DLC-Coating by Using the Pulsed D.C.-Arc-Process (PulsArc)

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A b s t r a c t

DLC-(Diamond-Like-Carbon)-coatings have been deposited using the pulsed d.c.-arc-process (PulsArc). This new method for DLC-coatings is characterized by a combination of the well-known d.c.-arc-process with a sequence of short pulses of high current. In this paper we demonstrate that the pulsed d.c.-arc technique (PulsArc) is suitable for the deposition of DLC-films. Coating rates up to 0,2µm/min are reached. Some polished HSS-slides have been coated using different mixtures of argon and argon/acetylene to form the plasma. The coated slides have been tested by different methods. The use of the gas mixture with acetylene leads to insulating films containing hydrogen. The micro hardness was found at values up to 4.600HV, the wear-coefficient at values in the range of $10^{-17}m^3/Nm$. These values are attributed to a high sp^3/sp^2-ratio as confirmed by Raman-spectroscopy. Finally the good correlation between the E-modulus measured by a laser-acoustic method and the Raman-spectra will be shown.

1. Introduction

Since carbon- and DLC-layers are characterized by low friction coefficients and a high hardness they are very interesting for industrial applications. The topical state of the technology of depositing these coatings are glow discharging, sputtering processes and the d.c.-arc-process. Only by sputtering and the d.c.-arc process it is possible to deposit carbon- or DLC-films without hydrogen or with a defined share of it.

The vacuum-arc process is a well-established deposition process in hard coating devices even for multi-layer systems /1/. The vacuum-arc generates a highly ionised plasma (ionisation rate about 70%). By superposing the d.c.-vacuum-arc with a sequence of short pulses at a high value of current the ionisation energy at the formed plasma will increase up to 50eV and more. An ionisation rate of nearly 100% will be obtained during the duration of the pulses /2/.

In principle the pulsed d.c.-arc process (PulsArc) is applicable without any gas in the chamber. By adding an inert gas to form the plasma the hardness of the deposited films decreases and a better homogeneity of the films thickness is available, especially for real machine parts or tools.

The pulsed d.c.-arc process (PulsArc) generates best physical conditions for the deposition of hard DLC-films. Using this method high deposition rates up to 0,2 µm/min are available, thus satisfying the requests by the industry.

The advantage of the vacuum-arc process is the comparatively simple equipment design as compared to that of the CVD-process. The realisation of the additional power supply, generating the sequences of short high-current pulses, is no technical problem.

2. Experimental

To carry out the experiments we used a small commercial vacuum-chamber of 600 x 600 x 600mm^3. The used arc-source is a commercial round type, produced by INOVAP, completed with a target made of pure carbon (graphite) with a diameter of 72mm and 12mm thickness.

We used a commercial available power supply generating a constant current at a value of 50A, completed with especially developed electronics for control. The power supply was added by a pulsed current source, which furnishes pulses with a peak current of 1.600A and a duration of 300µs. The repetition rate of the pulses is 100 Hz. The power of the pulses is about 30Ws at 1500A_{pulse}.

The arc-discharge has been ignited using a mechanical striker. The discharge burns continuously with a d.c.-current of 50A, superposed by the 300µs-current pulse sequences.

Using the d.c.-current superposed by the pulse sequences we did not need any complicated ignition device as reported in /1/. The different behaviour of the arc-spot was shown in /3/. We used HSS-slides with highly polished surfaces as substrates. The HSS-slides have been fixed on a turntable and turned around three axis' through the chamber. The turntables diameter is 370mm and the minimum distance between the arc-source and the target was 190mm. Each deposition process has been divided into short coating cycles (single layer). After each cycle a break of some minutes took place to cool down the substrates. Thus the deposition of the carbon layers has been carried out at substrate temperatures below 200°C.

For the coatings presented at this paper we used different mixtures of Argon or Ar/C_2H_2. The main coating parameters are listed in Table 1.

As reported in /3/ we remarked an increase of the arc's voltage corresponding to the value of the pulses maximum current. This results in a higher degree of ionisation of the carbon-plasma (nearby 100%) and an increased ionisation energy of the plasmas particles (up to 70eV).

3. Results

We analyzed the deposited films by different methods. The results are summarized in Table 2.

The hardness was tested by a Vickers-microindenter DUH-202 (Shimadzu). The program /4/ gives us the equivalent Vickers-hardness. The Young`s modulus was determined using laser-enhanced ultra-sonic emission /5/. The films thickness was determined by an optical method as well as using a ca-lotte-grinding gadget (calotest). The wear coefficient was determined using the calotest too. Calotests have been carried out with a speed of 600rpm using a WC-ball with a diameter of 20mm. We did not use any abrasive or lubricant solution. The deepest ball crater was found to be 0.6µm corresponding to a wear length of 1.226m. Figure 1 shows the wear coefficients resulting out of a series of ball craters on one test slide.

The sp^3/sp^2-ratio was investigated by Raman-spectroscopy. Figure 2 depicts the Raman spectra of one sample which consists of two broad bands known as the D- and the G-modes located at 1350cm^{-1} and 1550cm^{-1}, respectively /6/. The D band is related to sp^2-bonded graphite rings and the G band is related to all sp^2 sites. The disappearance of the D band is an indication for the increase of sp^3 bonding due to a de-creased probability for the occurrence of graphite rings. From numerical fits to the data for frequencies >

1200cm^{-1} based on two Gauss functions we calculate the area ratio of the D and G peak intensity which can be related to the sp^3/sp^2-ratio /6/.

The contents of hydrogen have been investigated with ERDA /7/. Figure 3 shows the ERDA-depth profile of sample 051001a. It shows the impact of hydrogen into the deposited carbon layer using the Ar-C_2H_2 – mixture to form the plasma.

4. Conclusions

The measurement of the different DLC-films on test slides shows that the pulsed d.c.-arc technique (PulsArc) allows to deposit DLC-films in a wide range of process parameters with good hardness and Young`s modulus. Micro hardness up to 4.600 kp/mm^2 was measured.

The best wear coefficient we found on DLC-coatings with a hardness below 3.000kp/mm^2, as shown in Figure 4 (except sample 51001b).

A small share of hydrogen in the carbon layer results in insulating films and leads probable to a lowered wear coefficient.

The ratio of sp^3/sp^2-content is in good agreement with the Young's-modulus as shown in Figure 5. It shows that high values of hardness and Young`s-modulus are corresponding to a decrease of the D band to G band intensity ratio measured by Raman spectroscopy.

Future aims are to fix a defined field of parameters for the deposition process and to reach deposition rates up to 0.2 µm/min. First tests are carried out just in time.

Acknowledgements

The work was supported by the SMWA of the Free state Saxony under grant No. FK 7709. The authors like to thank the Forschungszentrum Rossendorf Inc. and the Fraunhofer Institute of Material Research and Beam Technology Dresden for the assistance meanwhile the investigations.

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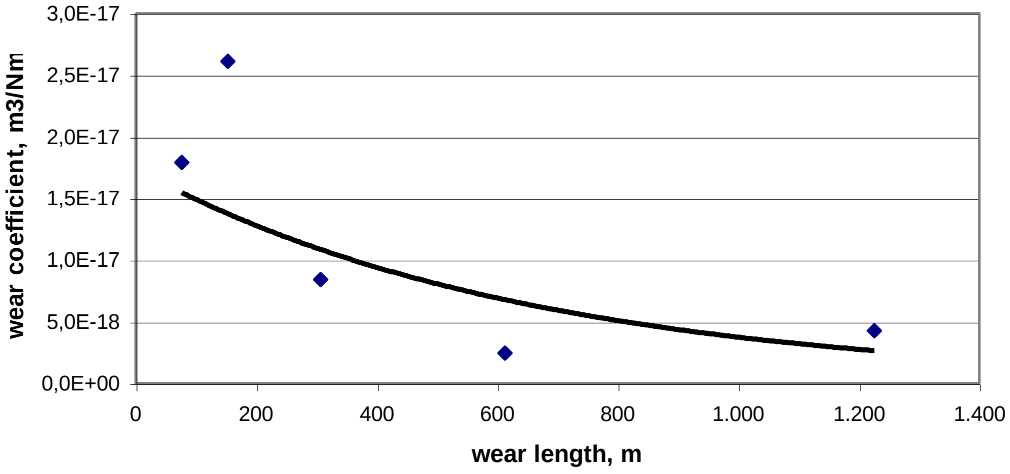

Fig. 1 Wear coefficients of a series of ball craters on sample 51001a corresponding to the wear length

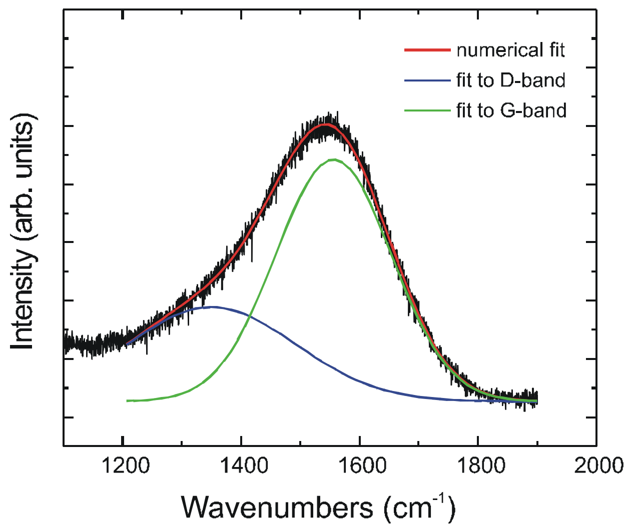

Fig. 2 Raman spectra of sample 51001a, fitted with two Gaussian peaks for the G- and D-mode

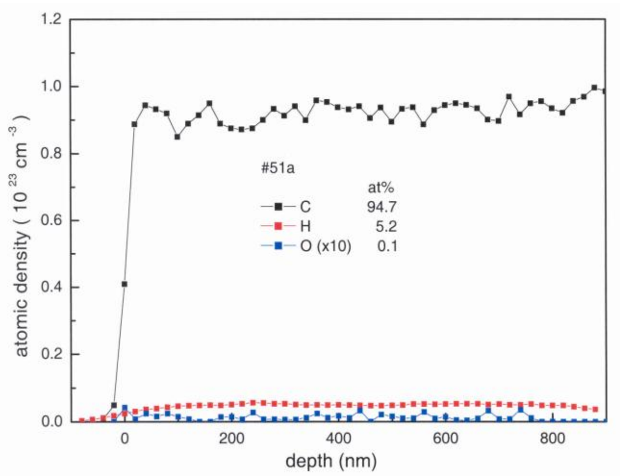

Fig. 3 ERDA-based depth profile of sample 51001a

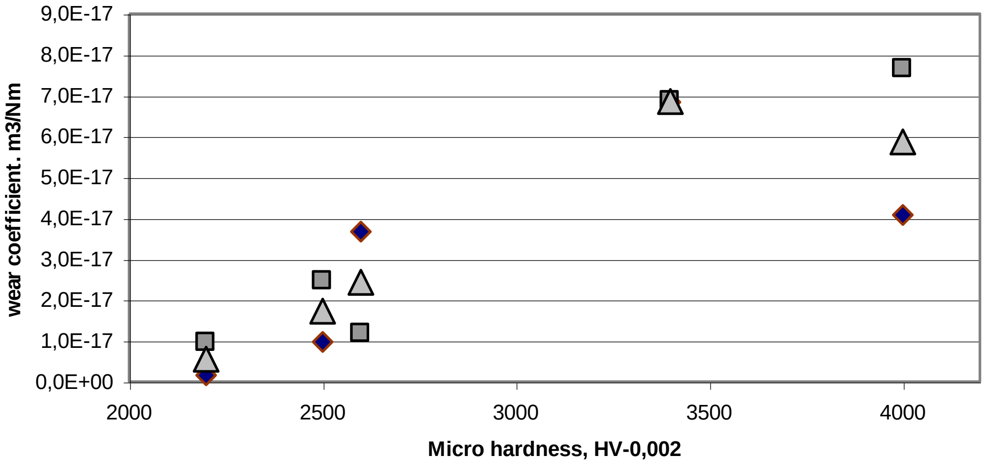

Fig. 4 Wear coefficients of a series of the samples depend on the micro hardness values

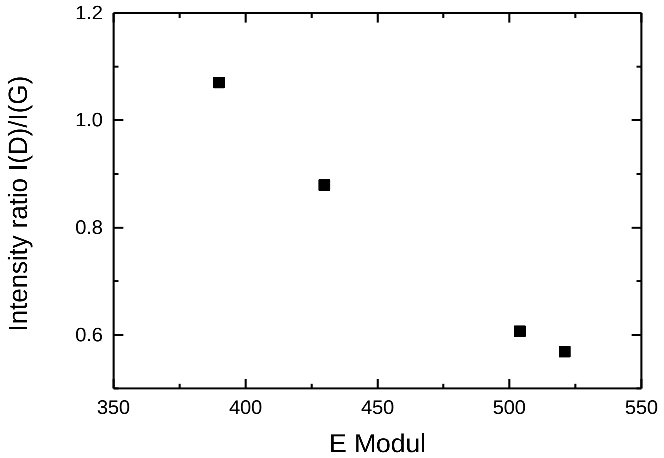

Fig. 5 Correlation between Young's-Modulus and the intensity ratio of D-/G-peak for the samples with the highest Young's-Modulus.

Number of Tested slide	DC-Current A	Pulse peak A	Pressure Pa	Temperature °C	BIAS V	Process gas mixture
41001*	50	1.500	5,0E-2	60	0	Ar / C_2H_2
51001b	50	1.500	5,0E-2	100	0	Ar
51001c	50	1.500	2,0E-1	60	-80	Ar
21001	50	1.500	1,0E-1	180	-80	Ar
31001	50	1.500	1,0E-1	60	0	Ar / C_2H_2
051001a*	50	1.500	5,0E-1	130	0	Ar / C_2H_2

*DLC-film includes Hydrogen

Table 1 Coating parameters for the coated HSS-slides

Number of the slide	Films thickness µm	Micro hardness HV_{2mN} kp/mm^2	Young`s modulus GPa	D/G band - ratio	Wear coefficient m^3/Nm	Electric resistance Ω/µm
41001*	0,7	2.600	334	0,57	1,7E-17	> 60 MΩ
51001b*	0,8	3.400	350	5,08	2,4E-17	> 4 MΩ
51001c	0,8	2.200	390	1,07	5,5E-18	205
21001	0,9	4.000	402	0,75	6,8E-17	31
31001	0,7	2.500	430	0,88	5,3E-17	134
051001a*	0,8	4.600	504	0,61	4,1E-17	30 kΩ

*DLC-film includes Hydrogen

Table 2 Summarized Parameters of the DLC films on the test slides