EFFECT OF TEMPERATURE AND pH ON THE METAL RELEASE FROM TiNi

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Lucrarea se bazează pe influența temperaturii şi a pH-ului asupra ionilor eliberați din nitinol. Probele de NiTi polisate mecanic au fost testate în saliva artificială Afnor de diferite pH-uri şi la temperaturi de 10-800C. Rezultatele au arătat că abilitatea nitinolului de a repasiva este redusă cu creşterea temperaturii. Cantitatea de ioni de Ni şi Ti eliberați a fost determinată cu ajutorul metodei de spectrometrie cu plasmă cuplată inductiv (ICPMS). Cea mai mare cantitate de ioni de Ni şi Ti eliberați în soluție a fost constatată în saliva artificială de pH 2, dar valorile sunt mai mici față de nivelul critic al cantităților care produc alergii.

This study is based on the influence of temperature and pH on the ion released from Nitinol. Mechanical polished NiTi were tested in Afnor artificial saliva with various acidities and at temperatures ranging from 10°C to 80°C. Results showed that the ability of Nitinol to repassivate is reduced with the increase of temperature. The amount of Ni and Ti ions released from TiNi was determined by inductively coupled plasma mass spectrometry (ICPMS) method. The highest amount of Ni and Ti ions released in solution was found in artificial saliva of pH 2, but the values were smaller than the critical level of quantities that produce allergies.

Keywords: nitinol, biocompatibility, titanium alloys, electrochemical measuremets, medical aplication

1. Introduction

Many bioalloys were intensively studied in the last decade [1, 2] and, despite their good corrosion resistance [3], their ion release even in small amount was evaluated and discussed taking into account that in many cases the investigations have shown that the metallic components of the alloys used in orthopedics and dentistry may be toxic and may dissolve in body fluids due to corrosion [4]. Every metal has its own intrinsic toxicity to cells, but the corrosion mostly determines the existing concentration. Thus, the corrosion resistance of the

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alloy and the toxicity of individual metals in the alloy are the main factors determining its biocompatibility.

The corrosion of metals in aqueous solutions takes place via an electrochemical mechanism. Different metals have different intrinsic aptitudes to corrode. Reactions taking place on the metal surface and in the specific environment may cause radical changes in this theoretical nobility. After implantation, the metal is surrounded by serum ions, proteins and cells, which may all modify the effect on local corrosion reactions. The corrosion behavior of a metal in non-physiological in vitro studies vs physiological in vitro studies may vary dramatically. Every implant metal corrodes inside the human body [5].

There are numerous factors which affect metal corrosion. The structure, composition and thickness of the passive layer are highly dependent on the metal itself and its environment [6]. Metals contain various elements, such as lattice defects, impurities and contaminants, which may affect the corrosion reaction. The different heat treatments and working processes change the grain size and energy state of the metal and cause surface heterogeneity [7, 8, 9]. All these factors may affect the passivation layer.

Nitinol, a nearly equiatomic nickel-titanium alloy discovered in 1962, has been studied extensively for biomedical applications, because of its unique shape memory effect, super-elasticity, as well a good biocompatibility [10]. In vivo study, TiNi alloys show cytotoxic reaction.

The aim of this study is to examine the effect of temperature and the pH on the metal release rate in artificial saliva with various acidities, with the prospect of reducing the toxicity risk due to metal ion release.

2. Experimental part:

Mechanical polished Nitinol (51.4% at Ni) was used in this study. The samples were cut in a cylindrical shape with the radius of 2 mm, height of 6 mm, and the tested area of 1.25 cm^2. The samples were polished with waterproof emery paper no. 400, 1000, and 2400, washed with deionized water and then dried at 80^0C.

The corrosion test method follows ASTM F2129 [11].

In order to assess the effect of temperature on the corrosion resistance of Nitinol, Afnor artificial saliva solution was cooled down or heated up to 10°C, 20°C (room temperature), 30°C, 50°C, 60°C, 70°C and 80°C, using a temperature controlled water bath. Artificial saliva Afnor was used as working solution using reagent of analytical grade. Table 1 presents the chemical composition of Afnor artificial saliva.

Table 1

Composition of Afnor artificial saliva

Compound	Concentration g/L
Na_2HPO_4	0.26
NaCl	6.70
KSCN	0.33
KH_2PO_4	0.20
KCl	1.20
$NaHCO_3$	1.50

The corrosion resistance of the samples was characterized in terms of their breakdown potential (E_b) and repassivation potential (E_p). In addition, the corrosion current density (I_{corr}) was also determined. The electrochemical parameters were detected by Voltalab PGZ 301 with VoltaMaster soft. The potentiodynamic polarization curves of the test specimens were measured from -0.8V towards the anodic direction with a scan rate of 2 mV/s. When 1.5V was reached, the scanning direction was reversed. The scan was finished when the potential reached again the value of -0.8V. For ion release, ICPMS analysis was performed in the static immersion in accordance with JIS T 0304 standard [12]. The concentrations of metals released into solutions were determined in ppb (ng/ml). Ni and Ti concentrations were analyzed by inductively coupled plasma-mass spectrometry (ICPMS). Metal concentration was measured in a clean room and the solutions for measurement were prepared on a clean bench (class 100). The analytical detection limits under these conditions were all below 0.05 ng/ml.

3. Results and discussion

A summary of the corrosion resistance of Nitinol tested between 10°C and 80°C is presented in Table 1 and in Fig. 1. The testing temperatures are between 10 and 80^0C, because of the fact that in oral cavity the temperatures are quite different depending on what we are eating. Temperature can also affect the nature of the environment by changing the solubility of a constituent that can affect the corrosion behavior of a material. Based on the shape of the polarization curves and inspection of the specimens after the tests, E_b coincides with the potential for oxygen evolution for samples tested between 10°C and 70°C. Therefore, the small shift in E_b for samples tested between 10°C and 70°C appears to be related to a change in the value of potential at which oxygen is being produced on the sample. It is important to note the small hysterisis between E_b and E_p, indicating superior ability of the material to repassivate and low susceptibility to crevice corrosion. Starting at 60°C, the samples start to exhibit a different corrosion behavior. Although E_b appears to still overlap with oxygen evolution, the ability of the material to repassivate after breakdown of the oxide layer is progressively

reduced. The samples tested at 80°C are characterized by a large hysterisis between E_b and E_p, suggesting that the material is less able to repassivate and more susceptible to crevice corrosion at that temperature.

Table 2

Corossion parameters of Nitinol at different temperatures

Temp [^{0}C]	E_b [mV vs SCE]	E_p [mV vs SCE]	I_{corr} [μA/cm^2]
10	1308	1285	2.1
20	1270	1070	2.8
30	1245	1050	3.11
37	1025	880	4.28
50	902	835	3.42
60	853	795	3.56
70	785	524	8.21
80	796	-21	9.54

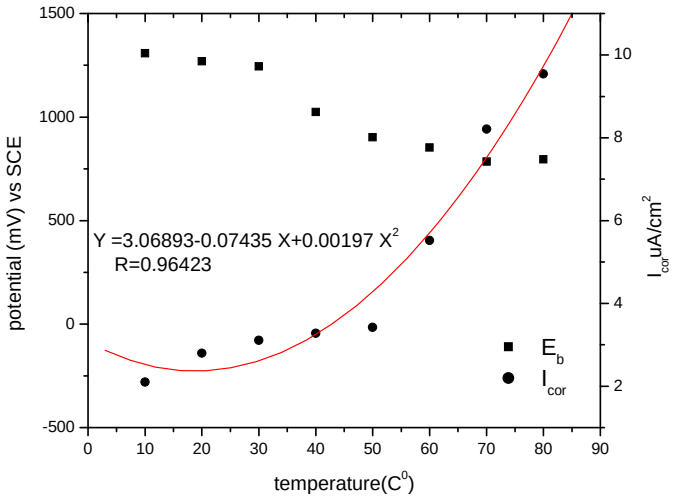

Fig. 1. Influence of temperature on breakdown potential and corrosion current.

The corrosion current density, which is directly related to the corrosion rate, appears to slowly increase as a function of test temperature. However, because I_{corr} are all within the same decade, it cannot be concluded that this increase in I_{corr} is significant within the temperature range studied. These results suggest that temperature affects the ability of Nitinol to repassivate. However, no other effects, such as on the corrosion rate of the material, were observed with a change in temperature.

A summary of the corrosion resistance of Nitinol tested at pH of 2, 7 and 10 at 37^{0}C is presented in Table 3. The cyclic polarization plots of TiNi in Afnor

artificial saliva are given in Figure 2. Polarization of NiTi in Afnor artificial saliva solution at a pH of 2 resulted in a shift of the curve toward greater values of potential. Similar to the previous study, E_b coincides with oxygen evolution. Therefore, the small shift in E_b can be related to a change in the potential at which oxygen is being produced in the solution. This result is in agreement with the Pourbaix diagram for water: more acidic pH shifts the oxygen evolution reaction to higher potentials [13]. The variation in E_p is similar to E_b so the material ability to repassivate is not affected. No major differences could be found between the samples tested at pH 7 and pH 10. Furthermore, no differences were found in the corrosion current densities between all groups.

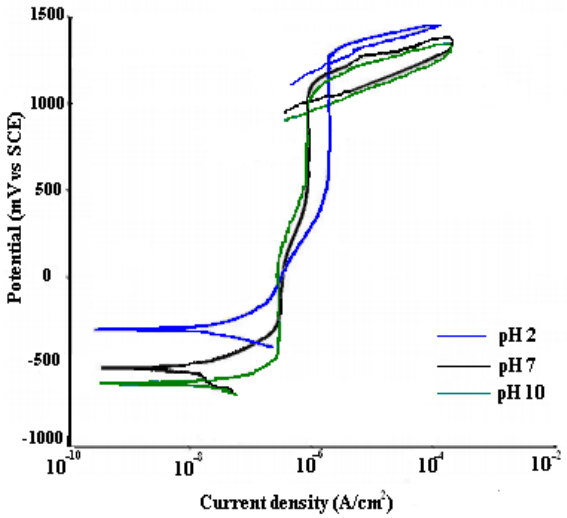

Fig. 2. Polarization curves of TiNi at various pH

Table 3

Electrochemical parameters of TiNi in artificial saliva with various acidities

Afnor artificial saliva	E_{corr} (mV)	E_b (mV)	E_p (mV)	E_b-E_p (mV)	I_{corr} ($\mu A/cm^2$)	I_{pass} ($\mu A/cm^2$)
pH 2	-316	1289	1232	57	2.12	7.58
pH 7	-535	1250	1050	200	1.02	1.96
pH 10	-660	1200	988	212	0.61	1.32

Because the variation of temperature between 10^0 and 80^0C did not show a higher influence on the corrosion currents, and the contact time of metallic implant at these temperatures is very short, it was studied the evolution of metallic ions release detached from implant onto artificial saliva with different pH at a temperature of 37^0C.

There has been great variation in the concentrations of nickel in human tissues reported in literature [14]. Standard reference values are still missing. The older methods of measurement and sample processing have involved many sources of error. The suggested normal nickel concentrations in human tissues are (microgram/kg of dry weight): 173 in lung, 62 in kidney, 54 in heart, 50 in liver, 44 in brain, 37 in spleen and 34 in pancreas [15]. Figures 3, 4 and 5 show the amount of Ni and Ti ions released from TiNi in Afnor artificial saliva after different immersion periods with various acidities.

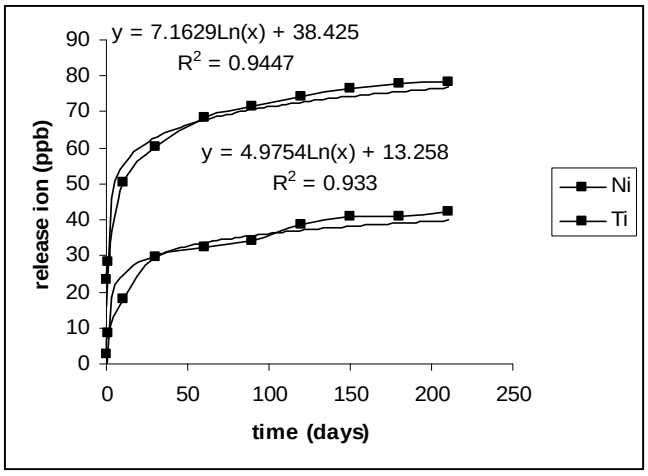

Fig 3. Release amount of Ni and Ti from TiNi in Afnor saliva at pH 2.

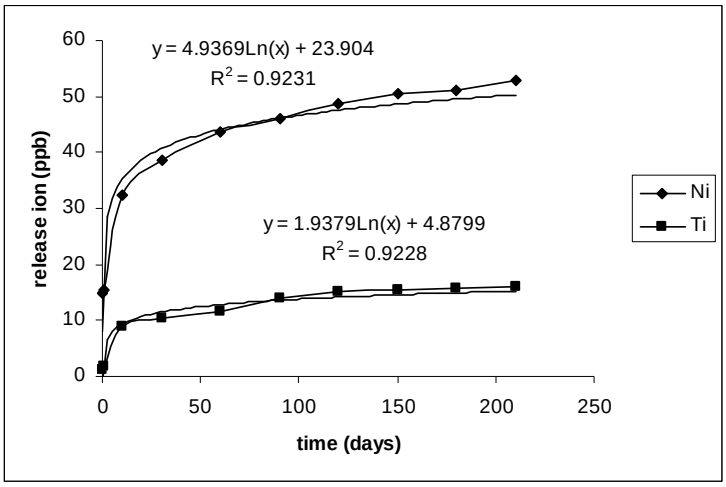

Fig 4. Release amount of Ni and Ti from TiNi in Afnor saliva at pH 7.

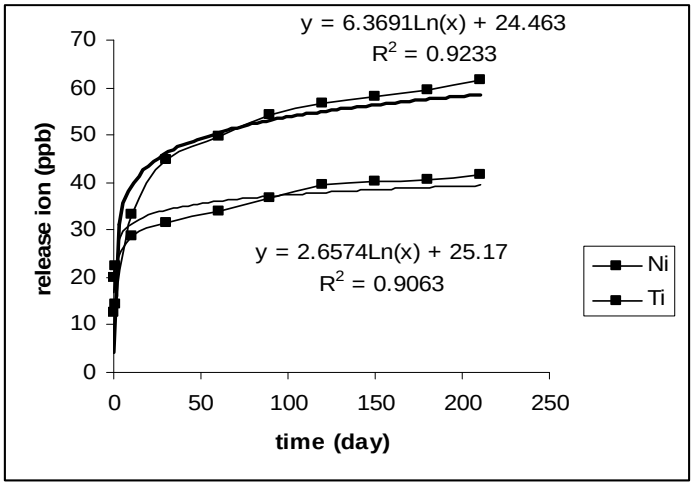

Fig 5. Release amount of Ni and Ti from TiNi in Afnor saliva at pH 10.

The dissolution rate was correlated with a logarithmic rule for all media studied. The release amount of metal ions increased with immersion period in all test solution, while the average ion release per day decreased with immersion period. The release amount of Ti ions compared to Ni ions was smaller in all media studied.

Results from the immersion test revealed that the highest amount of Ni ions released in pH 2 solution for 1 day was 28 ppb, much below the critical concentration (600-2500μg) that causes allergy [16] and the daily dietary intake level (300-500 μg) [17].

For the Ni and Ti ions release in pH 7 solution for 1day immersion period, the release amount was less than those obtained in pH 2 solutions. In the artificial saliva with pH 10 the amount of Ni ion release was slightly lesser than in a solution with pH 2. Slightly acidic saliva or basic saliva may provide a corrosive environment within the oral cavity [18]. This idea is sustained by the amount of Ti ions that is higher than in pH 2 saliva. An increase in the release of Ti ion represents the deterioration of the surface passive film (mainly TiO_2) on TiNi alloy [19]. This would lead to a concurrent increase in Ni ion release. The smallest amount of Ti ions release was measured in pH 7 artificial saliva, this amount being of approximately 5 times lower compared to Ti ions release in pH 2 artificial saliva.

The data obtained by ICPMS measurements were used to estimate the corrosion rate variation in time. Fig. 6 represents the corrosion rate variation in time in accordance with the immersion period.

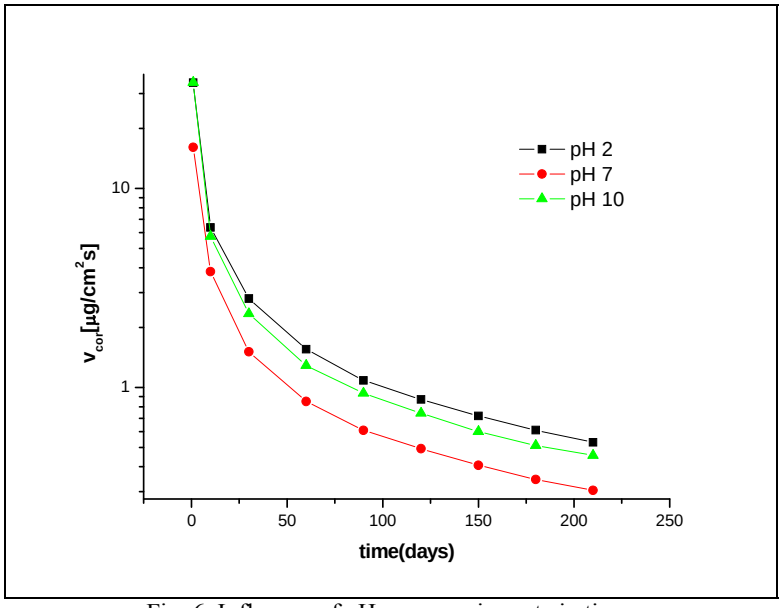

Fig. 6. Influence of pH on corrosion rate in time.

The corrosion rate is higher for the first hours of immersion and after 60 days the values become stationary. Based on the data detected with ICPMS, the average gravimetric value and the average penetration value for Nitinol in analyzed solution was computed. The obtained data are presented in table 4.

Table 4

Estimated values of the corrosion rate

pH of Afnor artificial saliva	k_g (g/m^{2}h) × 10^{-5}	I_p (mm/an) × 10^{-5}
2	2.37	3.22
7	1.4	1.91
10	2.8	3.90

Regarding the evaluation of stability to corrosion, we can admit that TiNi is "perfect stable" ($1 \cdot 10^{-3}$ mm/an).

4. Conclusions

An increase in temperature affects the resistance to localized corrosion of Nitinol by reducing the ability of the material to repassivate. The uniform corrosion rate of Nitinol was not affected by temperature.

The corrosion resistance of NiTi was not affected by a variation in pH, except for a change in the potential for oxygen evolution.

The average amount of Ni ions released per day from the tested TiNi in artificial saliva with various pH, was below the critical concentration specific in the case of allergy and under daily dietary intake level.

R E F E R E N C E S

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