



Tool Optimization for Dry Forming Applications – Optimized Surface Preparation of ta-C

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Abstract

Within this work, the development of roughness during vacuum arc deposition of ta-C thin films was investigated. By means of topography measurements of the plasma etching processes, adhesion layer- and ta-C deposition were investigated. These investigations were made for two materials tool steel 1.2379 and a stainless steel 1.4301 as well as different probe roughness. Material dependent differences in the ablation depth during the metal-ion-sputtering process are investigated. Furthermore the roughness of the samples after the deposition of a chromium adhesion layer is analyzed. From these investigations conclusions concerning an optimized probe roughness prior to the deposition can be made. Additionally the thin film preparation process and the pretreatment processes can be tuned for improved tribological coatings.

Keywords: PVD, etching, chromium, ta-C coating

1 Introduction

Amorphous carbon thin films are world-wide in the focus of research activities. The reasons are the fascinating physical properties which are interesting for basic research and industrial applications [1-3]. One reason to aim on carbon in electronic applications is the high electron mobility of graphitic crystalline carbon which originates from a 2D density of states [4]. However, besides this sp²-bonded graphitic form carbon also exists in a sp³-bonded amorphous state, a diamond-like form, which is electrically isolating, very hard and can be used as a tribological coating [5,6]. By varying the deposition conditions, it is possible to adjust the layer properties for an optimized performance [5]. Such diamond-like carbon coatings (DLC) can be produced by different processing technologies [7]. DLC coatings produced by PECVD processes are typically containing a higher concentration of hydrogen [7]. This reduces the hardness and wear resistance. In PVD processes, the carbon source consists of graphite. If the graphite is evaporated by arc discharge (vacuum arc PVD) under

ultra-high vacuum conditions, the resulting coating is a "pure" carbon layer. If such a layer consists predominantly of sp³-bonded carbon the coating is called tetrahedral amorphous carbon (ta-C). Ta-C coatings can reach up to 75% of the diamond hardness. Such hard amorphous carbon layers called Diamor® have been developed at the Fraunhofer Institute for Material and Beam Technology in Dresden [6].

As a result of the vacuum arc process, small graphitic particles (micro particles) emitted from the carbon source are incorporated in the coating, which leads to a disturbance of the layer growth and thus increases the roughness. Due to their poor bonding to the layer composite, these particles reduce the corrosion resistance. Pores or pinholes, as a result of the growth defects are positions with an increasing corrosion potential. This results in an under-migration of the layer by corrosion products and finally a local delamination of the coating [8, 9]. Particularly in the case of hard coatings such as ta-C, increased roughness degrades the running behavior of the friction system. This can lead to an increased friction and wear of the counter-body, for

instance. For this reason the development of the roughness over the entire coating process is investigated in this study. Furthermore, possibilities for roughness reduction during and after the coating process are discussed.

2 Experimental Methods

2.1 Sample preparation

To generate a defined roughness on the used steel probes, they were polished with SiC sandpaper of different grain sizes (500, 1000, and 4000). Isopropanol was used as a lubricant during grinding. Before grinding with a smaller grain size, the samples were cleaned with isopropanol.

After the first grinding steps, the samples were additionally polished on a turntable with a polishing cloth and an abrasive. The abrasive was a diamond dispersion based on alcohol and particles with sizes of 3 μm and 1 μm , respectively.

Before the samples can be coated in a vacuum process, a preliminary cleaning is required. In order to achieve good film adhesion, the substrate surface must be free of dust and organic impurities. Such a cleaning procedure has to be adapted to the materials used. For substrates 1.2379 and 1.4301 the cleaning was identical:

- Cleaning with acetone
- Cleaning with a foam
- Purification with deionized water
- Aqueous cleaning with a washing machine
- Washing with isopropanol
- Drying with dry nitrogen

After cleaning, the substrates were immediately mounted in substrate holders in the coating system. This prevents the substrate from being re-contaminated.

2.2 Vacuum arc coating technology

The investigations in this publication were made with a PVD coating system MZR 373 by Metaplas Oerlikon (see Fig. 1). This system can be used with a bias voltage of up to 1 kV, a mass-flow controlled gas environment. The typical base pressure of this system is between 10-4 Pa and 10-5 Pa (further details about design and mode of operation can be found elsewhere [10]). The coating system has 12 DC arc evaporators. Six of them are located on an adapter plate on the left and right side of to the chamber door. Each of them can be individually controlled and the maximum current is 100 A at a voltage of 30 V. More details on the correlation between arc current, ion energy and sp³ content can be found elsewhere [11].

The operation mode of the carbon coating system was a pulsed mode (frequency 100 Hz) to evaporate the carbon from disc shaped graphite cathodes. With the resulting high energy carbon species hard amorphous carbon coatings were deposit on steel plates.

After mounting the samples, the vacuum chamber was evacuated to a pressure of 5x10⁻⁴ Pa and heated three times for 5 minutes. After that, the samples were plasma cleaned. Subsequently a thin chromium layer was deposited as adhesion layer. Finally the functional carbon

layer was deposited at a temperature of 85 – 190 °C, respectively. To avoid softening of the hardened samples by high process temperatures, the deposition was carried out in cycles containing pauses to cool down.



Fig. 1: MZR 373 coating system by Metaplas Oerlikon.

2.3 Thin film characterization

The carbon layer thickness was measured by calotte grinding whereas the chromium layer thickness was determined with the help of spectroscopic ellipsometry in the range between 350 nm and 1050 nm (step width: 10 nm; spot size: 1.5 mm; measuring angles: 65°, 70° and 75°) from pre-ta-C-coated samples (see also [12]). The surface topographies of the uncoated and coated surfaces were measured with a mechanical profilometer with a resolution of 10 nm.

The modulus of elasticity of the coatings was measured using a laser-acoustic method (LAwave). The adhesion strength of the coated samples was determined according to the VDI guideline 3198 by a Rockwell C test. Through the penetration of the tapered test specimen into the coated probe, sample material is displaced. After setting an impression, the edge of the indentation was characterized with a light microscope and the resulting crack distribution is classified. The classification was ranging from 1 (no delamination, good adhesion) to 6 (total delamination of the rim area, no adhesion).

4 Results and Discussion

4.1 Roughness of ta-C on steel

In this section the influence of the substrate roughness on the final surface roughness after the coating processes is investigated. The investigated materials are typical construction materials, a stainless steel (1.4301) and tool steel (1.2379). The necessary substrate roughness is crucial, since in the production the relative production costs increase significantly with increasing surface quality [12].

The surface roughness R after the coating is composed of different components:

$$R = f(R^S, R^{MIS}, R^{Cr}, R^{taC}),$$

R^S represents the initial substrate roughness, R^{MIS} is the surface roughness after the sputtering, R^{Cr} the roughness from the Cr coating and R^D the roughness of the ta-C coating.

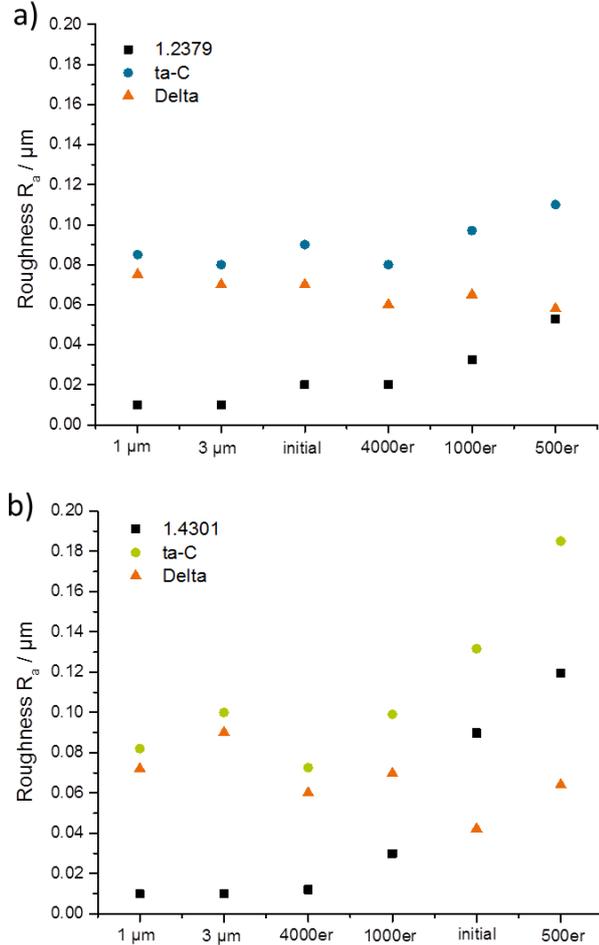


Fig. 2: Average roughness of 1.2379 steel and 1.4301 steel after different pretreatments and ta-C coating.

In the case of the substrate materials 1.2379 and 1.4301 (see Fig. 2), a smooth surface with $R_a < 20$ nm could be produced by polishing with $1 \mu\text{m}$ and $3 \mu\text{m}$ diamond suspension. The surfaces treatment with 1000er and 500er sandpaper grit resulted in higher roughness of 32 nm and 53 nm (1.2379) and 91 nm 123 nm (1.4301), respectively. In contrast to the 1.2379 steel, the relatively ductile 1.4301 is roughened much more by the same pretreatment methods (see Fig. 2 b). Just the pretreatment with $1 \mu\text{m}$ and $3 \mu\text{m}$ diamond suspension and a sandpaper grit of 4000er provide similar results.

After the deposition of $1.4 \mu\text{m}$ thick ta-C, the R_a roughness increased for all samples (see Fig. 2). Additionally the R_a values are increases with increasing substrate roughness. This depicts that the R_a value of the substrates is partly transferred from the substrate surface to the ta-C surface. In summary the increase in the R_a

surface roughness was in the range of $0.5 - 0.8 \mu\text{m}$ from the ta-C coatings

4.2 Influence of metal-ion sputtering

Prior to the deposition of ta-C the substrates were plasma treated (metal-ion sputtering), these cleaning removes of adsorbed water molecules and oxides from the surface. The influence of the sputtering time on the substrate roughness and the substrate removal is shown in Fig. 3. In this set of experiments we used polished substrates with an average roughness ~ 15 nm (1.4301) and 20 nm (1.2379), respectively. Within the etching process argon was used as a process gas. The ionization was reached by a DC arc-evaporator (current 75 A and voltage 20 V) at a base pressure of $4 \cdot 10^{-1}$ Pa. During the process a bias voltage of 750 V was applied between the substrates and the coating chamber. The samples were cleaned in two-fold rotation.

In Fig. 3a it is demonstrated that with an increasing cleaning time, the surface roughness increases. The increase in the roughness is approximately linear and reaches after 90 min. a R_a value of 53 nm (1.2379) and 38 nm (1.4301), respectively. Interestingly, the roughness of the tool steel increases as compared to stainless steel 1.4301. Experiments with samples, which were pre-treated with sandpaper grit 1000er, showed a similar increase in the surface roughness. From this we concluded that the increase of the roughness after the metal-ion sputtering does not depend on the initial substrate roughness, but on the material used.

Fig. 3b depicts that the ablation depth of the substrates increase with the sputtering time. It is noticeable that the ablation rate from the 1.2379 steel decreases at longer treatment durations (> 10 min.), but on the other hand it increases if stainless steel (1.4301) is used.

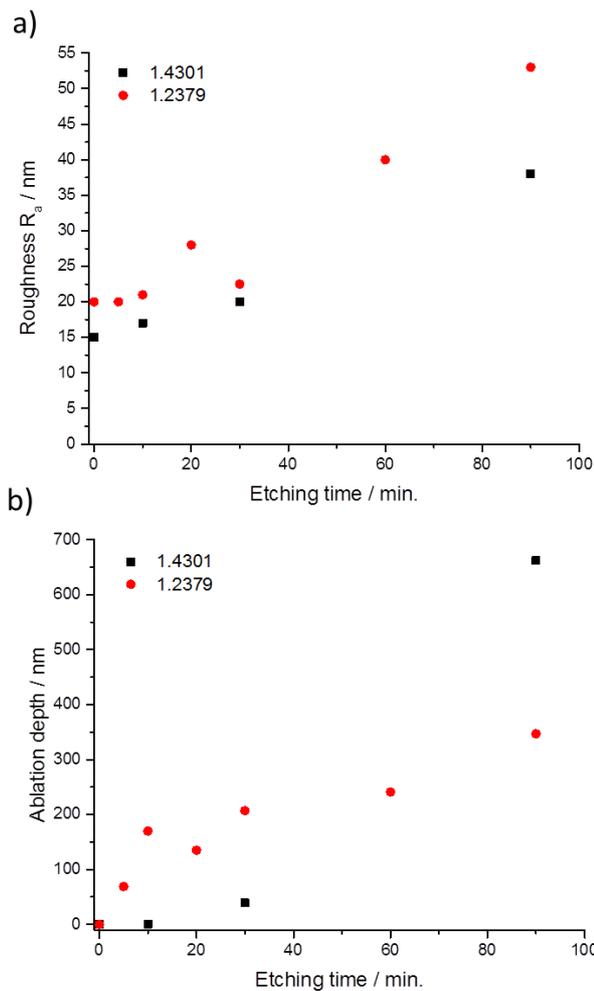


Fig. 3: a) Average roughness of 1.2379 steel and 1.4301 steel after metal-ion sputtering (etching time). b) Ablation depth after metal ion sputtering

4.3 Influence of the chromium adhesion layer on the substrate roughness

The influence of the chromium adhesion layer was exemplarily demonstrated on samples made of 1.2379 steel. After the above described plasma fine cleaning of 30 minutes, the samples were coated in double rotation with chromium.

The R_a of the chromium thin films shows no significant increase in roughness with increasing thicknesses. Rather, a decrease in the R_a value at a layer thickness of approximately 450 nm can be observed. Accordingly, the surface seems to be smoother in its micro-roughness. However, the increase in the R_z values indicates that there are more spikes at longer coating times. This can be attributed to an increase in the number of micro particles from the arc process.

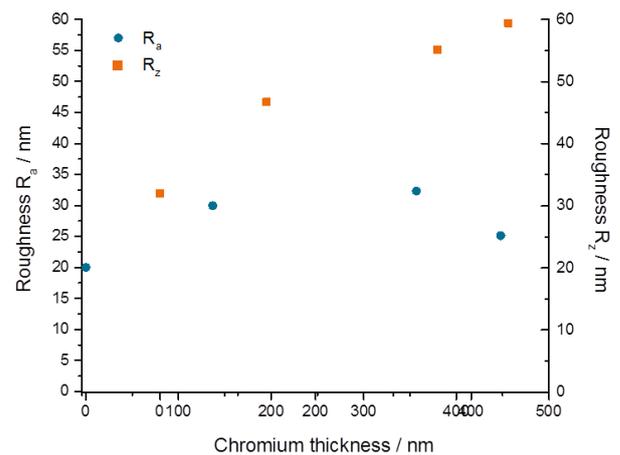


Fig. 4: R_a and R_z of chromium at different layer thicknesses.

5 Summary and Conclusion

In this paper, the coating procedure of ta-C with a pulsed arc process is investigated. From this investigation the main reason of the roughness development during the coating process can be attributed. We found that the use of different steels like 1.2379 and 1.4301, has only a minor influence on the resulting R_a roughness. The investigation of the influence of the substrate roughness and the roughness after ta-C coating can be summarized as follows:

- Polishing of the steel with grain sizes 1 μm or 3 μm results in comparable roughness.
- The substrate roughness is different for surface grinding.
- The roughness increases as a result of the coating process.
- In the case of polished samples, the R_a roughness increases by $\sim 0.05 \mu\text{m}$ per μm ta-C thickness.

Additionally we found major differences in the ablation depth during the metal-ion-sputtering process. The substrate ablation increased for tool steel (1.2379) but was smaller for stainless steel. In summary we found that:

- Roughness after metal-ion sputtering does not significantly depend on the substrate roughness.
- The substrate roughness increases with the etching time.

Investigating the roughness after the deposition of a chromium adhesion layer we found:

- An adhesion layer reduces the surface roughness compared to an plasma etched surface
- The R_a value drops after ~ 350 nm layer thickness.
- The R_z value increases with the chromium thickness, which indicates that the surface is covered with droplets.

Due to these investigations the highest roughness increase, during the coating process, could be attributed to the ta-C deposition.

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REFERENCES

- [1] Y. Lifshitz, Hydrogen-free amorphous carbon films: correlation between growth conditions and properties, *Diamond Related Materials* 5 (1996) 388-400
- [2] M. Chowalla, J. Robertson, C. Chen, S. Silva, C. Davis, G. Amaratunga, W. Milne, Influence of ion energy and substrate temperature on the optical and electronic properties of tetrahedral amorphous carbon (ta-C) films, *J. App. Phys.* 81 (1997) 139-147
- [3] S. Xu, L.K. Cheah, B.K. Tay, Spectroscopic ellipsometry studies of tetrahedral amorphous carbon prepared by filtered cathodic vacuum arc technique, *Thin Solid Films* 312 (1998) 160-169
- [4] A. Roch, T. Roch, E. Talens, B. Kaiser, A. Lasagni, E. Beyer, O. Jost, G. Cuniberti, A. Leson: Selective laser etching and laser patterning of metallic and semiconducting nanotubes in single walled carbon nanotube films, *Diamond and Related Materials* 45 (2014), 70-75
- [5] S.K. Field, M. Jarratt, D.G. Teer, Tribological properties of graphite-like and diamond-like carbon coatings, *Tribology International* 37 (2004) 949-956
- [6] B. Schultrich, V. Weihnacht, Tribologisches Verhalten von harten und superharten Kohlenstoffschichten, *Vakuum in Forschung und Praxis* 20 (2008) 12-17
- [7] J. Robertson, Diamond-like amorphous carbon, *Material Science and Engineering R* 37 (2002) 129-281
- [8] S.H. Ahn, J.H. Lee, J.G. Kim, J.G. Han, Localized corrosion mechanisms of the multilayered coatings related to growth defects, *Surface and Coatings Technology*, 177-178 (2004) 638-644
- [9] K. Reichel, Dissertation: Entwicklung und Charakterisierung von korrosions- und verschleißbeständigen Beschichtungen unter Einsatz des Arc-PVD-Verfahrens, VDI Verlag, 1991
- [10] J. Vetter, 60 years of DLC coatings: Historical highlights and technical review of cathodic arc processes to synthesize various DLC types, and their evolution for industrial applications, *Surface and Coatings Technology* 257 (2014) 213-240
- [11] B. Schultrich, Modeling of ta-C growth: Influence of the technological parameters, *Diamond Related Materials* 20 (2011) 785-792
- [12] R. Volk, *Rauheitsmessung Theorie und Praxis*, 1. Auflage, Beuth-Verlag, 2005