Fatigue Damage of Nitinol Stents in Simulated Physiological Solution

Petr Vlach [1,a], Štěpán Major [2,3b], Marek Musil [3,c] and Libor Jakl [4,c]

[1] Department of Chemistry, Faculty of Textile Engineering, Technical University of Liberec, Studentská 2, 461 17 Liberec 1, Czech Republic

[2] Institute of Theoretical and Applied Mechanics AS CR, Prosecká 809/76, 190 00 Praha 9, Czech republic

[3] Institute of Medical Biophysics, Faculty of Medicine in Hradec Králové, Charles University of Prague, Šimkova 870, 500 38 Hradec Králové 1, Czech Republic

[4] Faculty of Mechanical Engineering, Technical University of Liberec, Studentská 2, 461 17 Liberec 1, Czech Republic

[a] vlachpetr1@seznam.cz, [b] major@itam.cas.cz, [c] doc2008@seznam.cz, [d] libor.jakl@tul.cz

Keywords: Nitinol, Stent-Graft, Corrosion, Finite element analysis, Hanks Physiological Solution

Abstract Nowadays, stent-grafts are commonly used in vascular surgery. Stent-graft manufactures are confronted with two basic requirements: stents must have an "infinite'' life, stents must be made of the "thinnest'' wires (especially those at the brain). Stent-graft failure or device fatigue remains major concern for stent-graft manufactures and researches. Self-expanding stent-grafts are made of nitinol. The stent-grafts are mechanically loaded, and also the device is placed in very aggressive environment. The corrosion stability of Nitinol is strongly dependent on the surface preparation: grinding, polishing, chemical etching. This article deals with fatigue degradation of stent-grafts in corrosive environment.

Introduction

Nickel titanium, also known as nitinol, is a metal alloy of nickel and titanium, where the two elements are present in roughly equal atomic percentages. The term nitinol is derived from its composition and its place of discovery: (Nickel Titanium Naval Ordnance Laboratory). William J. Buehler and F. Wang [1,2], discovered its properties during research at the Naval Ordnance Laboratory in 1962. Nitinol alloys exhibit two closely related and unique properties: shape memory and superelasticity (also called pseudoelasticity). As a biomedical material, Nitinol has to meet several requirements: high corrosion resistance in chloride-rich medium and biocompatibility combined with suitable mechanical properties [3]. Nitinol is used for orthodontic treatments, and in cardiovascular surgery for stents, guide wires, filters, etc., in orthopaedic surgery for various staples and rods, and in maxillofacial and reconstructive surgery [4,5]. Probably the most common medical use of nitinol is construction of stent-grafts. Another example of the use of these materials in medicine are dental applications or use in prosthesis [6,7]. Cardiovascular stents are small cylindrical devices introduced in stenosed arteries to reopen the lumen and restore blood flow. if the stent fracture, free end of the broken wire penetrates into and injures the walls of the patient's artery. There then follows a proliferation of cells and the formation of scar tissue around the injury, similar to the scarring of other organic tissues. This reaction to the trauma subjects the artery to close,this constitutes the major mechanism of in-stent restenosis.

Nitinol contains about 50 % of nickel, which is a known allergen and carcinogen. Nickel release occurs in a patient's body [4], this process is associated with corrosion of the stent-grafts. In order to

diminish the release of nickel from Nitinol wires in the patient's body, numerous treatments have been used. Further untreated Nitinol (without a specially prepared protective coating) is protected by a layer comprised mainly of TiO_2, with a small amount of NiO in the outermost surface layers [8], but this natural protective coating is insufficient. Corosion resistence of Nitinol is a function of surface preparation, namely mechanical polishing, electropolishing, electropolishing,chemical passivation, straw-coloured or blue-coloured oxide deposition [9]. The corrosion rate is dependent on the surface preparation, being the lowest for the specimens treated by chemical passivation, and highest for the mechanically polished specimens [3,9].
A finite element analysis of stent grafts under representative cyclic loading conditions was presented in some works [10, 11], but these studies do not consider corrosion processes in the overall degradation of the stent. In this paper, a computational analysis of different stent–graft combinations and their impact on mechanical characteristics while undergoing cyclic pressure loads was carried out, employing the finite element solver ANSYS. We can assume that stents rupture first occur in regions with highest portion of deformation, but a fracture of the stent may occur due to corrosion in places where the protective layer is damaged. Protective layer can be damaged during stents manufacturing or surface layer can be damaged due to friction of individual wires of stents structure.

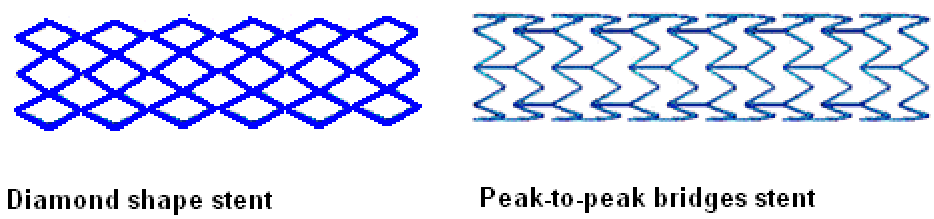

Fig.1. Stents-graft geometry.

Experimental details

Forty commercially available diamond-shaped stent-grafts made from knitted wires were examined. Knitted stent grafts were made from two different Nitinol alloys. Laser cutted stent-grafts with two different types of cut geometry (diamond-shaped, peak-to-peak bridges, see Fig.1) were used for fatigue experiments (Fifty diamond-shaped and Fifty stents with “peak-to-peak“ bridges geometry). Laser cutting is a typically method for stent production. Most of stents in the world are cutted. Both types of laser cutted stents were made from the same stock (NiTi tube with same diameter 25 mm and same chemical composition). Nominaly diameter of cutted stents was 12 mm and nominaly length 65 mm. Wall thickness of stock tube was 0.62 mm. These stents differ only in the cut geometry. The knited stents were made from wires with diameter 0.64 mm. Dimensions of the individual elements of all stents were approximately the same (compare diameter of wires 0.64 mm to the thickness 0.62 mm in he case of cutted stents). The examined stent-grafts were treated with four different surface treatments.
The specimens were refined by mechanical polishing and conventional ion implantation. In this which ions are extracted from plasma, accelerated, and bombarded into a device. In this study were surfaces refined with molybdenum (Mo) and carbon (C). The pulsed electron-beam modified the surface as deep as 10 nm for Mo and 30 nm for C. As example of bioactive surface was chosen surface refined with Heparin coating and passivation in HNO_3. . The Laser surface melting (LSM) of Nitinol using either argon as a shielding gas was used for 20 laser cuted stents. The Laser surface melting (LSM) of Nitinol using either argon as a shielding gas was used for 20 laser cuted stents. After LSM in argon, Nitinol revealed new phases, such as Ti_2Ni, $TiNi_3$ and martensite B19. Overview of applied surfaces and types of stents is shown the Table. 1.

The examined stents were strung on “artificial blood vessels”. Fatigue loading was simulated by the bending of “artificial blood vessels”.Electrochemical measurements or corrosion tests were performed in performed in a three-electrode corrosion cell. Measurements were performed in simulated physiological solution (This solution is known as Hanks salt solution.), with the following composition: 9 g/L NaCl, 0.5 g/L KCl,0.25 g/L NaH2PO4·2H2O, 0.35 g/L NaHCO3, 0.05 g/L Na2HPO4·2H2O, 0.19 g/L CaCl2·2H2O, 0.4 g/L MgCl2·6H2O, 0.06 g/L MgSO4·7H2O, 1 g/L glucose. The pH was adjusted to 5, 8 and 9 by the addition of HCl or NaOH solutions. The specimens were embedded in a teflon holder and exposed to Hanks simulated physiological solution at temperature 37.3±1 ^{o}C.

Table 1. Types of stents used in the experiments

<table>
<tr><td colspan="2">Surface treatment</td><td colspan="2">conventional ion implantation</td><td rowspan="2">Laser surface melting (LSM)</td><td rowspan="2">mechanical polishing (MP)</td><td rowspan="2">bioactive surface (BS)</td></tr>
<tr><td colspan="2">Geometry of atent-graft</td><td>Mo</td><td>O</td></tr>
<tr><td colspan="2">„diamond- shape“</td><td>10</td><td>10</td><td>10</td><td>10</td><td>10</td></tr>
<tr><td colspan="2">„peak-to-peak “ bridges</td><td>10</td><td>10</td><td>10</td><td>10</td><td>10</td></tr>
<tr><td rowspan="2">Knited stents</td><td>Alloy A</td><td></td><td></td><td></td><td>10</td><td>10</td></tr>
<tr><td>Alloy B</td><td>10</td><td>10</td><td></td><td></td><td></td></tr>
</table>

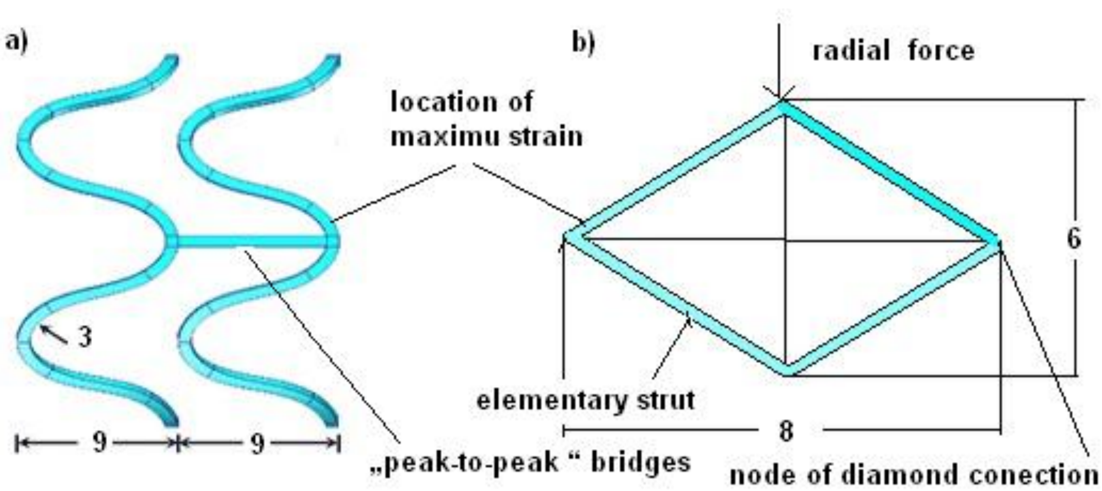

Fig.2. Geometry of elementary cels of stent grafts:

a) „peak-to-peak “ bridges; b) „diamond- shape“.

Numerical analysis.
ANSYS software was employed to study the mechanical behavior and fatigue performance of stents. Further calculations were carried out using FreeFem software. The exact calculations were carried out only for laser cutted stents. In the case of knitted specimens is calculation more complicated. The calculations made for knitted stents have only limited value. For the numerical analysis was chosen same method as in the work [10]. Contrary to conventional engineering materials, Nitinol

stent fracture is not stress based but strain based. The goal of numerical analysis was to determine locations of maximum stress, respectively, determination of maximum deformation.The calculation are based on equation for the structure(s) in the condition of static equilibrium, where zero body loads were applied:

$$div(\sigma_{ij}) = 0 \,, \tag{1}$$

where σ_{ij} are the stress tensor components of the applied load. One node in stucture must be fixed in the direction perpendicular to surface to prevent out-of-plane rigid body translation. Now we will discuss types of loading applied on stents. First crimping loading is applied on stents. Crimping is used to compress an expanded stent graft into a delivery system. The stent-graft with outer diameter of 25 mm was compressed into delivery system with internal diameter of 5mm.

In the artery are the stent-grafts under permanent compression, because stent–grafts are oversized in comparizon to the artery. This is made to prevent stent–graft migration. Stent–graft migration could lead to a endoleak. The arterial wall prevents the stent graft from completely expanding. Betwen the wall of the artery and the stengraft was assumed friction factor of 0.25. This load, however, seems to have a negligible influence on the fatigue life. The body of the stent-graft forms a vessel, in which blood flows under presure. The stent is periodicaly loaded by internal pressure applied on the stent-graft due to cyclic loading as a result of pulsatile blood flow. In the case of crimping (for diamond-shape stent-graft), it was found that the maximum strain is located on internal side elementar rod, near the diamond cell connection. The maximum strain location in the case of stent-grafts with „peak-to-peak " bridges geometry is shown in Fig. 2. The maximum crimping strain for „diamond-shape" stent-graft is 7.5% and 10% for stent-grafts with „peak-to-peak " bridges. Both these results are lower its critical threshold value of 12%. The calculated values are comparable with [10]. The calculated strains caused by flow of pressure fluid (blood), cyclic change of internal alternating pressure (the difference between 50mmHg (diastolic) to 150mmHg (systolic)) are shown in Table 1. The distribution of von Mises stress is similar to the stent shape. The stress concentrations in the contact region with artery is cause by the artery's deformations. Numerrical analysis shows that the highest risk of fatigue fracture is located at the strut´s internal tensile side, close to the conection of diamond cels or bridges. In the case of knitted stents is exact numerical analysis imposible, but but it can be assumed that the maximum strain is located on on internal side wires in nodes on the main body of stent-graft.

Table 2. Calculated maximum strains

Geometry of atent-graft	**strains caused by flow of pressure fluid [%]**	**Cyclic strain [%]**	**Radial force [N] at 100mmHg**	**Crimping strain cause by crimping for 1/5 of nominal diameter**
„diamond- shape"	0.52	0.35	1.85	7.5%
„peak-to-peak " bridges	0.66	0.62	1.27	10%

Experimental results

Fatigue loading was simulated by the loading on "artificial blood vessels". to the final fracture of an element stent. The results are shown in Fig. 3. This figure represents stent–graft constant-life diagram. One half of the samples was only loaded to the final fracture, while the other half of the samples were subjected to combination of corrosion degradation in Hanks solution and loading.

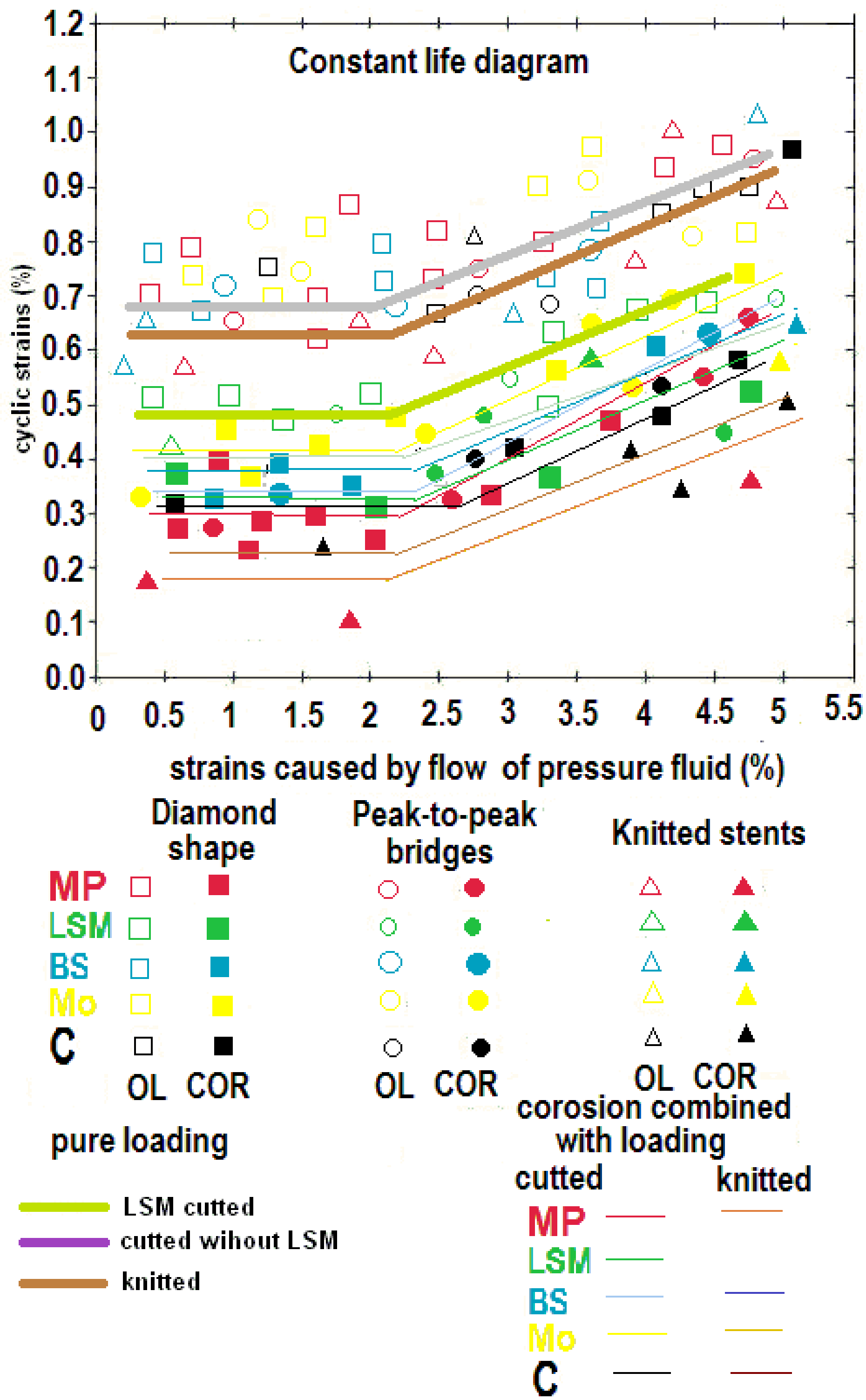

Fig.3. Stent–graft constant-life diagram. Not all points are plotted in the graph for clarity.

MP – mechanical polishing, LSM- laser surface melting, BS – bioactive surface,

Mo – surface refined with molybdenium, C - surface refined with karbon, OL- Loaded only,

COR- Corosion degraditioncombined with mechanical loading.

For the case of samples without causing corrosion degradation were drawn only three lines constant life. In this case very small differences are between cutted geometry stent-grafts. Influence of surface layers is not significant. The only exception was the LSM method. The laser surface melting surfaces have negative effect on fatigue resistance against mechanical loading. In the case of corrosion degradation are again combined results for „diamond- shape“ and „peak-to-peak “ bridges stents. The best corrosion protection ensures Mo surface for both laser cutted and knitted stent grafts. The knitted stents have a significantly lower corrosion resistance in comparison to the laser cutted stents. This effect can be explined in two ways:

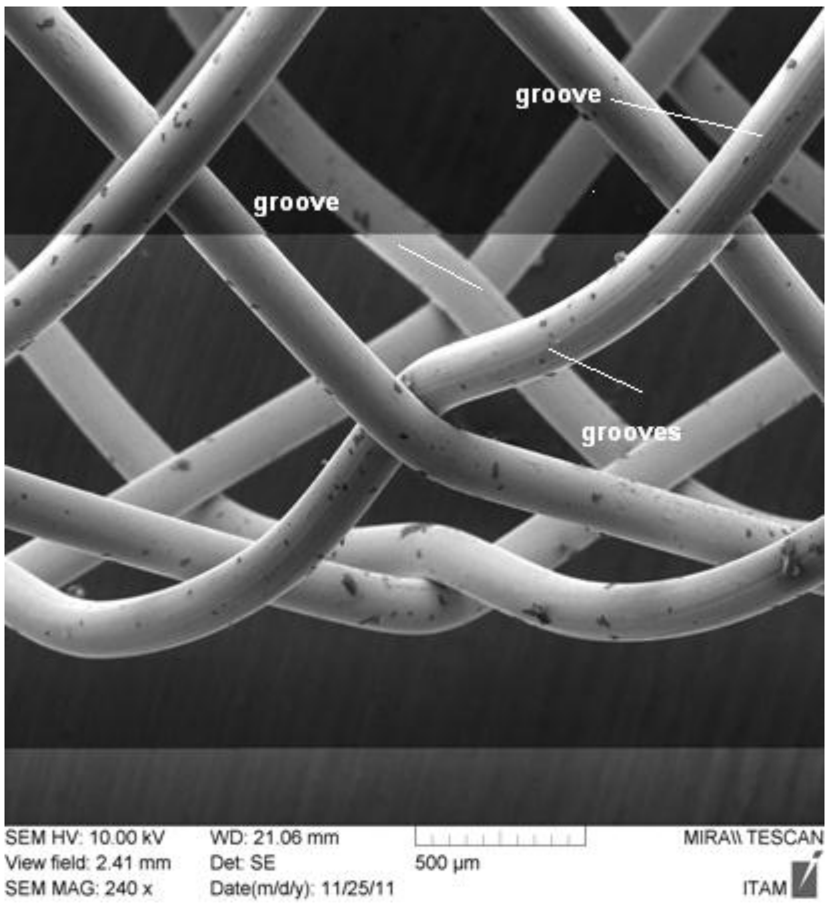

Fig.4. Grooves on wires surfaces

a) Long grooves were observed on the wires surfaces of knitted stent-drafts, see Fig. 4. These grooves are most likely caused by drag of wires in knitting process. These grooves often stretch on the entire length of the wire surface. Alsoon the surface of the wires used for stents manufacture has been observed similar grooves, but less frequently. Grooves are already generated in the production of wires. These grooves are not as deep as the grooves generated during knitting. These grooves reperesented not only stress concetrator, but mainly place of intense corrosion. Although, these grooves are covered with coating surface.

b) The second factor that apparently causes significant corrosion degradation of knitted stents is the mutual attrition of wires in the nodes. This friction causes damage to the protective surface layer. These sites are also characterized by the highest strain. This explanation of phenomenon is supported by the fact, that the loops at the ends of the stent are much less damage by corrosion wires in the nodes in the main body of the stent (The value of strain in the loops at the end of the stent and in nodes can be considered approximately equal.).

Summary.
The corrosion stability of Nitinol devices is strongly affected by the method of surface preparation. The laser surface melting surfaces have negative effect on fatigue resistance against mechanical loading. On the contrary, biosurfaces don't affect mechanical resistance. The stents rupture first occur in regions with highest portion of predeformation. The laser cutted stents have higher durability in high cycle region, but they are more sensitive to low cycle fatigue.

Acknowledgement
The author acknowledged the financial support provided by the Czech Science Foundation in the frame of the Project No. SVV-2011-262901 and Project Prvouk (Charles University of Prague). Special thanks go to ELLA-CS medical device development.

References

[1] W.J. Buehler, J.W. Gilfrich & R.C. Wiley, "Effects of low-temperature phase changes on the mechanical properties of alloys near composition TiNi," *Journal of Applied Physics* 34 (1963) p 475.
[2] F.E. Wang, W.J. Buehler & S.J. Pickart, "Crystal structure and a unique martensitic transition of TiNi," *Journal of Applied Physics* **36** (1965) p 3232-3239.).
[3] I.Milošev, B.Kapun, Materials Science and Engineering C, July 2011, in press
[4] S. Shabalovskaya, Int. Mater. Rev. 46 (2001) 1–18.
[5] S.A. Shabalovskaya, Bio-Med. Mater. Eng. 12 (2002) 69–109.
[6] T.W. Duerig, K.N. Melton, D. Stöckel, and C.W. Wayman, in Engineering Aspects of Shape Memory Alloys, Butterworth-Heinemann Ltd., London, 1990, p. 14-18.
[7] T.W. Duerig, K.N. Melton, D. Stöckel, and C.W. Wayman, in Engineering Aspects of Shape Memory Alloys, Butterworth-Heinemann Ltd., London, 1990, p. 369-393.
[8] D.J. Wever, A.G. Veldhuizen, J. de Vries, H.J. Busscher, D.R.A., J.R. van Horn, Biomaterials 19 (1998) 761–769.
[9] O. Cissé, O. Savadogo, M. Wu, L'H. Yahia, J. Biomed. Mater. Res. Part A 61 (2002), 339–345.
[10] C. Kleinstreuer, Z. Li, C.A. Basciano, S. Seelecke, M.A. Farber: Computational mechanics of Nitinol stent grafts, Journal of Biomechanics 41 (2008) 2370–2378
[11] X.Y.Gong, A.R. Pelton, T.W.Duerig, N. Rebelo, K. Perry, 2003.Finite element analysis and experimental evaluation of superelastic Nitinol stent. In: Proceedings of the International Conference on Shape Memory and Superelastic Technologies, Menlo Park, CA, pp. 453–462
[12] Cui Z, Man H, Yang X. The corrosion and nickel release behavior of laser surface-melted NiTi shape memory alloys in Hanks solution. Surf Coat Technol 2005;192:347–53. [13] T.W. Duerig, K.N. Melton, D. Stöckel, and C.W. Wayman, in Engineering Aspects of Shape Memory Alloys, Butterworth-Heinemann Ltd., London, 1990, p. 14-18.