can be observed in the Fig. 1 the thickness of the vanadium carbide layer (6.9 μm) is higher than the thickness of the vanadium nitride (5.7 μm) layer although the deposition time for each layer was the same (1.5 h). This fact is due to a higher deposition rate for vanadium carbide compared to vanadium nitride.

XRD analysis revealed the nature of the phases formed in the deposition process. Vanadium nitride single layer reveals the diffraction lines corresponding to hexagonal β-V_2N (PDF 01-071-0618) phase

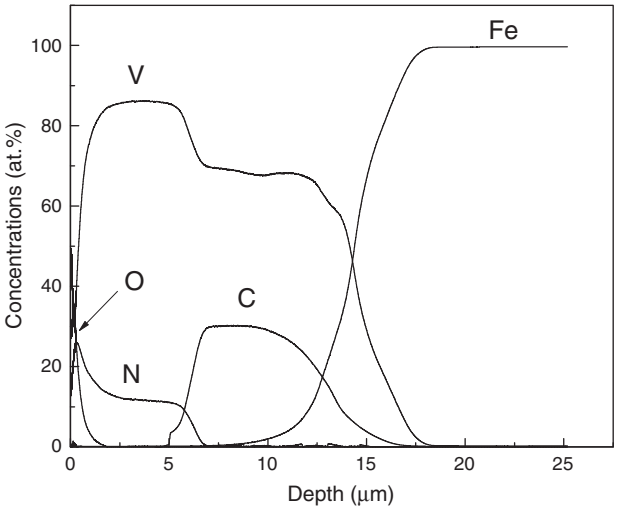

Fig. 1. GDOES depth profile for a VC/VN multilayer structure.