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Synthesis of a-C coatings by HPPMS using Ar, Ne and He as process gases

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ABSTRACT

Diamond-like carbon (DLC) coatings are used in numerous tribological applications, for example components of the automotive powertrain. The universal hardness HU of these coatings correlates with the sp^3/sp^2 bond ratio between the carbon atoms. Research on the synthesis of these coatings is upon physical vapor deposition (PVD) processes, especially the high power pulsed/impulse magnetron sputtering (HPPMS/HiPIMS). Synthesizing DLC coatings with a high sp^3/sp^2 ratio requires high energetic carbon ions, whose generation strongly depends on the HPPMS process parameters. Plasma diagnostics have shown that the energy of the carbon ions in the plasma strongly depends on the process gas mixture, the process gas pressure and the bias voltage. An increased fraction of high energetic carbon ions in the HPPMS plasma has been reported for process gases with a higher ionization energy as well as for higher bias voltage and lower process gas pressure. Therefore, the aim of this work is to investigate the correlation of the plasma parameters with the properties of DLC coatings. Ar, Ne and He were used as process gases. Process gas pressure and bias voltage were varied between $p = 0.5$–2.5 Pa and $U_B = -300$–0 V, respectively. The coatings were deposited in a high volume semi-industrial coating unit. It was observed that the coating properties strongly correlate with the results from the plasma diagnostics. Dependencies of the sp^3/sp^2 ratios and hardness on the ionization energy of the process gas, the process gas pressure and bias voltages could be found. Hardness values up to HU = 45 GPa have been achieved. In conclusion it can be claimed that synthesis of DLC coatings with high hardness is possible by HPPMS processes using process gas mixtures of Ar, Ne and He.

1. Introduction

Diamond-like carbon (DLC) coatings are used in numerous tribological applications, for example components of the automotive powertrain [1]. Further applications arise for example from magnetic storage discs or medical devices [2]. For these applications a high universal hardness HU as well as a low friction coefficient of the coatings within a tribological contact can lead to reduced component wear [3]. The universal hardness HU 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^2 rich DLC coatings are also named amorphous carbon (a-C). sp^3 bonds are similar to the diamond structure. Therefore, sp^3 rich coatings are called tetrahedral amorphous carbon (ta-C) [5]. Further modifications of the tribological behavior of DLC coatings are possible by means of doping with other elements. For example the incorporation of hydrogen (a-C:H) results in a reduced friction coefficient within dry friction environment whereas the doping with metals (a-C:Me) can enhance the wear resistance [6]. However, the focus of this work is on pure a-C coatings to isolate the influence of the carbon matrix from the influences of other elements within doped DLC coatings. Therefore, regarding the wear resistance of DLC coated components in tribological applications the percentage of sp^3 bonds has to be raised.

Physical vapor deposition (PVD) processes are appropriate to reach this aim. Especially the pulsed laser deposition (PLD) and the filtered cathodic arc (FCA) evaporation have been used for the deposition of DLC coatings with high sp^3/sp^2 ratios, so far. sp^3/sp^2 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 [7,8,9]. The higher roughness and defect density result in an increased friction coefficient and component wear. Therefore, for the industrial application an extensive post processing of the coated components is necessary to gain smooth and defect-free surfaces. As an alternative to the PLD and FCA coating technologies, magnetron sputtering (MS) provides smooth coatings and therefore no post processing is required. Nevertheless, conventional MS processes like the direct current (dc) or middle frequency (mf) MS do not provide sp^3/sp^2 bond ratios like PLD or FCA, since the ionization of carbon ions in the dcMS or mfMS plasma with a percentage $\eta < 5\%$ is too low [10,11]. Therefore, research is upon the high power pulsed/impulse magnetron sputtering (HPPMS/HiPIMS), which was firstly introduced by Kouznetsov et al. in 1999 [12]. In this process the power supply is pulsed with short pulses with a pulse length $t_{on} < 200$ μs and low frequencies $f < 2000$ Hz. Due to the very low duty

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cycle D < 40% very high peak power in the range of kW to MW can be achieved [13,14]. The influence of the HPPMS technology on the coating properties has been reported in several works [15–19]. Regarding the plasma the high power densities on the target result in a significantly increased ionization of the plasma of up to $\eta = 90\%$ as observed for a Ti target [20]. Regarding DLC coatings an increased ionization of the carbon species in the plasma was also observed, but did not exceed a percentage of 5% [21]. This value is too low to synthesize a-C or ta-C coatings with a high sp^3 bond percentage.

Therefore, various approaches have been conducted to increase the carbon ionization within the plasma as well as the kinetic energy of the carbon ions to gain a-C coatings with a high fraction of sp^3 bonds. Aijaz et al. [22] carried out experiments with varying bias voltages U_B, process gas pressure p and process gas on a laboratory scale. The variation of the process gas was based upon the assumption that the ionization of carbon atoms depends on the ionization mean free path λ_{miz} which correlates exponentially with the electron temperature T_e. Likewise, T_e correlates with the ionization energy E_i of the process gas. Therefore, Ne with an ionization energy $E_{i,Ne} = 21.56$ eV was compared to the conventional process gas Ar with $E_{i,Ar} = 15.6$ eV. It was assumed that an increased carbon ionization in the plasma could be observed. Comparable results were measured for the mass density in coatings, which correlates with the sp^3/sp^2 bond ratio, as proven in the work of Sarakinos et al. [21]. An increasing mass density was also observed for an increasing bias voltage U_B as well as a reduction of the process gas pressure [22]. Furthermore, several studies regarding the influence of varying HPPMS sources and pulse parameters on the DLC coating properties have been conducted on laboratory scale [23–26].

Nevertheless, regarding the former research activities there have been no comparable investigations in high volume coating units. Furthermore, the characterization of a-C coatings by means of HPPMS regarding application-oriented coating properties like the morphology and universal hardness HU has rarely been reported, so far. Therefore, in the first step of our work [27] the HPPMS carbon plasma within a high volume coating unit was analyzed by means of optical emission spectroscopy (OES) and energy resolved mass spectrometer (MaSp). The HPPMS pulse parameters pulse length t_{on} and frequency f were varied as well as the process gas pressure p and the process gas composition. In addition to Ar ($E_{i,Ar} = 15.60$ eV) and Ne ($E_{i,Ne} = 21.56$ eV), He with an ionization energy $E_{i,He} = 24.58$ eV was investigated. Since the ionization mean free path λ_{miz} should be further increased due to the higher electron temperature of the process gas [22], a further ionization of carbon compared to Ar and Ne was expected. The conducted plasma diagnostics showed an increasing carbon ionization and ion energy, especially for twice ionized carbon C++, for a reduced pulse length t_{on} and frequency f as well as a reduced process gas pressure. The most significant influence was observed for the process gas composition, shown in Fig. 1. An increased carbon ionization by a factor 10 was detected for Ne, compared to Ar. Regarding He the increasing factor was observed as 6 compared to He and 60 compared to Ar.

Therefore, the aim of this work was to synthesize a-C coatings with Ar, Ne and He as process gas and to correlate the coating properties with the plasma parameters. Furthermore, the process gas pressure p and bias voltage U_B were varied. The coatings were deposited in a high volume semi-industrial coating unit. Afterwards, the coating properties were analyzed by means of nanoindentation (NI), Raman spectroscopy (Raman), scanning electron microscopy (SEM) and confocal laser scanning microscopy (CLSM). The compound adhesion between the coatings and substrates was determined by means of Rockwell indentation.

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. 2. The coating unit has two cathodes, both equipped with a HPPMS power supply Sinex, Chemfilt Ionsputtering AB, Linköping, Sweden, which can also run in dcMS mode. The substrate table was positioned under the cathodes at two configurations. A position under a dcMS powered cathode with a zirconium target with purity of 99.99% was chosen (Fig. 2a) to synthesize a zirconium interlayer, which was used to increase the adhesion between the a-C coatings and the substrate. The substrate table was placed under a HPPMS powered cathode with a graphite target with purity 99,9% (Fig. 2b) to deposit the a-C toplayers with varying process parameters. The cathodes were oriented parallel to the substrate table. Each target size was 200 mm × 88 mm.

The coatings were synthesized on tungsten carbide substrates THM12 (universal hardness HU ≈ 20 GPa), Ceratizit GmbH, Empfingen, Germany, which were polished to an arithmetic mean roughness Ra ≈ 0.01 μm. The bulk of the substrate table was cooled down to a temperature $T = 18$ °C by a water cooling system, since an increased sp^3/sp^2 ratio can be expected for low substrate temperatures [28]. Prior to the

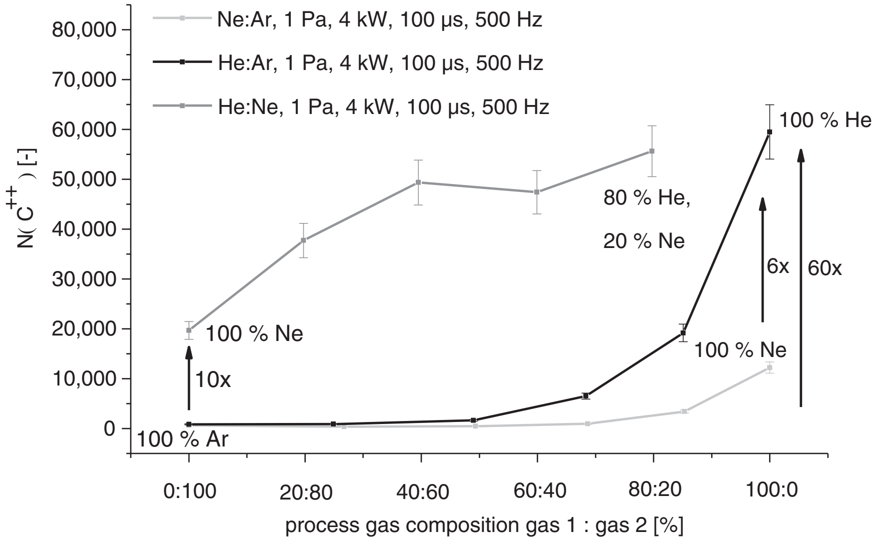

Fig. 1. Results of plasma diagnostics by means of MaSp during a HPPMS a-C process regarding the dependence of the carbon ion energy on the process gas composition. Gas 1 and gas 2 are defined in the figure legend [27].