Effect of surface etching and electrodeposition of copper on nitinol

E Ramos-Moore\textsuperscript{a,b,\ast}, A Rosenkranz\textsuperscript{a, b}, L F Matamala\textsuperscript{c}, A Videla\textsuperscript{c,b}, A Durán\textsuperscript{d} and J Ramos-Grez\textsuperscript{a,b}

\textsuperscript{a} Instituto de Física, Pontificia Universidad Católica de Chile, Santiago 7820436, Chile.
\textsuperscript{b} Centro de Investigación en Nanotecnología y Materiales Avanzados “CIEN-UC”, Pontificia Universidad Católica de Chile, Santiago, Chile.
\textsuperscript{c} Departamento de Ingeniería en Minas, Pontificia Universidad Católica de Chile, Santiago, Chile.
\textsuperscript{d} Departamento de Ingeniería Metalúrgica, Universidad de Santiago de Chile, Avda. Libertador Bernardo O’Higgins 3363, Casilla 10233, Santiago, RM, Chile
\textsuperscript{e} Departamento de Ingeniería Mecánica y Metalúrgica, Pontificia Universidad Católica de Chile, Santiago, Chile.

\ast evramos@uc.cl

Abstract. Nitinol-based materials are very promising for medical and dental applications since those materials can combine shape memory, corrosion resistance, biocompatibility and antibacterial properties. In particular, surface modifications and coating deposition can be used to tailor and to unify those properties. We report preliminary results on the study of the effect of surface etching and electrodeposition of Copper on Nitinol using optical, chemical and thermal techniques. The results show that surface etching enhances the surface roughness of Nitinol, induces the formation of Copper-based compounds at the Nitinol-Copper interface, reduces the austenitic-martensitic transformations enthalpies and reduces the Copper coating roughness. Further studies are needed in order to highlight the influence of the electrodeposited Copper on the memory shape properties of NiTi.

1. Introduction
Shape memory alloys (SMA) are known for a long time since the first observation of this effect was made in 1932 [1]. After that, intense fundamental research on this effect made it possible to generate commercial applications [2]. One of the most prominent and extensively studied SMA is Nickel-Titanium (NiTi), also known as Nitinol, which stands for Nickel Titanium Naval Ordnance Laboratory. Nitinol represents a highly ordered intermetallic phase with a nearly quasi equiatomic composition of 50 \% Ni and 50 \% Ti. Due to the fact that the shape memory effect can just be found in a very narrow concentration range, different alloying elements are typically used in order to increase this range and to enhance certain physical properties [3]. In this context, Niobium can be added to NiTi to generate an alloy with a wide hysteresis thus leading to a more pronounced two-way shape memory effect as well as better damping properties [4]. Copper can be used to narrow the transformation hysteresis, thus inducing high frequency response [5] and making it suitable for
micromechanical actuators. In terms of applications, NiTi-alloys are very interesting for the medical and dental sector since those alloys combine shape memory as well as pseudoelasticity with remarkable material properties such as good biocompatibility [6], corrosion resistance and good mechanical properties [7].

Despite the proved biocompatibility of NiTi [6], major concerns related to medical issues arise based upon the chemical composition and the high Ni content. It is well-known that Ni is highly toxic for the human body and it can be assumed that these concerns might decelerate the application of this alloy in the medical sector [7]. From the material’s point of view, the Ni release can be directly correlated to the corrosion resistance. Consequently, various surface treatments such as surface modifications or coatings can be thought of to improve and tailor the corrosion resistance as well as the biocompatibility [8,9]. Chemical and electrochemical methods such as electropolishing and chemical etching need to be considered since those methods can be utilized to avoid defective surface layers and oxidation of the surface [6]. Although antibacterial metals, such as Silver and Copper, can be toxic to the human body when its concentration exceeds certain threshold, the control of their adherence onto NiTi during coating deposition opens the possibility to improve the functionality of SMAs by adding the antibacterial property to the material surface.

In the context of medical or dental applications, two other aspects, namely biocompatibility and antibacterial properties, need to be addressed. An easy way to enhance the biocompatibility of SMA is to use a biologically active coating [6,7,10]. Regarding the antibacterial properties, different attempts have been made in order to induce an antibacterial function on SMA. Ahmed et al. [11] produced a biocomposite of gold nanoparticles and chitosan (natural polymer). This biocomposite was electrodeposited on NiTi to investigate the effect of this coating on biocompatibility and antibacterial effects. They could verify that this coating reduces the Ni release by a factor of 20. Additionally, due to the presence of the gold nanoparticles, an antibacterial effect could be observed. Another interesting approach to improve the antibacterial effect was the addition of Silver [12], but to the best of our knowledge, no systematic study on the electrodeposition of Copper on NiTi has being performed.

In this work, we study topographical, chemical and phase transformation effects of surface etching as well as Copper electrodeposition on Nitinol. Our hypothesis claims that etching may increase the surface area as well as the surface reactivity of Nitinol in order to improve the nucleation and growth of crystalline Copper coatings. Our results show interesting properties of the etching process as a way to further enhance the integration of Copper into the NiTi surface [13-15] thus combining shape memory and antibacterial properties.

2. Experimental Methods

Nitinol samples (Nitinol UNSPSC 30000000) were obtained from Kellogg’s Research Labs in form of plates (1 mm thick, 45 mm wide and 150 mm long). The composition of the samples was 50 at.% Ni and 50 at.% Ti. The etching treatment consisted in exposing one of the Nitinol sample face to a 10% HNO₃ solution during 24 hours at room temperature and no agitation. Atomic Force Microscopy (AFM), NanoWizard 3 Bioscience, was performed in order to measure the root mean square roughness (Sₐ) of the samples in averaged over an area of 100 µm x 100 µm. Electrodeposition of Copper onto the plate surface was done in a solution containing 40 g/l of Copper Oxide and 160 g/l of H₂SO₄ at room temperature. Both plates, NiTi cathode and Lead anode, had an active surface of 1 cm² for electrodeposition. The electrodeposition was performed under continuous stirring to reduce the diffusion layer. The current was controlled by a standard power source. Current intensity was kept constant at 200 A/m² for 20 minutes. Figure 1 depicts the experimental setup used to perform the electrodeposition. The plate mass weight was measured prior to and after electrodeposition in order to estimate the amount of deposited Copper.
Figure 1. Schematic diagram of the experimental setup used to perform the electrodeposition of Copper on the NiTi substrates.

The characterization of the samples was performed using a laser-scanning microscope OLS40-SU (Olympus) and a dual beam scanning electron microscope (SEM) Helios NanoLab TM600 (FEI) equipped with focus ion beam (FIB) system. Grazing incidence X-ray diffraction (GI-XRD) was performed using the X-ray diffractometer MPD PANalytical X’Pert with Cu Kα1 radiation ($\lambda = 0.15406$ nm) generated at 40 kV and 40 mA. The primary optic was divergent (slit of 1°) and the X-ray source was fixed allowing an angle of incidence of $\omega = 4^\circ$ between the X-rays and the sample surface. The secondary optic was divergent (slit of 1 mm) and the detector scanned between $2\theta = 5^\circ$ and $2\theta = 140^\circ$ with step size of $2\theta = 0,04^\circ$. Differential scanning calorimetry (DSC) was conducted using the equipment Perkin-Elmer DSC-6000 at the scanning rate of $10 \, ^\circ\text{C} \cdot \text{min}^{-1}$ in a rich N$_2$ atmosphere (99,95 % of purity).

3. Results and Discussion

3.1. Topography

Before the etching process on NiTi, the roughness $S_q$ measured by AFM was 320 nm, whereas after the etching process an increase in $S_q$ of 104 nm was observed. Therefore, an effective depth of around 50 nm produced by etching effect is estimated. Three Nitinol substrates were exposed to Copper deposition under the same experimental conditions. They were weighted prior to and after deposition, resulting in a Copper mass of $0.019 \pm 0.006$ g, which corresponds to $20 \pm 6$ µm of coating thickness. It is important to note that the calculated coating thickness is an average value due to differences in the distribution of electric field at the cathode surface. The samples were imaged using laser- and electron-scanning microscopy. Figure 2 shows optical images of the as-coated samples (inset) as well as top- and transversal-view images of the Copper coating electrodeposited onto Nitinol. As a standard procedure, Pt layers are deposited either by Ga-beam (Pt-Ga) and/or electron-beam (Pt-e) evaporation in the SEM microscope in order to avoid sample damage due to the impact of Ga ions during the FIB cut.
Figure 2. Top-view and transversal images of the Copper coating electrodeposited on Nitinol with and without etching pre-treatment. Pt layers are deposited prior to the FIB cut in order to avoid sample damage. Inset: optical micrographs of the as-coated samples showing the NiTi substrate and the Copper coating.

Laser-scanning microscopy (top images in Figure 2) show the presence of 2D dendritic-like structures at the surface of the Copper coating deposited on the Nitinol subjected to etching. These structures cannot be clearly observed for the other sample without etching, although both images were obtained under the same optical conditions. Dendritic structures in deposition of Copper have being observed for high voltages under current saturation [16-18]. Dendritic shapes in metals are related with the nucleation and growth kinetics in which free metal atoms continuously minimize the growth area by maximizing the surface energy.

The $S_q$ parameter determined by Laser-scanning microscopy was found to be 5.6 µm for the etched Nitinol sample and 16.3 µm for the non-etched Nitinol sample. Moreover, SEM/FIB cross-sections (bottom images in Figure 2) show defined Cu grains underneath the surface in both samples and a porous top layer of around 2 µm in the non-etched Nitinol sample. This layer might correspond to a discontinuity of the growth kinetics due to fluctuations of the deposition process such as excessive turbulences and/or local temperature variations in the electrodeposition solution [17,18].

3.2. Chemical Analysis

In order to study the species formed at the NiTi-Copper interface, GI-XRD was performed on both samples. All diffractograms were obtained using the same experimental conditions (optic, measuring time, step size and so on) by keeping the X-ray source at a fixed angle of 4° with respect to the sample surface and moving the detector to perform the 2θ-scan. With this geometry maximum information depth was approximately 4 µm. Figure 3 shows diffractograms with the respective peak assignment for both samples. Both samples show rather small NiTi peaks (PDF 35-1281) due to the small information depth and the absorption of the X-rays in the coating layer. In addition to that, both samples show strong Cu peaks (PDF 4-836), whereas only the etched sample shows several peaks that
correspond to the CuSO$_4$(5H$_2$O) (PDF 77-1900) due to reduction reactions. The reduction may have happened at the surface of the NiTi, which was directly affected by the etching process.

![GI-XRD patterns of the Copper coated NiTi samples with and without etching prior to electrodeposition.](image)

Figure 3. GI-XRD patterns of the Copper coated NiTi samples with and without etching prior to electrodeposition.

3.3. Thermal Analysis

In order to study the effect of the etching process and the electrodeposition of Copper on the thermal transformations of Nitinol, DSC was performed on three samples, namely: reference NiTi, etched NiTi and etched-coated NiTi. Figure 4 shows the endothermic (heating) and exothermic (cooling) behavior of those samples for two consecutive cycles in order to separate the information of the sample bulk from the adsorbents. The samples weight for the DSC analyses were 18.5 mg (Reference NiTi), 19.0 mg (Etched NiTi) and 36.0 mg (Etched and Cu-coated NiTi).
Figure 4. DSC curves measured on NiTi reference sample (A), NiTi after etching treatment (B), and NiTi after etching and Copper electrodeposition (C).
The reference and etched NiTi samples show the endothermic austenitic and exothermic martensitic phase transformation at similar temperatures below 40 °C. This is a well known behavior of NiTi and is associated with shape memory properties [2,19]. It is worth to note that the first cycle of the etched sample shows intense endothermic signals above 60 °C, which corresponds to surface diffusion and/or desorption of O-H based groups, including water.

In order to study the phase transformations, three parameters were analyzed: the starting transformation temperature ($A_S$ and $M_S$), the final transformation temperature ($A_F$ and $M_F$) and the enthalpy ($\Delta H_A$ and $\Delta H_M$). Table 1 resumes those parameters for the austenite and martensitic transformations. These temperatures correspond to the points where the curve crosses the straight baseline, whereas the enthalpies were estimated by integrating the DSC curves between both transformation temperatures. Typically, transformation from martensite to austenite undergoes a specific enthalpy change of around 15 J/g [20], but this value is very sensitive to changes in composition [21] and grain boundaries density [22].

Table 1: Temperatures and enthalpies associated with the austenite and martensitic transformations, for all the analyzed samples.

| Sample     | Austenitic Transition | Martensitic Transition |
|------------|-----------------------|------------------------|
|            | $A_S$ [°C] $A_F$ [°C] $\Delta H_A$ [J/g] | $M_S$ [°C] $M_F$ [°C] $\Delta H_M$ [J/g] |
| Reference NiTi | 17 40 4.6 | 31 11 3.9 |
| Etched NiTi   | 17 38 2.5 | 33 6 3.3 |

The etched-coated NiTi sample (Figure 4c) shows linear heating and cooling behavior due to the presence of Copper and no adsorbed H-O groups was observed. The linear behavior corresponds to materials with low heat capacities that experience high variation of temperature with low amounts of heat. In this case, although the specific heat of the Copper and Nitinol are similar [23], the Copper coating has a very low comparative mass and therefore behaves as a material with very low thermal capacity. Nevertheless, after derivation of the second DSC cycle, two small inflections can be observed for each endothermic and exothermic range. As shown in Figure 4, the endothermic inflections are observed between 18 and 25 °C as well as between 32 and 42 °C, whereas the exothermic inflections are observed in the intervals of 34 to 27 °C and 20 to 17 °C.

The analysis of the DSC data (see Table 1) shows that etching on Nitinol produced a reduction of 46 and 15% in the austenitic and martensitic transformation enthalpies, respectively. It is well known that changes in enthalpies might be produced by a lost of thermo-elastic energy after the generation of twins, impurities, defects and/or dislocations [19,20,24]. Moreover, the content of Cu in Ni-Ti-Cu alloys is known to directly affects the shape memory properties [21,25], suggesting and effect of Copper diffusion into Nitinol. We claim that etching consequently affects the surface of the Nitinol by generating energy sinks that modify the amount of energy driven to the shape memory effect.

Although our observations are interesting, they cannot be tracked back directly to phase transitions and therefore will be studied in more detail in a follow-up manuscript including mechanical testing such as stress-strain analyses.
4. Conclusions
1. Surface etching and electrodeposition of Copper coatings was successfully achieved on Nitinol substrates with shape memory properties.
2. Surface etching on Nitinol induces the formation of CuSO$_4$(5H$_2$O) at the Copper-Nitinol interface and reduces the surface roughness of electrodeposited Copper coating.
3. A reduction of austenitic-martensitic transformations enthalpies were observed after surface etching on Nitinol, suggesting an influence on the shape memory effect.
4. Further studies are needed in order to highlight the influence of the electrodeposited Copper on the memory shape properties of NiTi.

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