Surface & Coatings Technology 206 (2012) 2877–2883

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

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

Effect of the bias voltage on the structure of nc-CrC/a-C:H coatings with high carbon content

L. Yate *, L. Martínez-de-Olcoz, J. Esteve, A. Lousa

Departament de Física Aplicada i Óptica, Universitat de Barcelona, Martí i Franquès 1, E-08028 Barcelona, Spain

ARTICLE INFO

Article history:
Received 9 August 2011
Accepted in revised form 10 December 2011
Available online 21 December 2011

Keywords:
Nanocomposite coatings
Chromium carbide
Amorphous carbon
Cathodic arc

ABSTRACT

Nanocomposite coatings consisting of a hard nanocrystalline carbide phase and a-C:H amorphous matrix are the focus of many investigations because of their mechanical and tribological properties such as high hardness, low friction coefficient and high resistance to wear. In this work, nanocomposite coatings of nanocrystalline chromium carbide embedded in an amorphous matrix (nc-CrC/a-C:H) were deposited onto silicon substrates by cathodic vacuum arc deposition using a Cr target in an Ar/C_2H_2 gas mixture atmosphere. A linear magnetic shield was employed to reduce the macroparticle content in the films. A range of negative bias voltages from 50 to 450 V was applied to substrates during deposition. X-ray diffraction (XRD) analysis showed that amorphous or nanocrystalline thin films were formed in all cases. The hydrogen bonding in the material was studied by Fourier transform infrared spectroscopy (FTIR). X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and electron energy loss spectroscopy (EELS) were used to determine the carbon bonding and to study the presence of different forms of amorphous carbon. High resolution transmission electron microscopy (HRTEM) revealed a nanocomposite structure with chromium carbide nanocrystallites embedded in an amorphous hydrocarbon matrix. It was observed that the negative bias voltage significantly affected the carbon bonding and the hydrogen content.

1. Introduction

Hydrogenated amorphous carbon films (a-C:H) having sp^3 and sp^2 bond with various amounts of hydrogen have been studied in the last two decades due to their good mechanical and tribological properties [1,2]. The major challenges in these coatings are low adhesion to substrates, high internal stresses and poor thermal stability above 350 °C [3–5]. To overcome these issues a widely studied possibility was to introduce carbide-forming metals like W, Mo, Nb, Ti or Cr. As a result, the internal stress decreases, the adhesion to substrate increases and mechanical properties rest unchanged. Improvement of the adhesion is based upon the idea that a composite material within the carbon matrix may accommodate internal stresses and decrease the stored strain energy [6,7]. In particular, nanocomposite coatings made of a hard nanocrystalline carbide phase embedded in an amorphous nonhydrogenated or hydrogenated carbon matrix (a-C, a-C:H) have been recently studied, showing a good combination of mechanical and tribological properties [6,8,9]. On the other hand, it is clear that the structure of nanocomposite films will strongly depend on the growth conditions. In particular, the nature and the competitive formation of the nanocrystalline CrC and the a-C:H matrix phases can be strongly influenced by the intensity of ion bombardment [10,11], though this fact has not been extensively studied in the literature.

Among the scarce literature related to coatings of the C–Cr system, only a few works have clearly identified by TEM the presence of a nanocomposite structure. In all these works, the deposition technique was magnetron sputtering. One of the most significant contributions is that of Gassner et al. [9,12–14] who used magnetron sputtering of a Cr target in an Ar/CH_4 atmosphere at a constant working pressure of 0.4 Pa to study the effect of varying the CH_4 partial pressure between 0.1 and 0.2 Pa, at two values of the negative bias voltage (50–150 V). The carbon content in the samples was between 35 and 55 at.%. The samples deposited at a negative bias voltage of 50 V were amorphous irrespective of the CH_4 partial pressure. On the other hand, the samples deposited at a negative bias voltage of 150 V showed an increase of the crystallinity as the CH_4 partial pressure was increased, and the HRTEM image depicted the structure of a nanocomposite of metastable fcc CrC nanocrystallites embedded in an amorphous carbon matrix. Singh et al. [15] used d.c. magnetron sputtering of a Cr target in an Ar/CH_4 atmosphere (ratio of 5.33/1) at a total pressure of 2.66 Pa and a fixed negative substrate bias voltage of 1000 V to study the effect of varying the magnetron current between 150 and 360 mA. The deposited samples presented carbon contents around 50 at.%. The HRTEM image of the sample with a relative composition C/Cr ≈ 10 revealed the formation of a nanocomposite with CrC nanocrystallites embedded in an amorphous carbon

---

* Corresponding author. Tel.: +34 93 403 92 24; fax: +34 93 403 92 18.
E-mail address: l.yate@ub.edu (L. Yate).

0257-8972/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2011.12.015

matrix. The diffraction rings of the CrC nanocrystallites were identified to be the reflections of the metastable fcc CrC structure.

The influence of the deposition parameters on the structure of the nc-CrC/a-C:H coatings deposited by magnetron sputtering is not yet well understood. Moreover, this lack of knowledge is even greater for nc-CrC/a-C:H deposited by other plasma-based PVD techniques like cathodic arc evaporation (CAE) for which, to the best of our knowledge, there are no published studies in the literature.

In a previous paper [16], we studied the effect of the C_2H_2 pressure on the composition and crystalline structure of coatings deposited by cathodic arc evaporation (CAE) using a Cr target and a fixed value of the substrate bias voltage. The deposited films were polycrystalline and the deposition of highly textured Cr_3C_2 coatings was achieved for low values of the acetylene gas partial pressure. In this work, we focus on the opposite range of relatively high acetylene gas partial pressure. In this conditions we study the effect of varying the ion bombardment intensity by applying different bias voltages on the composition and structure of nc-CrC/a-C:H coatings.

2. Experimental details

nc-CrC/a-C:H nanocomposite thin films were deposited onto Si (100) substrates in a cathodic arc deposition system, under various bias voltages. A magnetic shield was placed between the cathode and the substrates in order to reduce the occurrence of droplets in the film. A scheme of the setup of the shielded cathodic arc system used in this study is shown in Fig. 1. The configuration of the magnets in the cathode and the shield allows the coupling of both magnetic fields and the resulting magnetic field forces drive the ions ejected from the cathode towards the substrates. A pure Cr metal cathode (5.8 cm in diameter) was used as source material. The base pressure of the chamber was under $5 \cdot 10^{-4}$ Pa and was obtained by means of a 1000 l/s diffusion pump backed with a mechanical pump. Prior to deposition, the polished silicon substrates were sputter cleaned with a negative bias of 500 V in a 25 Pa Ar atmosphere for 5 min. In order to improve the adhesion of the coating on the substrates, a Cr layer of ~10 nm was deposited onto silicon substrates by cathodic arc deposition in pure Ar atmosphere at 0.1 Pa, 3 sccm Ar flow rate, and with a negative bias voltage of 500 V applied to the substrate holder. Subsequently, C_2H_2 was introduced in the chamber with a gradual flow increase from 0 to 100 sccm for the first 5 minutes up to a total pressure of 6 Pa in order to deposit a carbon gradient thin layer. Finally, the main chromium–carbon layer with constant composition was deposited at a total pressure of 6 Pa during a deposition time of 15 min. A high concentration of metal in the coating is preferred near the film-substrate interface in order to improve adhesion and to reduce internal stresses, and a low concentration of metal is desired at the coating surface to maximize surface hardness and wear resistance. All samples were grown with the substrate holder heating facility turned off and the cathode d.c. current was constant at 65 A. The negative bias voltage has been switched on during the whole deposition process and has been different for each deposition: 50, 150, 250, 350 and 450 V.

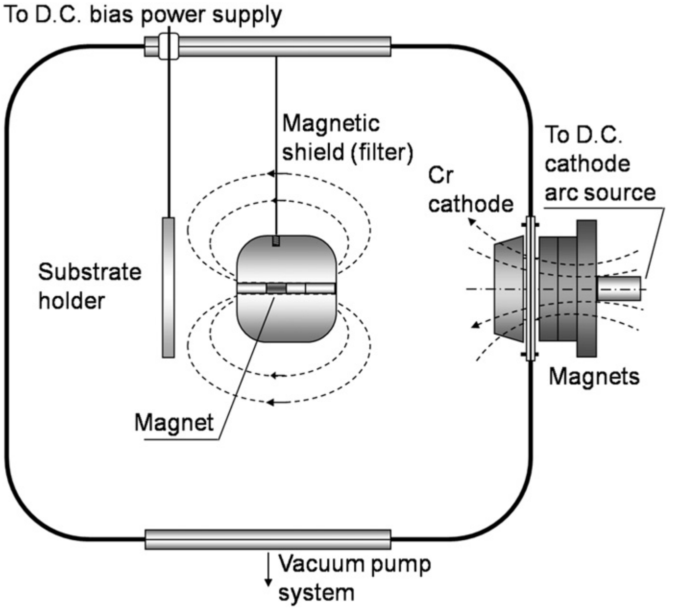

Fig. 1. Scheme of the setup of the shielded cathodic arc deposition.

After deposition, films were cooled down in the low pressure Ar atmosphere and later, they were transferred out of the chamber for characterization. Film thicknesses were determined by profilometry with a Dektak 150 profilometer and the deposition rate was obtained dividing the thickness by the deposition time. The morphology of the samples was evaluated using a field emission scanning electron microscope, FE-SEM (HITACHI S-4100FE) and an atomic force microscope, AFM (Park Systems XE-70). The roughness values were calculated from the AFM measurements using the XEI 1.7.3 image processing software over an imaged area of $60 \times 60\ \mu m^2$. X-ray diffraction (XRD) analysis was conducted for structural investigations of the coatings using a Philips-MRD diffractometer. In the XRD analysis the samples were tilted 4° from the normal in order to disengage from a diffraction peak of a very high intensity from the Si substrate. Raman spectra of the films were recorded with use of a Jobin-Yvon T64000 spectrometer in the 700 cm^{-1} to 1900 cm^{-1} range. This spectrometer was equipped with a 2 mW Ar^+ laser light source (488 nm). Infrared reflectance measurements were performed using a FTIR BOMEM DA3 spectrometer under vacuum conditions. Secondary ion mass spectroscopy (SIMS) analyses were accomplished using an Atomika 488 apparatus using an oxygen ion beam of 9 keV and 500 nA. X-ray photoelectron spectroscopy (XPS) analyses were performed by means of a PHI 5500 Multitechnique system (Physical Electronics) with a monochromatic X-ray source (Al Kα 1486.6 eV) after an initial short etching of the sample surface in order to remove contamination. High resolution cross-section images were obtained in a TEM microscope (JEOL JEM 2100) working at 200 kV. Electron energy loss spectroscopy (EELS, JEOL JEM 2010F TEM) was used to obtain information on carbon hybridization. EELS analysis was performed in the core loss region between 230 and 650 eV, where the K-edge of the carbon and L-edge of the chromium are located.

3. Results and discussion

The profilometry analyses indicate that a central zone of about 4 cm^2 has a practically uniform thickness. This central zone was used for the different characterizations done on the samples. The thickness and deposition rate of the samples are shown in Table 1.

To investigate the feasibility of the magnetic shield on the filter of macroparticles, the surface morphology of the nc-CrC/a-C:H coatings was studied by scanning electron microscopy and atomic force microscopy. A cross-section SEM image of the sample deposited at a negative bias voltage of 50 V is shown in Fig. 2. It is clearly seen

Table 1
Thickness and deposition rates, roughness (obtained from AFM analysis) and sample compositions (as obtained from XPS analysis).

Negative bias voltage (V)	Thickness (μm)	Deposition rate (μm/h)	Roughness, Ra (nm)	C (at.%)	Cr (at.%)	O (at.%)
50	0.8	2.4	15	51.7	23.1	25.3
150	0.7	2.1	26	50.7	21.3	28.0
250	0.6	1.7	3	59.2	21.7	19.1
350	0.4	1.4	4	66.0	31.5	2.5
450	0.4	1.2	1	72.4	25.1	2.5