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PAN-BASED CARBON FIBERS DEPOSITION ON NiTi SURFACE

The main objective of the work was to create a layer of carbon nanofibre on the surface of the NiTi shape memory alloy. The coating process was carried out in three stages. First, polyacrylonitrile was deposited by electrospinning. Then it was stabilized at temperatures up to 250°C. The last stage was the carbonization performed below 1000°C. The microstructure of the obtained coatings was observed using a scanning electron microscope. The X-ray diffraction techniques were applied to analyze the coating structure. After the polyacrylonitrile deposition, the fibers had an average diameter of about 280 nm, and the final fibers were almost twice as tiny. The applied steps also changed the phase and crystalline state of the fibers, finally leading to the formation of amorphous-nanocrystalline graphite.

Keywords: Electrospinning; carbon fibers; PAN fibers; nitinol

1. Introduction

The surface functionalization of implantable materials is an issue of particular importance in biomedical engineering. A number of solutions attractive for their material properties face difficulties with the tissue or cellular response. In contrast, a large group of materials have favorable biological properties with inadequate mechanical or physicochemical properties. Skillful combinations of these extreme material solutions provide an alternative approach to meet the needs and growing demands of clinicians and patients.

The gold standard for materials used in cardiac surgery is nitinol which is often used in orthopedic and cardiac as well as veterinary implants [1,2] is due to its mechanical (strength, shape memory) and physicochemical properties. In some cases, it is necessary to protect the nitinol surface from the external environment to inhibit the further release of nickel in the prolonged contact with the material. On the other hand, improving surface properties may enhance the cellular response by regulating clotting (cardiology) and improving the cell adhesion (orthopedics). The existing solutions employ either temporary polymer layers or DLC carbon layers which admittedly are biocompatible and athrombogenic. Yet these properties persist for a relatively short period of time and the texture of such implants does not stimulate the bone cell proliferation [3].

A new approach would be to functionalize the nitinol surface layer by its nanostructuring with e.g. a layer of carbon nanofibers whose biomedical potential is widely discussed in the literature [4,5]. There is no literature data on carbon nanoforms used as modifying agents for metallic surfaces but their high compatibility and biocompatibility leads us to believe that such a NiTi/nanocarbon fibers (NCF) surface would be attractive to many somatic cells [3]. Carbon nanofibers are characterized by diameters ranging from a few to several hundred nanometers and come in many structural subtypes which can be considered a transitional form between carbon nanofibres (CNF) and multi-wall carbon nanotubes (MWCNT). The most important types of CNFs that differ in structural and textural ordering include: electrospun carbon nanofibers, gas-phase synthesized nanofibers, herringbone nanofibers and nanowires [6].

The most popular method of yielding pure and therefore biosafe carbon fibers is the thermal conversion of polymer fibers (e.g. from cellulose, lignin, polyacrylonitrile, polyvinyl alcohol or polyfluorovinilidene) to form carbon nanofibers by methods known from the textile technology [4]. Therefore, our work aimed to create a protective CNF coating on the shape memory NiTi alloy's surface to protect and functionalize its surface.

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2. Materials and methods

Commercially available 15×10 mm NiTi plates with a chemical composition close to equiatomic were used as a substrate for applying carbon fibers. The alloy surface was preliminary polished on abrasive papers and then in the SiO₂ slurries to 1 μm gradation. The applied procedure assured that measured roughness by means of Ra and Rz was 0,023 and 0,179 μm, respectively.

The commercial polyacrylonitrile (PAN) powder (Sigma-Aldrich) was dried under anhydrous conditions at 80°C for 3 h, then the spinnable 12% wt. solution was prepared using dimethylformamide (DMF) as a solvent. The solution was homogenized for 24 h with a mechanic stirrer. Additionally, the ultrasonic homogenization was applied (1min) prior to electrospinning. The polymer solution was introduced into nozzles connected to a 12.5 kV high-voltage power supply. The potential difference between the nozzle and the collector (a steel plate with the NiTi substrate) initiated the extraction of the polymer jet. The process was carried out for one hour at room temperature with 30% humidity. The polymer fibers were subjected to the thermal conversion. The first stage involved oxidation (230-260°C) when the PAN chain was cyclized and some heteroatoms removed (called oxyPAN). The second stage involved the low-temperature carbonization (930-970°C). The process was carried out under protective conditions in order to remove residual heteroatoms and obtain the post-oxidation of the turbostratic carbon structure (called CNF).

After each deposition stage, the SEM observations of the NiTi substrate and layers were carried out on JSM-7100 F TTL LV (Jeol Ltd., Tokyo, Japan) with the accelerating voltage of 15 kV. The microscope was also equipped with an energy dispersive spectrometer (EDS) NORAN Vantage for the chemical composition determination.

The phase identification was performed based on the diffraction patterns measured at room temperature using an X-ray X'Pert (PANalytical, Almelo, the Netherlands) diffractometer with copper radiation (CuK1 and 2). The measurements were car-

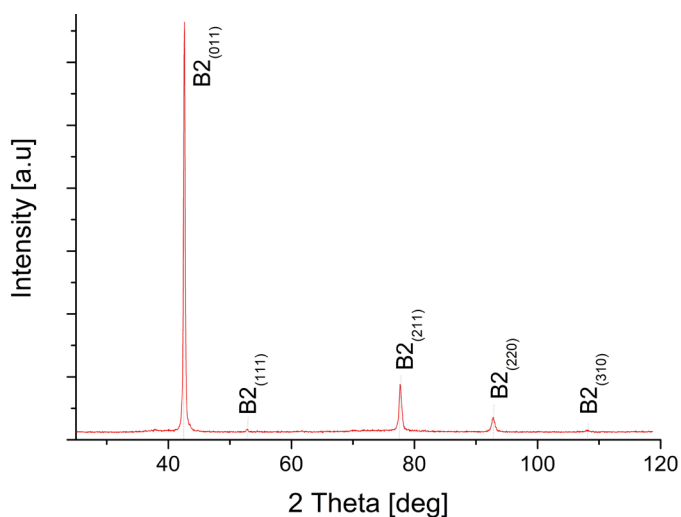


Fig. 1. X-ray diffraction pattern measured for NiTi matrix

ried out in two geometries: the standard Bragg-Brentano (BB) or the constant grazing incidence angle of the X-ray beam (GIXD). The diffractograms measured in the Bragg-Brentano geometry were registered in an angular 2θ range: 10-140°, in a step-scan mode with the step of 0.04°. On the other hand, the diffractograms using the GIXD method were measured at a constant angle of incidence of the primary beam α: 5°, 2.5°, 1°, 0.5°, 0.3°, 0.2°. The GIXD geometry diffraction patterns were measured in an angular 2θ range: 5-90°, in a step-scan mode with the step of 0.5°. The measurement time was adjusted to receive the appropriate counting statistics. The phase identification used the ICDD-PDF-4+ (International Centre for Diffraction Data) database.

3. Results and Discussion

3.1. Characteristics of the NiTi substrate material

The substrate of the CNF layers was the NiTi alloy with the measured average chemical composition of 49.34at.% Ti and 50.66at.% Ni, respectively. In the β phase, the nickel predominance meant that the reversible martensitic transformation would occur below room temperature. This fact was confirmed by the X-ray diffraction studies (Fig. 1). The measured diffraction pattern contained only diffraction lines belonging to the parent phase with a B2-type structure (ICDD card no. 03-065-0917). However, in addition to the parent phase, the microscopic observations revealed fine precipitates of the non-transformable Ti₂Ni equilibrium phase (Fig. 2). Its quantitative share was lower than the X-ray limit of detection. Hence, the lines of this phase were not visible in the diffraction pattern.

3.2. Preparation and characterization of CNF layers

The electrospun PAN nanofibers were converted to CNF using a two-step heat treatment: stabilization and carbonization (Fig. 3). During the stabilization process, the cyclization

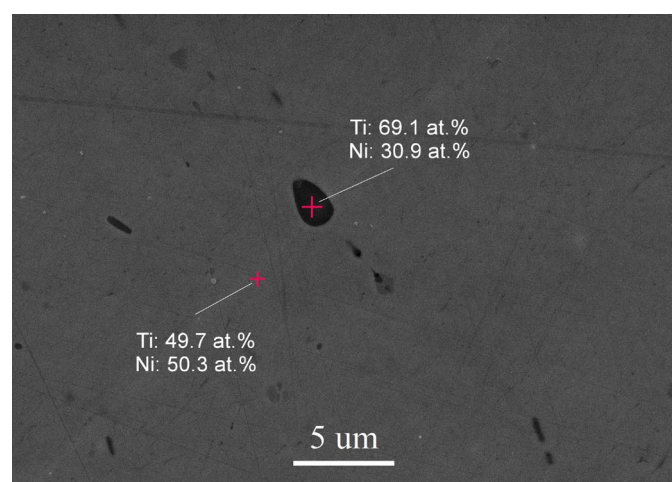


Fig. 2. SEM image with the results of chemical composition measured for NiTi matrix

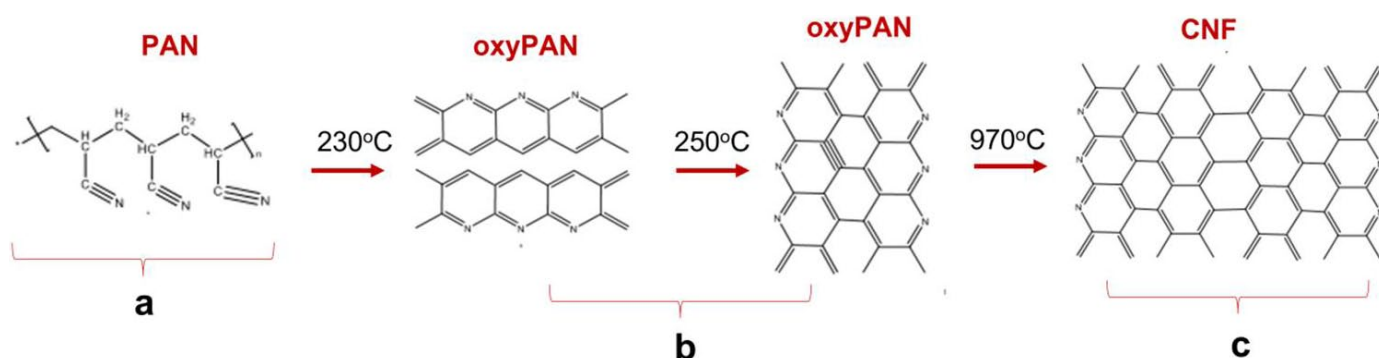


Fig. 3. Scheme of thermal conversion of PAN polymer fibers (a) to oxyPAN (b) to carbon nanofibers, CNF (c)

and dehydrogenation process occurred at 220-280°C in the air (Fig. 3a), forming a ladder structure of a series of connected C-N aromatic rings (Fig. 3b). The stabilization was critical in preserving the nanofiber structure during the high-temperature carbonization. The carbonization is usually carried out at a high temperature (>900°C) in inert atmosphere (nitrogen or argon) where the aromatic structure is grown and the heteroatoms like nitrogen are eliminated (Fig. 3c) [4,7,8]. The structure and microstructure were studied respectively after the deposition process (electrospun PAN layer), after stabilization – oxyPAN, and after carbonization – CNF.

3.2. Characterization of electrospun PAN deposit

The deposited PAN coatings adhered well to the surface of the NiTi alloy, covering its surface tightly. However, their microstructure and structure changed depending on the deposition stage. Fig. 4 shows the microscopic images taken at various production stages. Thanks to electrospinning, the coating was formed of micrometric fibers gradually elongating to reach hundreds micrometers (Fig. 4a). Regardless of the production stage, the fibers revealed a circular cross-section shape (Fig. 5). Oxidation did not significantly affect the coatings morphology. After oxidation, the surface morphology was very similar to the one previously described for the PAN deposition (Fig 4b). The last stage – carbonization – introduced a small morphological change. It consisted in the slight undulation of the fibers in a plane parallel to the substrate (Fig. 4c). A significant effect of the manufacturing steps was noted in the fiber diameter. The average fiber diameter was determined from the microscopic images (Fig. 6). Depending on the manufacturing step, it decreased from 281 nm to 112 nm for PAN and CNF, respectively. Also noteworthy was the change in the standard deviation value which also decreased from 54 nm to 17 nm, which proved the homogenization of the fibers morphology.

The morphology changes resulting from the technological conditions of the various stages of CNF production were followed by the structural changes in the fibers and the NiTi substrate. The X-ray diffraction was used to determine how the manufacturing parameters affected the phase and structural changes. Fig. 7 shows the GIXD patterns measured for the NiTi

sample after the polyacrylonitrile deposition. For the higher angle of incidence of the X-ray beam ($\alpha = 5^\circ$), the penetration depth of the X-rays was the greatest and it decreased with the incidence angle fall.

This effect translated into the PAN layer share and the NiTi matrix in the penetrating beam, which affected the diffraction lines' intensity. Hence, the diffraction lines originating mainly from the NiTi substrate were visible in the diffraction pattern measured at the angle $\alpha = 5^\circ$ (Fig. 7a). The phase identification showed that the B2 parent phase (ICDD card no. 03-065-0917) and the B19' martensite (ICDD card no. 03-065-0365) were present. The deformation of the surface layer during its polishing may have caused the martensite induction. Furthermore, as a one-way shape memory phenomenon, after heating in the oxidation process – the temperature of 230-250°C, martensite was restored to the B2 parent phase. This fact is confirmed by the results of X-ray diffraction studies of the NiTi substrate and will be discussed later in the article. In addition, a low-intensity peak belonging to polyacrylonitrile (ICDD card no. 00-048-2119) was visible at about $17^\circ 2\theta$. By lowering the measurement angle α to 0.2° , the volume fraction of the NiTi/PAN phases changed in favor of PAN (Fig. 7b). Hence, the diffraction patterns measured at an angle of 0.2° increased the intensity of diffraction lines originating from polyacrylonitrile. These lines were broadened and indicated the amorphous-nanocrystalline form of PAN.

The temperature raised to 230-250 degrees to oxidize PAN eradicated the martensite introduced in the surface layer by polishing. The diffraction pattern measured at a constant angle $\alpha = 5^\circ$ lacked the diffraction lines previously identified for the PAN sample (Fig. 8a). This means that the temperature of the oxidation treatment was sufficient to transform the martensite into the B2 parent phase. Furthermore, for this phase, reflexes (110), (200), and (210) were identified. On the other hand, the PAN presence was confirmed by the lines with increased intensity: (010) and (300). The diffraction pattern measured at the α angle of 0.2° revealed that the PAN lines increased their intensity at the expense of the B2 parent phase ones (Fig. 8b).

After the carbonization process at the temperature of 970°C, the layer-substrate adhesion decreased so much that the layer could be removed and subjected to the diffraction tests using the classical Bragg-Brentano method. The measurement result for the layer alone is shown in Fig. 9. Primarily, the diffraction

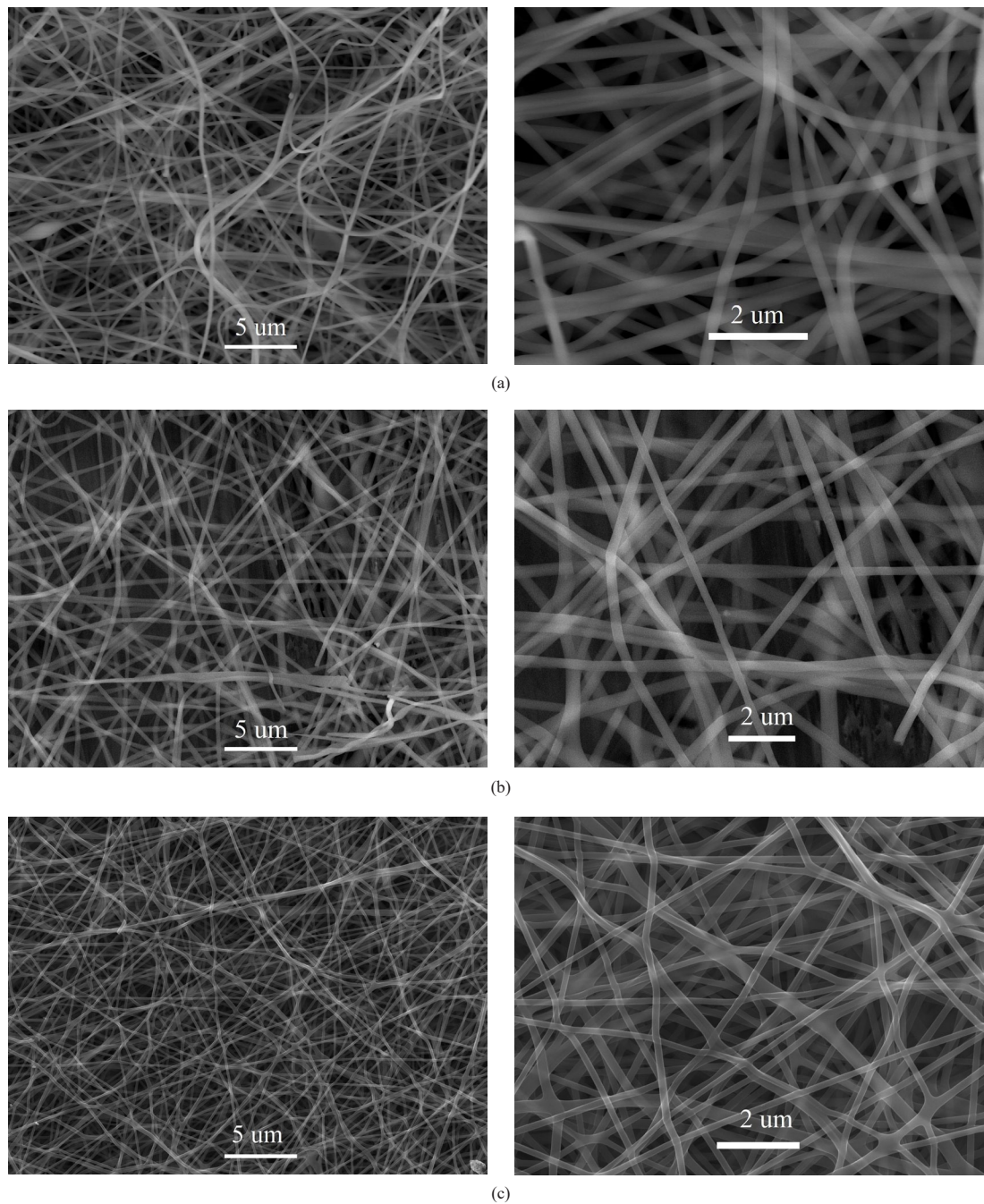


Fig. 4 SEM images observed for PAN (a), oxyPAN (b) and CNF (c) deposits

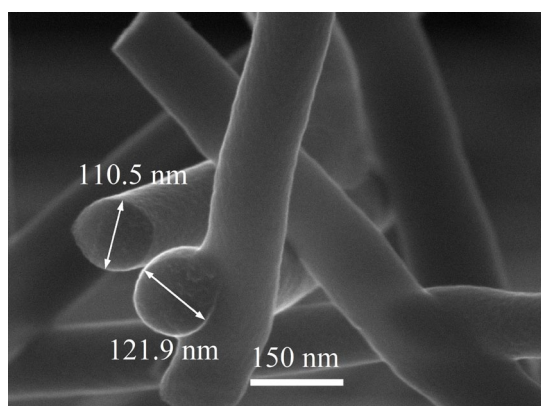


Fig. 5. SEM image observed for cross-section of oxyPAN deposit

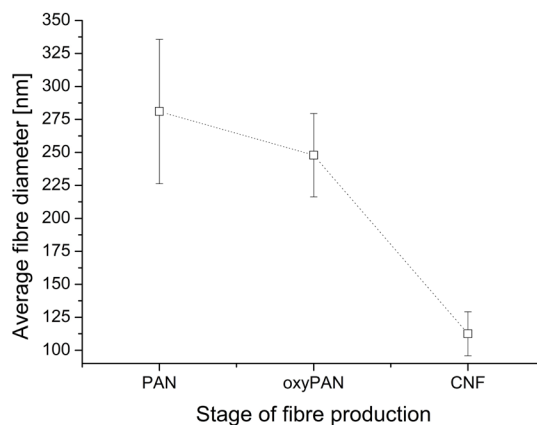


Fig. 6. Average fibre diameter determined for CNF production stages

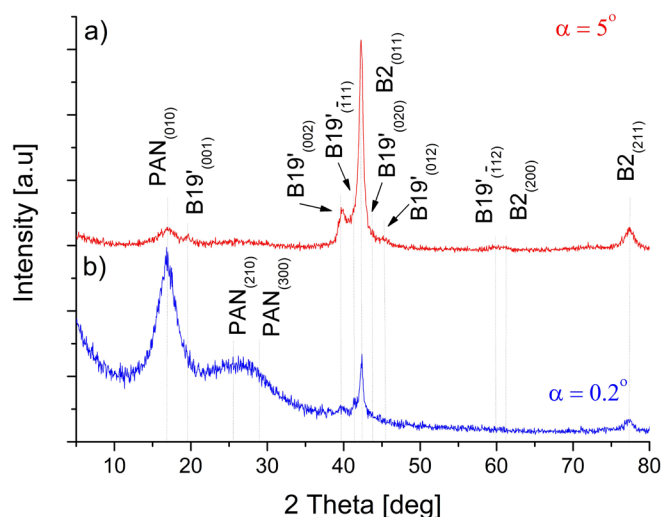


Fig. 7. GIXD diffraction patterns measured for NiTi/PAN, for α angle 5° (a) and 0.2° (b)

lines belonging to graphite (Gr) were identified (ICDD card no. 00-025-0284). There were also visible lines with low intensity originating from the PAN – practically slightly above the background fluctuations (ICDD card no. 00-048-2119). These facts confirm that almost the whole layer volume was CNF.

The crystalline evolution of the produced fibers was evidenced by the width of the diffraction line measured at half its intensity (FWHM). The Williamson-Hall method was used to calculate the mean crystallite size and lattice strains from the FWHMs. The results are summarized in Fig. 10. The fibers in the PAN coating had an average crystallite size of about 4.5 nm. After the oxidation process that required raising the temperature to 250°C and providing energy, the crystallites grew to about 7 nm. However, the PAN coating carbonization led to its internal reconstruction. As a result, graphite with an average crystallite size below 2 nm was formed. In addition, the energy supply reduced the internal strain from almost 4% after the PAN deposition to 1% in the CNF. This effect also proved the stabilization of the CNF fiber structure.

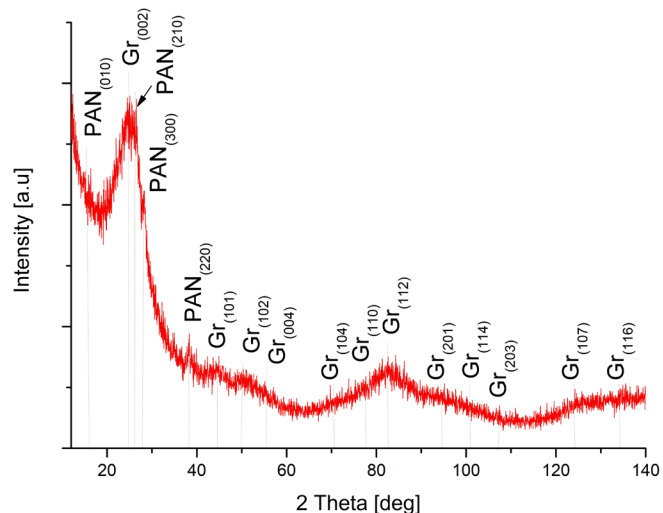


Fig. 9. X-ray diffraction pattern measured for CNF deposit

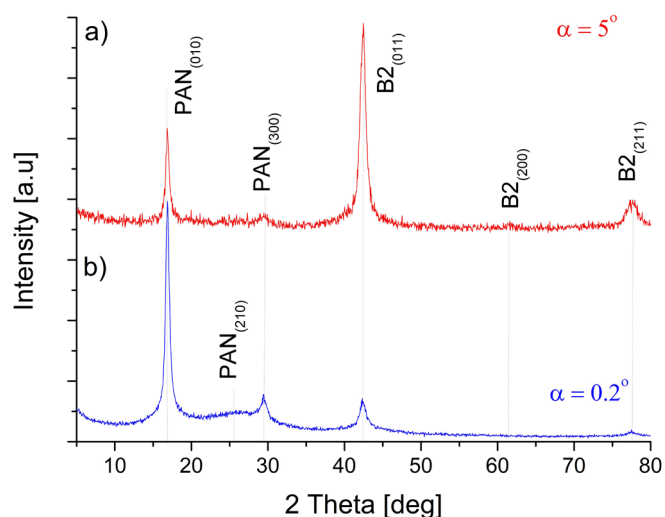


Fig. 8. GIXD diffraction patterns measured for NiTi/oxyPAN, for α angle 5° (a) and 0.2° (b)

4. Summary

The presented results show the preliminary approach to functionalizing the surface of NiTi alloys with the carbon fiber coatings via the electrospinning deposition supported by the thermal treatment. The multi-stage process reduced the diameter of nanofibers and their chemical and phase form. After the first two stages, the fibers diameter was about 280 nm and 250 nm, respectively, and they adhered well to the surface of the alloy. The carbonization process led to the fibers shrinkage to about 100 nm in diameter with the simultaneous phase reconstruction from PAN to graphite. In addition, the carbonization formed the fibers with an amorphous-crystalline structure. Even though the internal strain in the fibers was reduced to only 1%, the shrinkage of the CNF diameter introduced enough stress between the coating and the NiTi matrix. As a result of that, the coating could be easily removed. The problem how to improve the fibers-substrate adhesion needs further studies which will be particularly important regarding the conditions of the implant performance.

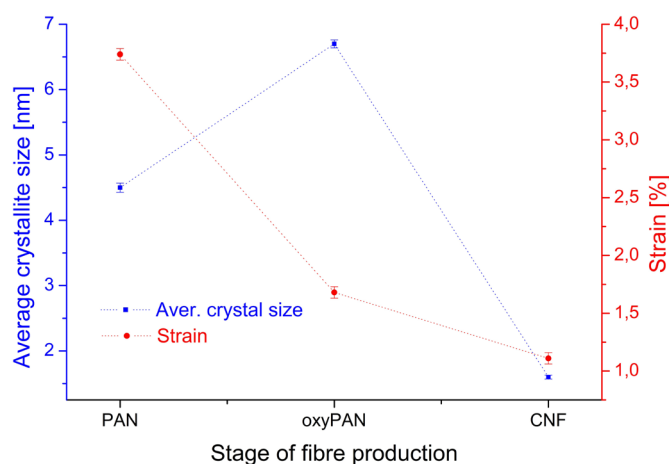


Fig. 10. Average crystallite size and strain on stages of CNF production deposited on NiTi substrate

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