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Excimer laser treatment of NiTi shape memory alloy biomaterials

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Abstract

NiTi Shape Memory Alloys (SMA) are potential biomaterial candidates. However, due to its possible corrosion in physiological solution, dissolution of toxic Ni might be happening, rendering this material nonbiocompatible. We have used excimer laser surface treatment to improve corrosion resistance of NiTi SMA plates. Potentiodynamic tests in physiological Hank's solution show that the laser treatment performed in air improved all corrosion parameters. The surface is homogenized and a Scanning Electron Microscopy (SEM) observation indicates a decrease of corrosion pit size and numbers. Laser treatment improvement resistance is explained by a combination of the homogenization of the surface by melting, the hardening due to N incorporation and the thickening of the oxide layer.

Keywords: NiTi shape memory alloy; Laser surface treatment; Corrosion resistance; Biomaterials

1. Introduction

The superelasticity and shape memory properties of NiTi alloy make it a potential material for new biomedical applications. One of the advantage of NiTi shape memory staples over the more conventional stainless steel or Ti_6Al_4V staples is their ability to be easily inserted with a mallet and a staple holder and, by recovering its initial converging prongs shape, it holds the two pieces of the bone, by exerting a pressure which avoid the backing out of the bone and facilitates the healing [1]. Since the staple becomes a long term implant, the constitutive materials of the staple must be biocompatible, the device must be strong enough to counteract opposing forces and the staple has to be formable.

NiTi biocompatibility and corrosion resistance have not been completely proven. First, Castelman and Motzkin [2], widely studied Nitinol biocompatibility and found that titanium could be considered as a physiologically stable material [2,3], while nickel is involved in allergic process, toxicity and even carcinogenic reaction if present in high amount [2,3]. The biocompatibility is closely related to the corrosion resistance of the material in the human body or a simulated media [4]. Indeed, the Ni^{2+} and Ti^{2+} ions release is a degradation by corrosion of the metallic elements Ni and Ti from the NiTi alloy. While some authors [5–7] claimed that NiTi has a good corrosion resistance in some physiological solution simulating aggressive conditions found in human body (presence of Cl^- and OH^- in the electrolytic media), other authors [8–10] noticed some localized corrosion with a poor reproducibility of the results. These discrepancies could be explained by

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the difference of both surface roughness or porosity [11] and phase [12].

As the corrosion resistance, and thus the biocompatibility, seems to depend on the surface properties of the alloy, many surface treatments have been considered. Efforts to improve the corrosion resistance by covering the surface with bioceramics (TiN and CTiN) thin film failed due to the cracking of the coating upon the large deformation due to the memory effect [9]. However, oxide films obtained by heating at 900°C for 10 min produced the same positive results on corrosion resistance as biocompatibility and cracks did not appear but the whole bulk of the sample is heated, modifying the transition temperatures of the alloy. Lombardi et al. [13] reported the improvement of corrosion resistance by Tetrafluoroethylene plasma coating due to the induced surface homogeneity improvement but no tests upon large deformations have been performed. The enhancement of pitting and crevice corrosion resistance was also noticed with N^+ implantation [14]. The N^+ bombardment zone trended to swell causing intense lateral compressive stresses and then the implanted layer trended to become harder.

In this work, the use of the Laser Surface Melting (LMS) has been investigated to improve the corrosion resistance of NiTi alloy. LSM process has been proved to improve the corrosion resistance of the 304 stainless steel, the CuCr alloy, the Al 2024-T6, the white and gray irons, and zirconium alloys [15–19]. In the LSM process, the absorbed energy is instantaneously transferred to the lattice and melt quickly the near surface regions. When the laser is removed, the metallic subsurface quenches quickly the melted layers which provides refinement in the surface microstructure, chemical homogenization of the surface, removal of inclusions, and possible metastable phases. Over all the other surface treatments, LMS presents the advantages of being a simple technique to modify the surface without affecting the bulk properties by forming a well adherent corrosion resistant layer.

2. Experimentals

Equiatomic NiTi shape memory alloy samples are supplied by AMP Développement (France). They are characterized by a martensitic finish of $M_f = -23 \pm 5$°C and an austenitic finish temperature of $A_f = 23 \pm 5$°C. Original plates were cut with a diamond saw in small pieces of 20 mm × 10 mm × 1.5 mm. The plate surfaces were mechanically polished with an alumina polishing powder (1–0.05 μm) during 5 min for each polishing degree. All the samples were first degreased with methanol in an ultrasonic bath for 5 min, and then rinsed with distilled water and dried with running compressed air.

A pulsed (30 ns) excimer laser (MPB Technologies, model AQX 150) has been used immediately after the cleaning. This laser operated at 248 nm (KrF) delivers a 8×22 mm^2 emergent beam at a repetition rate of $R = 12$ Hz. Photon energy of ~ 4.8 eV is strongly absorbed by metal, which avoids an excessive depth of the treatment. The plates have been treated in air by performing a raster scan over a 10×10 mm^2 surface. The optical laser system uses a 5 cm focal distance lens focusing the beam to an elliptical spot of $A = 3$ mm^2. We have found that the best results are obtained at a laser intensity of $I = 1200$ mJ/cm^2 and at a scan speed of $V = 2$ mm/s.

3. Corrosion tests

The corrosion resistance was evaluated according to the method developed by Lombardi et al. [15]. Potentiodynamics anodic polarization measurements were carried out at 37°C in a Hank's physiological solution of the following composition: NaCl 8 g/l, KCl 0.4 g/ℓ, $NaHCO_3$ 0.35 g/ℓ, KH_2PO_4 0.06 g/ℓ, Na_2HPO_4 0.0475 g/ℓ, glucose 1 g/ℓ. This corresponds to 0.5% of chlorine and a pH 7.4. A standard three-electrodes was used consisting of a 4 cm^2 platinium plates, a saturated calomel electrode (SCE) and the NiTi sample whose only 7×8 mm^2 is exposed to the solution. All potentials were expressed with respect to the SCE electrode. Experiments were performed from a potential of -800 to 2000 mV versus the open circuit at a rate of 0.5 mV/s.

Fig. 1 shows typical corrosion behavior of two treated and three untreated samples. The cathodic part of the curve for the three untreated samples superimpose over each other, while their pitting po-

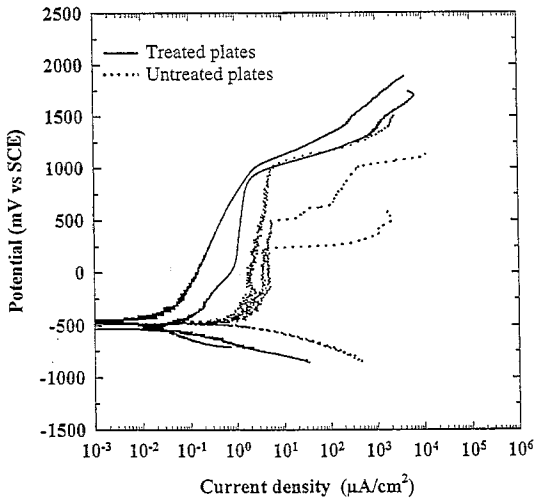

Fig. 1. Voltamperograms of the two treated and three untreated plates. The x-axis corresponds to the log of the absolute value of the current density.

tentials vary from one sample to an other, suggesting that the pitting resistance is not reproducible. Table 1 summarizes the corrosion parameters for all samples. The corrosion and/or passivation current densities are two orders of magnitude lower for the treated samples suggesting that the material is more resistant to generalized corrosion. In addition, the laser treatment doubled the autopassivating range, yielding to a greater resistance to pitting corrosion. Note that some untreated and treated plates showed an increase of the current density for nobler potentials than 1 V. This increase is not due to pitting but to the oxygen evolution which screens the real increase due to pitting.

Table 1
Sample corrosion parameters

Samples	Untreated plates	Treated plates
E_{cor} (average) (mV versus SCE)	−478	−595
E_p (minimum) (mV versus SCE)	> 240	> 948
I_{cor} (average) (μA/cm^2)	2.20	0.06
I_{pass} (average) (μA/cm^2)	4.2	0.09
Minimum autopassivating range (mV)	> 715	> 1543

4. Materials microstructure and composition

Optical microscopy observations showed inclusions and scratches in the NiTi matrix of the untreated plates. The observations after corrosion tests revealed different colors and pits on the corroded surfaces of those samples. The comparison of the microscopic photographs showed that the laser treatment induces homogenization of the surface by melting. However, some craters and ripples still persisted.

As seen in Fig. 2a, scanning electron microscopy (SEM) observations show that, after the corrosion test, the pits on the untreated plates measure about 400 μm maximum at a stopping experimental potential of 1400 mV (vs SCE). For the treated samples, the pit number and size are so small that they required a higher magnification. Indeed, the maximum pit size on the treated plates is only 7 μm at

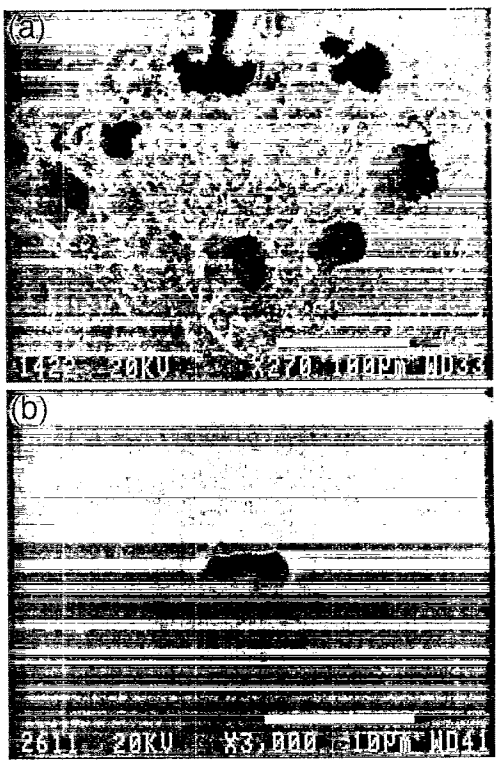

Fig. 2. SEM micrograph of a corroded untreated plate (a) and of a corroded treated plate (b).

Table 2
Relative concentration of surface elements as measured by XPS

Sputtering time (min)	Sample	Ni (%)	Ti (%)	O (%)	C (%)	N (%)	Ar (%)
0	untreated	5.1	15.3	43.6	34.5	—	—
	treated	2.0	18.3	40.2	34.9	4.5	—
8	untreated	24.5	23.6	31.0	17.2	—	3.7
	treated	4.4	29.2	37.2	18.1	7.5	3.7
18	untreated	32.0	22.1	16.0	24.8	—	5.1
	treated	13.1	29.1	29.2	17.1	7.2	4.1

the potential 1800 mV (vs SCE). In addition, the EDAX analysis indicated that Si and Al are present in the inclusions on the surface. This contamination probably comes from the polishing materials.

Auger electron analyses suggest that the effect of the laser treatment is to enhance an oxygen incorporation in the material resulting in a disproportion of the Ni/Ti ratio probably due to a preferentially titanium oxide layer formation on the surface. The thickness of the oxide layer has been measured at 50% height of the oxygen profile and is less than 7.5 nm for the untreated plates, indistinguishable from the carbon contamination layer for the untreated polished plate. The oxide layer increased to about 20 nm for the laser treated plates.

Table 2 summarizes the relative atomic concentrations of nitrogen, titanium, nickel, oxygen and carbon as measured by X-ray photoelectron spectroscopy (XPS). The measured concentrations after 8 min or 18 min Argon sputtering (≈ 30 Å/min) can be interpreted as those found in the depth. Nitrogen is present only in the laser treated samples. While Ti varies similary on both treated and untreated samples, Ni is more prononcely depleted on the surfaces treated samples. These results suggest that the laser treatment performed in air yields to the formation of a titanium oxinitride which could act as protective corrosion layer.

5. Conclusions

We showed that the corrosion behavior of NiTi sample was improved by Laser Melting Surface. A two orders of magnitude decrease of corrosion and passivation current densities was obtained on LMS treated plates. This treatment induced a thickening of the oxide layer, a nitrogen incorporation and a surface homogenization, increasing the autopassivation range from 715 to 1543 mV for the treated plates. Modifications to the laser system is being done to treat more complex geometries like staples. These results will be published later.

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