CORROSION AND BACTERIAL RESISTANCE OF ZrN, DLC COMP a-C:H AND MULTICOMP TiN/TiAIN COATINGS USED IN MEDICAL

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Abstract

The study presents the results of the corrosion resistance and bacteriological research of DC01 steel protected by ZrN, DLC COMP a-C:H and MULTICOMP TiN/TiAlN coatings applied by PVD method (Physical Vapour Deposition). The experiment was divided into two stages. The first part was concentrated on the corrosion resistance of analyzed coatings affected by selected corrosive solutions typical for hospital environment: Ringer's solution and 0,9% NaCl. The second part bacteriostatic or bactericidal properties of two strains of bacteria - *Pseudomonas aeruginosa* and *Staphylococcus aureus* were assessed.

It has been proved that the coatings used in the study present good corrosion resistance and bacteriostatic properties.

Keywords: corrosion resistance, bacterial resistance, ZrN coating, DLC COMP a-C:H coating, MULTICOMP TiN/TiAlN coating

1. INTRODUCTION

Metallic materials used in medicine are protected against corrosion by metallic coatings and paint coats among others. Some elements of medical equipment are also protected by the Ni, Cr, Cu coatings, and zinc hot-dip galvanizing or galvanizing.

We can observe increasing popularity of multi-layered coatings, built of various phases, e.g. TiNi, TiAlN, TiAlC, CrN, applied by PVD and CVD methods [2]. The PVD method (Physical Vapour Deposition) consists in physical deposition of thin layers coming from the gas phase. The achieved layer has 3 - 5 μm thickness. It is characterised by high hardness,which most often ranges from 2000 to 3000 HV, and it ensures abrasive wear resistance. Thanks to that, this protection method is broadly used in automobile and aviation industries. They are also applied to protect cutting tools, drills, as well as implants and medical tools. Despite of excellent mechanical and tribological properties, the coatings applied by use of PVD technology may pose poor corrosion properties, due to their structural defects and pores. When multi-layered coatings are used, it helps to reduce the problem [3].

The selection of a effective corrosion protection for steel is important particularly in a hospital environment. The metallic coating destruction is related to the appearance of corrosion, which in consequence leads to adhesion and growth of bacterial cells [4,6]. A patient is in danger of infection as long as the bacterial flora remains on the surface of hospital, diagnostic or rehabilitation equipment [4,5]. Corrosion and protective properties of are a very important thing to be considered during surface modification, but it also improves the biocompatibility of the materials used by medicine. The fact is crucial in case of medical tolls, implants or elements which stay direct contact with skin or mucous membrane. One criterion of biocompatibility of materials is bacteriostatic properties [6].

The authors started a research which aim is to assess the effectiveness of protecting steel elements, with coatings applied by PVD method (Physical Vapour Deposition). The research was divided into two stages. The first part was concentrated on the evaluation of corrosion resistance of the coatings, exposed to the activity of selected corrosive solutions. The second part was focused on the bacteriostatic and bactericide properties.

2. SAMPLES PREPARATION

The DC01 steel was selected for the research in form of cold-rolled sheet-metal, size 1000 x 2000 mm, and thickness 3 mm, used for medical equipment production. Chemical composition of material used in experiment was as follows: 0,07 %C; 0,02 %P; 0,016 %S; 0,49 %Mn; 0,034 %Al; 0,060 %Si; 0,056 %Cu; 0,013 %Cr; 0,032 %Ni. Carbon and sulphur were marked by a carbon and sulphur LECO CS-125 analyzer, however the rest of elements were marked by ICP-OES spectrometer.

Samples of 10 mm diameter were cut out of accidentally selected areas of sheet metal, which were grinded by discs (grain size 80 and 120) and then polished.

On the samples prepared in this way, the ZrN, DLC COMP a-C:H and MULTICOMP TiN/TiAlN coatings were applied by PVD method. Their quality is presented in images from scanning electron microscope SEM EVO MA 25, produced by Zeiss (Fig. 1-3).

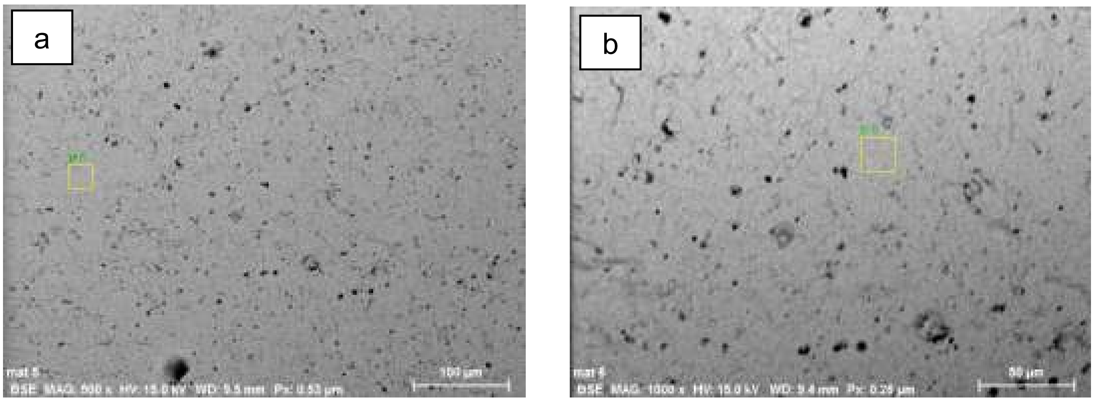

Fig. 1 The example of the sample surface, covered with ZrN, magnification: a - 500x, b - 1000x

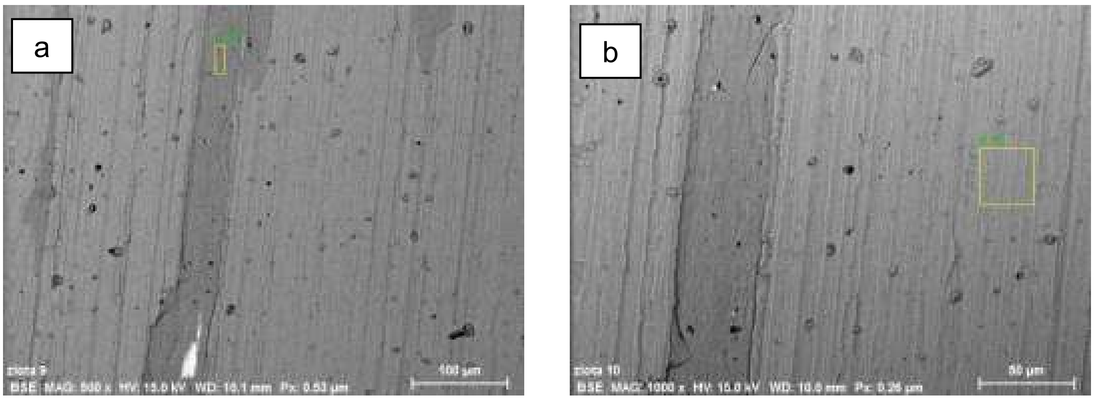

Fig. 2 The example of the sample surface, covered with MULTICOMP TiN/TiAlN, magnification: a - 500x, b - 1000x

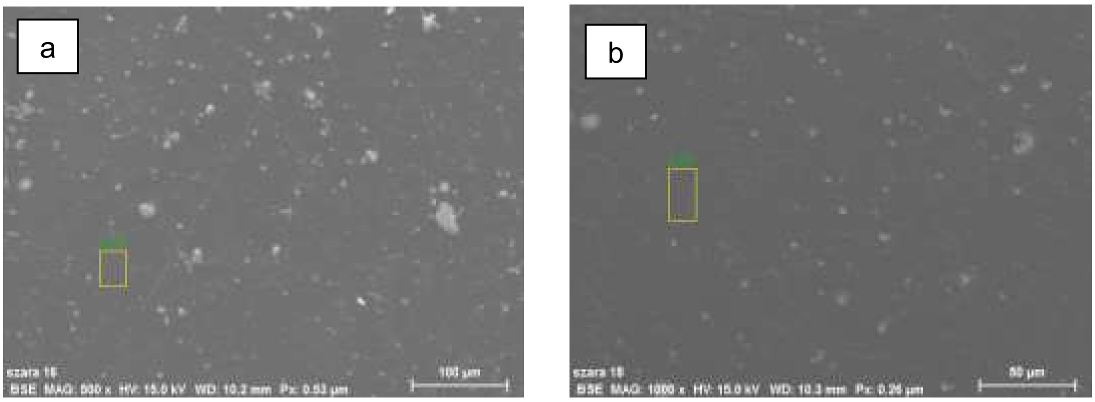

Fig. 3 The example of the sample surface, covered with DLC COMP a-C:H, magnification:
a - 500x, b - 1000x

The analysis of qualitative and quantitative composition of the examined samples was conducted by use of EDS microanalyzer, produced by Brucker, which was applied to the scanning electron microscope. The average results of the analysis are presented in Table 1.

Table 1 The qualitative and quantitative composition of the examined samples

Coating	The content of elements in DC01 steel by weight [%]							
	Zr	N	Ti	Al	O	C	W	rest
ZrN	81	10	-	-	-	7	-	2
MULTICOMP TiN/TiAlN	-	23	72	4	-	-	-	1
DLC COMP a-C:H	-	7	-	-	1,5	86	4	1,5

3. CORROSION RESISTANCE EVALUATION

The electrochemical research of corrosion resistance was based on potentiodynamic method in corrosive solutions oxygenated in a result of free contact with the air, corrosive solutions (Table 2), in 37 °C.

Table 2 *Characteristics of corrosive solutions*

Corrosive solutions	Concentration / qualitative and quantitative composition
Ringer's solution	0,2 g/l K_2HPO_4, 0,26 g/l Na_2HPO_4, 0,33 g/l KSCN, 1,5 g/l $NaHCO_3$, 0,7 g/l NaCl, 0,13 g/l $(NH_2)_2CO$, 1,2 g/l KCl, pH 8,5
0,9% NaCl	9 g NaCl / 1000 g solution

The research was conducted by use of a measurement system consisting in the Autolab PGSTAT302N potentiostat, no. AUT83628 produced by ECO CHEMIE B.V. company, which cooperates with the Nowa 1.7 software, by Metrohm Autolab B.V. The samples surface was measured before each measurement, washed by acetone, and conditioned in the examined solution for 1 hour.

The electrode prepared in this way was then placed in the side stub pipe in electrochemical cells (400 cm^3 capacity), equipped with water coating and connected to the Julabo ED 5 thermostat, which ensures the precision of regulation by ± 0,1 °C. The system was connected to the A probe, together with a reference electrode, were placed in a lid. Its role was fulfilled by calomel electrode (NEK, Hg / $Hg_2Cl_{2(s)}$ /

KCl(nas.)) of the +244 mV potential compared to NEW in temperature 25 °C with Haber-Ługgin's capillary at the end. The capillary end was situated about 1 mm away from the researched electrode surface - the sample.

The research was conducted by use of linear polarization method with potentials ranging from -0,1 V to 0,1 V, with the current range 1 mA and scanning rate 0,001 V/s, and by potentiodynamic method in cyclic voltammetry, with potentials ranging from -0,1 V to 1,6 V, and scanning rate 0,1 V/s, according to the EN ISO 10271:2012 standard.

By comparing the experimental curves with the curves described by the Tafel equation the following parameters were determined: the corrosion current density j_{kor} [nA/cm²], and the following values were calculated: the corrosion potential E_{kor} [mV], measured from the minimum on the polarization curve, the corrosion rate V_p [mm/year] and the polarization resistance R_p [MΩ]. Furthermore, the stationary potential OCP (equilibrium potential) as potential change over time by potentiostatic method was determined.

The results, which were the average of three measurements, are compared in Table 3. The polarization curves in Ringer's solution and 0,9% NaCl for the steel covered with ZrN, DLC COMP a-C:H and MULTICOMP TiN/TiAlN coatings, are presented in Figure 4.

Table 3 The results of the measurement of corrosion resistance of steel covered with, in corrosion solution

Established parametres	ZrN		DLC COMP a-C:H		MULTICOMP TiN/TiAlN	
	Ringer's solution	0,9% NaCl	Ringer's solution	0,9% NaCl	Ringer's solution	0,9% NaCl
OCP	-0,34	-0,38	-0,23	-0,36	-0,28	-0,39
E_{kor} [mV]	-345,40	-394,06	-236,30	-373,03	-291,48	-407,02
j_{kor} [µA/cm²]	108,51	83,73	127,35	289,75	377,78	264,67
R_p [Ω]	1,91	1,10	3,62	0,80	1,61	0,88

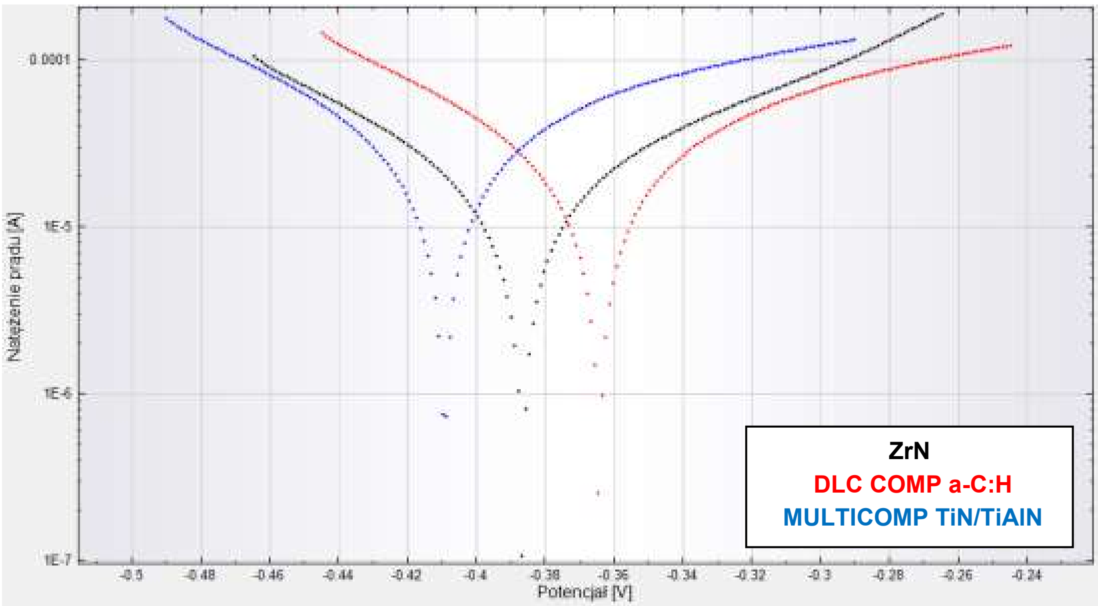

Fig. 4 The polarization curves in the 0.9% NaCl solution for the steel covered with ZrN, DLC COMP a-C:H and MULTICOMP TiN/TiAlN coatings

4. BACTERIOLGICAL RESERCH

The samples made of DC01 steel covered with coatings such as ZrN, DLC COMP a-C:H and MULTICOMP TiN/TiAlN were assessed. The *Pseudomonas aeruginosa ATCC 27853* and *Staphylococcus aureus ATCC 29213* bacteria were cultured on a medium of agar and blood agar (Fig. 5). The incubation period equaled 24 hours, and the temperature was 36 ^oC. The cultured bacteria strains were covered with samples for the incubation time.

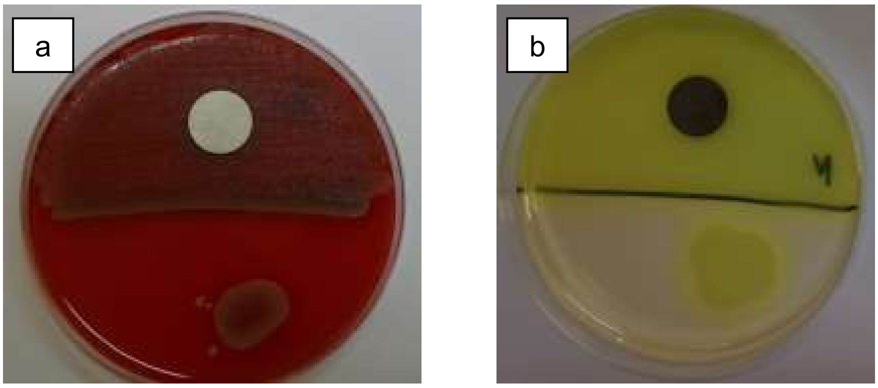

Fig. 5 The image of the medium with samples applied: a – ZrN coating, Blood agar, *Staphylococcus aureus*, b – DLC COMP a-C:H coating, Agar, *Pseudomonas aeruginosa*

When the incubation period finished, the samples were removed and the macroscopic surface was evaluated. All the coatings proved to be bacteriostatic (Fig. 6).

A small area of inhibition around the samples was observed in case of *Pseudomonas aeruginosa*, especially when the MULTICOMP TiN/TiAlN coating was applied. It implies bactericidal properties. The reference point was other bacterial strain culture without the application of samples and with samples without coatings.

In the first case, the bacteria growth was uninhibited. The samples presented only slight properties hindering bacteria growth.

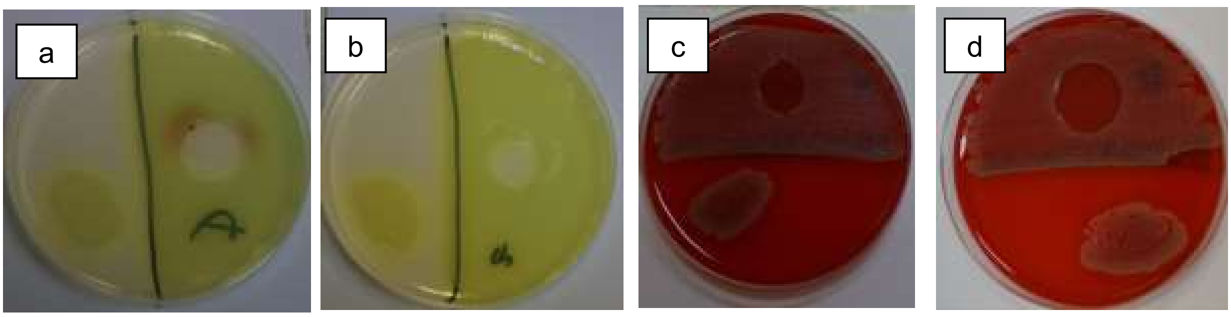

Fig. 6 The image of the medium without samples applied: a - MULTICOMP TiN/TiAlN , Agar, *Pseudomonas aeruginosa*, b – ZrN, Agar, *Pseudomonas aeruginosa*, c - DLC COMP a-C:H, Blood agar, *Staphylococus aureus*, d - MULTICOMP TiN/TiAlN, Blood agar, *Staphylococus aureus*

5. THE SUMMARY AND FINDINGS

5.1. Corrosion resistance research

The value of open circuit potential OCP, depending on the corrosive environment, equals from -0,34 to -0,38 in case of ZrN coating, from -0,23 to -0,36 for the DLC COMP A-C:H coating, and from -0,28 to -0,39 for

MULTICOMP TiN/TiAlN coating. The most positive OCP value was observed in case of DLC COMP A-C:H coating, both in Ringer's solution and in 0,9% NaCl solution. The lowest OCP value in Ringer's solution was achieved for ZrN coating, and in 0,9% NaCl solution it was the lowest for MULTICOMP TiN/TiAlN coating. It may be assumed that the DLC COMP A-C:H coating has the best stability, in both corrosion environments, and provides the best corrosion protection for DC01 steel, out of all researched coatings.

The corrosion potential $E_{kor,}$ depending on the environment, ranged from -345,40 to -394,06 mV for ZrN coating, from -236,30 to -373,03 mV for DLC COMP A-C:H coating and from -291,28 to -407,02 mV for MULTICOMP TiN/TiAlN coating. The highest value of corrosion potential was obtained for DLC COMP A-C:H coating, both in Ringer's solution and 0,9% NaCl solution. It may be stated that the coating is the most resistant to corrosion processes in examined environments.

The density of corrosion current varies from 83,73 to 108,51 μA/cm^2 for ZrN coating, from 127,34 to 289,75 μA/cm^2 for DLC COMP A-C:H coating and from 264,67 to 377,78 μA/cm^2 for MULTICOMP TiN/TiAlN coating. The highest density was reported in Ringer's solution in case of MULTICOMP TiN/TiAlN coating, the lowest in 0,9% NaCl solution for ZrN coating. According to these values it may be supposed that the most aggressive corrosion environment is Ringer's solution for MULTICOMP TiN/TiAlN coating, and the least aggressive is NaCl solution for ZrN coating, similarly to Ringer's solution for the coating.

The achieved values of polarization resistance R_p range from 1,10 to 1,91 Ω for ZrN coating, from 0,80 to 3,62 Ω for DLC COMP A-C:H coating, and from 0,88 to 1,61 Ω for MULTICOMP TiN/TiAlN coating. The highest corrosion resistance was observed in steel samples with the DLC COMP A-C:H coating in Ringer's solution, and the lowest in 0,9% NaCl solution.

5.2. Bacteriological research

All examined coating proved to have bactericidal properties in macroscopic evaluation. After standard incubation, the growth of *Staphylococcus aureus* and *Pseudomonas aeruginosa*, placed under the samples was not observed.

CONCLUSION

Accelerated corrosion examination of DC01 steel, covered with ZrN, DLC COMP a-C:H and MULTICOMP TiN/TiAlN coatings proved that DLC COMP a-C:H coating states good protective properties and significantly delays corrosion and that it way it may be utilized in human body.

Bacteriologic examination confirmed all coatings to be bacteriostatic and on that basis, the possibility of using them in dentistry, prosthetics and orthodontics occurred.

Summarizing all the above findings, it may be stated that DLC POMP a-C:H coating is the best one since it meets the requirements of corrosion and bacteriological criteria, and it is possible to be used inside human body.

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