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Structure and properties of nitrided surface layer produced on NiTi shape memory alloy by low temperature plasma nitriding

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ABSTRACT

NiTi shape memory alloys are used for bone and cardiological implants. However, on account of the metallosis effect, i.e. the release of the alloy elements into surrounding tissues, they are subjected to various surface treatment processes in order to improve their corrosion resistance and biocompatibility without influencing the required shape memory properties.

In this paper, the microstructure, topography and morphology of TiN surface layer on NiTi alloy, and corrosion resistance, both before and after nitriding in low-temperature plasma at 290 °C, are presented. Examinations with the use of the potentiodynamic and electrochemical impedance spectroscopy methods were carried out and show an increase of corrosion resistance in Ringer's solution after glow-discharge nitriding. This surface titanium nitride layer also improved the adhesion of platelets and the proliferation of osteoblasts, which was investigated in in vitro experiments with human cells. Experimental data revealed that nitriding NiTi shape memory alloy under low-temperature plasma improves its properties for bone implant applications.

1. Introduction

NiTi shape memory alloys are becoming increasingly widespread in medicine, where they are used as bone and cardiological implants: for spine correction, to connect bones, to seal the septum interventriculare or for stents. However, their use in implantology, due to the nickel content of approx. 50% and the metallosis effect, i.e. the migration of the alloy constituents, especially nickel, into the surrounding tissue, means that their resistance to corrosion needs improvement. This is accomplished through the use of various methods of surface treatment, which form e.g. layers of titanium oxide, titanium nitride, carbon coatings such as DLC (diamond like carbon) or NCD (nanocrystalline diamond), pyrolitic carbon, or polymeric and ceramic layers [1–20]. The methods include: electrochemical oxidation, including spark oxidation, ion implantation, RFCVD, glow discharge nitriding and laser treatment. A limitation in the application of the mentioned surface treatment methods is the temperature of the process, which as shown in the studies [6,17], should not be higher than 300 °C. It was found that when this temperature is reached during glow-discharge nitriding, the secretion process of intermetallic phase Ni_4Ti_3 begins and the martensitic transformation mechanism changes from single-stage to two-stage form, which causes the transformation hysteresis loop to extend. It also affects tension forces within the alloy, which in turn changes its superelastic properties and thus its performance. Titanium nitride – TiN, due to its good resistance to frictional wear and biocompatibility, is being widely studied for its potential applications in medicine. The studies also encompass the processing of NiTi alloy [6,8–19]. In medical applications, the microstructure, surface topography and nanotopography of TiN play an important role [21,22].

The gas, laser and plasma nitriding processes currently used are carried out at high temperatures (≥600 °C), resulting in, among other things, the formation of sublayers composed of type Ti_2Ni, Ti_3Ni intermetallic phases with a thickness of up to 2 μm. The thickness is primarily dependent on the process time [14,15,23,24]. Both the equilibrium phases do not possess the properties which are needed to induce the shape memory or superelasticity effect. The high elastic modulus of the surface layer can cause problems leading to crack formation and increased corrosion under dynamic loads

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[28]. Nitriding of complex shaped surfaces is also carried out by means of plasma immersion ion implantation. The produced layers are approx. 2–3 μm thick [9,23,24]. These layers increase corrosion, wear resistance and biocompatibility. Titanium nitride layers also protect the human body against nickel release [8,16].

However, the current surface engineering techniques used for NiTi must take into account the specific functional properties of the alloys, and the surface layer produced should be resistant to shape-memory-effect-induced mechanical deformation in the range of several percent. Hence, the layers formed on the shape memory alloys should be thin, have a diffusive nature, a homogeneous structure and provide the possibility of processing complexly shaped workpieces. These conditions are met by surface treatment involving glow-discharge low-temperature plasma nitriding, which has been proven in the case of nitriding or oxynitriding of NiTi or Ti6Al4V titanium alloys [6,17,26]. Application of cathodic sputtering in the course of glow-discharge nitriding makes it possible to produce surface defects in the crystalline structure, remove the surface oxide layer [25], reduce the concentration of nickel in the top layer of the NiTi alloy [20], which intensifies the formation of diffusive layers of titanium nitride – TiN and allows the temperature of the nitriding process to be reduced to approx. 300 °C [6,17], making it possible to process workpieces with complex shapes [25,29,30]. In addition, the high chemical affinity of titanium to atomic nitrogen present in low-temperature plasma, has a significant impact on the formation of titanium nitride [25,27]. Therefore, the aim of the study was to produce thin, corrosion-resistant diffusive nanocrystalline titanium nitride layers with a surface topography ensuring good osteoconductivity.

2. Research methodology

NiTi shape memory alloy (50.8% Ni) was investigated. Samples measuring Ø 8 mm × 1 mm were ground down to 1000 grit, and were afterwards polished with an Al_2O_3 aqueous suspension and then degreased with acetone. The glow discharge nitriding process was conducted at a temperature of 290 °C for 30 min in an atmosphere of pure nitrogen (99.999%) and at a working chamber pressure equal to 1.6 hPa. During heat-up, immediately before nitriding, the samples were subjected to cathodic sputtering in a gaseous mixture of argon and nitrogen (volume 3:1) at a pressure of 0.3 hPa for 10 min. The temperature was controlled by a thermocouple and a Rayomatic pyrometer.

The structure of the nitrided layers was investigated using a transmission electron microscope (JEM 3010, JEOL). The microscopic observations were carried out on cross-sectional specimens. The specimens were prepared using the ion polishing method. An X'Pert Pro diffractometer was used to carry out X-ray grazing diffraction (GIXD) examinations to determine the phase composition of the samples. The radiation CuKα with wavelength = 0.15418 nm was used. The angle of the beam was set to 0.2°. Surface topography was observed using scanning electron microscope (Hitachi, S-3500N) with the acceleration voltage of 15 kV in SE (secondary electron) mode and was measured by means of a Wyko NT 9300 scanning optical profilometer. Surface morphology was analyzed using Vecco atomic force microscope with Multimode VIII controller (tapping mode, tip model ACSTA, AppNano).

Corrosion resistance examinations were carried out by means of the impedance and the potentiodynamic method using an Autolab PGSTAT 100 potentiostat in Ringer's solution consisting of: NaCl – 7.0 g/dm^3, KCl – 0.075 g/dm^3, $CaCl_2 \cdot 2H_2O$ – 0.1 g/dm^3, $NaHCO_3$ – 0.1 g/dm^3 at 37 °C. Prior to electrochemical studies, the samples were exposed to a corrosive solution in current-free conditions for 24 h. Impedance examinations were conducted in a three-electrode setup: the test electrode – reference electrode (saturated calomel electrode) – auxiliary electrode (platinum), with the frequency ranging from 10^5 to 10^{-3} Hz and the amplitude of sinusoidal signal 20 mV. Impedance spectra were analyzed with the use of EQUIVCRT Baukamp programme. Equivalent circuit with two time constants $R_1(Q_2[R_2(R_3Q_3)])$ was used, which is generally applied in the case of materials susceptible to pitting corrosion. Obtained spectra are presented in the form of Bode plot. Potentiodynamic tests were conducted in an identical tri-electrode setup, up to a potential of 1500 mV. The test material was polarized with a potential sweep rate of 0.2 mV/s.

The titanium nitride layers produced and the NiTi alloy were used to grow Normal Human Osteoblasts (NHOst, Lonza, USA). The cells were grown on an osteoblast basal medium (Lonza) enriched with foetal bovine serum (50 ml/500 ml medium), ascorbic acid (0.5 ml/500 ml medium), GA-1000 (0.5 ml/500 ml medium) antibiotics, in a humid atmosphere of 95% air and 5% CO_2 at 37 °C. The medium was changed every 48 h. Cells in the BulletKit® (Lonza) incubation medium with a concentration of 3×10^4/500 μl were applied onto polished NiTi samples in initial state and after glow discharge nitriding. The cells were then incubated for 24, 48 and 144 h at 37 °C. Following incubation, the culture was rinsed with a phosphate buffered saline solution (PBS, Lonza), and the settled cells were fixed in 4% glutaraldehyde for 30 min at 4 °C, then rinsed in a cacodylic buffer, in accordance with the procedure of preparing biological material for examinations employing a scanning electron microscope. The prepared specimens were vacuum coated with a ca. 10–15 nm layer of gold using a JFC-1200 JEOL fine coater. They were then tested under a scanning electron microscope (JSM-7600F, JEOL) with the acceleration voltage of 5 kV in LEI (lower secondary electron image) mode.

Adhesion and aggregation tests of blood platelets on the surface of NiTi alloy in initial state and after producing of TiN layer were performed with the use of platelet rich plasma (PRP), prepared on the basis of the blood of healthy donors. The plasma was incubated on the surface of the samples for 2 h at 37 °C. After this time, the non-adhering cells were rinsed off, while the adhering ones were fixed for testing under a scanning electron microscope according to the same procedure as in the case of osteoblast cultures.

Adsorption of albumin on samples was investigated after incubated with fresh human plasma for 2 h at a temperature of 37 °C. Biofilm produced on the surface was fixed in 4% paraformaldehyde and 70% methanol. Albumin in biofilm was visualized with specific primary rabbit anti-human antibody (1:1000, LifeSpan BioSciences) followed by secondary goat anti-rabbit antibody conjugated with Alexa Fluor 555 (1:1500, Invitrogen) and analyzed using confocal microscope (Olympus, Germany). The amount of albumin was counted with use of the morphometric programme Imaris (Bitplane).

3. Results and discussion

Observation of the electrons transmission through the nitrided layer shows microstructure of the cross section of the layer (Fig. 1a and b). At the middle magnifications the layers reveals their high smoothness of the top surface layers. Inside the layers there exists the contrast, which proves an inhomogenity of the layers structure. Near the top part of the layers the areas of brightness contrast can be seen. It means that these areas characterize the lower density or are more amorphous phase. HRTEM observations showed a nanocrystalline structure of this layer (Fig. 1b). Under the TiN diffusive layers, a strongly deformed region of B2 matrix phase was observed [6]. The thickness of the TiN layer formed depends on the process time and ranges from ca. 30 nm for a 30 min process at 290 °C, and 70 nm for a process lasting 50 min at the same temperature. Thus, lowering of the temperature of the glow-discharge