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Full Length Article

# NiTi shape-memory alloy oxidized in low-temperature plasma with carbon coating: Characteristic and a potential for cardiovascular applications

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ABSTRACT

Surface layers currently produced on NiTi alloys do not meet all the requirements for materials intended for use in cardiology. Plasma surface treatments of titanium and its alloys under glow discharge conditions make it possible to produce surface layers, such as TiN or $TiO_2$, which increases corrosion resistance and biocompatibility. The production of layers on NiTi alloys with the same properties, and maintaining their shape memory and superelasticity features, requires the use of low-temperature processes. At the same time, since it is known that the carbon-based layers could prevent excessive adhesion and aggregation of platelets, we examined the composite a-CNH + $TiO_2$ type surface layer produced by means of a hybrid method combining oxidation in low-temperature plasma and Radio Frequency Chemical Vapor Deposition (RFCVD) processes. Investigations have shown that this composite layer increases the corrosion resistance of the material, and both the low degree of roughness and the chemical composition of the surface produced lead to decreased platelet adhesion and aggregation and proper endothelialization, which could extend the range of applications of NiTi shape memory alloys.



## 1. Introduction

Intensive development of medical technologies and surgical procedures has placed new and more stringent requirements on the biomaterials used. Data from a 2015 BBC report on the use of intelligent materials indicates that their global share will increase by 10.2% annually until 2019, when it will reach a value of $42.2 billion [1]. Among these materials are shape-memory alloys (SMAs), whose role is becoming increasingly more apparent. The most commonly used SMA is Nitinol, which is an alloy of titanium and nickel with an almost equal atomic ratio [2,3]. Its unique properties, i.e. the uni- and bidirectional shape memory effect as well as superelasticity based on its diffusion-free thermoelastic martensitic transformation make it possible to design innovative implants, such as clamps for spinal correction, plates for osteosynthesis, orthodontic wires or self-expanding stents [4–6]. The biocompatibility of NiTi alloys is currently the subject of numerous studies [7–9]. Their self-passivating properties make these alloys highly resistant to corrosion, however their biocompatibility requires improvement due to their high nickel content, which as nickel can migrate to the surrounding tissues in the form of ions (metallosis effect). Nickel demonstrates cytotoxic and carcinogenic properties [10,11]. For this reason, various surface engineering techniques are used including oxidation in air and water, or electrochemical techniques such as oxidation, laser nitriding, glow-discharge nitriding, ionic implantation, deposition of carbon, ceramic or polymeric coatings [12–16]. As demonstrated by our previous studies, treatment in glow-discharge conditions can render some very good results [17]. Glow-discharge nitriding can be carried out at lower temperatures, i.e. up to 300 °C. Such conditions make it possible to retain the unique properties of NiTi alloys, since at higher temperatures, precipitation of the $Ni_4Ti_3$ phase is observed, which affects shape memory and superelasticity [18]. The high chemical affinity of titanium to oxygen or atomic nitrogen makes it possible to produce tight, nanocrystalline layers on the surface of a NiTi alloy, with a thickness and surface topography controlled by the process parameters. Titanium oxide – $TiO_2$ (rutile) and tita-

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nium nitride – TiN-type layers or mixtures of titanium oxides and nitrides produced on titanium and its alloys are biocompatible and ensure increased corrosion resistance as well as improved biological properties [19–22]. Apart from ensuring exhibiting the standard features of a biomaterial, NiTi materials used in cardiology need to ensure reduced blood clotting on the surface of the implant. The hemocompatibility of the surface can be increased by using amorphous carbon layers, which demonstrate antithrombogenic properties [23–25]. Increased corrosion resistance is also of high importance when using the alloy in the production of implants for minimally invasive surgery (e.g. stents), as it limits and even eliminates the metallosis effect.

Hence the objective of the study was to produce on the NiTi alloy surface a composite oxide layer with an external amorphous carbon coating modified with nitrogen and hydrogen – a-CNH, and to define its properties in the aspect of its application on cardiovascular implants.

## 2. Materials and methods

A NiTi shape memory alloy (50.8% at. Ni) was investigated in disc-shaped samples measuring 8 mm in diameter and 1 mm in thickness. Before the processes, the material was ground with 800-grit abrasive paper and washed. The glow discharge oxidizing process was conducted at a temperature of 290 °C for 30 min in air with a working chamber pressure of 1.6 mbar. The temperature was controlled by a thermocouple. Carbon coatings were formed on the oxidized layers via the RFCVD method in an atmosphere of $CH_4 + N_2 + H_2$, at a pressure of $1 \times 10^{-2}$ mbar and an RF generator power of 600W for 15 min.

The structure of the produced layers was investigated with the use of a High Resolution Scanning Transmission Electron Microscope (HRSTEM) with Bright Field (BF) and High-Angle Annular Dark Field (HAADF) detectors, under an acceleration voltage of 200 keV (HD2700, Hitachi). Observations of the structure of the layers were carried out along their cross-sections. Samples measuring $15 \times 3 \times 5$ μm were prepared for HRSTEM using the Focused Ion Beam (FIB) lift-out technique and an Ion Scanning Microscope, and were then thinned to approx. 100 nm using a gallium ion beam with an energy of 40 kV. A linear distribution of oxygen, titanium and nickel in the oxidized layer was also executed.

Surface topography was assessed using a Wyko NT 9300 scanning optical profilometer and a Vecco atomic force microscope with a Multimode VIII controller (tapping mode, tip model ACSTA, AppNano). Roughness parameters were measured by analysis of $480 \times 640$ μm areas (optical profilometer) and $10 \times 10$ μm (AFM) areas.

Corrosion resistance was assessed on the basis of potentiodynamic measurements with the use of an Autolab PGSTAT 100 potentiostatat at a temperature of 37 °C in Ringer's solution consisting of: 7.0 g/dm$^3$ NaCl, 0.075 g/dm$^3$ KCl, 0.1 g/dm$^3$ $CaCl_2 \cdot 2H_2O$ and 0.1 g/dm$^3$ $NaHCO_3$ at 37 °C and a chloride ion content of 4.33 g/dm$^3$. Prior to the assessments, the samples were exposed to a corrosive solution in current-free conditions (approx. 2 h) in order to stabilize the corrosion potential. Potentiodynamic examinations were conducted in a three-electrode setup: the test electrode – reference electrode (saturated calomel electrode) – auxiliary electrode (platinum), at a potential range from approx. 200 mV below the corrosion potential ($E_{corr}$ – 200 mV) up to 600 mV. The tested material was polarized with a potential sweep rate of 0.2 mV/s. Corrosion current density and the corrosion potential were determined using the Tafel extrapolation method.

The hemocompatibility of the produced composite layer was assessed by examining the adhesion and aggregation of blood platelets and endothelial cell adhesion and proliferation on the surface of NiTi in the initial state and NiTi with an oxidized layer and an outer carbon coating produced in the mentioned hybrid process, with the platelet-rich human plasma (PRP) and human cell line HUVECs (Human Umbilical Vein Endothelial Cells; Lonza) used, respectively. The incubation of PRP with the samples at 37 °C lasted 2 h. HUVECs with an initial concentration of $3 \times 10^4$/sample were incubated on the material surface for 2 h, 72 h or 6 days in a humid atmosphere of 95% air and 5% $CO_2$ at 37 °C. The non-adhering cells from PRP or HUVEC populations were rinsed off and then the settled cells were fixed in 4% glutaraldehyde for 30 min at 4 °C, rinsed in a cacodylic buffer and dehydrated. Then they were coated with an approx. 10–15 nm layer of gold (using a JFC-1200 JEOL fine coater) and tested under a scanning electron microscope (JSM-7600F, JEOL) in LEI mode (lower secondary electron image) with an acceleration voltage of 5 kV.

Results were presented as means and standard deviations. Statistical analyzes were performed using the Fisher and t-Student tests at the significance level $\alpha = 0.05$.

**Table 1**
Surface roughness of NiTi alloys in their initial state and after a hybrid process (a-CNH + $TiO_2$ composite layer) (optical profilometer).

| Method | Sample | $R_a$ [μm] | $R_q$ [μm] | $R_z$ [μm] |
|---|---|---|---|---|
| Optical profilometer | NiTi | 0.251 ± 0.111 | 0.398 ± 0.052 | 6.030 ± 0.837 |
| | a-CNH+ $TiO_2$ | 0.154 ± 0.005 | 0.201 ± 0.009 | 2.510 ± 0.443 |
| AFM | NiTi | 0.129 ± 0.057 | 0.163 ± 0.077 | 1.147 ± 0.392 |
| | a-CNH+ $TiO_2$ | 0.079 ± 0.011 | 0.097 ± 0.013 | 0.722 ± 0.047 |

*Abbreviations:* $R_a$ – roughness average; $R_q$ – root mean square roughness; $R_z$ – mean height of the five highest peaks above the average line decreased by an average of five lowest valleys below the average.

## 3. Results

### 3.1. The composite layer microstructure

TEM images show the microstructure of the composite layer produced via a hybrid process (Fig. 1). There is an outer zone of carbon coating, which is an amorphous, a-CNH-type layer, as demonstrated by our earlier work [26], and an oxidized layer. As a result of oxidation under glow discharge conditions the titanium oxide is formed, which is $TiO_2$ (rutile)-type with nanocrystalline structure shown by HRSTEM examinations (Fig. 1b, b'), as we also reported in our previous studies [18,19]. No nickel was detected in this layer (Fig. 1c). Directly under the produced layer of titanium oxide ($TiO_2$) a transition zone is observed (Fig. 1a,c) formed in the initial stage of glow discharge oxidation as a result of the high chemical affinity of titanium to active oxygen present in low temperature plasma [18]. The thickness of a titanium oxide layer is approx. 25 nm, while that of an a-CNH coating is approx. 35 nm after 15 min of an RFCVD process and it depends on the duration of the process.

### 3.2. Surface topography

Surface topography assessments have shown a reduced surface roughness following oxidation and carbon coating deposition both in the micro-scale (optical profilometer) and in the nano-scale (AFM) (Table 1). The decrease in roughness parameters in the case of the evaluated materials is evident and ranges from 30% to 50%. So it can be stated that the a-CNH coating first forms in places where the surface energy is the highest, i.e. by filling in any voids in the surface of the oxidized $TiO_2$ layer (Fig. 2).

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