Surface & Coatings Technology 238 (2014) 216–222

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Temperature dependence of the residual stresses and mechanical properties in TiN/CrN nanolayered coatings processed by cathodic arc deposition

F. Lomello [a,b,*], M. Arab Pour Yazdi [c], F. Sanchette [d], F. Schuster [e], M. Tabarant [b], A. Billard [a,c]

[a] LRC CEA-IRTES-LERMPS-UTBM, site de Montbéliard, 90010 Belfort cedex, France
[b] DEN/DANS/DPC/SEARS/LISL CEA Saclay, 91191 Gif-sur-Yvette, France
[c] IRTES-LERMPS-UTBM, site de Montbéliard, 90010 Belfort cedex, France
[d] Institut Charles Delaunay, Laboratoire des Systèmes Mécaniques et d'Ingénierie Simultanée — UTT, Antenne de Nogent-52, Pôle Technologique de Haute-Champagne, 52800 Nogent, France
[e] CEA Cross-Cutting program on Advanced Materials Saclay, 91191 Gif-sur-Yvette, France

ARTICLE INFO

Article history:
Received 3 September 2013
Accepted in revised form 30 October 2013
Available online 9 November 2013

Keywords:
Cathodic arc deposition
Titanium and chromium nitrides
Superlattices
Mechanical properties
Tribological properties

ABSTRACT

Nanolayered TiN–CrN coatings were synthesized by cathodic arc deposition (CAD) on M2 tool steel substrates. The aim of this study was to establish a double-correlation between the influence of the bilayer period and the deposition temperature on the resulting mechanical–tribological properties.

The superlattice hardening enhancement was observed in samples deposited at different temperatures — i.e. without additional heating, 300 °C and 400 °C. Nonetheless, the residual compressive stresses are believed to be the responsible for reducing the hardness enhancement when the deposition temperature was increased. For instance, sample deposited without additional heating presented a hardness of 48.5 ± 1.3 GPa, while by increasing the processing temperature up to 400 °C it was reduced down to 31.2 ± 4.1 GPa due to the stress relaxation. Indeed, the sample deposited at low temperature which possesses the thinnest bilayer period (13 nm) exhibited better mechanical properties. On the contrary, the role of the interfaces introduced when the period is decreased seems to rule the wear resistance.

1. Introduction

It is well known that nanostructuring by layering two transition element nitrides permits to enhance the mechanical properties compared with standard multilayered coatings, the so-called superlattice coatings [2,3]. Many authors concentrated the studies around the nanolayered coatings after the publication of Cahn [4]. This author suggested that by creating alternated layers of different materials, it would be possible to create an efficient dislocation barrier. As a consequence, the inhibition of dislocation motion due to the layer coherency strains increases the total interface area, thus obliging to glide throughout the layers [5]. The second condition is to decrease layer thickness with the aim of avoiding the dislocation generation (≈100 atomic layers or less) and its pile-up. The strength improvement can be explained by applying the formula $Q = (G_A - G_B) / (G_A + G_B)$ where G_A and G_B are the shear moduli of the single constituents [6]. For this reason, it is necessary to possess differences in terms of elastic constants.

In the literature many studies have *experimentally* shown the hardness and the elastic moduli enhancement for different binary nitride systems [7,8]. Indeed, Ducros et al. ascribed the hardening effect to the accommodation of lattice parameter mismatch at the isostructural nitride/nitride interface which is reliable for inducing local strain, therefore impeding the dislocation motion [9].

Tribological properties are also improved in nanolayered coatings as shown by Mendibide et al., since the cracking is deviated at the interfaces due to a fluctuating stress field [10]. Furthermore, Ducros et al. and other authors attributed the enhanced tribological behavior to the higher hardness accompanied by the formation of TiO_2 and Cr_2O_3 during wear tests which allow to reduce the coefficient of friction [8,11]. These oxides provide an external protection to the wear scar.

In this study, TiN/CrN nanolayered coatings were produced by vacuum cathodic arc deposition. These processes are one of the most suitable due to the higher energy ion bombardment during growth [1,12]. The choice has been made thinking in the future *industrial up-scaling*.

As a matter of fact, the production of hard coatings with different periods could be easily up-scaled into industrial reactors only by varying the turntable principal rotation as shown by Ducros et al. [13]. Furthermore, in their work, the authors showed that deposition of nanolayered coatings on cutting tools was the optimal solution for machining Ni based superalloys. It allows to reduce the machining forces, thus limiting the built-up edge phenomenon which consequently leads to increase the tool lifetime [8,14].

During the sample production, deposition parameters such as turntable rotation speed, which permits to control the period thickness, as

* Corresponding author at: CEA Saclay, Bât. 391, 91191 Gif-sur-Yvette, France. Tel.: +33 1 69 08 44 08.
E-mail address: fernando.lomello@cea.fr (F. Lomello).

0257-8972/$ – see front matter
http://dx.doi.org/10.1016/j.surfcoat.2013.10.079

well as the deposition temperatures, were varied in order to obtain a range of mechanical properties. The main aim of the study was to contribute to the actual knowledge about the temperature effects on the mechanical–tribological properties of nanolayered thin films.

2. Material and methods

Multilayer coatings were deposited by using a machine IMD 700 Plassys system equipped with 4 random arc BMI sources (100 mm in diameter) and a threefold rotating substrate was used. The turntable speed of the threefold rotating substrate was set in the 1 → 4 revolutions per minute (rpm) range. Pure titanium and chromium targets (Purity 99.99%) were mounted in opposite direction following the configuration as shown by Ducros et al. [13].

AISI M2 HSS substrates (63 HRc — $\Phi = 30$ mm) were employed in this study. Substrates were degreased in alcohol before deposition.

Argon etching was performed at 0.3 Pa in pure argon (bias ≈ −800 V) during 30 min prior to perform Cr etching in pure Ar at 1 Pa (bias ≈600 V) for 10 min ($I_{Cr} = 60$ A). Subsequently, the coatings were deposited in pure nitrogen atmosphere at a pressure of ≈2 Pa with −150 V of bias voltage (MDX 10 kW, Advance *Energy*). In order to quantify the temperature effect on the mechanical–tribological properties, samples were deposited at different temperatures in the substrate holder without additional heating (labeled as RT) – final temperature ≈250 °C – at 300 °C and at 400 °C. All the experimental conditions are resumed in Table 1.

The fracture cross-section and polished surfaces were observed by means of a thermal field emission scanning electron microscope (FE-SEM JEOL JSM-7800F).

The X-ray diffraction pattern evolution was performed by using a *XRD Bruker D8 Focus* device in a θ–2θ mode ($CoK_{\alpha}1$ radiation — $\lambda = 1.788970$ Å).

Profile composition was measured by glow discharge optical emission spectroscopy (GD-OES). Depth profile analysis on substrates was conducted by means of *Horiba RF GD-Profiler 2* equipped with a 4 mm. diameter copper anode and operating in Ar atmosphere. GD-OES measurements were carried by operating a radio frequency discharge, a pressure of 650 Pa and 30 W of power [15,16]. Profiles were analyzed by using *Jobin Yvon Quantum Intelligent Quantification* software.

Hardness and the effective Young's modulus $E^* = E / (1 - \nu^2)$ – where E and ν are the Young's modulus and Poisson ratio respectively – of coatings were measured by means of a nanohardness tester (NHT CSM Instruments) using a *Berkovich* diamond tip from loading/unloading curves. The *Oliver and Pharr method* [17] was employed. Final values were calculated from an average of 40 indentations with imposed penetration depths shallower than 10% of the coating thickness, according to the Bückle's rule [18]. Young's modulus values thus obtained could be overestimated because of the substrate influence on thin film elastic response for relative indentation depth above 1–2% of coating thickness [19].

Residual stress was determined using a bending method. Curvature of steel foils was measured by optical profilometry (ALTISURF 500) and the stress level was deduced from the Stoney's Equation [20].

Ball-on-disk tests were performed by using a CSM tribometer. As counter material, a WC/Co ball of 6 min diameter was employed. The tribological tests were conducted following fixed conditions: in air, a constant load of 10 N, a wear track nominal diameter of 10 mm, a sliding velocity of 100 mm s^{-1}, a sliding distance of 600 m, a relative humidity between 33 and 39%RH and a temperature range of 19–25 °C.

A white-light profilometer (ALTISURF500) allowed to measure the 2-D profiles of the wear scars after ball-on-disk tests at four different areas. The resolution is 10 nm on the height measurements (*z*-height), while its spatial resolution is 0.5 μm (*x* direction). In the present study, the scanning speed was fixed at 15 μm s^{-1}.

Table 1
Deposition parameters.

Target current	≈100 A
Target voltage	≈−20 V
Nitrogen pressure	2 Pa
Substrates	M2 HSS, 63 HRc
Bias voltage range	−150 V
Turntable rotation speed	1 → 4 rpm
Deposition time	90 min
Deposition temperature	≈250 °C, 300° & 400 °C

3. Results

3.1. Structure and composition analyses

The XRD diffraction patterns are shown in Fig. 1. The scanning speed was fixed at 0.02 $2\theta \cdot s^{-1}$ for these patterns in the 30–60° range. The crystalline microstructure matches with the NaCl-B1 face-centered cubic (FCC)-type structure of titanium and chromium nitride (JCDD cards # 03-065-0565 and # 01-077-0047).

A conventional growth is observed corresponding to the (111) lowest packing density and the lowest strain energy [21]. Nevertheless, in samples processed at 4 rpm, two first-order positive and negative satellite reflections appeared along the (1 1 1) reflection, thus confirming the superlattice structure. This phenomenon is often observed when the modulation period of two materials (high density of interfaces) with similar NaCl-B1 type structure and lattice parameters is reduced [1]. In this particular case, the result is the formation of a microstructure following a specific growth direction (1 1 1) through the interfaces.

For a sake of clarity, the X-ray diffraction patterns containing the two first order satellite peaks around the (1 1 1) reflection are presented in Fig. 2.

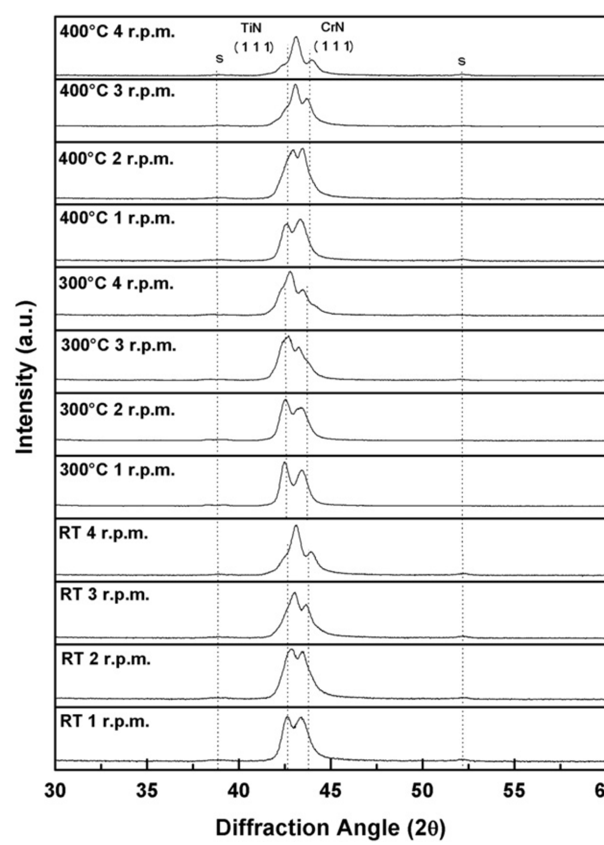

Fig. 1. X-ray diffraction patterns of TiN/CrN coatings deposited at different conditions ("s" = indexes of the substrate peaks).