

IMPROVEMENT OF THE CORROSION RESISTANCE OF EQUIATOMIC NiTi SHAPE MEMORY ALLOY FOR MEDICAL IMPLANTS BY THE ELECTROPOLISHING METHOD

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Autorii au studiat comportamentul la coroziune al aliajului cu memoria formei NiTi (50,6 % at.) utilizând metoda lustruirii electrochimice, pentru îmbunătățirea rezistenței la coroziune și testul pitting pentru verificare. Considerând aplicațiile medicale ale aliajului (proteze arteriale - stenturi și alte implanturi), îmbunătățirea rezistenței la coroziune este una din preocupările principale, în special datorită conținutului ridicat de nichel, care este alergen, toxic și cancerigen. O suprafață foarte netedă va îmbunătăți rezistența la coroziune, ceea ce duce implicit la scăderea cantității de atomi de nichel care vor interacționa cu organismul uman. În plus, față de îmbunătățirea rezistenței la coroziune, punem în evidență o metodă utilă de stabilire a condițiilor optime pentru lustruirea electrochimică. Suprafețele lustruite electrochimic au fost analizate prin microscopie de forță atomică, iar suprafețele supuse testului de coroziune au fost analizate prin microscopie optică.

The authors studied the corrosion behaviour of the NiTi shape memory alloy (50.6 at. %) using the electropolishing method for improving its corrosion resistance and the pitting test to evaluate the results. Considering the medical applications of the alloy (stents and other implants), improving the corrosion resistance is one of the main concern, especially because of the high amount of nickel content, which is allergen, toxic, and cancerous [1]. A smooth surface will improve the corrosion resistance; hence it will decrease the rate of nickel atoms that will interact with the human body. Besides improving the corrosion resistance, we pointed to a useful method for establishing the optimal conditions for electropolishing. The electropolished surfaces were analysed by AFM (atomic force microscopy), and the corrosion tested surfaces were analysed by optical microscopy.

Keywords: NiTi shape memory alloy, implant, electropolishing, corrosion

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1. Introduction

NiTi shape memory alloy has a very good corrosion resistance, similar to pure titanium. However, the presence of nickel in the alloy creates reluctance in using the material for a long period of implantation, e.g. 10-20 years. In order to avoid the nickel interaction with the human body, several methods have been developed, such as mechanical methods (polishing), chemical (etching), electrochemical (electropolishing), thermochemical treatments, metallic or polymeric coatings etc [1].

In our study we consider that the smoother is the surface, the higher the corrosion resistance will be [2].

Therefore, a smooth surface, with no mechanical defects (scratches, superficial deformations, rough surface), coated with protective layers shall increase the biocompatibility of the implant.

In this paper, we studied the influence of electropolishing on the roughness of the surface, using AFM and we tested the corrosion resistance using the pitting test.

Electropolishing is often used to improve the smoothness of the materials' surface. The analysed material is immersed in an electrolyte bath as the positive electrode. Applying a direct current to the electrodes a process of removing a thin layer of material will take place. In this way, the microscopic rough peaks are removed from the surface of the material, resulting a smooth surface. The method is simple and recommended for medical implants and devices, even of a complex shape [1, 2].

The factors of influence of the electropolishing method that affect the corrosion rate and depth are: the composition and concentration of the electrolyte bath and its components, the working temperature, the agitation rate and current density.

2. Materials and methods

In our experiments, the samples were first polished on sandpaper starting from very fine grit size (P150) to ultrafine grit size (P2000), followed by P3000 and P8000 diamond paste polishing. Then, the samples were corroded in a $HF:HNO_3:H_2O$ (1:5:4) solution for 120 seconds [2]. Finally, the samples were electropolished in different conditions [3, 4].

To optimize the working conditions we used a two level factorial design of the experiment (table 1).

Table 1.

Two level factorial design for the electropolishing method.

Run	Voltage, [V]	Corrosion time, [sec.]
1	3	60
2	9	60
3	3	120
4	9	120

The voltage and corrosion time were used as factors of influence. The electrolyte was a solution of $H_2SO_4:CH_3OH:H_2O$ (1:4:5). Two levels of voltage (3 and 6 V) and time (60 and 120 seconds) were chosen.

The resulted surface was analysed by AFM. The prepared samples were tested by pitting corrosion method, and the corroded surface was analysed by optical microscopy.

3. Results and discussion

3.1. AFM analysis of the electropolished surface

The surface of all 4 samples was studied by AFM (fig. 1 – 4). In fig. 1 and 2, the 3D views of the electropolished surfaces are presented for the samples used in our experiment. In two of the cases (fig. 1. a, c) the surfaces are much smoother than in the other two (fig. 1. b, d). The peaks in fig. 1.b, d are higher than in fig. 1. a, c, due to the higher voltage used. As a result of a longer electropolishing time at the same voltage (fig. 1. c, d), the peaks are not necessary shorter (run 4, fig. 1.d). The round shape of the peaks is to be noticed in run 2 and 4 (fig. 1.b, d).

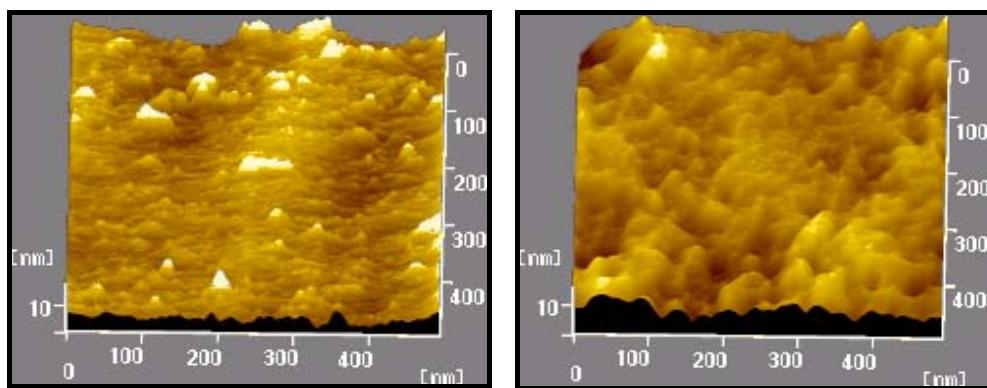


Fig. 1.a, b. 3D view of the electropolished areas for 4 samples (width: 500 nm).

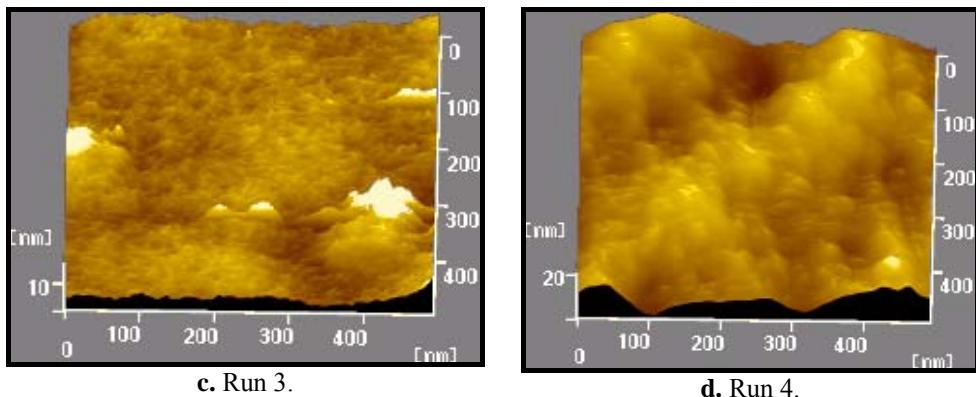


Fig. 1.c, d. 3D view of the electropolished areas for 4 samples (width: 500 nm).

For a larger area of the electropolished surface the same results can be noticed (fig. 2). The peaks on the third sample (fig. 2.c) are much lower than all the others. In fig. 3 and 4 there are presented the frontal views of the analysed surfaces from fig. 1 and 2.

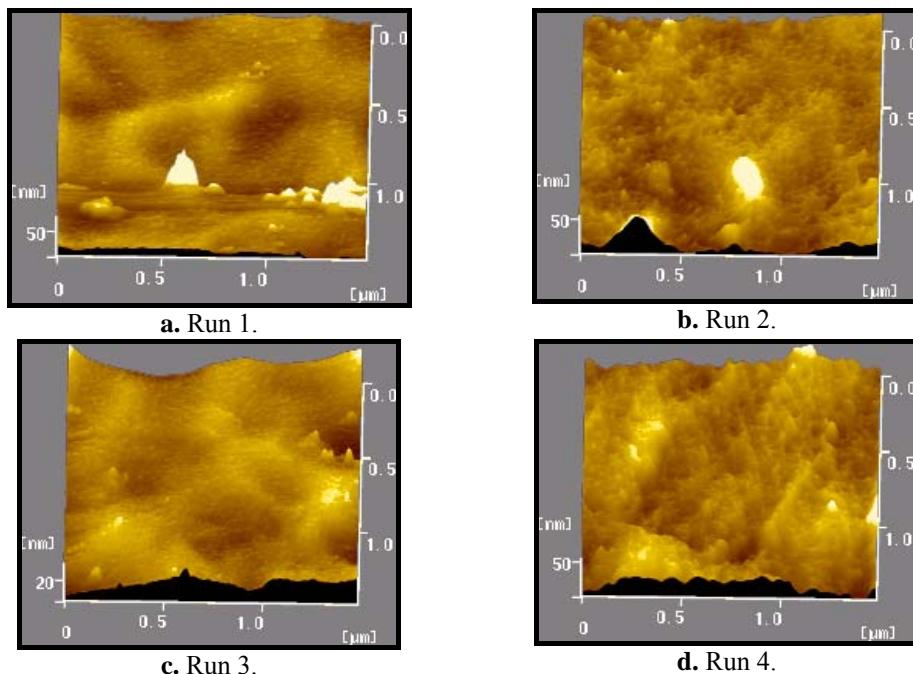


Fig. 2. 3D view of the electropolished areas for 4 samples (width: 1500 nm).

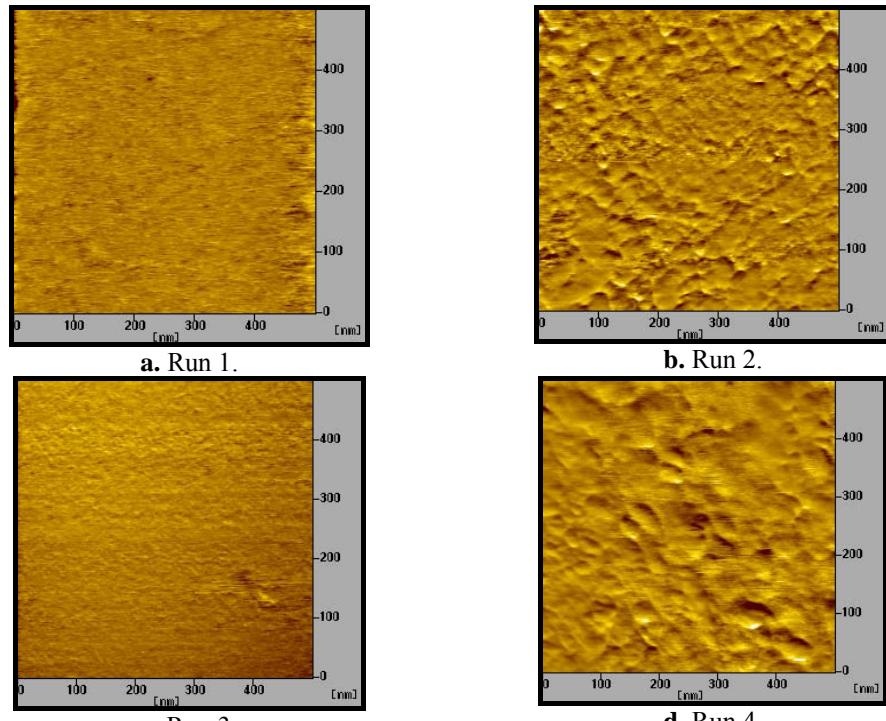


Fig. 3. Frontal view of the electropolished area (fig. 1).

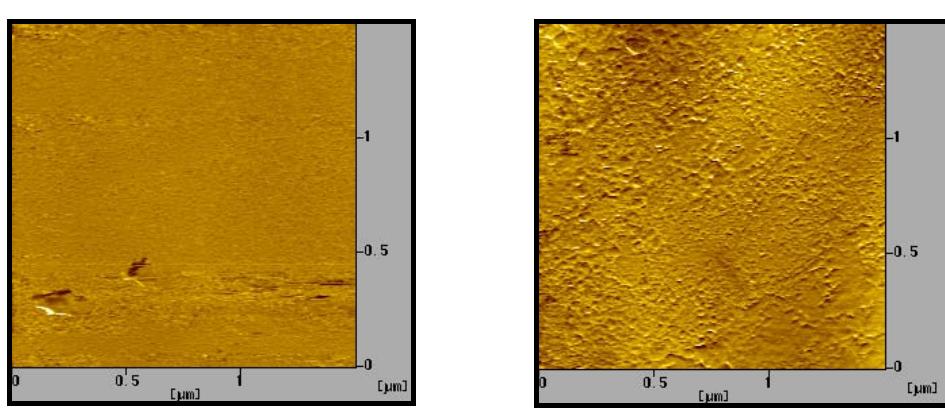
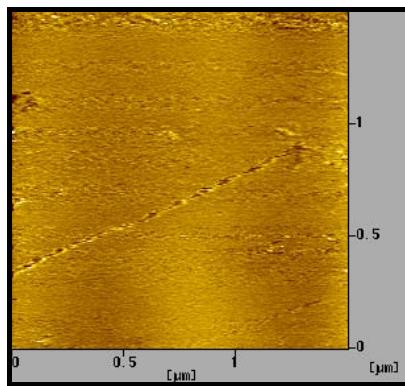
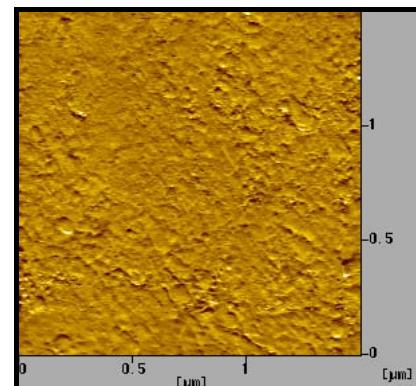


Fig. 4.a, b. Frontal view of the electropolished area (fig. 2).



c. Run 3.



d. Run 4.

Fig. 4.c, d. Frontal view of the electropolished area (fig. 2).

In fig. 5-8 the profile view on different directions is presented, generated by AFM. Based on the profile view, we measured the average height of the peaks for all 4 samples. The average height of each sample's profile is considered the result (response) of the factorial design (table 2). Attention should be paid to the shape of the peaks, because it has an important influence on the tissue-material interaction [1].

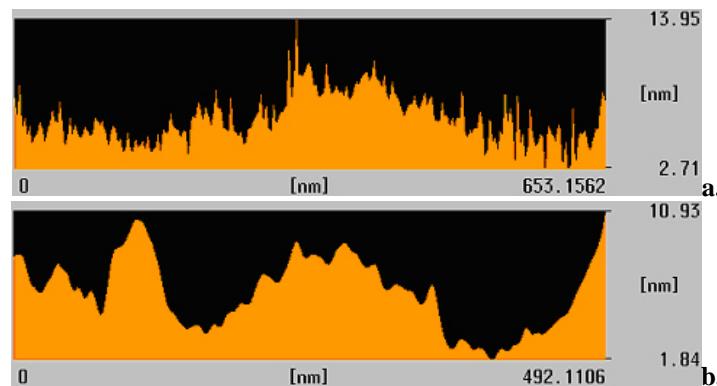


Fig. 5. The profile view of sample #1 on two different directions.

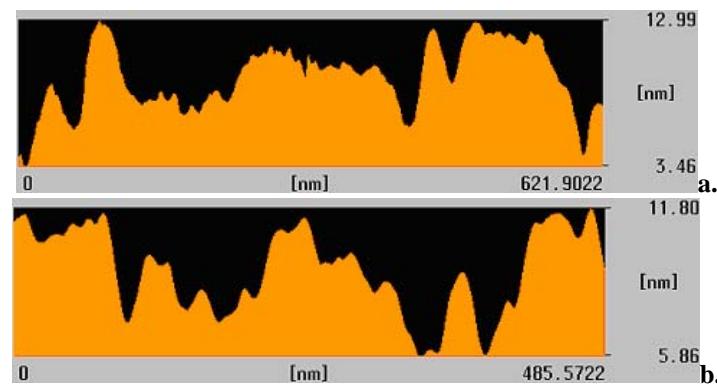


Fig. 6. The profile view of sample #2 on two different directions.

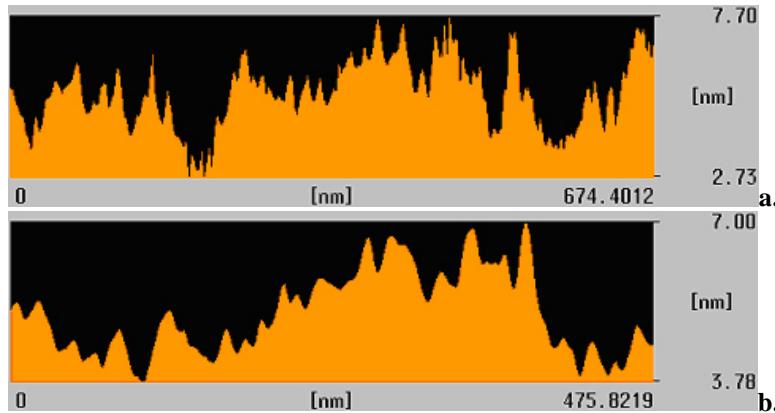


Fig. 7. The profile view of sample #3 on two different directions.

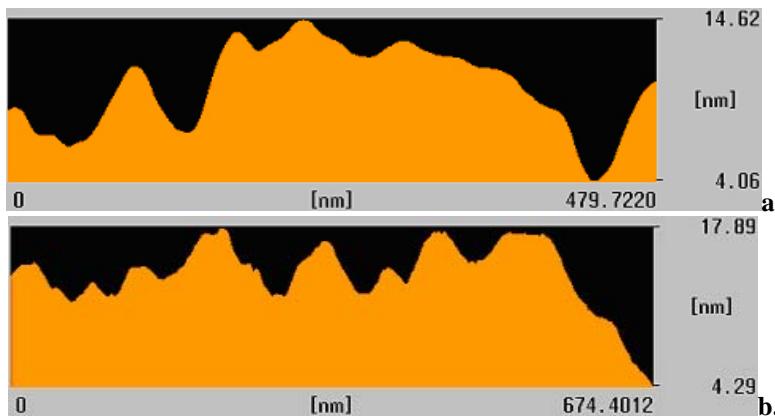


Fig. 8. The profile view of sample #4 on two different directions.

Table 2
The average height of the peaks for all 4 samples

Run	$h_{min}, [nm]$	$h_{max}, [nm]$	$h_{average}, [nm]$
1	1.84	13.95	7.35
2	3.46	12.99	8.81
3	2.73	7.70	5.36
4	4.06	17.89	10.49

In fig. 9 we present the data from table 2 in a graphical form. At a low voltage (test 1 and 3), the average height of the peaks is decreasing with the time of the electropolishing, but at high voltage (test 2 and 4) the removing of the material is stronger, so that the average height is higher. Analysing the obtained data, we can conclude that run #3 is the most efficient among all four.

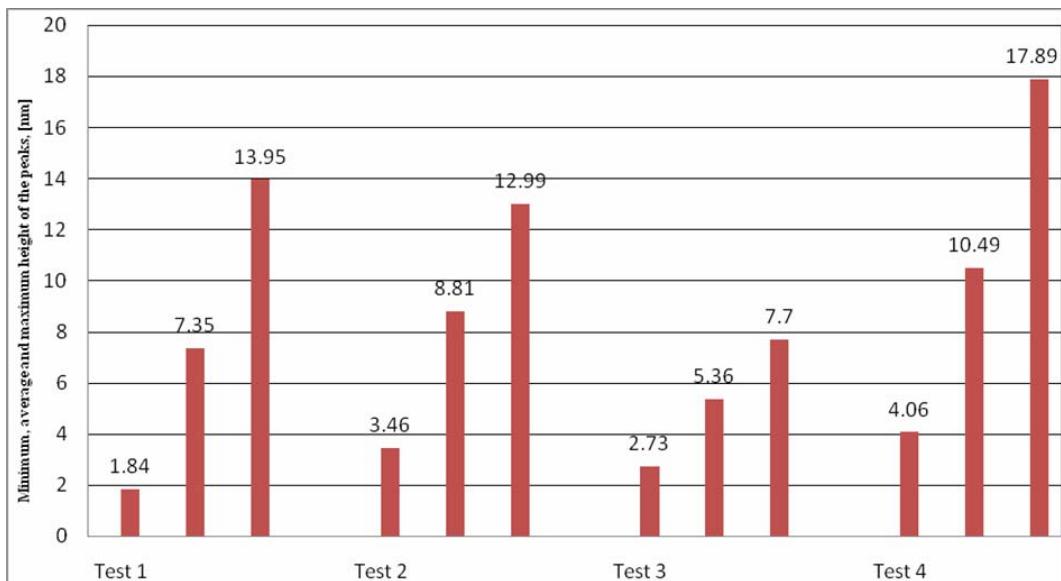


Fig. 9. Graphical representation of the average height of the peaks.

3.2. Pitting test and optical microscopy analysis

Following the electropolishing, their corrosion resistance was checked using the pitting test (ASTM G48-2000), as a fast, simple and easy to analyse method. The samples were analysed by optical microscopy.

For the pitting test the samples were immersed into an aqueous solution of $FeCl_3$, at room temperature, and checked at every 24 hours, when the solutions were also refreshed. The samples were tested for 72 hours.

In fig. 10-13 are presented the micrographs of the tested samples.

It is interesting to observe that for all 4 samples there is a great improvement of the quality of the surface, if we compare them to the simple chemical corrosion method [1, 2].

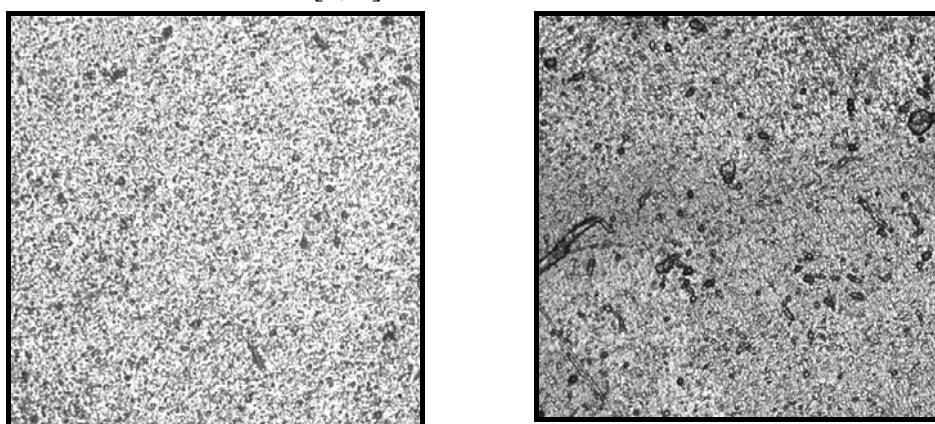


Fig. 10. The optical micrograph of sample 1 after the pitting test (200 x).

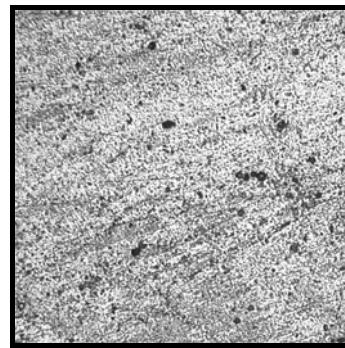
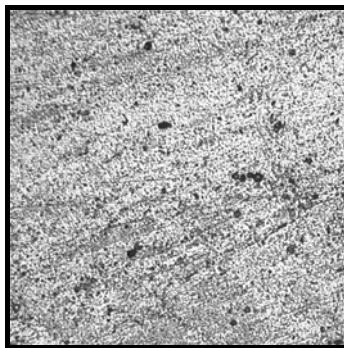


Fig. 11. The optical micrograph of sample 2 after the pitting test (200 x).

An unexpected result was obtained for the third sample, which though having the lowest value for the average height of the peaks, was the most corroded.

We consider this behaviour to be the result of the geometry (shape) of the peaks, which is very sharp. The sharp shape of the peaks will make them easier to be removed and also to become centers for a deeper corrosion.

The peaks of samples 2 and 4 have rounded shapes, which are harder to be removed. This is why samples 2 and 4 show a better corrosion resistance.

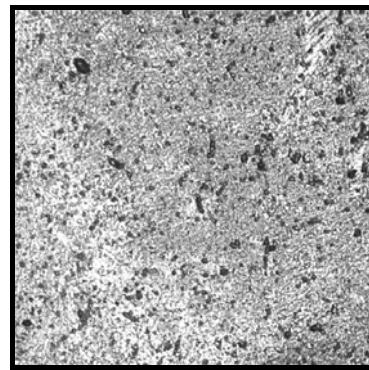
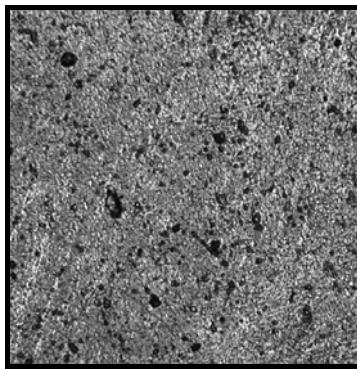


Fig. 12. The optical micrograph of sample 3 after the pitting test (200 x).

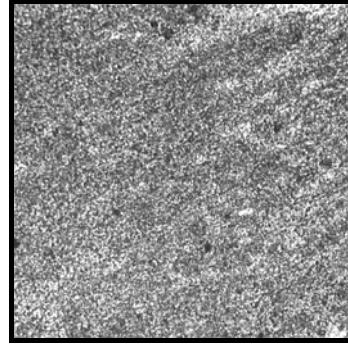


Fig. 13. The optical micrograph of sample 4 after the pitting test (200 x).

Because of a good geometry of the peaks sample 4 has the best corrosion resistance, in spite of its highest peaks.

4. Conclusions

Our experiments have pointed to several aspects concerning the improvement of the corrosion resistance of *NiTi* shape memory alloy intended to be used for biomedical implants.

1. Electropolishing is a simple and efficient method to improve the corrosion resistance of a certain material because of its strong influence on the quality of the surface. The method is also more effective than the simple chemical corrosion method [2].

2. In case of *NiTi* shape memory alloys, used for medical applications, improving the corrosion resistance will definitely reduce the possibility that Ni atoms interact with the human body fluids or tissue.

3. Using a simple factorial design of the experiment makes easier to observe the influence of some analysed factors (in our case the voltage and the time).

4. The AFM is a helpful method to understand the role of peaks shape, and to notice that only the low height of the peaks doesn't improve the corrosion resistance of the material. A rounded shape of the peaks is also required to increase the corrosion resistance.

5. The design of the experiment allows to find the optimal conditions for the experiment.

6. The method is applied for medical devices such as implants where the corrosion resistance must be very high [1].

7. We recommend further electropolishing tests on *NiTi* alloys, considering more factors of influence (temperature, electrolyte type etc). Also, for future tests, the weight of the samples, before and after the pitting test, should be considered.

R E F E R E N C E S

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