Chemical procedures for Ti-alloy based metallic surface modification

I. ŞTIRBU[a], P. VIZUREANU[a], R. CIMPOEŞU[a]*, M. LUNGU[b], M. BERNEVIG[a], R. F. POPA[c]
[a]*Science Materials Department, Faculty of Materials Science and Engineering, "Gheorghe Asachi" Technical University of Iasi, Prof. dr. docent Dimitrie Mangeron Rd., No. 59A, 700050, Iasi, Romania*
[b]*Scholar group "Gh. Duca", Vifor Haiducul Rd , No. 34, 900317, Constanța, Romania*
[c]*Surgery Department, University of Medicine and Pharmacy "Gr. T. Popa", University str. no. 16, 700115, Iaşi, Romania*

Surface enhancement of titanium based alloys is made through different methods and improves the biofunctionalization of alloy and the deposition capacity of nonmetallic thin layers (hydroxyapatite or polymers). Thin coatings deposition on metallic substrates represents an improvement method of material properties, especially those used in the medical field as in-contact body applications. Few chemical engraving methods based on acid solution attack of the surface were used to prepare a Ti-based alloy wire surface. The surface area activation was calculated and chemical and microstructure analyses were performed using X-ray energy dispersive analyze and scanning electrons microscopy (2 and 3D) to establish the applied solution effects.

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1. Introduction

Surface modification and coating of Nitinol (an acronym for NiTi Naval Ordnance Laboratory), a family of nearly equiatomic NiTi alloys with shape memory and superelastic properties, is a subject of numerous recent studies directed at improving the material's corrosion resistance as well as its biocompatibility through elimination of Ni from the surface. This chemical element is known to be allergenic and toxic, though essential for the human body. Although it has been shown that the amount of Ni recovered in biological studies in vitro may be either very low from the beginning or drop to undetectable levels after a brief exposure to biological environments [1, 2], 'the nickel case' keeps reappearing. Thus, the recent results obtained on commercial ready-to-use orthodontic wires showed that the Ni release varied in a wide range from 0.2 to 7l g cm^2 [3]. Moreover, it has been reported that the Ni release can actually significantly increase with time [4, 5], maintaining a high level up to 8 weeks and even for a few months [6, 7], indicating the need for better understanding of the material/surface interface. Surface modifications have been used on metal-base biomaterials in order to improve chemical, mechanical and physical properties like wear resistance, corrosion or electro-corrosion resistance, biocompatibility, and surface wettability.

Based on the number of published papers on Nitinol surfaces, especially recently, one might conclude that this issue indeed deserves serious attention. Various techniques and protocols have been used for surface treatments; among them mechanical and electrochemical treatments, chemical etching, heat treatments, conventional and plasma ion immersion implantation, laser and electron-beam irradiation, design of bioactive surfaces, and a proper technique can easily be lost in that jungle of publications. Some of the procedures that were developed originally for pure Ti and their application to Ti- based alloys not only may not bring any improvement but, rather, can cause surface damage because of inevitable other elements involvement.

The electrochemistry of Nitinol is poorly explored. Until recently, there have been no studies on electro-polishing and anodizing of this material. This situation is gradually improving with the publications of papers on electro-polishing processes in various electrolytes [8], and anodizing in various solutions and voltage regimes [9]. The effect of chemical etching (passivation) in $HF+HNO_3$ aqueous solutions on Nitinol surface chemistry has also been studied [10].

In this study the effects of few chemical modification methods of the metallic surfaces are analyzed to improve the adhesion on Ti-Ni alloy with further superficial thin layers that can be deposited (in our case hydroxyapatite - HA). We also estimate the effective surface increase area based on the traces made on the material after chemical attack.

2. Experimental details

A superelastic equiatomic NiTi shape memory alloy [11] acquisitioned from Saes Getters Group was prepared through different engraving solution for thin layers deposition operation. The shape memory alloy has 50.5 % Ni and 49.5% Ti mass percentages and an oxide layer on the wire surface. The material surface was "attack" with different solutions like 48% H_2SO_4+18 % HCl, $HClO_4$

solution at a temperature of 65 ºC for 60 min., and acid-HF40% + $HNO_3$60% solution at 65ºC temperature and 60 min. time [12-14]. Microstructure of alloy surface before and after chemical treatments was analyzed using scanning electrons microscopy (SEM – VegaTescan LMHII) with a secondary electrons (SE) detector and 30 kV tension of gun lamp. Insights on 3D information on the surface (like the holes profile or depth) were realized using VegaTescan software (based on the secondary electrons spatial distribution) and were use to appreciate the depths on the surface after chemical preparation used for calculus of new activated area. Using X-ray dispersive energy analyze (EDAX) equipment chemical analysis were performed on 2.5 mm^2 surfaces following the Ni and Ti percentage evolution and also the other elements appearance on the surface like oxygen, fluorine, sodium or carbon [15].

3. Experimental results

Various techniques and standards have been used for surface treatments; among them mechanical (sanding) and electro-chemical treatments (anodizing), chemical etching, heat treatments (for TiO increasing percentage), conventional and plasma ion immersion implantation, laser and electron-beam irradiation, design of bioactive surfaces, and a proper technique can easily be lost in that jungle of publications [16-21].

The surface state of shape memory alloy NiTi is presented in Fig. 1 at 250x power amplification of the image and a 50 µm scale. Can be observing a smooth surface of the material obtained from the element manufacturing that had a preparation necessity for better adhesion of the superficial layers ready for deposition.

Further the chemical etching was made using the same engraving method to process the material surface in a more concentrated solution of 48% H_2SO_4 18% HCl, and the results are shown in Fig. 1 through electron microscopy, changes in light intensity and 3D surface analysis. As shown in Fig. 2 *a* and *b* the attack of this solution on the surface material was manifested violent on the smart material surface affecting the surface of the alloy intensively.

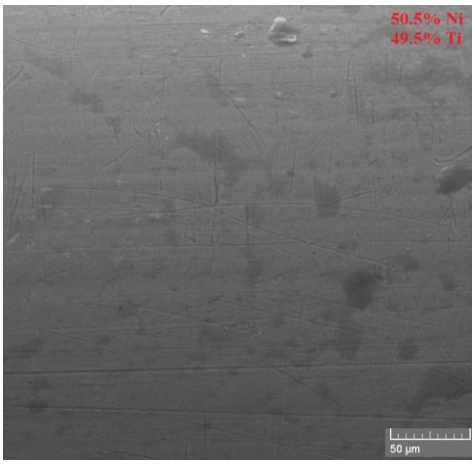
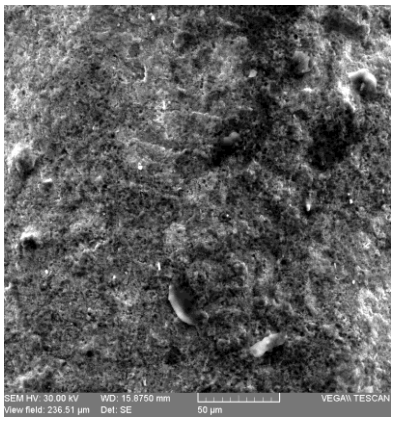


Fig. 1. SEM microscopy of initial NiTi state surface, 250x.

a



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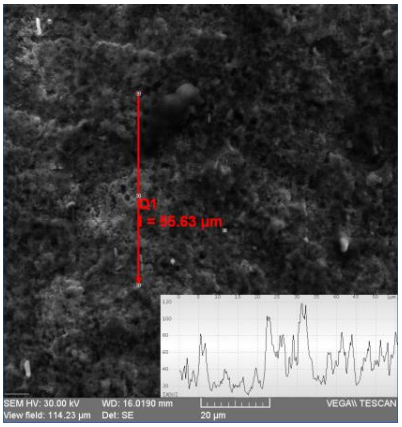
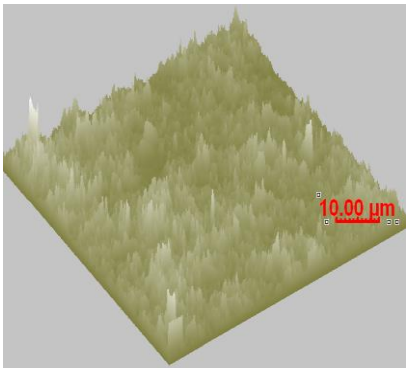


c



d

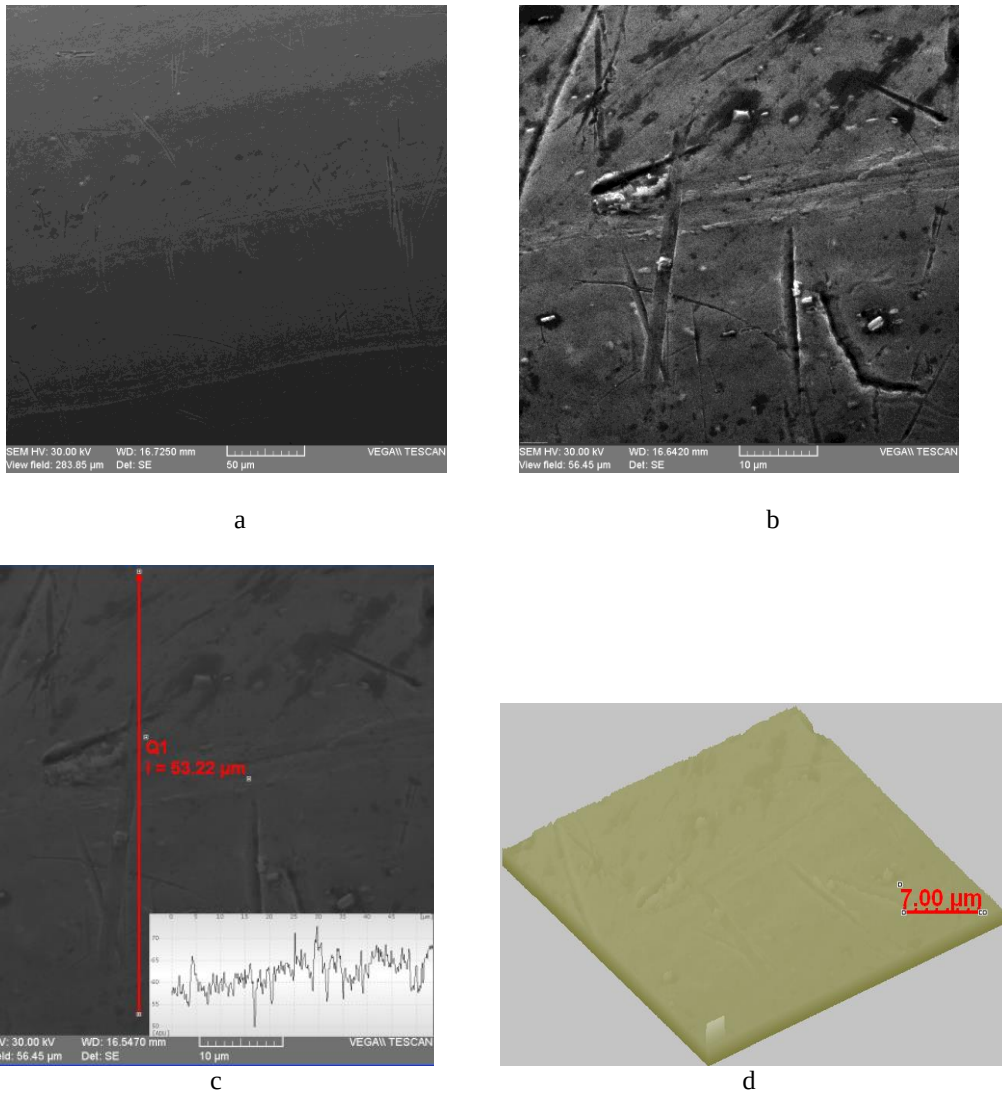
Fig. 2. NiTi shape memory alloy surface for different amplification powers and positions; a) 100x, b) 1000x, c) variation of light intensity on the surface and a length of 55 µm, d) 3D analysis of the material surface chemically etched.

Change in light intensity variations was performed on the 55 µm distance showing a large variation between 20 and 120 ADU based on the engraving effects of the field describing this area as quite affected than the original surface, Fig. 2 *c*). This is confirmed by the 3D surface analysis, Fig. 2 *d)*, where at a scale of 10 µm of the surface we observe a modify surface comparing with the initial state with traces of 5 µm as a media diameter with a 100% occurrence on the surface. In Table 1 are presented the chemical elements identified on the surface material after chemical etching and present a loss of titanium percentage (from 49.5 to 46.5), an element that react with the acid solution. Also carbon is observed on the surface as a chemical reaction product after the chemical procedure.

Tabel 1. Chemical Composition of the Shape Memory Alloy Surface After his Immersion in Solution of 48% H_2SO_4+18% HCl.

Chemical Element	[wt. %]	[at %]	Error [%]
Nickel	51.5	43.6	0.2
Titanium	46.5	48.3	0.2
Carbon	1.9	8.1	0.4
	100	100	

As a second solution the NiTinol engraving continue with processing of the material surface in a not so aggressive solution of $HClO_4$ at 65ºC temperature for 60 minutes. Surface appearance after this process is represented in Fig. 3 by electrons microscopy, *a*) 100x and *b*) 1000x, light intensity distribution in *c*) and 3D surface analysis.



a b

c d

Fig. 3. SEM microscopy of NiTi superelastic alloy surface at various power amplifier; a) 1000 x and b) 5000 x after immersing it in $HClO_4$ solution at a temperature of 65°C for 60 minutes maintaining time.

Changes in light intensity falling in 55-70 ADU range relatively different from the initial state of the surface material but in a reduce manner, fact that does not recommend this surface for deposition because the initial fall in the surface is properly etched, Fig. 3 *d*. From the 3D representation of the entire surface can be observed some traces, inhomogeneous distributed, with rectangular shape having around 5 µm length, 1 µm width and a media of 2 µm depth.

Table 2 present the chemical composition of surface material that is observed as a percentage of oxygen due to surface oxidation, especially of titanium, which decreased in wt%.

In the third experimental case we used an acid-$HF_4$0% + $HNO_3$60% solution at 65ºC temperature and 60 min. time. The material is presented in Fig. 4 by electrons microscopy technique at different amplification powers *a*) 1000x and *b*) 5000x and size effects are observed in this acidic solution like craters between 0.1 and 5 µm on the entire surface.

Table 2. Chemical Composition of the Alloy Surface After Immersion of NiTi in $HClO_4$ Solution at a Temperature of 65°C for 60 Minutes Maintaining Time.

Chemical element	[wt.%]	[at.%]	Error [%]
Nickel	52	44.8	0.1
Titanium	47	49.1	0.3
Oxygen	1.01	6.5	0.4
	100	100	

Light intensity falling on initial domain and have a very close variation to the original surface of shape memory alloy wire even though now the material is now heavily engraved.

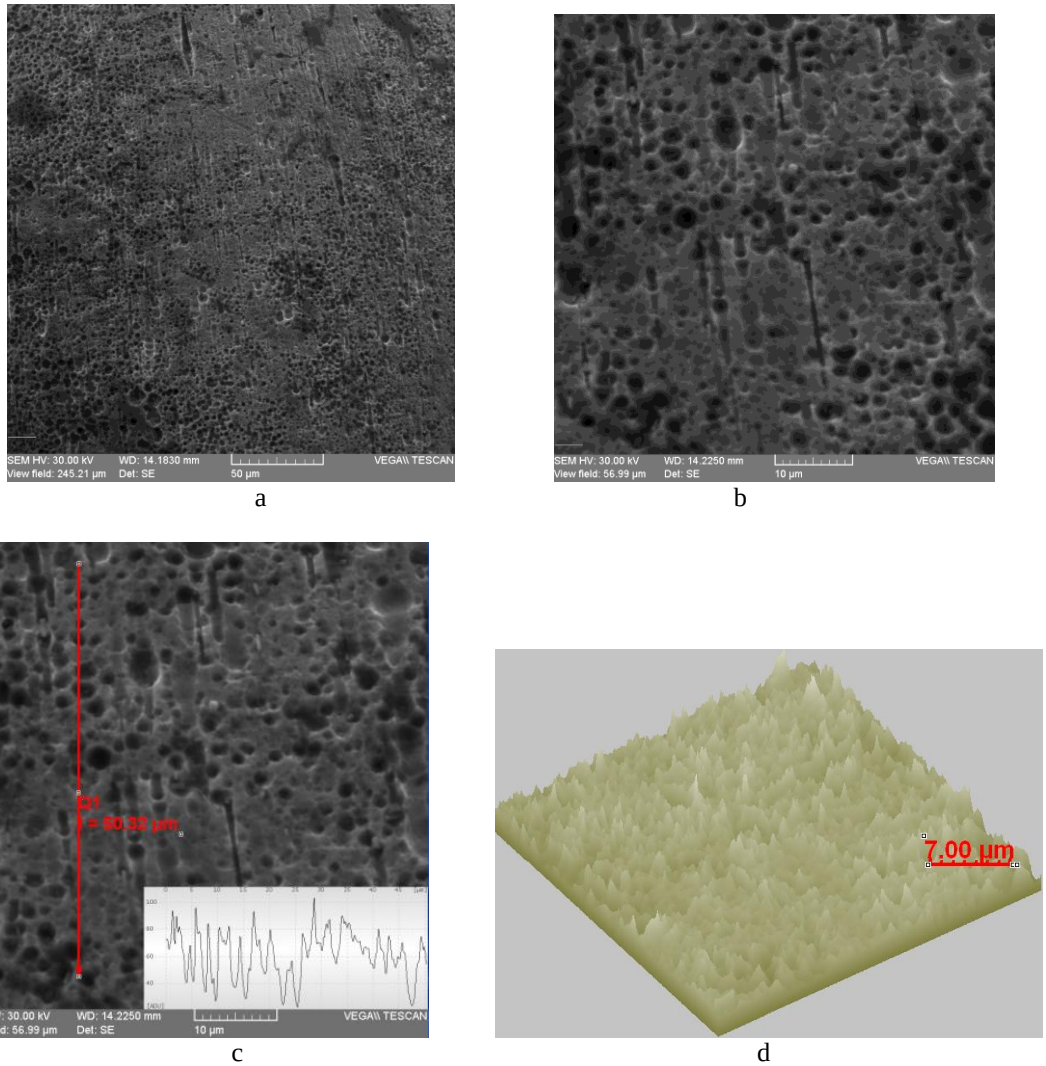


Fig. 4. Electron microscopy analysis - SEM of surface of the shape memory material after immersion in solution HF40% + 60% HNO3 at 65°C for 60 minutes at two amplification powers; a) 1000x and b) 5000 x.

The 3D microscopy of the material, Fig. 4 *d* shows a uniform surface engraved with deep craters on average, Fig. 4 *c*, which can hold an average proper HA material suitable immersion method. Traces with 4µm diameters are observed on the entire surface having approximate 3µm depths, Fig. 4 d).

Based on the shape, size and uniformity of surface material effects on the metallic titanium based alloy surface the HF40% + HNO_3 60% solution is most proper of the acid solutions for etching the surface of superelastic nitinol material. The chemical composition, Table 3, present an intense surface material fluoridation, fluor element being beneficial for medical applications of metallic and nonmetallic materials [22], but whose influence on subsequent deposit of shallow surface layers is not sufficiently investigated.

Table 3. Chemical Composition on the Surface of Titanium Alloy After its Activation Process in Solution HF40% + 66% HNO_3 at 6°C for 60 Minutes.

Chemical element	[wt.%]	[at. %]	Error [%]
Nickel	48.4	34.4	1.3
Titan	37.8	32.9	1.1
Fluor	10.9	24.1	3.5
Oxygen	2.03	7.1	0.4
Chlorine	0.8	1.5	0.1
	100	100	

Atomic percentages of titanium and nickel are still keeping a close proportion of properties suitable for smart alloys even if it is only the surface of this material. Chemical etching and electro-polishing of NiTi can be used for surface structuring as well.

The research on the surface of nitinol material preparation by chemical methods will continue in a further article using other attack solutions also observing the microstructural surface aspect and chemical behavior in the same time with the variation of TiO thin layer and the deposited layers mechanical, physical and chemical properties.

4. Conclusions

Trying to improve the surface properties of these materials for depositions of superficial thin layers is considered a solution among the increase and evolves of TiO thin layer. Different engraving solution was used to improve the surface of material for adhesion with thin deposited layers the results being based on micrographic analyze (macro and micro areas analyzed) and chemical composition observation at the surface as well. Nitinol materials are widely used in the medical field, many applications being in direct contact with the human body. For deposition process a solution of HA is proposed with particle dimension of 0,61 μm so all the engraving methods are suitable to sustain and improve the adhesion of the new thin layer material. Also based on the dimensional determination of the chemical process traces (length or diameter and depth) comparing with the initial state of the material (figure 1) we obtain a functionalized area improved with 99.5 % in the 48% H_2SO_4+18 % HCl, solution case, an increase with 28.56% in the second case, $HClO_4$, and 299.9 % increase of surface contact area for the acid-HF40% + HNO360% solution case.

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*Correspondent author: ramonahanu@yahoo.com