BARRIER EFFECT OF DLC THIN FILMS FOR POTENTIAL APPLICATION IN BIOMEDICINE

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Abstract

The aim of the presented paper was the investigation of the barrier properties of Diamond Like Carbon (DLC) thin films used for biomedical applications. The DLC films were prepared by the Plasma Enhanced Chemical Vapour Deposition (PECVD) from methane. Stainless steel AISI type 316L was used as a substrate. Samples were placed on the excitation RF electrode. The self-bias ranged from -700V to -800V and the deposition time varied from 1 min to 15 min. The working gas methane pressure during process was 20 Pa. Morphology of obtained DLC layers was characterized by AFM and SEM microscopy and the coating thickness by calotest method. The surface chemical composition was identified by EDS analysis. The coated samples as well as the pure substrate were tested for leaching of allergenic nickel into environment. Physiological solution was used as a model matter for this purpose. The content of nickel in the solution was monitored using ICP-OES analysis. The obtained results proved that the barrier effect was achieved even in case of 50 nm thick DLC film.

Keyword: DLC film, PECVD, barrier, nickel, leach

1. INTRODUCTION

As the modern technology is developed further, new materials and also new procedures are introduced into medicine. One of the branches that can profit from newly possessed knowledge is the implantology. The number of implants is growing every year [1 - 5]. In many applications (especially in orthopedics) the metal implants are irreplaceable by any other material and in many cases the first choice is the medical stainless steel AISI 316L (1.4404 EN) that contains 12% of Ni. Allergic reaction to metals is rare; however it can result in serious health problems when it occurs. Allergy to nickel was reported for 13% of population, allergy to cobalt for 3% and to chromium for 1% [2, 5 - 9]. Allergy to metals can result in eczema, impaired wound and fracture healing, infection-mimicking reactions, effusions, pain, urticaria and vasculitis etc. [2 - 5, 7 - 9]. Proving the allergy to implant is difficult and probably due to high complexity there are no relevant data to this given problem (according to the author's best knowledge). It can take several years before the allergy reaction occurs and it can show also in case of the patients with negative contact test [2, 4, 5]. It is also important to differ between allergy and infection.

Relatively complicated situation can be solved by using barrier coatings that can also improve the properties of the surface. Often ZrO_x coatings are used [10] or carbon thin films can be applied [11 - 19]. In recent years, lot of attention has been paid to the above mentioned carbon thin films as these are biocompatible and have excellent mechanical properties. Therefore the carbon coatings are very promising for bioapplications.

This work is focused on barrier properties of the diamond like carbon (DLC) coatings deposited on the medical stainless steel AISI 316L using Plasma enhanced chemical vapor deposition (PECVD). The bias of the substrate and the treatment time were varied. Barrier effect of the DLC coating of various thicknesses was studied by measuring the nickel leaching from substrate to the physiologic saline solution.

2. MATERIAL AND METHODS

The rectangle-shaped specimens of polished stainless steel type AISI 316L (1.4404 to EN 10088) of 30 x 50 mm and 2 mm thick were used. The substrates were washed in isopropanol in ultrasonic cleaner and dried in laboratory oven. The deposition of DLC thin films was carried out in the low-pressure PECVD reactor with planparallel plate electrodes. The bottom electrode was capacitively coupled to the RF power generator (13.56 MHz) via matching unit. The excitation electrode was used as a substrate holder. DLC thin films were deposited for various substrate biases (-700 V, -750 V, -800 V), times (1, 2, 5, 10, 15 min) and powers delivered to the excitation electrode (160 W, 180 W, 200 W). The methane (CH4) was used as the working gas. The flow rate of CH4 was 15 sccm while the working gas pressure during process was 20 Pa. Before the deposition itself the substrate was cleaned in argon plasma for 5 min.

The layer thickness was measured by the calotest method. Morphology of obtained DLC layers was characterized by AFM (Atomic Force Microscopy) and SEM (Scanning Electron Microscopy). The surface chemical composition was estimated by EDS analysis (Energy-dispersive X-ray spectroscopy).

The coated samples as well as the pure substrate were tested for leaching of allergenic nickel into environment according to UNI EN 1811:2011 - Standard on nickel release. However this standard relates to nickel contact allergies. Therefore the experiment was adapted slightly: Physiological saline solution was used instead of artificial sweat solution as a model matter for this purpose. The content of nickel in 45 ml of test solution was monitored after 1 and 6 months (instead of 1 week) of interaction of the samples using ICP-OES analysis.

Leaching of nickel was tested using stainless steel substrates coated with DLC films and two types of reference samples. All samples had covered bottom, sides and edges by nitrocellulose lacquer so the functional surface, on which the physiological solution had exposed, was 8cm^2. The both referential samples were from stainless steel AISI 316L. One of them had 8 cm^2 of uncoated surface and the second one was completely covered by nitrocellulose lacquer. The content of nickel in the solution was monitored using ICP-OES analysis.

3. RESULTS AND DISCUSSION

Evaluation of the layer morphology using SEM and AFM analysis did not show any considerable changes neither by self-bias nor by time dependence (Fig. 1 – Fig. 5).

From AFM pictures is evident the structure of the grains in stainless steel with texture after rolling (Fig. 3 – Fig. 5). This structure remained also after deposition of DLC layers. The DLC deposition only resulted in rounded edges of particular grains (Fig. 1, Fig.2).

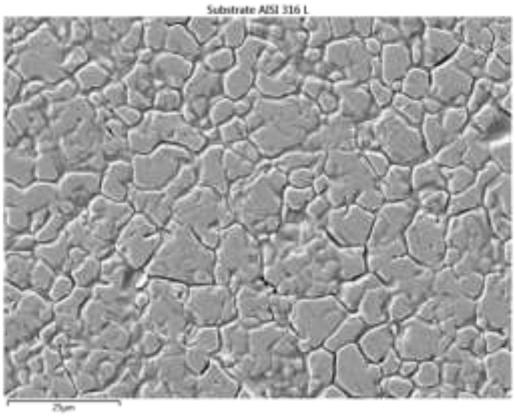

Fig. 1 SEM of substrate AISI 316L

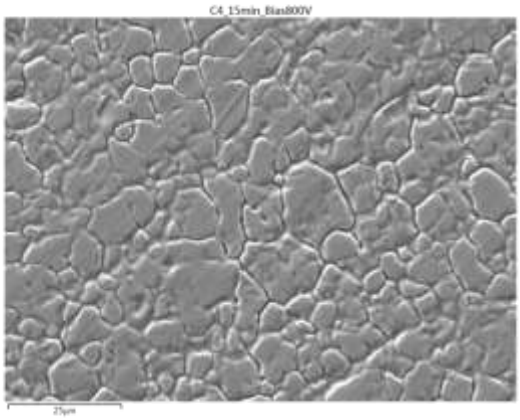

Fig. 2 SEM of DLC film; -800V,15min

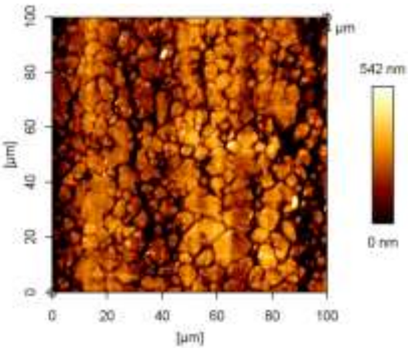

Fig. 3 AFM of substrate AISI 316L

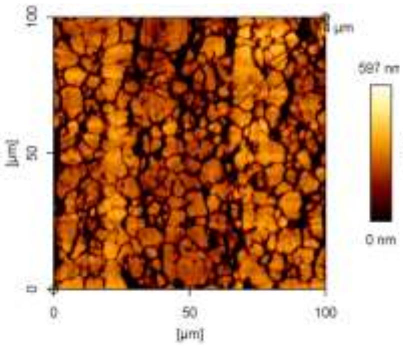

Fig. 4 AFM of DLC film; -700V,1min

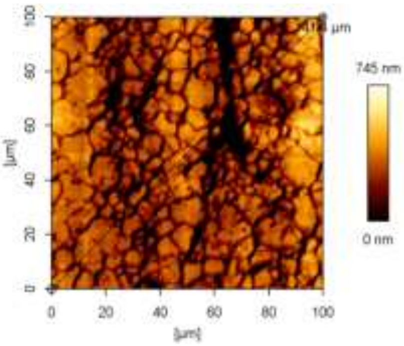

Fig. 5 AFM of DLC film;-800V,15min

The relation between deposition conditions and thickness of deposited layer is summarized in Fig. 6. The thickness of the layers varied from 50 to 270 nm and did not linearly grow with the deposition time as was presumed. A significant carbon layer growth is observed during first two minutes of deposition regardless of the self-bias. For longer deposition times the thickness of the layers decreased. That was probably caused by ion bombardment which could densify or sputtered the layer away. This is also supported by the fact that the biggest thickness difference is observed for the highest self-bias (-800 V).

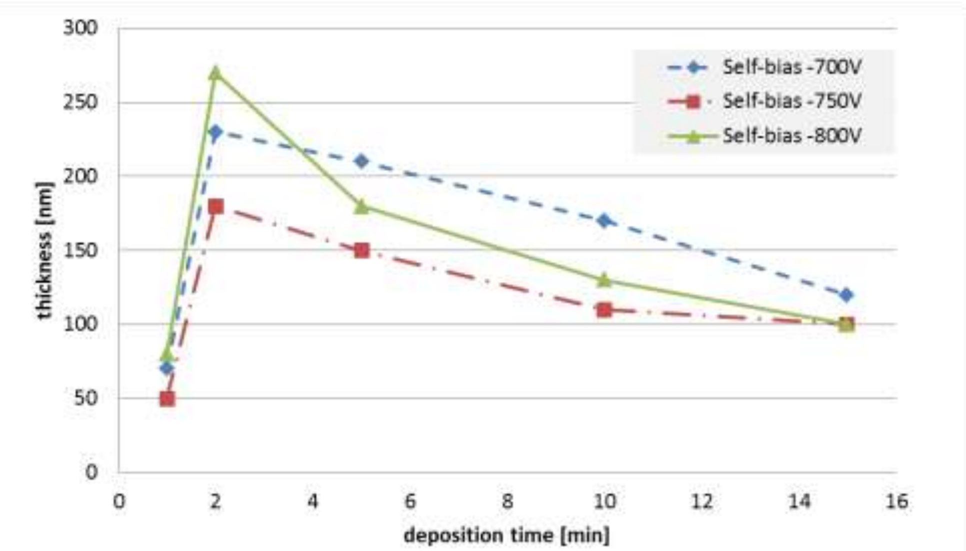

Fig. 6 Graph to show effect of deposition conditions on thickness of DLC films

EDS analysis results of the surface of the samples are summarized in Table 1. As was expected, DLC layers with 15 min duration of deposition have higher content of carbon than layers which were deposited just 1 minute. In comparison of samples which were deposited 15 min has the highest content of carbon the one with the lowest self-bias (- 700 V). That relates its higher thickness and the theory that higher self-bias on the sample causes densifying or sputtering of the layer (see Fig.6). In accordance with the growth of the layer and increasing content of carbon the content of other elements on the surface of the sample decreases.

EDS analysis allowed us to estimate the chemical composition of the surface to depth of approximately 2 μm. However the thickness of the layers is always lower than this value. That is why in all cases the chemical composition of the substrate exhibits as well. The specifications of chemical composition of the surface from EDS are therefore not relevant for evaluation of barrier dispositions of the thin films.

Table1 EDS analysis of stainless steel AISI 316L substrate and DLC films

sample	C [Wt%]	Si [Wt%]	Cr [Wt%]	Mn [Wt%]	Fe [Wt%]	Ni [Wt%]	Mo [Wt%]	W [Wt%]
AISI 316L	3.5	0.4	16.6	1.4	66.1	9.8	2.3	0.2
-700V/1min	7.8	0.3	15.9	1.3	63.2	9.4	1.9	0.2
-700V/15min	38.2	0.2	10.9	0.9	42.3	6.9	1.3	0.1
-750V/1min	7.9	0.3	15.9	1.3	63.1	9.4	1.9	0.2
-750V/15min	33.9	0.3	11.6	0.9	45.3	6.5	1.4	0.1
-800V/1min	7.7	0.4	15.9	1.3	63.3	9.4	1.9	0.2
-800V/15min	35.3	0.2	11.4	0.9	44.3	6.5	1.4	0.2

The amount of nickel that leached from the surface of the samples into the physiological solution is adduced in Table 2. From final results is clear (/evident) that from 1cm^2 of unmodified medical stainless steel AISI 316L leached into the test solution 0.113 um of nickel already after 1 month. We are not aware of any limit, which would define allowed nickel leaching of implants. There is just a limit for contact allergies to fashion jewellery which is 0.5mg/cm^2/week. Although the amount of leached nickel from AISI 316L was after one month almost 5x lower then this limit, the implants interact with tissue over a long period. Later it might occur serious problems which would lead to reoperations that is why we reckon this amount alerting.

As we can see from results in Table 2, the all DLC layers (even the 50nm thick as well) made a barrier to diffusion of nickel into the test solution for at least 1 month. Even after a half-year-long interaction with the physiological solution was any of the DLC layers damaged, flaked off or corroded. However the lacquer cover damaged by few samples after this time and that destroyed the results of nickel leaching through the DLC layer (see Table 2 - marked *). These samples were eliminated. We still continue working on adjustment of the nickel leaching test to ensure the contact of the test solution just with the functional part of the sample (that means with the layer).

After the half-year-long exposition of DLC layers in the test solution 4 samples with the highest self-bias and 3 samples with the lowest self-bias confirmed the barrier effect of the layers. Nickel did not leach neither from the sample with -750V self-bias and the lowest thickness of DLC layer (50nm).

Table 2 Content of nickel in the physiological saline solution monitored using ICP-OES analysis

bias [V]	reference	reference	-700V					-750V					-800V				
deposition time [min]	AISI 316L	all lacquer	1	2	5	10	15	1	2	5	10	15	1	2	5	10	15
DLC film thickness [nm]	0	-	70	230	210	170	120	50	180	150	110	100	80	270	180	130	100
Ni [μg/cm²/ 1 month]	0.11	under the limit detection	under the limit detection					under the limit detection					under the limit detection				
Ni [μg/cm²/ 6 month]	0.22	0.11	0.27	under the limit detection			0.22	under the limit detection	0.48*	1.40*	0.27	1.88*	2.53*	under the limit detection			

*damaged lacquer

4. CONCLUSION

In our work were studied the properties of the DLC layers prepared under various deposit conditions. The thickness of the layers ranged from 50 to 270 nm. The layers copied the structure of the grains in the substrate from stainless steel AISI 316L. All layers proved barrier effect for allergenic nickel after one month of interaction with the physiological solution. By 8 samples with the DLC layer nickel was not found in the test solution even after a half year. Standard on nickel release UNI EN 1811:2011 can be with certain adjustment applied also for long-term testing of nickel leaching from implant materials. The results in the study suggest that DLC films are suitable for biomedical application as barrier layers for allergenic nickel.

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