with NCD layers the shift of corrosion potential was observed in more positive values. Moreover the corrosion rates of Ti with both NCD layers are order of magnitude smaller than for Ti without NCD. The both NCD coatings have comparable values of corrosion rate and polarization resistance. Investigated samples with different NCD coatings have similar impedance characteristics and the same equivalent electrical circuit.

Obtained electrochemical results show different corrosive features of NCD layers deposited on Ti using two different techniques - pitting corrosion did not occur on Ti/NCD RF samples, but it occur on Ti/NCD MW/RF despite of thicker NCD layers. Microscopic investigations made for Ti/NCD MW/RF show that localized corrosion process is joined with surface microstructure - pitting corrosion take place on whole crystallites surface with preferable orientation. These differences in corrosive features may be joined with changing of surface layers different for used deposition techniques. In electrochemical aspect the new method MW/RF PCVD (despite of existing breakdown at 3.4V) is better in comparison with RF PCVD, because there is no anodic peak in potential range 1-3V. Therefore it can be supposed that the presence of graphitic (sp2) material on NCD layers deposited by MW/RF PCVD method is smaller.

Summarizing obtained results can be stated that MW/RF PCVD technique requires subsequent improvement of the main parameters of NCD deposition processes on Ti so that the breakdown will be eliminate or the breakdown potential will be shifted to maximum value.

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PROPERTIES OF NiTi - SHAPE MEMORY ALLOY AFTER MODIFICATION BY RF PCVD METHOD

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Abstract

The DLC (diamond-like carbon) and NCD (nanocrystalline diamond) layers coat made implants of medical steel 316 L, titanium and titanium alloys [1]. These layers have excellent properties such as: high hardness, good biocompatibility to various types of cells, good adhesion to implants [2], wheres implants with diamond layer have good corrosion resistance in body fluids. Result received for these materials are encourage to modification other materials for example shape memory alloy NiTi. Nitinol is often used material in interventional cardiology, orthodontics and urology [3]. Shape memory alloy charackterizes of return to designed shape, superelasticity, thermomechanical behavior [3]. This phenomenons are proceeded thanks to the martensite transformation. Modification in high temperature perhaps cause failure martensite transformation which influence on the material properties change.

***Key words**: nitinol, diamond layer, RF PCVD method*

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Introduction

Nitinol - equatomic shape memory alloy is often used material to production of vascular stents, filters, implants in orthopedics and orthodontics [3]. NiTi is characterized by an unique combination of properties, superelasticity, thermomechanical behavior, low density and shape memory. These are very favourable phenomenons taking into account the difference of size of blood-vessels where the implants are predicted to be introduced. Phenomenons in NiTi are proceeded thanks to martensitc transformation. The term martensitic phase transformation describes the formation during cooling or during loading with an external stress of the austenite high temperature phase [9]. In this phenomenon occurs atoms re-organise. This transformation dose not change the chemical composition. Results of this transformation are new crystal lattice.

All materials, which are implanted, should fulfill many factors, they could not cause allergic response or inflammatory reaction. They must exhibit biocompatibility - the ability of the human body to endure the implants without destruction of the tissue. They must have a specific system of mechanical properties - good adhesion, good corrosion resistance in body fluids.

Although studies have demonstrated the good corrosion resistance and biocompatibility of Nitinol [4], but the high nickel content at this alloy (54,5 to 57% weight) makes possible dissolution by corrosion and it still remains a concern. The corrosion ions caused failure cells and allergic response. In this emergency implants is rejected.

Due to assure biocompatibility implants on NiTi investigations over modification NiTi [3] are conducted. Our investigation qualifies NiTi properties after coated it them with nanocrystalline diamond layer manufactured by RF PCVD (Radio Frequency Plasma Chemical Vapour Deposition) method [5]. Idea of this method has consists in the process of activated of dense plasma in methane in a radio frequency filed 13,56 MHz. Manufacturing process of diamond layers consisted of two stages: ion etching of surface NiTi and diamond layer deposition on this surface.

NCD layer manufactured by RF PCVD is biocompatibility [6]. It does not cause allergic reactions and it does not contribute inflammation. Implants with NCD layer have good corrosion resistance in body fluids.

Materials and methods

In these tests were used NiTi samples delivered by Memory Metalle (Germany) such as:
- disks (diameter = 4,6 mm and thickness - 2 mm)
- ribbons (thickness - 0,63 mm, width -3,34 mm and lenght - 40 mm). Surface ribbons preparation dark grey oxide.

On this samples were manufactured diamond layer by RFPCVD (Radio Frequency Plasma Chemical Vapour Deposition) method [5]. Parameters of coating process shows TABLE 1. Before the RF PCVD process samples were mechanical polished and ultrasonic cleaned.

Samples' surface and structure after test was observed on the metallographic microscope and scanning electron microscope SEM. The microhardness of pure NiTi and NiTi with diamond layer were also examined. It was bending strength measurement pure NiTi and NiTi coated diamond layer.

Results and discussion

Before and after the NiTi samples coating by diamond layer X-ray analysis were made samples surface were observed by SEM.

FIG. 1a. shows results of clear disks analysis and in the table is range of content of elemenets. It can be seen that Ni and Ti are principals elements of this alloy. Surface of NiTi disk shows FIGURE 1b.

FIG. 2a. shows results of clear ribbons analysis and in the table is range of content of elemenets. It can be seen that Ni and Ti and O are principals elements of this alloy. Surface of NiTi ribbon shows FIGURE 2b.

FIG. 3a. shows analysis results of disks with diamond layer and in the table is range of content of elemenets. Surface of NiTi disks with diamond layer shows FIGURE 3b.

FIG. 4a. shows analysis results of ribbon with diamond layer and in the table is range of content of elemenets. Surface of NiTi riboon with diamond layer shows figure 4b. It can be seen that diamond layers is constant and uniformity.

NiTi structure

Structure of NiTi disks and ribbons was observed by metallographic microscope.

The view of pure NiTi disk structure shows FIG.5a. On

	ETCHING		COATING		
	Potential [V]	Time t [min]	Potential [V]	Time t [min]	Flow of gas process [cm^3/min]
NiTi disks	840-860	5 - 8	700-750	6 - 9	20-30
NiTi ribbons	700-740	4 - 7	680-720	3 - 5	20-30

TABLE 1. Parameters of RF PCVD process.

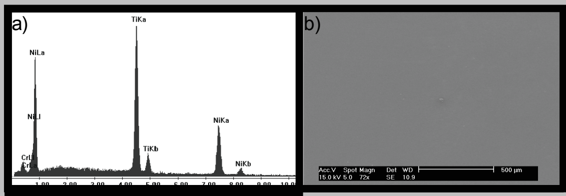

FIG. 1. Clear NiTi disks :a) results of X-Ray analysis, b) SEM view.

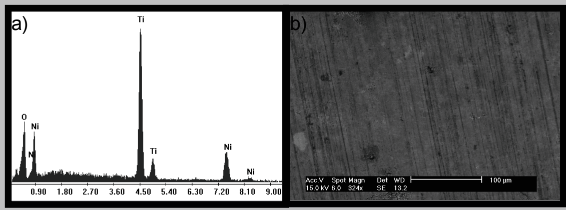

FIG. 2. Clear NiTi ribbon: a) results of X-Ray analysis, b) SEM view.

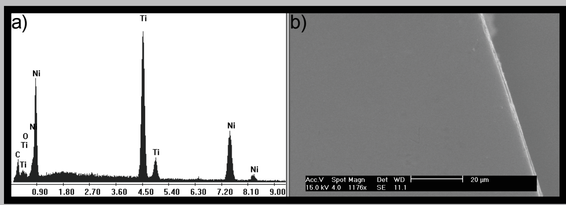

FIG. 3. NiTi disk with diamond layer: a)result of X-Ray analysis, b) SEM view.

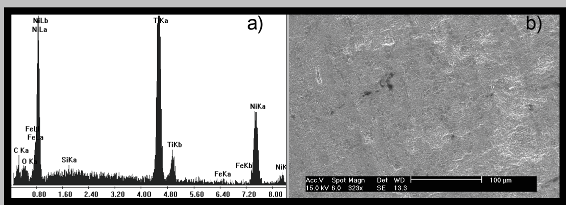

FIG. 4. NiTi ribbon with diamond layer: a)result of X-Ray analysis, b) SEM view.

the FIG. 5b was showed structure of NiTi disk after RF PCVD process. It can be seen that diamond layer on the NiTi ribbon is constant.

The view of NiTi disk structure pure ribbon shows FIG.6a. On the FIG.6b was showed structure of NiTi ribbon after RF PCVD process.

Pictures show that structure of disks and ribbon after coating changed.

Microhardness

Was mesurement before and after RF PCVD process microhardness of NiTi.. Microhardness was made on the 6 clear NiTi samples and 6 samples with diamond layer. Results of these tests are shown in TABLE 2. It can be seen that microhardness after coating changed. During the RF PCVD process followed strengthen material.

Bending

Clear NiTi ribbon and NiTi ribbon with diamond layer were bending. FIG.7,8 show results of these test. It can be seen that NiTi samples after RF PCVD process did not return to original shape. Structrue of NiTi change. RF PCVD process makes the plasticity properties lower.

Differential Scaning Calorimetry

On the clear NiTi and NiTi with diamond layer were made differential scanning calorimetry (DSC). Measurements were made in range temperatures from -50 to 250°C. The flow gas in the time test was 50ml/min. FIG.9 shows curve DSC

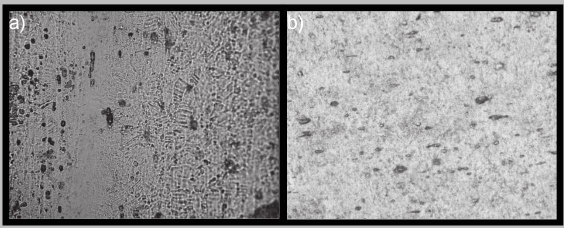

FIG. 5. View of NiTi disk structure- metallographic microscope - magnification 275x: a)clear NiTi, b) NiTi with NCD.

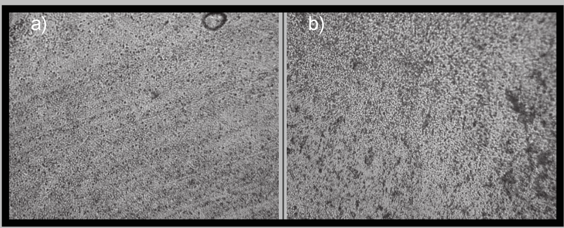

FIG. 6. View of NiTi ribbon with diamond layer structure - metallographic microscope -275x: a)clear ribbon, b) ribbon with NCD.

clear NiTi under heating and cooling. It can be seen that temperatures transformation Ap upon heating to amount 10°C and temperature transformation Mp upon cooling to amount 20°C.

FIG.10 shows NiTi curve DSC with diamond layer under heating and cooling. It can be seen that temperature transformation Ap upon heating to amount 30°C and temperature transformation Mp upon cooling to amount 10°C.

Microhardness NiTi– average for 6 samples	
Before RF PCVD	After RF PCVD
291 HV	370 HV

TABLE 2. Microhardness NiTi- average for 6 samples.

Conclusions

Investigations results show that modification by Radio Frequncy Plasma Chemical Deposition method NiTi does not satisfy expectations. Modification NiTi caused lower mechanical properties instead high them. The SEM images of diamond layer on the NiTi surface shows that layer is homogeneous and coats surface of NiTi samples very good but structure tests of NiTi shows that RF PCVD process caused material's change. High temperature during the process coating that's the problem, which destroits shape memory. phenomenon. Test DCS showed that RF PCVD process changes transformation temperatures upon heating an upon cooling. This is very unfavourably phenomenos. Material after RF PCVD does not good shape memory and superelasticity.

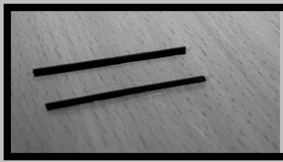

FIG. 7. Clear NiTi after bending.

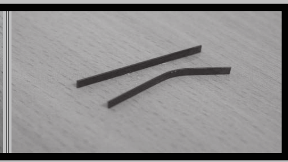

FIG. 8. NiTi with diamond layer after

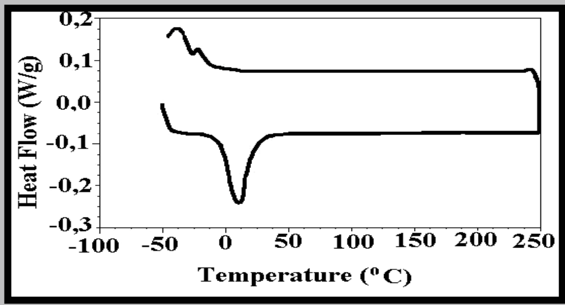

FIG. 9. Curve DSC clear NiTi.

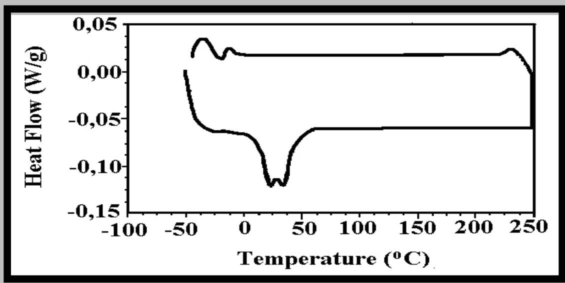

FIG. 10. NiTi DSC curve after RF PCVD process.

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