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Chemical etching of nitinol stents

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At present the main cause of death originates from cardiovascular diseases. Primarily the most frequent cause is vessel closing thus resulting in tissue damage. The stent can help to avoid this. It expands the narrowed vessel section and allows free blood flow. The good surface quality of stents is important. It also must have adequate mechanical characteristics or else it can be damaged which can easily lead to the fracture of the implant. Thus, we have to consider the importance of the surface treatment of these implants.

In our experiments the appropriate design was cut from a 1.041 mm inner diameter and 0.100 mm wall thickness nitinol tube by using Nd:YAG laser device. Then, the stent was subjected to chemical etching. By doing so, the burr created during the laser cutting process can be removed and the surface quality refined. In our research, we changed the time of chemical etching and monitored the effects of this parameter. The differently etched stents were subjected to microscopic analysis, mass measurement and in vivo environment tests. The etching times that gave suitable surface and mechanical features were identified.

Key words: *stent, Nitinol, chemical etching, metallic surface area*

1. Introduction

At present the main cause of death originates from cardiovascular diseases, which primarily affect the elderly but can affect the young as well as a result of genetic features and unhealthy lifestyle. Smoking, lack of exercise, consumption of unhealthy foods, stress, high blood pressure, diabetes mellitus, hyperlipidaemia and last but not least genetic inheritance taint the likeliness of the development of these illnesses. In case of a significant vascular narrowing stents can be used to restore the normal blood flow. In most cases stents are haemocompatible metal meshes laser cut from a tube and treated accordingly. During catheterisation of peripheral or coronary arteries a contrast material is injected in the patient's vessels to help X-ray visibility. In some cases markers are put in the stent so the physician can place and position the stent by monitoring the X-ray images [1]–[3].

Two categories of stents can be distinguished depending on the vessel needing expansion. One is the balloon expandable stent, which material is generally 316L austenitic stainless steel, Co-Cr alloy or Pt-Cr alloy [4]. The other group is the so-called self-expanding stents. Usually these are used in peripheral vessels. These stents require not only to be biologically compatible but also to be greatly flexible as these implants can be subject to external forces that can result in deformation. Without flexibility the stents would not gain back their original shapes after the elapse of the forces that had caused the deformation. Thus, these types of stents should be made of some sort of shape memory alloy. Materials such as nickel-titanium, the so-called nitinol alloy, Nb-alloy or Ta-alloy can serve this purpose [5].

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Other than the biological compatibility, the smoothness of the stent surface touching the tissue is also important.

An implant with rough surface quality would irritate the tissue beign directly touched, thus the organism would not accept it causing excessive cellular (proliferative) reaction. In terms of stents it is not extraordinary that restenosis (re-narrowing of expanded vessel sections) happens. If so, the long-term success of these interventions is limited, because blood flow will be again limited by the growing vascular tissue inside of the stent [6]. A common method is to coat the part of the stent which is touching the tissue with some kind of "organism friendly" polymer in order to decrease the occurrence of complications. In some cases an anti-proliferative drug (for example, paclitaxel, sirolimus, everolimus) is put on the stent or in the coating to reduce the chance of restenosis [7], [8]. Another solution to refine the surface quality and compatibility is to apply surface treatment. Traditional surface treatments for biomaterials include mechanical polishing, electropolishing, chemical etching, heat treatments, sandblasting and short pinning [9].

Schweizer et al. showed that a simple layer-by-layer (LbL) deposition of positively charged chitosan and negatively charged heparin can be used to efficiently modify the native surface of both NiTi and Ti without any previous treatments [10].

The effect of chemical etching in HF + HNO_3 aqueous solutions on nitinol surface chemistry has been studied by Shabalovskaya et al. [11]. Chemical etching of nitinol is known to be efficient for the elimination of defective surface layers and surface oxidizing [12], [13].

The corrosion behaviour of nitinol in the body is also of critical importance because of the known toxicological effects of nickel. Some surface treatments (e.g., chemical etching, electropolishing) improve the biocompatibility and inhibit the migration of nickel. The stability in the physiological environment is dependant primarily on the properties of the mostly TiO_2 oxide layer that is present on the surface [14].

O'Brian et al. investigated a passivation process for polished nitinol wires and vascular stent components, after being given a typical shape setting heat treatment. Surface analysis indicated that the passivation reduces Ni and NiO content in the oxide and increases TiO_2 content [15].

The success of chemical etching depends on the applied etchant, the temperature of etching and the timing of etching. In our research, we conducted in vitro and in vivo experiments to identify the time interval. In this study, a cooperative work between engineers and a medical research team was carried out and the samples were placed in the carotid arteries of rats and histology analysis was also performed. The diameter of these vessels is around one-tenth of the human carotid arteries, thus the developed and produced stents had to be equally smaller than the vasodilator implanted in a human being. However, the distal left anterior descending coronary artery in human has a diameter similar to that of the stents used in our experiments [16]. The aim of our research was to reproduce and securely achieve the produced nitinol alloy stents' etching phase and mainly to identify the optimal etching time.

2. Materials and methods

The first step in the stent production is to create the desired mesh design. In our experiments, a tube with a 1.041 mm inner diameter and 0.100 mm wall thickness was used, with chemical consistency of 56.8% wt% Ni, balance wt% Ti, 0.021% O, 0.0012% H, 0.002% C, any single trace element <0.005%. Then the designed sample was cut by using Nd:YAG solid-state laser. The laser cutting mechanism is based on the reaction of neodymium with an yttrium–aluminium-garnet crystal, resulting in a coherent monochromic (1064 nm wavelength) laser beam. This heats and melts the material at the location of contact. The protecting gas (argon) used during the laser cutting process blows the melted material out from the hole creating the cutting surface. A number of parameters determine the cutting quality and by optimising them adequate cutting can be attained.

Despite the cutting being performed with optimal parameters, burr still had been created on the stent and not all pieces had dropped out. Figure 1 shows the stent parts with burr after the laser cutting process. This implant does not comply with the conditions of implantation in a living organism, thus it needs treatment. This justifies the need of chemical etching following the laser cutting process (Fig. 2).

During the chemical etching process the material and the applied etchant (which is different for every material) get in chemical reaction. As a result a new compound is created from the atoms generated on the surface of the material together with the components of the etchant and this results in the shrinking of the material.

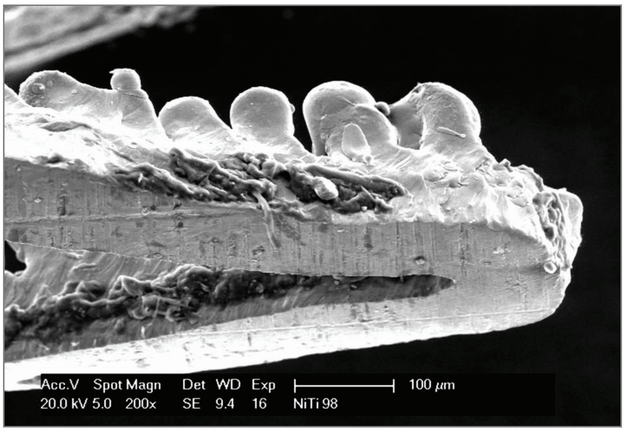

Fig. 1. Struts of the laser cut stent with burr

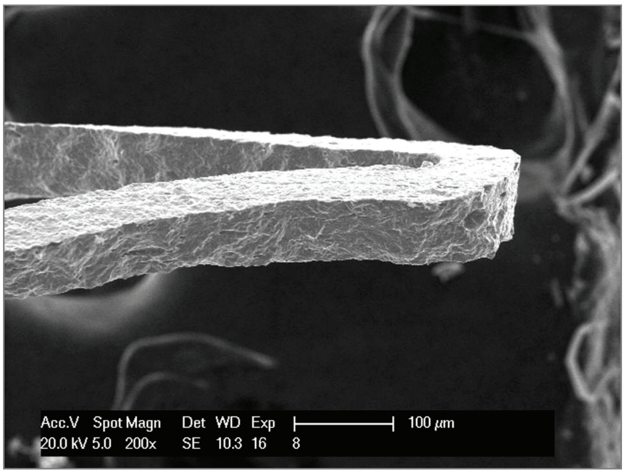

Fig. 2. The struts of the stent after 220 s etching

The chemical etching intensity is influenced by the following parameters: the time of etching, the type of etchant and its temperature. The applied etching pickle contains hydrogen chloride (HCl) and nitric acid (HNO_3) with dilution ratio of 1:3. The compound of acids was attenuated with distilled water (50 cm^3 etching pickle added to 150 cm^3 distilled water). The etching process was performed in ultra-sound cleaning equipment, which helped the removal of burrs and residues. The rest of the parameters were not changed during our experiment.

We considered the etching successful if the strut, created during the laser cutting process, was totally removed; the assisting cuttings, where the laser cut starts dropped out completely and the strut did not get damaged disabling its further usage. The etching time was changed every 20 seconds between 180 and 300 seconds. 180 seconds were the starting period, because the removal of the burr created during laser cutting was not possible in shorter time, while the struts became largely damaged after 300 seconds. In these experiments, 21 pieces of stents were treated that were categorised into 7 groups. We etched stent groups for the same period of time, thus this way we could examine the reproduction of the process as well.

During chemical etching the structure and mechanical features of stents change. The strut characteristics of a given stent pattern and material determine its protecting ability against external forces. One important parameter is the width of the struts. This plays an important role not just in the mechanical properties but also in the behaviour in the in vivo environment, since this determines the surface size contacting directly with the living organism which is called MSA – Metallic Surface Area. It is practical to have it in the smallest size to decrease the harmful effects to the organism; however, this may be at the expense of mechanical properties.

Stereo-microscopic images were taken before and after the chemical etching to measure the width of struts. Image analyser software was used to measure the exact strut width. The measurements were taken on 2 different struts of a stent and each strut at 4 points. We did the same process on all stents before and after etching.

The stent's mass was measured prior and after the chemical etching. Firstly, the implants were cleaned with ethanol to remove any grease, other impurities and remaining etchant. Then, the mass of the samples was measured on an analytical scale (0.0001 g accuracy).

3. Results

The measurement of the struts shows how their width changes in relation to the time of chemical etching. The changes of the stent struts are presented in Figs. 3–10. The width examined is indicated with arrows in Fig. 3.

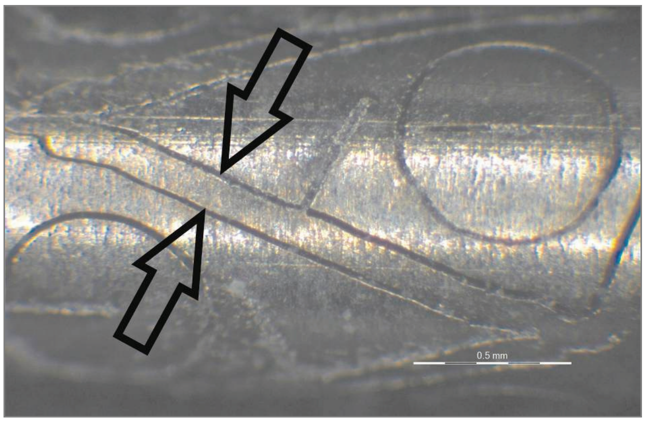

Fig. 3. Laser cut stent struts

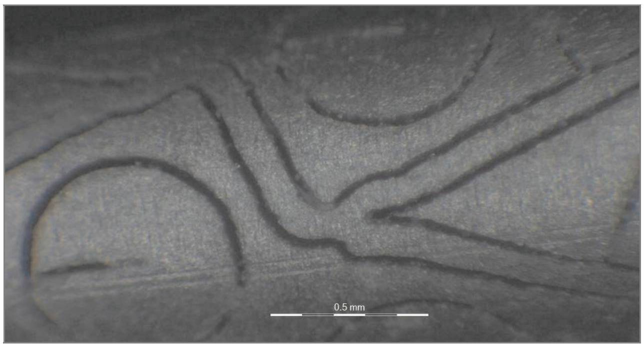

Fig. 4. Stent struts etched for 180 seconds

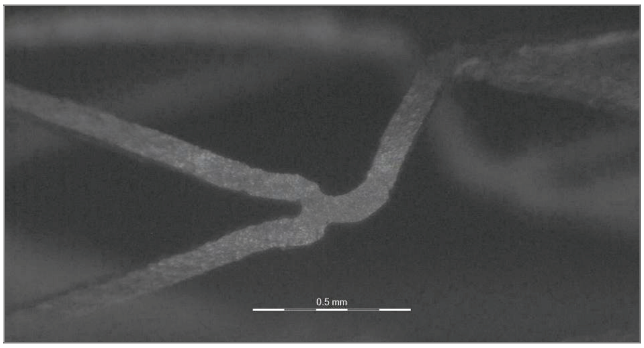

Fig. 5. Stent struts etched for 200 seconds

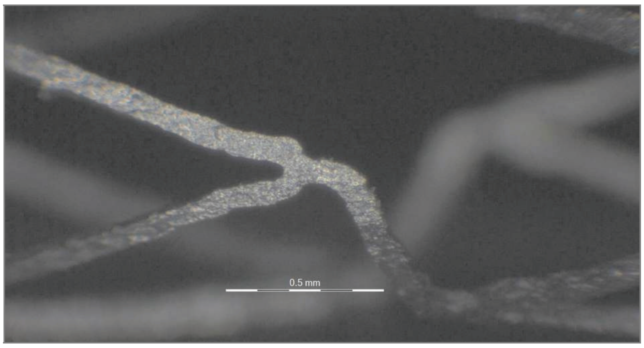

Fig. 6. Stent struts etched for 220 seconds

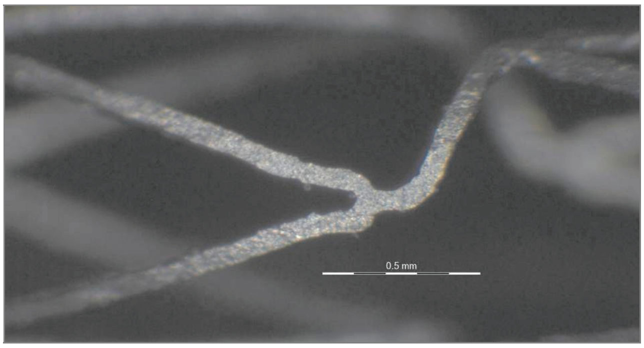

Fig. 7. Stent struts etched for 240 seconds

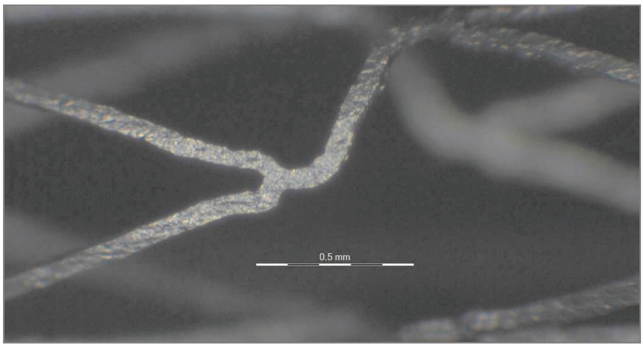

Fig. 8. Stent struts etched for 260 seconds

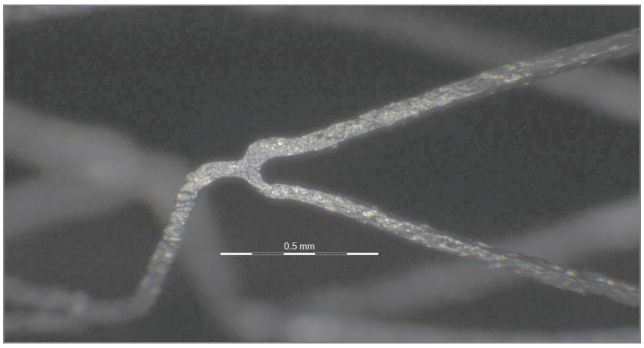

Fig. 9. Stent struts etched for 280 seconds

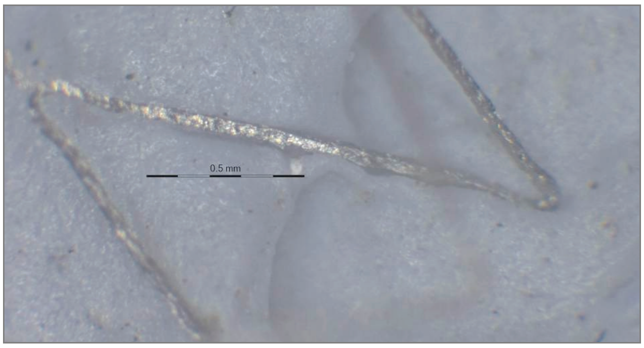

Fig. 10. Stent struts etched for 300 seconds

Figure 10 shows that the stent struts had thickened so heavily that they became fractured. Decreasing the struts width causes the implant to drop its mass. The stent's mass may influence the reactions and effects evoked in the organism.

By analysing the images taken of the differently etched stent struts and the diagram illustrating the numeric values as well, the shrinkage of width in relation to longer etching time can be clearly seen (Fig. 11). It is obvious that the width of struts had not been exactly the same prior to the cutting. The highest measured value was 116.7 µm, the smallest was 95.4 µm and the average strut width was 106.7 μm. The laser cutting process gives explanation for this. Even the slightest inaccuracy can cause noticeable changes in the cut sample and in the width of stent struts when cutting small size. In terms of larger samples this error would only cause slighter changes correlated to the whole stent. The stent's mass was decreased by increasing the time of etching (Fig. 12).

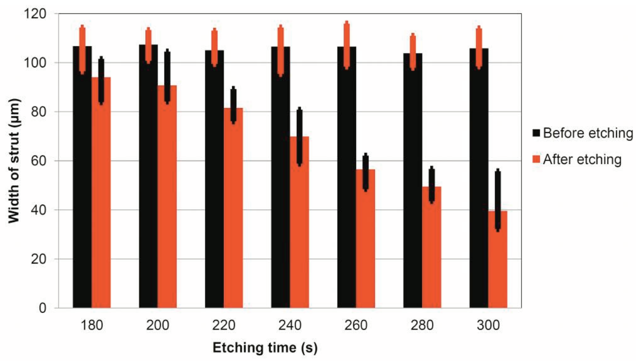

Fig. 11. Changes of strut width of the analysed stents

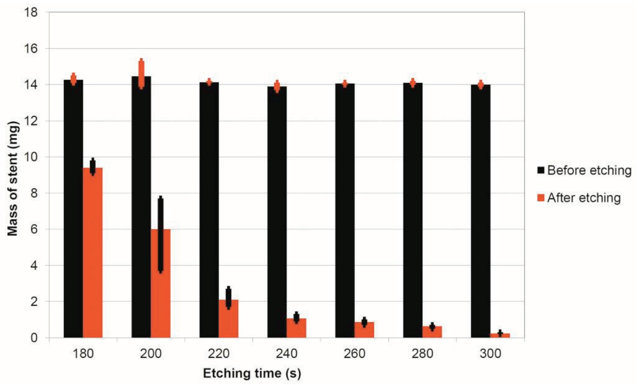

Fig. 12. Changes of the mass of stents

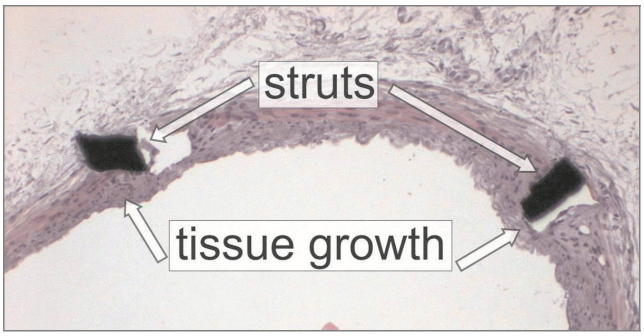

Fig. 13. The histology photo taken 28 days after placing a strut in the rat's carotis

By analysing the histological preparations of the rat carotid arteries with the implanted nitinol stents we could observe a relevant vascular stenosis due to neointimal hyperplasia inside the stents treated by chemical etching only. Figure 13 shows a hematoxylin and eosin stained carotid artery cross section 28 days after stent implantation. Neointimal proliferation first occurs next to the stent struts, then becoming concentric and significantly narrowing the vessel. Although cellular proliferative reaction – due to direct pressure by the stent to the intimal and medial layer of the artery – cannot be completely avoided, it may be further reduced by decreasing the endothelial damage by further treatment of the stent surface.

4. Discussion

One can see in Fig. 11 that after 180 seconds of etching the width of the struts decreased less than 10%. A 300 second long etching resulted in width decreasing by about 60%, so there is additional ~50% compared to the 180 second etching time. We can conclude that the etching process is accelerating in the aspect of strut width decreasing. During the process we have to take into account that the thickness of the strut is also decreasing. Therefore, the height of sidewalls is decreasing, too. The material–acid contact surface is also decreasing. In the case of decreasing contact surface, the material removal is slowing down. Figure 12 verifies this theory because the mass decreasing slows down with time. If we assume that the volume of the acid is unlimitedly great compared to the stent volume, we can find that decreasing the contact surface does not cause acceleration of the etching. So, there is another explanation of the accelerated strut width decreasing. The width decreasing speed is changing significantly between 220 seconds and 240 seconds. The characteristic change is also observable in Fig. 12. At this point the width decreasing speed is accelerated while the summarised material removal is decelerated. Therefore, we have to find two different processes, which have opposite influence on material removing. One of these processes can be decelerating material removal by the decreasing contact surface. Another process is the change of localized etching speed on the sidewalls, which accelerates the material removing from the side of the struts. We can explain these changes by the change in the chemical composition around the laser cut [17]. During the laser cutting the constituents can burn out or their ratio can vary. This modified composition reacts more intensively with the picking bath than the base material itself.

Based on the results obtained we can state that the burrs created during the laser cutting process can be removed with an HCl-HNO_3-water etchant mixture. This composition is different from the mixture in

Shabalovskaya's work but appropriate and not too circumstantial to use like the hydrogen-fluoride content etching pickle [9].

According to our optical and electron-microscopic tests we found that the optimal stent etching period is between 200–240 seconds. This time interval differs from the applied etching time in other researchers' work [9]–[15] because there the stent geometry was not examined. In the case of other stent sizes this treatment time may be different because of the different sizes and the different laser cut parameters. This etching time period overlaps with the range of changes in the strut width decreasing. The etching during this time is probable to remove all of the modified material caused by laser cutting.

The geometries of the implant and the surface treatments (e.g., chemical etching, electropolishing) influence the mechanical and other properties (e.g., flexibility, Metallic Surface Area) of the stents [18]. By changing the time of chemical etching we can reach different properties. The struts must be resistant to the cyclic stress tiring which depends on the condition and the age of the patient [19], [20].

The surface treatment methods (e.g., chemical etching, electropolishing) change the resistance to the corrosion behavior of implants which is an important property [21], [22]. To observe this behavior further in vitro and in vivo studies are needed.

Acknowledgements

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References

[1] NELSON B.D., *Expandable Metal Stents: Physical Properties and Tissue Responses*, Techniques in Gastrointestinal Endoscopy, 2001, Vol. 3, 70–74.

[2] LIM I.A.L., *Biocompatibility of Stent Materials*, MURJ, 2004, Vol. 11, 33–37.

[3] JUSTICE J., YACONO C., *Use of drug-eluting stents for patients with coronary heart disease*, JAAPA, 2009, Vol. 22(8), 30–34.

[4] MENOWN I.B.A, NOAD R., GARCIA E.J., MEREDITH I., *The Platinum Chromium Element Stent Platform: from Alloy, to Design, to Clinical Practice*, Adv. Ther., 2010, Vol. 27(3), 129–141.

[5] MIGLIAVACA F., PETRINI L., MASSAROTTI P., SCHIEVANO S., AURICCHIO F., DUBINI G., *Stainless and shape memory alloy coronary stents: a computational study on the interaction with the vascular wall*, Biomech. Model Mechanobiol., 2004, Vol. 2(4), 205–217.

[6] WEINTRAUB W.S.A., *The pathophysiology and burden of restenosis*, Am. J. Cardol., 2007, Vol. 100(5A), 3K–9K.

[7] PUSKÁS Z.S., TOLDI Á.I., GINSZTLER J., *Measuring the Heparin Binding Capability of Polyurethane-Coated Stainless Steel Stents with a Label-Free Biosensor*, Materials Science Forum, 2010, Vol. 659, 331–335.

[8] MANI G., MACIAS C.E., FELDMAN M.D., MARTON D., OH S., AGRAWAL C.M., *Delivery of paclitaxel from cobalt–chromium alloy surfaces without polymeric carriers*, Biomat., 2010, Vol. 31(20), 5372–5384.

[9] SHABALOVSKAYA S., ANDEREGG J., HUMBEECK J.V., *Critical overview of nitinol surfaces and their modifications for medical applications*, Acta Biomaterialia, 2008, Vol. 4, 447–467.

[10] SCHWEIZER S, SCHUSTER T., JUNGINGER M.M., SIEKMEYER G., TAUBERT A., *Surface Modification of Nickel/Titanium Alloy and Titanium Surfaces via a Polyelectrolyte Multilayer/ Calcium Phosphate Hybrid Coating*, Macromolecular Materials and Engineering, 2010, Vol. 295(6), 535–543.

[11] SHABALOVSKAYA S., ANDEREGG J., LAABS F., THIEL P., RONDELLI G., *Surface conditions of nitinol wires, tubing, and as-cast alloys: the effect of chemical etching, aging in boiling water, and heat treatment*, J. Biomed. Mater. Res., 2003, Vol. 65B, 193–203.

[12] VOJTECH D., FOJT J., JOSKA L. NOVÁK P., *Surface treatment of NiTi shape memory alloy and its influence on corrosion behavior*, Surface and Coatings Technology, 2010, Vol. 204(23), 3895–3901.

[13] SHABALOVSKAYA S., RONDELLI G., UNDISZ A., ANDEREGG J.W., BURLEIGH T.D., RETTENMYR M.E., *The electrochemical characteristics of native nitinol surfaces*, Biomat., 2009, Vol. 30, 3662–3671.

[14] CLARKE B., CARROLL W., ROCHEV Y., HYNES M., BRADLEY D., PLUMLEY D., *Influence of nitinol wire surface treatment on oxide thickness and composition and its subsequent effect on corrosion resistance and nickel ion release*, Journal of Biomedical Materials Research, Part A, 2006, Vol. 79A, 61–70.

[15] O'BRIEN B., CARROLL W.M., KELLY M.J., *Passivation of nitinol wire for vascular implants – a demonstration of the benefits*, Biomat., 2002, Vol. 23(8), 1739–1748.

[16] DODGE J.T., BROWN B.G., BOLSON E.L., DODGE H.T., *Lumen diameter of normal human coronary arteries. Influence of age, sex, anatomic variation, and left ventricular hypertrophy or dilation*, Circulation, 1992, Vol. 86(1), 232–246.

[17] KATONA B., NAGY P., BOGNÁR E., HIRSCHBERG K., *Development of nitinol stents: etching experiments*, Materials Science Forum, 2013, Vol. 729, 240–245©, Trans Tech Publications, Switzerland. DOI: 10.4028/www.scientific.net/MSF.729.240

[18] SZABADÍTS P., PUSKÁS Z.S., DOBRÁNSZKY J., *Flexibility and trackability of laser cut coronary stent systems*, Acta of Bioengineering and Biomechanics, 2009, Vol. 11(3), 11–18.

[19] MARIUNAS M., KUZBORSKA Z., *Influence of load magnitude and duration on the relationship between human arterial blood pressure and flow rate*, Acta of Bioengineering and Biomechanics, 2011, Vol. 13(2), 67–72.

[20] CHAICHANA T., SUN Z., JEWKES J., *Hemodynamic impacts of left coronary stenosis: A patient-specific analysis*, Acta of Bioengineering and Biomechanics, 2012, Vol. 15(3), 107–112.

[21] BURNAT B., WALKOWIAK-PRZYBYŁO M., BŁASZCZYK T., KLIMEK L., *Corrosion behaviour of polished and sandblasted titanium alloys in PBS solution*, Acta of Bioengineering and Biomechanics, 2013, Vol. 15(1), 87–95.

[22] WALKE W., PRZONDZIONO J., *Influence of hardening and surface modification of endourological wires on corrosion resistance*, Acta of Bioengineering and Biomechanics, 2012, Vol. 14(3), 93–99.