ARTICLE IN PRESS

Surface & Coatings Technology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Advanced deposition of hard a-C:Me coatings by HPPMS using Ne as process gas

K. Bobzin, T. Brögelmann, N.C. Kruppe, M. Engels*

Surface Engineering Institute, RWTH Aachen University, Kackertstr. 15, 52072 Aachen, Germany

ARTICLE INFO

Keywords:
PVD
DLC
a-C:Me
HPPMS
Mass spectrometer
Raman spectroscopy

ABSTRACT

Diamond-like carbon (DLC) coatings are used in numerous tribological applications, for example on highly-loaded components of the automotive powertrain. The high hardness and low roughness of these coatings contribute to the reduction of the component wear in tribological contact. It has been shown that hard a-C coatings with a low roughness can be deposited by means of high power pulsed magnetron sputtering (HPPMS) using Ne as process gas. Furthermore, the doping of a-C coatings with metals is the subject of current research. These a-C:Me coatings exhibit significant changes of the coating properties, which might contribute to a performance increase in tribological applications. Hence, in the present work a-C:Me coatings were successfully deposited in a high-volume semi-industrial coating unit by means of a hybrid process using one direct current magnetron sputtering cathode with a Zr target and one HPPMS cathode with a graphite target, using Ne as process gas. Furthermore, coatings were deposited using two HPPMS cathodes. The deposition of coatings using both types of processes was conducted in order to evaluate the influence of dcMS and HPPMS on the coating properties and the economic efficiency of both processes, respectively. The average power of the cathode with the Zr target was varied in the dcMS mode and in the HPPMS mode, whereas the cathode with the C target was powered constantly in HPPMS mode. A densification of the microstructure was observed for the HPPMS processes. Furthermore, different ratios of C and Zr in the coating were obtained, which resulted in a varying phase composition. Coatings with a maximum universal hardness HU = 25 GPa and arithmetic mean roughness Ra = 0.03 μm could be deposited.

1. Introduction

Diamond-like carbon (DLC) coatings are used in numerous tribological applications, for example on highly-loaded components of the automotive powertrain [1]. Further applications arise for example from magnetic storage discs or medical devices [2]. The hardness of the coatings as well as a low friction behavior of the coated components contribute to the reduction of the component wear in tribological contact [3]. Hence, an increased component lifetime is obtained. Amongst others, the universal hardness correlates with the sp^3/sp^2 bond ratio between the carbon atoms [4]. The bonding state sp^2 is related to the graphite structure of carbon. sp^3 bonds are similar to the diamond structure. In amorphous carbon coatings both bonding states exist in a disordered mixture. With respect to the nomenclature, sp^2 rich DLC coatings are also named amorphous carbon (a-C), sp^3 rich coatings are called tetrahedral amorphous carbon (ta-C) [5]. Besides the sp^3/sp^2 bond ratio, the doping of a-C or ta-C coatings with other elements can also influence the universal hardness as well as further coating properties and hence the behavior of the coated component in the tribological contact. In this context it was reported that the incorporation of H to a-C coatings, so-called a-C:H, results for specific tribological systems in a reduced friction coefficient within dry friction environment, compared to a-C coatings [6]. Furthermore, a doping of these a-C:H coatings with metals results in a significant enhancement of the coating properties. For example, it was reported that the incorporation of metals (Me) to a-C:H coatings results in an increasing universal hardness and friction coefficient in tribological contact [7,8]. In the referenced works this was attributed to the formation of a nanocomposite structure, which results from the formation of crystalline nanometer-size MeC grains within the a-C:H matrix [8]. Other influences on the coating properties have been found for an increasing H content, which reduces the universal hardness and intrinsic stress of the coating [9]. A reduced intrinsic stress was also reported for the incorporation of F and Si [10]. Either increasing or decreasing values of the universal hardness and the intrinsic stress were found for the incorporation of N [11–13]. A conclusion on the doping of a-C coatings is

---

* Corresponding author.
E-mail address: engels@iot.rwth-aachen.de (M. Engels).

http://dx.doi.org/10.1016/j.surfcoat.2017.07.089
Received 27 March 2017; Received in revised form 6 July 2017; Accepted 7 July 2017

Please cite this article as: Bobzin, K., Surface & Coatings Technology (2017), http://dx.doi.org/10.1016/j.surfcoat.2017.07.089

given by Vetter [14].

Beneath the above described influence of the chemical composition on the properties of DLC coatings, the deposition technology is also a significant influencing factor with respect to the coating properties. Conventionally, a-C:H coatings are deposited by means of the plasma-enhanced chemical vapor deposition (PECVD) technology. However, in order to deposit hydrogen free a-C coatings with and without further doping elements, the PECVD technology cannot be used. Hence, physical vapor deposition (PVD) processes must be utilized [14]. Within the PVD, the pulsed laser deposition (PLD) and the filtered cathodic arc (FCA) evaporation are conventionally used for the deposition of DLC coatings with high sp^3/sp^2 bond ratios. sp^3/sp^2 bond ratios higher than 80% were reported [5]. However, coatings deposited by PLD or FCA exhibit high defect densities and surface roughnesses, for example caused by emitted particles from the target, so-called droplets [15–17]. The higher roughness and defect density result in an increased friction coefficient and component wear in tribological contact. Therefore, for the industrial application an extensive post processing like grinding or polishing of the coated components is necessary to gain smooth and defect-free surfaces [4]. As an alternative to the PLD and FCA coating technologies, magnetron sputtering (MS) provides smooth coatings. Nevertheless, conventional MS processes like the direct current (dc) or middle frequency (mf) MS do not provide sufficiently high sp^3/sp^2 bond ratios like PLD or FCA, since the ionization of C ions in the dcMS or mfMS plasma with a percentage $I < 5\%$ is too low [18,19]. Therefore, recent research has been upon the deposition of a-C and a-C:Me coatings, using the high power pulsed magnetron sputtering (HPPMS), which was firstly introduced by Kouznetsov et al. in 1999 [20]. The influence of the HPPMS technology on the properties of various coating systems has been reported in several works [21–26]. Furthermore, it has been shown that using a dcMS/HPPMS hybrid process results in coating properties which can be classified between the coating properties of deposited coatings by means of dcMS and HPPMS processes. Meanwhile the deposition rate and hence the economic efficiency is increased, compared to HPPMS processes [27,28]. However, for HPPMS as well as dcMS/HPPMS processes, the ionization of C atoms within the plasma is too low to deposit a-C and a-C:Me coatings with a sp^3 bonds portion, which is comparable to PLD or FCA processes [29]. To overcome this issue, Ne was introduced as process gas, since the ionization energy $E_{i,Ne} = 21.56$ eV exceeds the ionization energy of Ar $E_{i,Ar} = 15.6$ eV and leads to an increased C ionization [29]. In previous works of Sarakinos et al. [29], Aijaz et al. [30] and Bobzin et al. [31,32] it was proven that using Ne instead of Ar as process gas significantly enhances the ionization in the C plasma [29–31], which results in a-C coatings with an increased sp^3/sp^2 bond ratio, 20% higher density [29,30], increased universal hardness up to HU = 45 GPa and smooth surface topography [32]. An increasing mass density was also observed for an increasing bias voltage U_B as well as a reduction of the process gas pressure [30,32]. Furthermore, several studies report the influence of varying HPPMS sources and pulse parameters on DLC coating properties [33–36].

According to the above described works, it can be expected that the deposition of a-C:Me coatings, using HPPMS technology and Ne as process gas, could result in coatings with enhanced coating properties and a high performance in tribological systems, compared to a-C:H:Me coatings by means of PACVD or a-C:Me coatings by means of PLD and FCA. Furthermore, using a dcMS/HPPMS hybrid process could lead to a higher economic efficiency with respect to the deposition rate. Hence, in the present work for the first time extensive investigations on a-C:Me coatings are presented, which were deposited in a high-volume semi-industrial coating unit by means of different dcMS/HPPMS hybrid and HPPMS processes, respectively. The process parameters were adapted to our previous work on the deposition of a-C coatings by means of HPPMS, using Ne as process gas [32]. Due to the promising results of graded a-C:H:Zr coatings in tribological systems [1,37], the transition metal Zr was chosen as doping for the formerly deposited a-C coatings. Furthermore, promising results on the coating properties of ZrC coatings by means of a magnetron sputtering process with a Ar/CH_4 process gas mixture have been reported by Kumar et al. [38].

In the present work, the average power of the cathode with the Zr target was varied in order to obtain different ratios of C and Zr in the coatings: Hence, phase transitions from Zr + ZrC to stoichiometric ZrC and crystalline ZrC grains in an amorphous a-C matrix can be expected for an increasing carbon content in the coating [8,39], which result in strongly varying coating properties. These coating properties were analyzed by means of scanning electron microscopy (SEM), glow discharge optical emission spectroscopy (GDOES), X-ray diffractometry (XRD), Raman spectroscopy (Raman), transmission electron microscopy (TEM), nanoindentation (NI) and confocal laserscanning microscopy (CLSM). Furthermore, the compound adhesion between the substrates and the coatings was determined by means of Scratchtest.

2. Materials and methods

2.1. Coating unit configuration and process parameters

The presented investigations were carried out using a high-volume semi-industrial scale PVD coating unit, PVT550, PVT GmbH, Bensheim, Germany. The coating chamber has a dimension of 500 mm × 500 mm × 500 mm, Fig. 1. Two cathodes are available, both equipped with a HPPMS power supply Sinex, Chemfilt Ionsputtering AB, Linköping, Sweden, which can also run in dcMS mode. One cathode was equipped with a Zr target with a purity of 99.99%. The other cathode was equipped with a graphite target with a purity 99.90%. Each target size was 200 mm × 88 mm. The cathodes were mounted so that the target surfaces were oriented perpendicularly to each other. The substrate table was positioned centrically under the cathodes as shown schematically in Fig. 1, which is not true to scale.

In order to obtain comparable results to our previous work on a-C coatings [32], especially the compound adhesion between substrate and coating, the a-C:Zr coatings were deposited on tungsten carbide substrates THM12 with a universal hardness HU ≈ 20 GPa, Ceratizit GmbH, Empfingen, Germany, which were polished to an arithmetic mean roughness Ra ≈ (10 ± 2) nm. The bulk of the copper substrate table was cooled down to a temperature $T = 18$ °C by a water cooling system to keep the substrate temperature as low as possible, since an

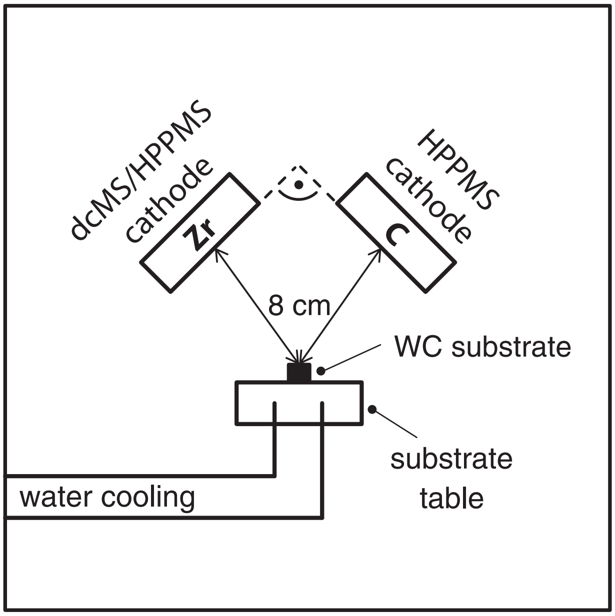

Fig. 1. Setup within the vacuum chamber of the high-volume semi-industrial scale PVD coating unit for the a-C:Zr coating deposition.