

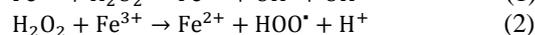
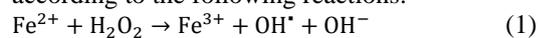
Effects of Fenton's Reagent on Surface Modification of Nitinol Shape Memory Alloy for Biomedical Applications

R. Asghari¹ J. Khalil-Allafi^{2*}

1- Introduction

Nickel-titanium alloys are one of the most widely used medical alloys known as Nitinol. Superelasticity, biocompatibility, shape memory properties and corrosion resistance make these alloys superior to other applied materials in medicine. One of the main reasons for the good biocompatibility of Nitinol is the faster oxidation of titanium than nickel at the alloy surface; therefore surface modification of Nitinol seems essential to improve its performance.

In 2007 for the first time, the effect of Fenton's oxidation in surface modification of nitinol alloys was studied and presented a biocompatible and flexible coating as a low-temperature process for the modification of Nitinol surface. The Fenton reagent is referred to a mixture of H₂O₂ and iron ions, in which H₂O₂ is converted by Fe²⁺ to hydroxyl radicals (OH[·]) with higher oxidation potential than H₂O₂. Hydroxyl radicals are used as non-selective and highly active oxidizing agents. Fenton's oxidation is carried out by catalytic decomposition of H₂O₂ to hydroxyl radicals according to the following reactions:



Fe²⁺ initiates the reaction and catalyzes the H₂O₂ decomposition resulting in production of OH[·]. This radical has a non-coupled electron and is one of the most reactive oxidizing agents.

In this study, Fenton's oxidation has been investigated to create a protective oxide layer against corrosion on a Nitinol alloy, and an attempt has been made to optimize the operating conditions to provide a more corrosion resistant layer. For this purpose, temperature and time factors are considered as variables and Ringer solution have been used as the test environment to measure corrosion behavior and created layer biocompatibility.

2- Materials and Methods

Nitinol specimens with 50.8, 49.1, 0.05 and 0.04 atomic percent of Ni, Ti, C and O elements respectively were prepared using wire-cut to produce disks in a thickness of 1mm and 12.7mm in diameter.

The time and temperature of the oxidation process were considered as test variables and thus the samples were grouped in accordance with Table 1.

Table 1 Grouping of samples under the oxidation process

time\temperature	60°C	65°C	70°C
24 hours	60C24h	65C24h	70C24h
36 hours	60C36h	65C36h	70C36h

Specimens were subjected to Fenton's oxidation under different conditions in 6 groups and the seventh group was used as control with chemically polished surface finish. Preparation of Specimens was performed in three steps according to ASTM F86. All specimens were grinded and then chemically polished with a solution containing H₂O, HF and HNO₃ in a 5:1:4 ratio for 5 min. Afterwards, ultrasonic wash in acetone for 10 min was applied to samples and then dried.

Fenton's reagent was supplied according to Table 2. The initial concentration of H₂O₂ was equal to 5% and H₂O₂/Fe²⁺ ratio in molar concentration was 2000/1. FeSO₄.7H₂O was employed as a source of iron ions, and the solution pH value was set to 3 by adding HF.

Table 2 Fenton's solution components

Solution components	H ₂ O ₂	Distilled water	FeSO ₄ .7H ₂ O
Quantity	20 ml	380 ml	11.3 mg

Fenton's oxidation was performed for groups 1-6 at a specified temperature and time according to Table 1 in the absence of light with stirring, then were washed in distilled water and dried.

To simulate body fluids condition, Ringer's solution was used as the test environment. To characterize the created oxide surfaces, A 25-gram Vickers microhardness test was performed by the M-400-G1/G2/G3 device and the SEM photographs were made using the Cam Scan MV2300 device. The device used for the AAS test was the Analytic Jena-novAA400 model with graphite furnace atomizer. For this test, oxidized samples and a control sample were placed in different containers of Ringer's solution with stirring, for 15 days at 37°C. Potentiodynamic polarization test was carried out using SCE as reference electrode.

3- Results and Discussion

Comparison of the VHN indicates that, the higher time and temperature, the higher VHN, which is attributed to higher thickness of the coating. Fig. 1 shows the SEM micrograph for 70C24h and 70C36h samples using backscattered electrons representing the crack-free surfaces. Cracks are favorable places for the oxide layer fracture and nickel release, which can be associated with serious implications for medical implants biocompatibility. Cavity-like points at the surface of the oxide layer are surface porosities attributed to over-etching.

¹ M.Sc. Faculty of Materials Engineering, Sahand University of Technology.

^{2*} Corresponding Author, professor, Faculty of Materials Engineering, Sahand University of Technology, Tabriz, Iran
Email: Allafi@sut.ac.ir

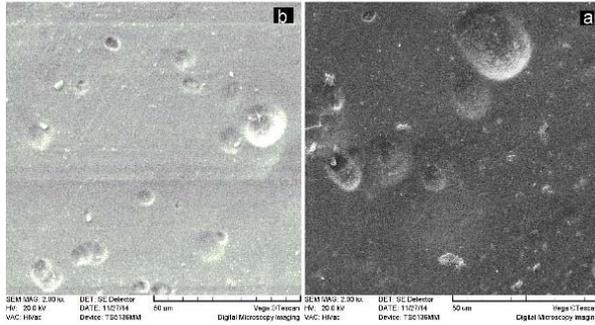


Fig. 1 The SEM micrograph of NiTi samples after Fenton's oxidation (a) 70C24h; (b) 70C36h

Investigation of Nickel release rate in Ringer solution is implemented using atomic absorption spectrometry. The amount of nickel released from the control sample is about $1.685 \mu\text{g} \cdot \text{L}^{-1} \cdot \text{mm}^{-2}$. The results indicate that the amount of nickel released from the Fenton oxidized samples after 15 days of immersion in Ringer solution is less than $0.006 \mu\text{g} \cdot \text{L}^{-1} \cdot \text{mm}^{-2}$, which is significantly lower than the daily safe intake of nickel to the body. Thus, from the aspect of biocompatibility, created surfaces nickel release tends to zero.

Table 3 provides a comparison of current density and corrosion potential values for oxidized samples. In the study of the effect of oxidation time on the corrosion behavior, there is no steady trend. At 60°C , increasing the oxidation time in the Fenton solution increases the corrosion resistance, in return at 65°C and 70°C , whatever the oxidation process time prolongs, the corrosion resistance decreases.

Table 3 corrosion potential and current density for oxidized samples

Sample number	Oxidation temperature ($^\circ\text{C}$)	Oxidation time (hrs)	Current density ($\text{mA} \cdot \text{cm}^{-2}$)	Corrosion potential (V)
60C24h	60	24	$5/316 \times 10^{-5}$	-440
60C36h		36	$4/235 \times 10^{-5}$	-464
65C24h	65	24	$4/102 \times 10^{-5}$	-520
65C36h		36	$4/457 \times 10^{-5}$	-475
70C24h	70	24	$4/143 \times 10^{-5}$	-476
70C36h		36	$6/717 \times 10^{-5}$	-464

It can be concluded that although the increase of the oxidation time in all samples increases the volume of the oxide layer, the thickening of the oxide layer does not always mean an improvement in corrosion behavior and, as can be seen, for different temperatures, the effect of the process time will be different. Oxidation operations at high temperatures can have a negative effect on shape memory properties.

Keeping the process time constant, polarization graphs are used to study the effect of temperature of the Fenton oxidation process on corrosion behavior. Fig. 2 shows the polarization diagram of samples oxidized for 24 hours. Among these, 65C24h having a more negative potential, exhibits the least corrosion current. After that, the 70C24h sample has a better

corrosion resistance. Generally, in 24 hours, higher temperatures provide a more resistant coating than 60°C .

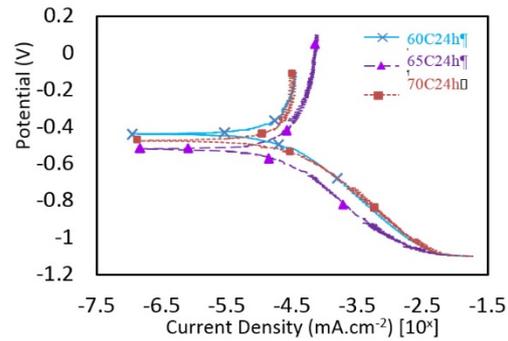


Fig. 2 polarization diagrams for 60C24h, 65C24h and 70C24h

In 36 hours, as shown in Fig. 3, there is not much difference between the corrosion potential of the specimens. However, the comparison of current density (Table 3) shows the increasing trend of corrosion current with temperature growth, which means better corrosion resistance at lower temperatures during oxidation time of 36 hours. Elevating the oxidation temperature accelerates the surface oxidation and increases the possibility of formation of porosities and fine cavities, which leads to a loss of corrosion resistance.

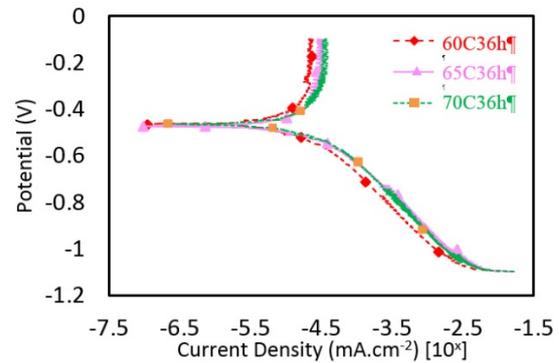


Fig. 3 polarization diagrams for 60C36h, 65C36h and 70C36h

4- Conclusions

Increasing the thickness of the oxide layer does not necessarily result in increased corrosion resistance and biocompatibility, and there can be no absolute and steady effect on corrosion behavior by increasing or decreasing the time and temperature of oxidation in the studied cases, but it can provide the optimal estate. The optimum time and temperature for this process is immersion in a Fenton Reagent solution at 65°C for 24 hours, which provides the best results for corrosion and biocompatibility between the examined conditions.