Properties of Super-hard Carbon Coatings deposited by a pulsed DC-Arc-Process

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1. Introduction

Super-hard Carbon Coatings (SHC) show a typical tetrahedral bonded amorphous structure without hydrogen. Coatings on steel with a thickness of several micrometers are characterized by a hardness of more than 3.500 HV0.002 and a good adhesion (HF1) on the steel substrates as well as on other hard materials.

The pulsed DC-Arc-process is an effective method to deposit super-hard carbon coatings (SHC) on tools and machinery components. This coating technique is working similarly to the well-known vacuum arc process. In addition, here high-current pulses are superposed to the DC-current sustaining the vacuum-arc discharge. To allow homogeneous deposition three pulsed arc evaporators are implemented in a PVD-coating system. Deposition rates up to 100 nm/min can be obtained on the rotating substrates (threefold rotation).

New results to the physical properties of SHC-coatings on steel substrates and hard materials are presented in this contribution. The pulsed DC-Arc-process opens new opportunities to optimize coating conditions and process schedules.

The SHC-coating results are characterized by hardness measurement using nano indentation, friction and wear testing using oscillating sliding tests, as well as structural analysis. The mechanical, tribological and structural results and their dependence on deposition conditions are discussed. In the conclusion it is shown, how the properties of the coatings can be improved by the modification of deposition parameters.

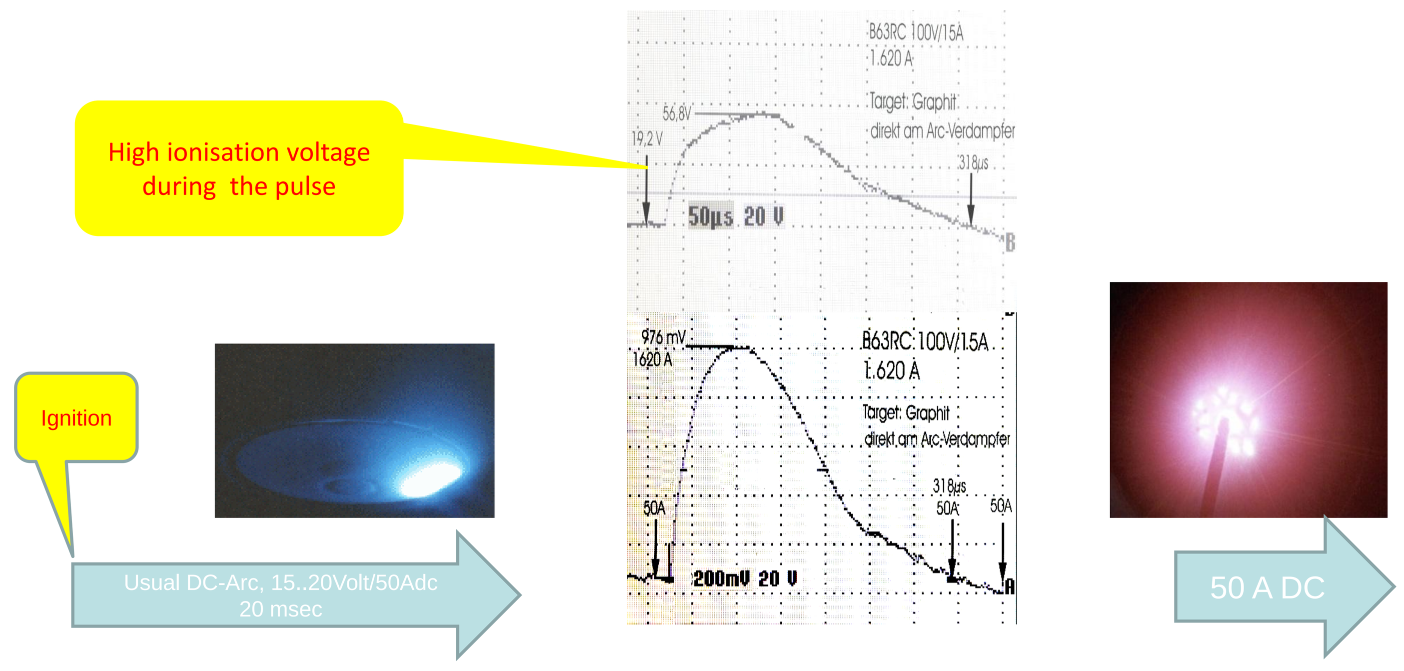


Figure 1: The pulsed DC-arc-process:
The arc discharge ignites in same way as a normal DC-arc-process and runs with 50 up to 100 A DC. If the DC-arc is running a special current source superposes a high current-pulse of 1600 A to the DC-arc discharge. A high ionisation voltage during the pulse is typical for this kind of discharge.

2. Coating Technology

Hydrogen-free Diamond like Coatings with a hardness higher than 3000 HV can be produced only with PVD-Arc-Technologies. Here, we use an equipment with pulsed arc sources. The distance of the cathodes to the substrate is 150 to 450 mm. The substrates rotate in three axes inside the vacuum chamber. The pulsed DC-arc-process works without any additional reactive gases at a pressure of 5x10^{-3} Pa. Figure 2 shows such a coating system with three pulsed DC arc sources. The DC current is superimposed by pulses with a peak current of 1.600 A, a pulse length of 300 µsec at a repetition rate of 100 Hz.

The arc discharge is ignited in same way as a normal DC-arc-process and runs at 50 to 100 A DC. A special current source superposes a high current pulse of 1600 A in the peak to the DC-arc discharge. During the DC-arc phase a single or few arc spots are moving very slowly over the surface of the cathode. In the beginning of the pulse phase a lot of spots arise and move quickly. At the end of the pulse phase only a few of them survive to sustain the DC current.

Figure 1 illustrates the principle of the pulsed DC-process on Carbon.

Process parameter	value, unit	Stable working range
Discharge voltage	15 V	
Discharge current, dc	50 A	25..100 A
Discharge voltage, during pulsing	> 70V	
Pulse current for each source	1.600 A	500 A..2.500 A
Distance to the substrate	150 mm	
Depositon rate	> 0.1 µm/min	>0.1 µm
Substrate moving	three axes	
Chamber pressure	< 5x10^{-3} Pa	10^{-6}..10 Pa
Deposition temperature	< 200°C	25°C … 300°C
Cooling water energy loss	< 15%	

Table 1 shows the Parameter of the pulsed DC-Arc process. For industrial application of the process the following facts are important:

- ✓The process is usable in a wide range of DC-current and chamber pressure without significant change in film properties.
- ✓The high efficiency arc sources have a small loss of energy by cooling water. Its possible, that the target temperature don't influence the coating result.
- ✓Residual gases from atmosphere or bad vacuum conditions are not crucial for the coating result. [4] reports the influence of N_2, CH_x and other gases on the film properties.

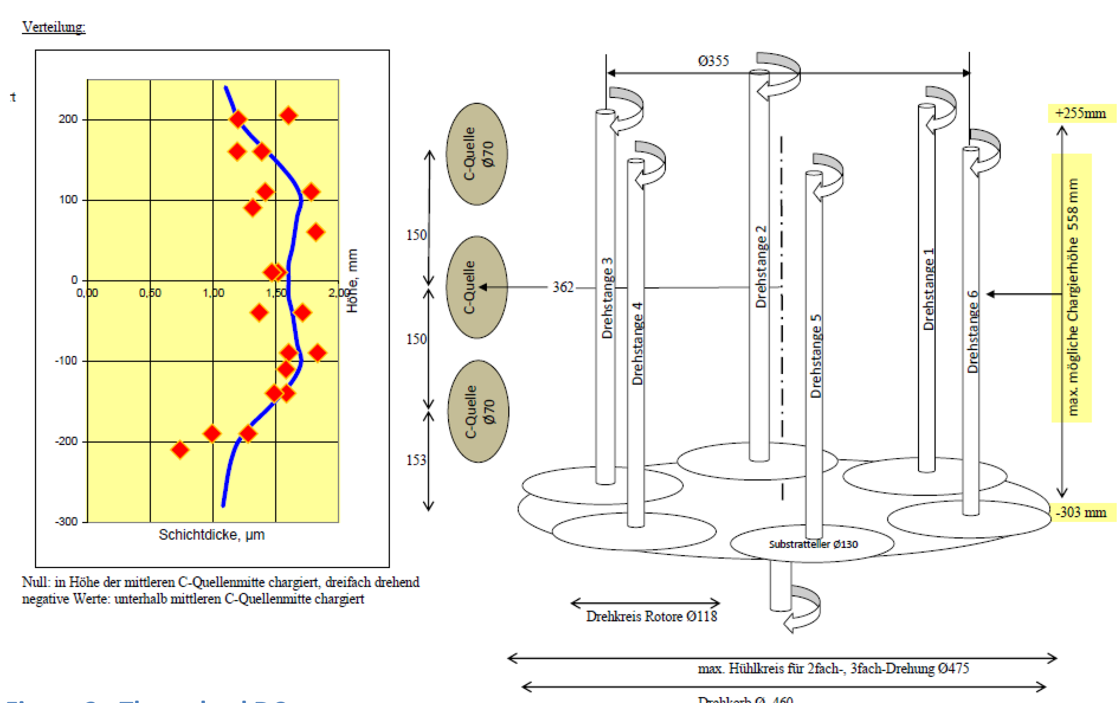
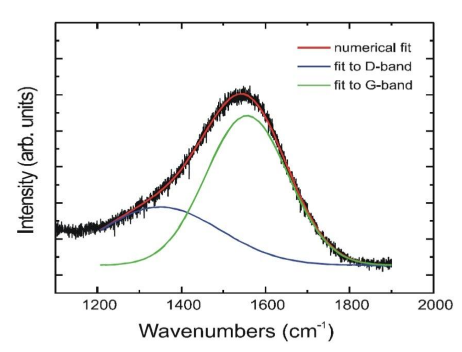


Figure 2: The pulsed DC-arc-process:
Layer thickness homogeneity (left)
Coating chamber geometry for a coating system with three pulsed DC arc sources (right)

3. Properties

The first important feature of the super-hard carbon films is the high hardness of more than 45 GPa. Super-hard carbon films are amorphous but with a high amount of diamond like bindings. In figure 3 the determination of sp^3-binding content is illustrated. The second important feature is the adhesion of the super-hard carbon film on steel and hard ceramics. The adhesion of super-hard carbon films on steel is illustrated in Figure 4 determined with Rockwell-indentation and micro-scratch test [4].



G-Peak : on 1580cm^{-1}, graphite, descended from sp^2-bindings, carbon **atom couples**

D-Peak : on 1350cm^{-1}, disordered, descended from sp^2-bindings, **carbon atom rings**

ID/IG : sp^3-content: 0.20-> 20%
0.16->33%
0.08->59%
0.00->85% -> ta-C-structure

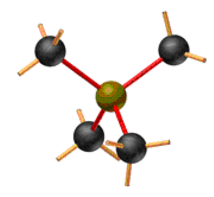
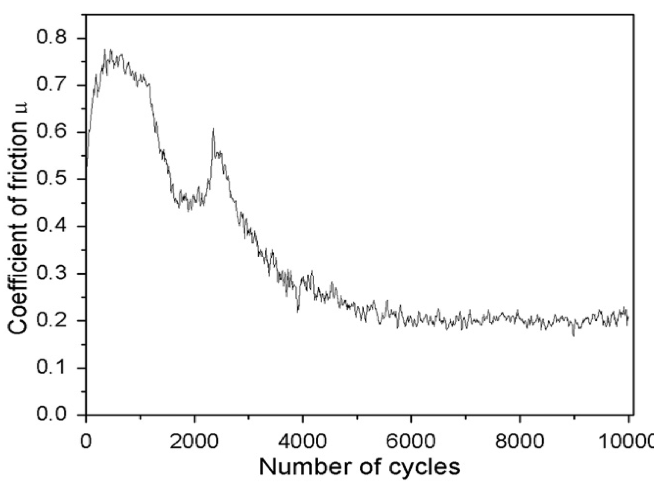


Figure 3: Raman spectroscopy:
The analysis of G-Peak and D-Peak reveals a high sp^3-amount (more than 85 %)

Property	value, unit
Hardness, GPa	45 ± 2
Young's modulus, GPa	385 ± 6
Internal stress, GPa	-1.9 ± 0,2
Critical Load Lc2, N	71 ± 3
Friction coefficient	0.09 ± 0,02
Coating wear rate, m^{3}N^{-1}m^{-1}	1,3 x 10^{-17}
Wear rate of counterpart	4.8 x 10^{-18}

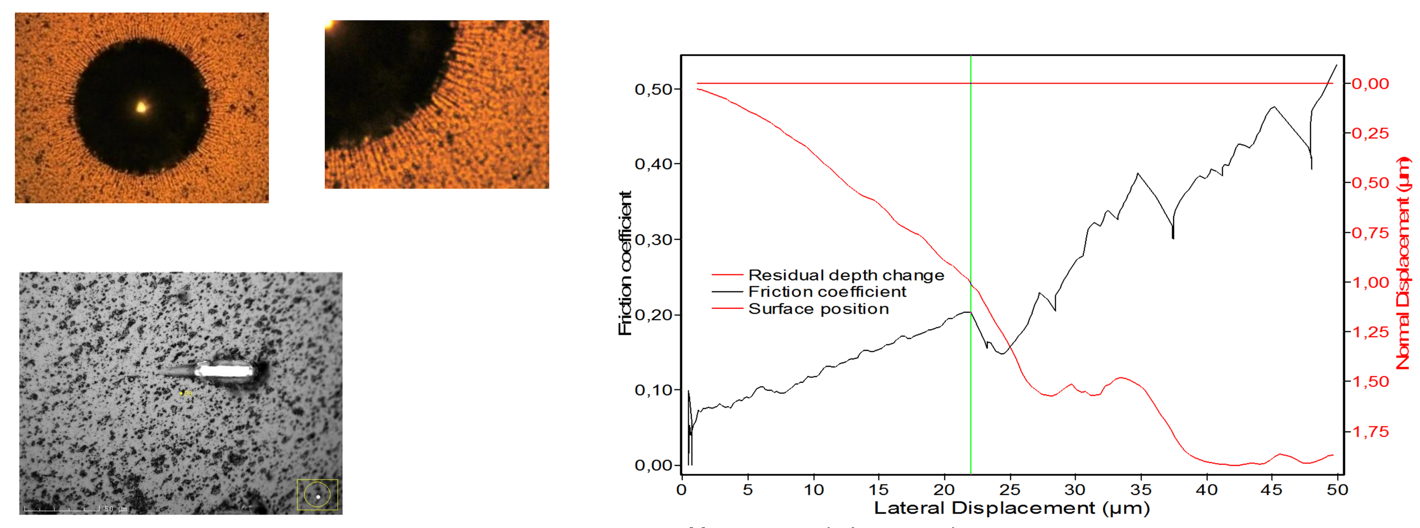
Table 2 gives values for different properties of the of the super-hard carbon coatings, measured at the University of Koszalin [2] on a multilayer coating with 1.5 µm super-hard carbon (ta-C) on top. The Hardness was measured using a Berkovich indenter and a constant depth of 0,3 µm. The critical load was determined with the scratch method. A type C rockwell indenter moved on the film whereas the normal load was linearly increased. The critical load Lc1 is the load value which is associated with the first cracks in the film and Lc2 is the load where full delamination of the film is observed.



The diagram on the left side shows the coefficient of friction of a super-hard carbon film, measured using the pin-on-disk method under dry conditions. A higher value of the friction coefficient during the initial period of the test is characteristic for super-hard carbon films(ta-C). After the running-in the COF drops to 0.2 and remains stable for the remaining time of the test. By means of micro-scratch-test a COF of below 0.09 has been measured [5].

Rockwell-indentation

Micro-scratch test
(diamond tip radius 7.5 µm)



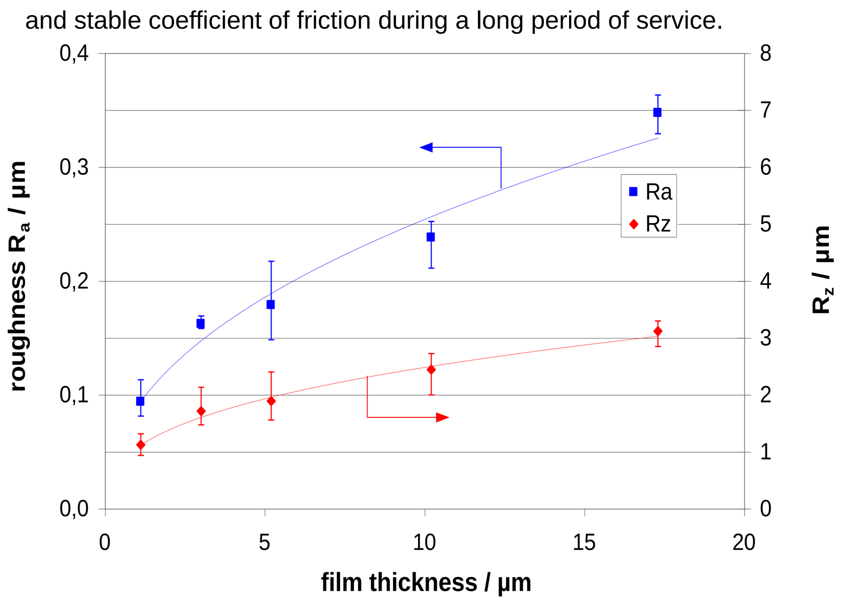
Scratch on a ta-C sample after loading from 0 to 1300 nm (HSS-substrate, 2.0 µm)

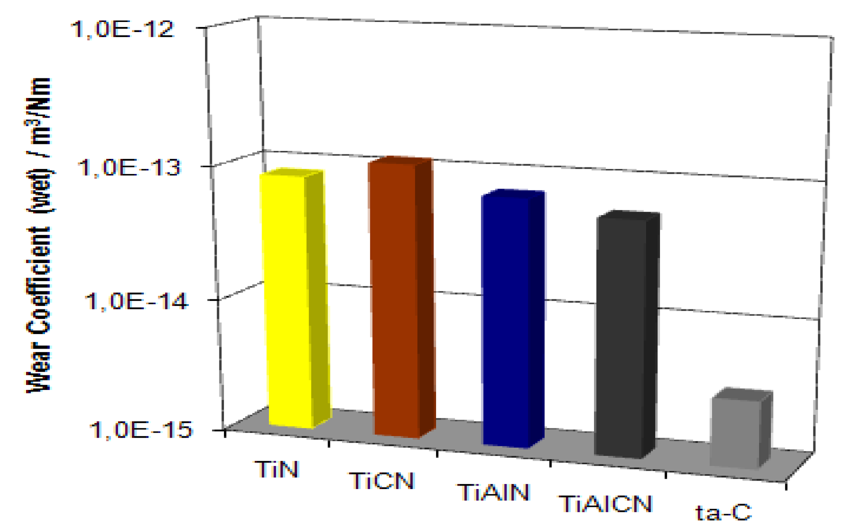
Measurement during a scratch test with a final load of 1300 nm (HSS-substrate, 2.0 µm)

Figure 4: Adhesion on HSS materials [4]:
The Rockwell-indentation shows HF1. With micro-scratch test a friction coefficient of 0.05 ..0.10 was measured [5]. The 2 µm films cracks at 600 mN.

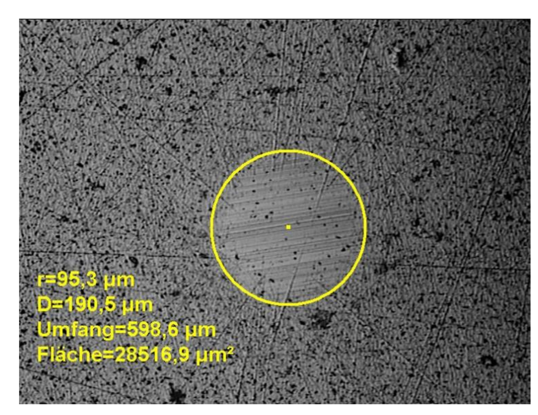
4. Conclusions and Discussion

Super-hard carbon films (ta-C) combine high hardness with a low coefficient of friction. This combination makes them well suited as tribological coatings on steel and hard ceramic substrates. Some applications of this coating are shown in figure 6. The advantage of the super-hard carbon is the high hardness and a wear coefficient which is five times better compared to well known hard coatings in industrial use (see figure 5). The disadvantage is the high surface roughness after deposition. The roughness of the hard carbon film depends on film thickness (see diagram below) and causes a high coefficient of friction in the initial stage of use. But after a running-in period or polishing the super-hard carbon (ta-C) is characterized by an excellent and stable coefficient of friction during a long period of service.





Comparision of wear coefficients (wet) of hard coatings measured with a 1 µm diamond suspension and steel balls.



Calo-wear-calotte grinded with a steel ball on ta-C-film, 2.0 µm (HSS-Substrate, Al_2O_3-Suspension), wear coefficient: 3x10^{-16} m^3/Nm

Figure 5: Wear coefficient compared to other hard coatings on HSS-steel:
On hard carbon films a wear rate of about 3 x 10^{-15} m^3/Nm (or even better) has been measured using a steel ball. This is five times better compared to the well-known TiN.

Mills and hobs

Knifes and cutters

Tools for punching

Motor components

Figure 6: Applications on HSS and HM-substrates:
Cutting tools for non-ferrous materials, motor components, machinery parts, industrial knifes and cutters, tools for the textile industry

Acknowledgements
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