Surface & Coatings Technology 205 (2011) 4471–4479

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Microstructure and mechanical properties of W-C:H coatings deposited by pulsed reactive magnetron sputtering

Andrzej Czyżniewski [a,*], Witold Gulbiński [a], György Radnóczi [b], Marianna Szerencsi [b], Mieczysław Pancielejko [a]

[a] Koszalin University of Technology, Institute of Mechatronics, Nanotechnology and Vacuum Technique, Raclawicka 15-17, 75-620 Koszalin, Poland
[b] Research Institute for Technical Physics and Materials Science, Budapest, Hungary

ARTICLE INFO

Article history:
Received 21 April 2010
Accepted in revised form 21 March 2011
Available online 26 March 2011

Keywords:
Carbon based coatings
Pulsed magnetron sputtering
Microstructure
Nanoindentation
Scratch test
Ball on disk test

ABSTRACT

Reported are results of microstructure, mechanical and tribological properties studies for thin, amorphous hydrogenated carbon based coatings with tungsten content from 4.7 at.% up to 10.3 at.%. Studied coatings have been deposited by pulsed, reactive magnetron sputtering on substrates under planetary rotation. Resulting coatings, characterized by transmission electron microscopy (TEM) also at high resolution (HREM), show multilayer structure consisting of sub-layers of W-C:H type, with alternately high and low tungsten concentration. Thickness and number of sub-layers depend on rotation speed of planetary substrate holder. An average tungsten concentration decreases with increasing partial pressure of reactive gas (C_2H_2) during deposition. More insight into the microstructure of coatings provided HREM analysis showing crystalline precipitations of about 1–2 nm in size as well as tungsten-rich and tungsten-poor W-C:H sub-layers. Raman spectra confirm presence of amorphous, hydrogenated carbon (a-C:H) phase in the coatings. Microhardness of studied coatings depends on tungsten content and increases from 10.7 GPa to 13.7 GPa, for 5.1 at.% and 10.3 at.% of tungsten content, respectively. The highest cracking resistance and best adhesion ($L_{c2}=78$ N and HF1) has been achieved for coatings containing 4.9 at.% of tungsten and a sub-layer thickness of 5 nm. Tribological processes occurring in the coating–coating contact zone are dominated by graphitization and oxidation of W-C:H coating. Very low friction coefficient (0.04) and low wear rate seems to be an effect gaseous micro-bearing by tribo-generated carbon oxides and methane as well as hydrogen released from the coating. In the W-C:H-steel contact zone a tribo-layer composed of iron and tungsten oxides mixed with graphite-like products is growing at the surface of steel counterpart. This tribo-layer becomes a barrier restricting direct contact of steel with the coating and thus preventing it from further intense wear.

1. Introduction

Thin, carbon based coatings of a-C, a-C:H and X-C:H (X = W, Ti, Cr, Si, F.) type often classified as Diamond Like Carbon (DLC) are widely studied in terms of their potential tribological applications, particularly in automobile industry [1–3]. Usually an application oriented research is aimed at elaboration of coatings showing high adhesion, particularly to steel substrates, high cracking resistance and good tribological properties, i.e. low friction and high wear resistance. Very important but often underestimated is a proper selection of the coating material and its properties in terms of specific features of tribo-contact, like counterpart material and lubrication conditions. A proper selection of materials for tribo-couple should result in low wear of both, the coating and a counter surface as well as low friction.

X-C:H coatings are usually deposited by reactive magnetron sputtering [4–16]. During deposition processes, coated items are mounted at a stationary or planetary substrate holder system. With the planetary substrate holder system, cyclic movement with respect to sputtering sources results in multilayer structure of these coatings, where concentration of metal changes in consecutive sub-layers. A detailed discussion of multilayer growth mechanism was published elsewhere [12,13]. Architecture and properties of such multilayer coatings, i.e. number and thickness of sub-layers as well as metal content depend on deposition system geometry, substrate rotation speed and flow of carbon carrying reactive gas [12–14].

There are only few reports in the literature showing that hardness, wear resistance and toughness of W-C:H coatings are affected by such a multilayer structure [13,14]. Indeed there is a lack of knowledge on a way how the coating architecture and tungsten content affect their tribological properties and adhesion. It is known that a metal (Me) content in the Me-C:H coatings determines the fraction of carbide phase (MeC) in an amorphous a-C:H matrix. In general, advantageous tribological properties are observed when metal content remains below 20 at.% [4,7–12,16]. According to the results of our former

* Corresponding author. Fax: +48 94 3478489.
E-mail addresses: andrzej.czyzniewski@tu.koszalin.pl (A. Czyżniewski), witold.gulbinski@tu.koszalin.pl (W. Gulbiński), radnoczi@mfa.kfki.hu (G. Radnóczi), redeine@mfa.kfki.hu (M. Szerencsi), mieczyslaw.pancielejko@tu.koszalin.pl (M. Pancielejko).

0257-8972/$ – see front matter
doi:10.1016/j.surfcoat.2011.03.062

studies [9,10], W-C:H coatings deposited in a stationary conditions, have shown low friction (<0.1) and high wear resistance for tungsten content below 10 at.%.

The aim of this work was to show how the microstructure and composition of W-C:H coatings, deposited with planetary substrate holder system by pulsed, reactive magnetron sputtering, depends on deposition conditions. Moreover, relations between structure of coatings and their mechanical as well as tribological properties were studied.

2. Experimental details

2.1. Deposition of coatings

The W-C:H coatings have been deposited in the system shown in Fig. 1. Two ARC-MAG sources operating in magnetron or arc mode and equipped with chromium (99.8%) and tungsten (99.99%) targets of 100 mm in diameter, have been used. The ARC-MAG sources were powered by DC-arc or pulsed magnetron supply. Planetary substrate holder was also pulse biased. Application of pulsed power at the frequency of 100 kHz, with 1 kHz modulation, to magnetron sources and substrates as well, enables stable, arc free deposition and limits plasma heating of the substrate. Working gases (Argon, 99.995% and acetylene, 96.8%) were introduced to the deposition chamber through flow meters driven by Flow Controller MGC-147 coupled with the Baratron® 250B pressure control system (MKS Instruments). Coatings were deposited on circular (32 mm in diameter), 3 mm thick substrates made of 100Cr6 bearing steel. Substrates have been subjected to the heat treatment resulting in hardness of 8.3 GPa. They have been then grounded and polished to the surface roughness $R_a \leq 0.02$ μm. Bearing balls made of 100Cr6 steel, 10 mm in diameter, hardened to 8.3 GPa and polished to $R_a \leq 0{,}02$ μm, have been used for friction tests in coated and uncoated states. For TEM studies, coatings have been deposited on single crystalline (100) silicon wafers.

Prior to deposition, substrates of all types have been ultrasonically cleaned in organic solvents and alkaline detergents. The final operation was cleaning in organic solvent vapor and drying with compressed nitrogen. The technological chamber has been pumped down to the ultimate pressure of 2×10^{-3} Pa. Substrates were heated using a radiation heater up to the temperature of approximately 120 °C. Before deposition ion cleaning in Ar plasma was done during 10 min at 1500 V and Ar pressure of 10 Pa. To improve adhesion and crack resistance of W-C:H coatings, Cr under-layer followed by Cr/W transition interlayer was deposited. Chromium was deposited by a combination of vacuum arc evaporation (ARC) and pulsed magnetron sputtering (MAG) techniques, to achieve Cr interlayer with high adhesion to steel substrate [17]. In the next step acetylene flow rate was gradually increased up to required value and deposition of W-C:H coating was continued to the thickness of about 2 μm. The most important parameters of deposition process are shown in Table 1. Deposition of coatings containing less than 10 at.% of tungsten requires high concentration of acetylene in the working atmosphere. It results in nearly total coverage of the target by tungsten carbide and amorphous carbon layer. Due to limited electrical conductivity of reaction products, target poisoning usually leads to process instabilities (arcing), particularly during DC sputtering. To overcome this problem, pulsed sputtering was used in this study. To achieve satisfying reproducibility of deposited coatings in terms of their chemical composition, prior to each deposition cycle, tungsten cathode of ARC-MAG source was cleaned from reaction products by vacuum arc evaporation (ARC). Target cleaning operation is particularly important after deposition performed at high acetylene concentration in the working atmosphere.

2.2. Characterization of coatings

Chemical composition of coatings was checked by Energy Dispersive X-ray Spectroscopy (EDS) method whereas hydrogen content was estimated by Energy Recoil Detection Analysis (ERDA). Their microstructure was examined by Scanning Electron Microscopy and Transmission Electron Microscopy (TEM-Philips CM20 operating at 200 kV), also at high resolution (HREM), using Jeol 3010 microscope operating at 300 kV. Micro-Raman T64000 (Yvon-Yobin) device equipped with an Argon laser (514.5 nm) was used to study phase composition of coatings and sliding wear products. Hardness and elastic modulus were evaluated by nanoindentation technique using Fischerscope 2000. A Berkovich diamond tip was used at a maximum indentation depth of 200 nm. Adhesion of the

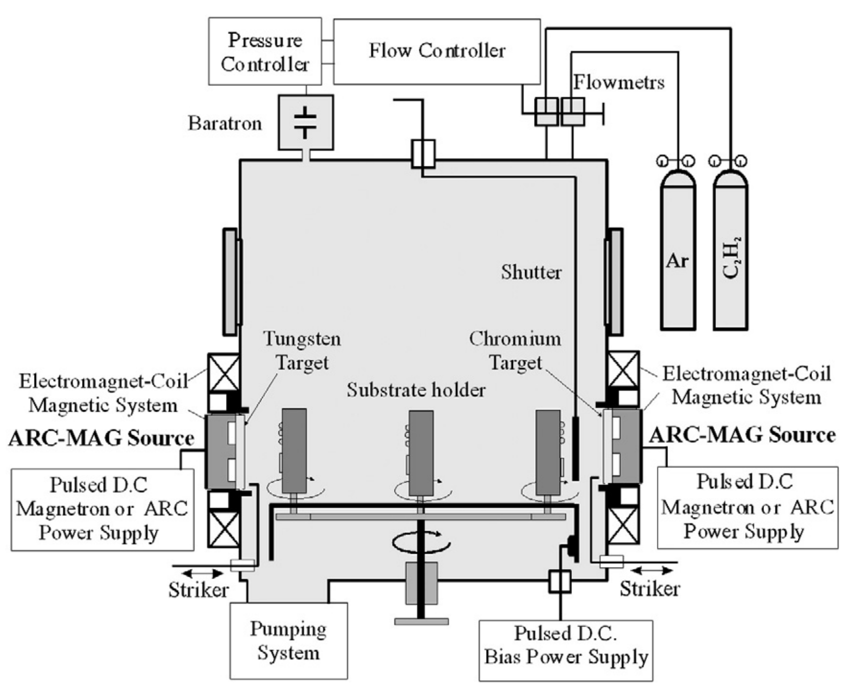

Fig. 1. Deposition chamber equipped with two planar ARC-MAG sources and substrate holder with planetary rotation.