

DYNAMICS OF NONLINEAR PROCESSES OF CORROSION OF NIKEL-TITANIUM AND TRANSITION OF NICKEL IONS IN BIOLOGICAL MEDIUM

Nasakina E.O., Kolmakov A.G., Sevostyanov M.A., Zabolotny V.T., Sergiyenko K.V.

Institution of Russian Academy of Sciences A.A. Baikov Institute of Metallurgy and Material Science RAS,
Moscow, Russia, e-mail: nacakina@mail.ru

Research of corrosion resistance of nanostructural nickel-titanium and his biomedical composite with Ta surface layer received by a method of physical vapor deposition is conducted. Samples were placed in mediums imitating physiological liquids, with pH from 1.68 to 9.18. 3 types of nitinol samples were used: in an initial state, after thermal (annealing) and surface mechanical treatment. The greatest release of nickel ions was observed in solution with the sourest environment and samples after annealing. Release of nickel ions in solution with composite samples wasn't observed.

Keywords: nickel-titanium, nanostructural nitinol, nanocomposite, tantalum, corrosion resistance, depassivating action, pitting formation.

Introduction

Nickel-titanium alloys (also known under the general name nitinol) are widely recognized as the material which is ideally suited by its mechanical properties for production of various products, including medical implants [1 - 4]. For example, medical devices of stent type existing only couple of decades gain the increasing popularity and are implanted practically in all human body. And consequently, they are exposed to both mechanical influence from tissues and electrochemical from physiological liquids, various both in structure and in acidity of medium. The presence in the nitinol of nickel (rendering toxic, allergic, cancerogenic, mutagenic impact on an organism, etc. [5 - 8]) causes the necessity of research and increase of corrosion resistance of a material to action of aggressive environment of an organism.

In works of different authors represent absolutely various duration (up to constant) and values (from shares to hundreds of mg/l) of nickel ions release from microstructural nitinol into environment [9 - 15]. Properties of a material can be changed by nanostructuring, creation of nanocomposite with a tantalum surface layer has to render still greater effect.

In this work corrosion resistance of nanostructural nitinol (Ni-55,91 weight %, Ti-44,03 weight %) in an initial state, after volume thermal (annealing) and surface mechanical treatment and a composite "basis — nitinol, tantalum surface layer" was defined.

Materials and Methods

For research of corrosion resistance in this work was decided to pick up and prepare the solutions which acidity would match with acidity of physiological liquids. Since in a human body pH changes almost from 1 to 9 (for example, 1.53–1.67 norm of gastric juice; 3.8–4 in wall area of intestines; 7.34–7.43 norm of blood; 8.5–9 in a large intestine, etc.), it was decided to carry out tests at several values of pH.

Thus the sour environment of a stomach and intestines is created by solutions of hydrochloric acid of low concentration which in vitro (in case of corrosion of metal samples) are very difficult for reproducing at the set level. Therefore for reproduction of these sour environments and the alkaline environment of the bottom departments of intestines the corresponding standard buffer solutions with pH 1,68, 3,56, 4,01 and 9,18 were picked up, and for receiving of the neutral environment of plasma of

blood and tissues 0,9 weight % sodium chloride solution (physical solution) was used (Tabl. 1). Also for comparison hydrochloric acid solution with pH 1,56 was used. Research was conducted on wire samples of equal length with a diameter of 280 microns with total mass of 32,6 mg per 100 ml of buffer solution. The analysis of probes was carried out on sequential atomic-issue spectrometer with induction plasma.

Table 1 - Structure and acidity of buffer solutions

pH	Structure
1,68	Potassium tetraoksalat ($\text{KH}_3\text{C}_4\text{O}_8 \times 2\text{H}_2\text{O}$), 0.05 M
3,56	Potassium acid tartrate ($\text{C}_4\text{H}_5\text{O}_6\text{K}$), 0.025 M
4,01	Potassium acid phthalate ($\text{C}_8\text{H}_5\text{O}_4\text{K}$), 0.05 M
7,39	Sodium chloride (NaCl), 0.9 wt%
9,18	Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \times 10\text{H}_2\text{O}$), 0.05 M

For research of corrosion properties of nitinol with surface layers at their creation metal tantalum was used. The choice was based on that this metal possesses: high biological compatibility with living tissues; extreme resistance to influence of any organic and inorganic acids (including "aqua regia"), to oxidation by oxygen and reaction with hydrogen to 280 °C; galvanic similarity to nitinol.

Results and discussion

Research of corrosion resistance in this work meant definition: 1) whether nanostructural nitinol exposed to interaction with the liquid environment (in any parameters imitating physiological liquids) in which it is; 2) what impact on this interaction character of this medium (structure or acidity) and treatment of nitinol sample (mechanical, thermal, structural) renders. Samples of four types were used: initial nanostructured nickel-titanium (sample 1), it after volume thermal (sample 2) and surface mechanical (sample 3) treatment, a composite with a nitinol basis and tantalum surface layer (sample 4).

Mechanical treatment was made for the purpose of increase of corrosion resistance of nitinol products due to improvement of quality of a surface: removals from it of pollution, reduction of roughness and, therefore, the total area of the surface treated to action of hostile environment, etc. Thermal – for giving to a material of an optimum set of mechanical properties.

Measurements of elements concentration in studied solutions were made in 10, 25, 45, 60 and 75 days from the experiment beginning (i.e. entering of samples into solutions). Results of measurements are summarized in table 2 ("-" designate concentration less than 0.0066 mg/l) and shown in figures 1 – 6. In table 2 results of research of all samples in solution with pH 9,18 and a sample 4 in general aren't given as in these two cases it wasn't observed of an release of metals in solution (in the second case in a month for which the sample stayed in solutions; in the first case for all time of research). Therefore further we will consider behavior only of samples 1, 2 and 3 in solutions with acidity 1,68 – 7,39.

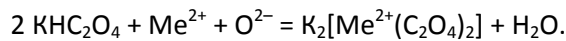
Figure 1 demonstrates that corrosion in solution with acidity 1.68 is observed, that concentration of metals ions increases over time, however its relative increase decreases (etching of metals from a surface decreases), that the release of nickel ions is more than of titanium, however titanium ions

nevertheless are present. This regularity remains in all four studied solutions in case of all three samples. In literary data when considering nitinol corrosion a mention of an release of titanium wasn't found. In case of buffer organic sour salts dissolution of the titanium explainable by occurrence of chemical interaction. The example of possible interaction of ions of nickel and titanium with potassium tetraoxalate is given below:

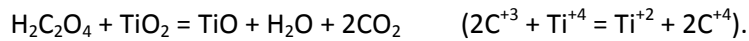
Table 2 - Results of research of corrosion resistance.

pH	Time, days	Concentration of an element in solution, mg/l					
		Sample 1		Sample 2		Sample 3	
		Ti	Ni	Ti	Ni	Ti	Ni
1,68	10	1,3010	2,1300	4,0000	6,2000	0,4700	0,7100
	25	1,9000	2,9700	6,0000	9,0000	0,6600	0,9700
	45	2,3040	3,6720	9,0750	9,9675	0,7900	1,2200
	60	3,1320	4,2780	10,0800	10,7250	0,7900	1,2300
	75	3,2220	4,3800	10,1250	10,7625	0,7900	1,2400
3,56	10	–	0,0500	–	0,1000	–	0,0340
	25	–	0,1800	–	0,4000	–	0,0700
	45	–	0,3780	0,0750	0,6075	–	0,1200
	60	0,0342	0,4500	0,0900	0,6900	–	0,1300
	75	0,0360	0,4920	0,0975	0,9150	–	0,1350
4,01	10	–	0,0300	–	0,0380	–	0,0110
	25	–	0,0600	–	0,0700	–	0,0200
	45	–	0,0740	–	0,1395	–	0,0240
	60	0,0066	0,0900	–	0,1425	–	0,0250
	75	0,0066	0,1020	–	0,1875	–	0,0255
7,39	10	–	0,5000	0,0138	0,8750	–	0,0420
	25	–	0,7600	0,0500	1,3300	–	0,1200
	45	0,0100	0,9420	0,0900	1,5450	–	0,1500
	60	0,2202	0,9780	0,9750	1,6050	–	0,1550
	75	0,2400	1,0260	0,1800	1,6800	–	0,1570

The example of possible interaction of ions of nickel and titanium with potassium tetraoxalate is given below:



Thus it is possible to assume that present at solution oxalic acid acts as a reducer in relation to titanium dioxide of TiO_2 average structure making a protective layer (nonstoichiometrical oxide film with the presence of Ti^{+3} ions) of grains and sample as a whole:



As potassium tetraoxalate isn't physiological liquid and serves in this experiment only for creation necessary pH, there was a desire to compare its action on an alloy to effect of hydrochloric acid (answering for the sour environment of gastric juice). The sample 1 was placed in solution of HCl in the distilled water with concentration of 0,0275 mol/l that by calculations corresponded pH 1.56. In 10 days concentration of nickel in solution was 1.94 mg/l and titanium — 0.515 mg/l. According to the table 2 the nickel and titanium release in solution of tetraoxalate was 2.13 and 1.3 mg/l respectively. Herewith pH in solution of acid changed to 2. It is possible to make a conclusion that in a quantitative sense corrosion of nitinol in these two solutions is close in a nickel release.

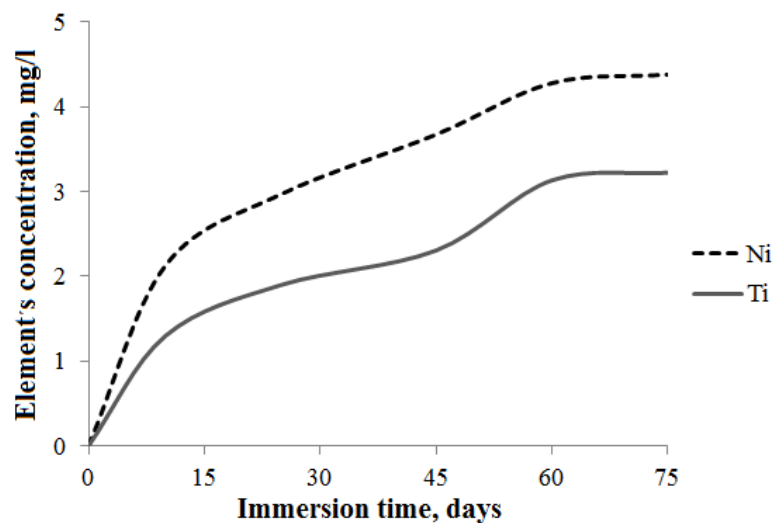


Fig.1. Dependence of concentration of nickel and titanium in solution with acidity 1.68

from sampling time for sample 1

When comparing influence of a processing type on corrosion resistance of samples (fig. 2, 3) it is very noticeable that samples after annealing are most subject to corrosion, and surface mechanical treatment strongly increases corrosion resistance of initial nitinol (as expected). Undesirable influence of heat treatment on corrosion resistance can be explained by occurrence of processes of

recrystallization of the external cold-hardened (strengthening) layer on a surface of initial nitinol formed during its receiving. According to literature the heat treatment necessary for stabilization of mechanical properties at a temperature from 400 to 1000 °C always leads to considerable deterioration of corrosion resistance [16-18]. Regularity remains in all environments.

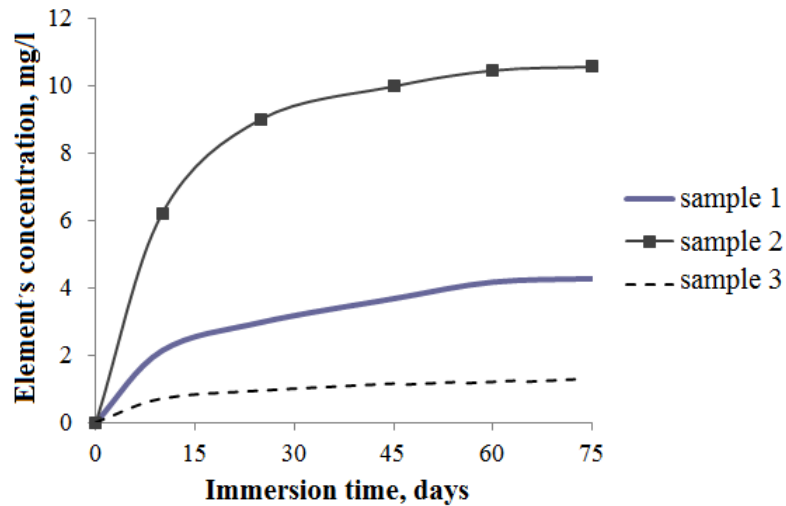


Fig.2. Dependence of concentration of nickel in solution with acidity 1.68 from sampling time for samples 1, 2 and 3

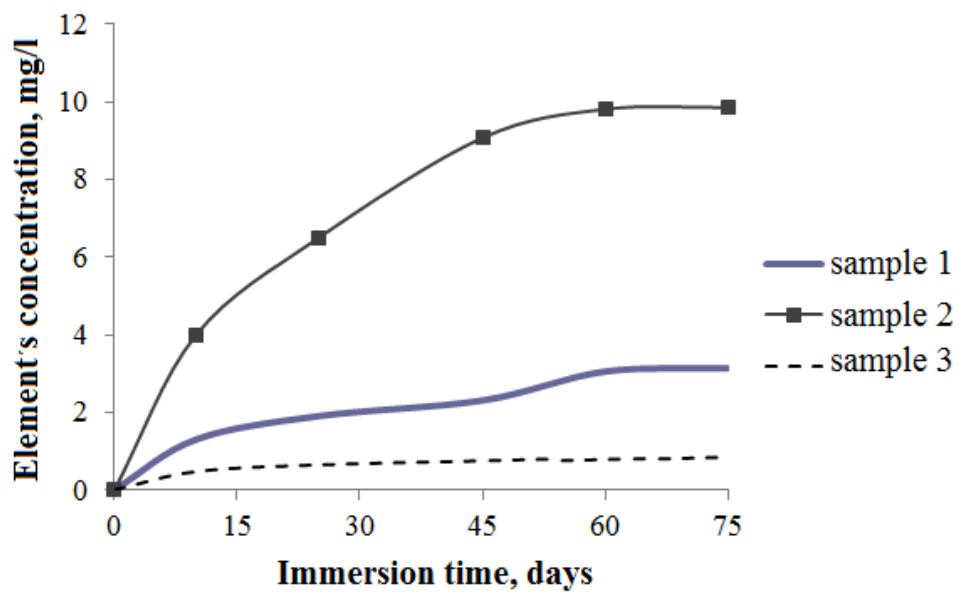


Fig. 3. Dependence of concentration of the titanium in solution with acidity 1.68 from sampling time for samples 1, 2 and 3

Corrosion of sample of the same type considerably increases with increase of solution acidity except for physical solution with pH about 7.39 (fig. 4 – 5). It meets expectations. On the one hand, the release of metals ions increases in process of acidity increase that in the theory corresponds to increase of "acid" concentration, i.e. aggression of the environment. On the other hand, the high release of metals (it is more, than at solutions with acidity 4.01 and 3.56) shows physical solution – rather concentrated source of chlorine ions.

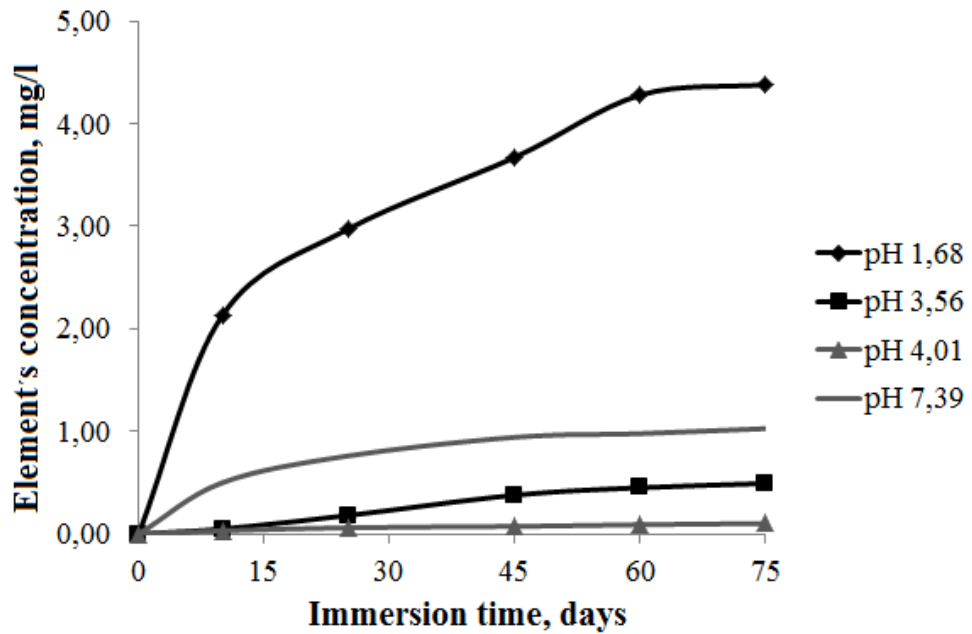


Fig. 4. Dependence of concentration of nickel in studied solutions from sampling time for sample 1 at various acidity

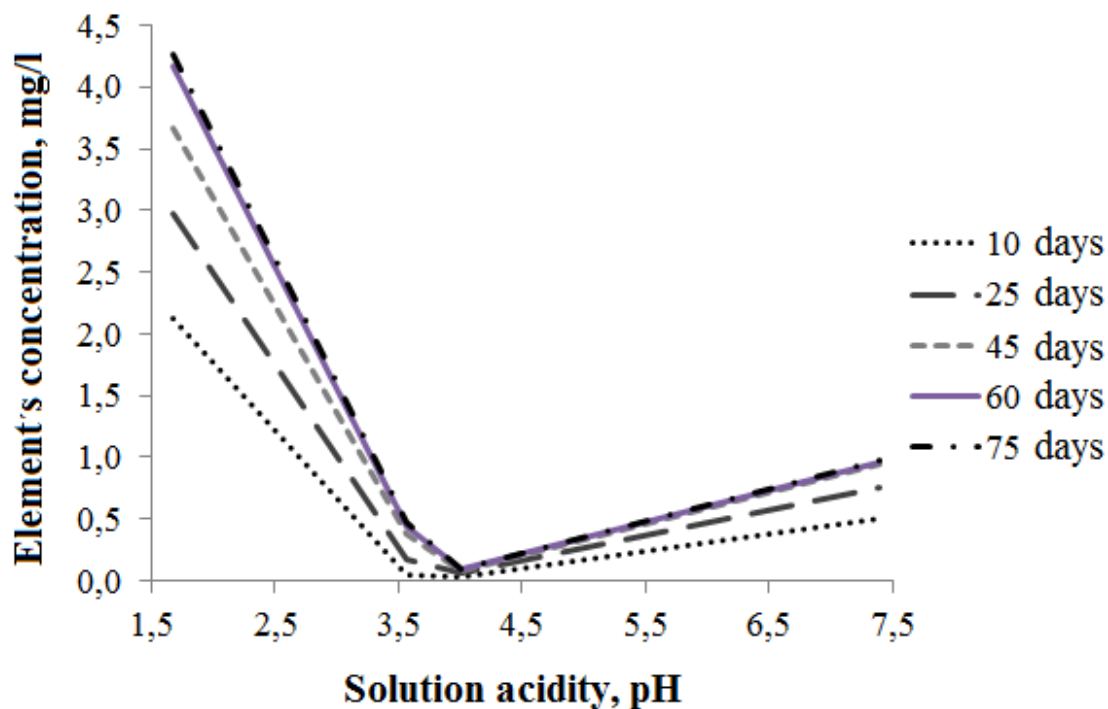


Fig.5. Dependence of concentration of nickel in studied solutions from their acidity at various time of sampling for sample 1

Chloride ions, as known, are the ions activators of corrosion providing depassivating, pitting formation action. Corrosion destruction of this type happens at chromic and the chromic-nickel alloys, aluminum and its alloys, nickel, zirconium, titanium in environments in which along with a passivator – an oxidizer (including the dissolved oxygen) activating anions (Cl, more Br and F, etc.) are present, for example, in NaCl solutions, in sea water, in solutions of chloric iron, at mixes of hydrochloric and nitric acids, etc.

At the same time the titanium is considered well resistant in the oxidizing environments containing ions of chlorine. Values of potential of pitting formation in 0.1-M NaCl at 25 °C are given below, V: Ni (+0,28); Ti (+12,0). Therefore unexpected there was a presence at solution of titanium ions at such large number. Here it is possible to suggest that it is connected with nanostructure of nitinol: nanodimensional grains on a surface when nickel leaching from it collapse and also let out in solution large amount of titanium. And though titanium isn't considered as "harmful" to human body also in quantities much exceeding received, it is possible nevertheless to note that the nanostructure has double impact on corrosion resistance of nitinol.

Conclusion

The nickel release in solutions with investigated nanostructural nitinol is less than the average quantity specified about microstructural nitinol in solution with any acidity; mechanical treatment allows to increase its corrosion resistance by 2–3 times, and tantalum surface layer (at least within 1 month) reduces corrosion to zero. Regularities of corrosion changing depending on acidity and composition of solutions meet expectations (the greatest concentration of metals is observed in solution with pH 1.68, slightly smaller in physical solution).

REFERENCES

1. Shabalovskaya S. On the nature of the biocompatibility and medical applications of NiTi shape memory and superelastic alloys. *Bio-Medical Materials and Engineering*, 1996, Vol. 6, pp. 267 – 289.
2. Gunter V.E., Khodorenko V.N., Yasenchuk Y.F., Chekalkin T.L. *Nikelid titanium. Medical material of new generation*. Tomsk, 2006, 296 p.
3. Gunter V.E., Yiting V.I., Monasevich L.A. *The shape memory effects and their use in medicine*. Novosibirsk, Nauka Publ., 1992, 742 p.
4. Stoeckel D. Nitinol medical devices and implants. *Minimally invasive therapy & allied technologies*, 2000, Vol. 9, pp. 81–88.
5. Fils V.A. *Harmful chemicals. Inorganic compounds of elements of groups I-VIII*. – Leningrad, Chemistry, 1988, 512p.
6. Takamura K., Hayashi K., Ishinishi N., Yamada T., Sugioka Y. Evaluation of carcinogenicity and chronic toxicity associated with orthopedic implants in mice. *Journal of Biomedical Materials Research*, 1994, No. 28, pp.583-589.
7. Uo M., Watari F., Yokoyama A., Matsuno H., Kawasaki T. Dissolution of nickel and tissue response observed by X-ray scanning analytical microscopy. *Biomaterials*, 1999, No.20, pp. 747- 755.
8. Wataha J., O'Dell N., Singh B., Ghazi M., Whitford G., Lockwood P. Relating nickel-induced tissue inflammation to Ni release in vivo. *Journal of Biomedical Materials Research*, 2001, No. 58, pp. 537- 544.
9. Wever D.J., Veldhuizen A.G., de Vries J., Busscher H.J., Uges D.R.A., van Horn J.R. Electrochemical and surface characterization of a nickel–titanium alloy. *Biomaterials*, 1998, Vol. 19, pp. 761–769.
10. Shabalovskaya S.A., He Tian, Anderegg J.W., Schryvers D.U., Carroll W.U., Van Humbeeck J. The influence of surface oxides on the distribution and release of nickel from Nitinol wires. *Biomaterials*, 2009, No.30, pp. 468 – 477
11. Hu T., Chu C., Xin Y., Wu S., Yeung K.W.K., Chu P.K. Corrosion products and mechanism on NiTi shape memory alloy in physiological environment. *Journal of Materials Research*, 2010, Vol. 25, pp. 350 – 358.
12. Trepanier C., Venugopalan R., Messer R., Zimmerman J., Pelton A.R. Effect of passivation treatments on nickel release from Nitinol. *Society for Biomaterials: Proc. 6th World Biomaterials Congress Transactions*. Minneapolis: Society for Biomaterials, 2000, pp. 1043.
13. Barrett R.D., Bishara S.E., Quinn J.K. Biodegradation of orthodontic appliances: part I, biodegradation of nickel and chromium in vitro. *American Journal of Orthodontics and Dentofacial Orthopedics*, 1993, Vol.103, pp. 8 – 14.
14. Tomić S., Rudolf R., Brunčko M., Anžel I., Savić V., Čolić M. Response of monocyte-derived dendritic cells to rapidly solidified nickel-titanium ribbons with shape memory properties. *European cells and materials*, 2012, Vol.23, pp. 58-81
15. Ryhanen J., Niemi E., Serlo W., Niemela E., Sandvik P., Pernu H., Salo T. Biocompatibility of nickel–titanium shape–memory metal and its corrosion behavior in human cell cultures. *Journal of Biomedical Materials Research*, 1997, Vol.35, pp. 451 – 457.
16. Trepanier C., Tabizian M., Yahia L.H., Bilodeau L., Piron D.L. Effect of modification of oxide layer on NiTi stent corrosion resistance. *Journal of biomedical materials research*, 1998, Vol.43, pp. 433- 440.
17. Trepanier C., Fino J., Zhu L., Pelton A.R. Corrosion resistance of oxidized Nitinol. *Proceedings of SMST-2003*. Monterey, CA; 2004, pp. 267 – 276.
18. Zhu L., Trepanier C., Fino J., Pelton A.R. Oxidation of Nitinol and Its Effect on Corrosion Resistance. *ASM Materials & Processes for Medical Device Conference*. Cleveland, 2004, pp.156–161.