



## Titanium Oxide (TiO<sub>2</sub>) Coatings on NiTi Shape Memory Substrate Using Electrophoretic Deposition Process

V. Khalili \*, J. Khalil-Allafi, H. Maleki-Ghaleh

Department of Material, University of Sahand, Tabriz, Iran

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### ABSTRACT

The aim of the present research is to convert bioinert surface of NiTi to bioactive and biocompatible surface. In order to develop a bioactive and corrosion resistant film on NiTi, electrophoretic deposition process was done and TiO<sub>2</sub> particles were deposited on the NiTi surface. Suspensions including TiO<sub>2</sub> particles were prepared using a mixture of acetone and n-butanol (0%, 30%, 60%, 80% and 100% acetone) without using any dispersant. Sedimentation test was used to characterize the suspensions. SEM investigations on surface morphology of coatings shows deposition within 0% acetone cause to crack-free and dense coating with relatively coarse grains and high corrosion resistance.

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## 1. INTRODUCTION

NiTi shape memory alloys were introduced in the late 1970s for medical applications due to their significant properties such as superelasticity, high resistance to fatigue and corrosion. However, their applications development in the medical engineering took many years due to not well-defined bioactivity and biocompatibility of them [1]. Two important factors in medical applications of NiTi as an implant are (i) reduction of releasing the Ni<sup>3+</sup> ions and reduction of corrosion in vivo [2] (ii) increased bone adhesion to the surface of NiTi alloy [3]. In order to reduce releasing of Ni<sup>3+</sup> ions, to increase bone adhesion to the metal implant surface, and minimize their direct contact with body fluids, TiO<sub>2</sub> coatings have been used on metallic implants. TiO<sub>2</sub> coating has proper anti-bacterial and biocompatibility properties [4].

Various deposition methods such as chemical vapor deposition, physical vapor deposition, sol - gel, plasma spray, tape casting, etc. have been used to develop TiO<sub>2</sub> coatings [5]. One of the most useful methods for this purpose is electrophoretic depositional (EPD). In 1994, Matthews et al. [6] used electrophoretic deposition of the TiO<sub>2</sub> layer to prepare the solar cells. EPD has the

advantages such as simplicity, low cost, good control of deposition microstructure by setting-up deposition parameters and so on, EPD is a two-step process. The first step is the motion of charged particles in suspension towards the electrode of opposite charge, under the applied electric field. The second step is deposition of charged particles on the electrode and formation of a dense layer [5].

There are three phases of TiO<sub>2</sub> in atmosphere: anatase, rutile and broket. Pure anatase gradually transforms to rutile in air at approximate temperature of 600°C. The transformation temperature range depends on many factors and varies in the range of 400-1200°C [7]. Presence of impurities in the raw materials may accelerate or retard this phase transformation. Another factor that can be under impact, is particles size [8]. Rutile is desirable phase in clinical applications due to the high corrosion protection of metallic implants and high biocompatibility. Also anatase phase has bioactivity properties [4].

Different types of organic [9] and water suspensions [10] have been used to EPD TiO<sub>2</sub> particles. Generally, in order to prevent cracks and delamination of coating, some adhesives such as PVC and PVP are added to the suspension. However, the adhesive-free suspension is preferred, because in the presence of adhesive materials

\*Corresponding Author Email: v\_khalili@sut.ac.ir (V. Khalili)

the mobility of electrons in the electrode decrease and also impurities in the deposition increase [11].

In the present work, TiO<sub>2</sub> thin films were developed using EPD process on NiTi substrate. First of all, in order to achieve TiO<sub>2</sub> bioactive and biocompatible coatings without any crack and impurities which originated from dispersed and adhesive materials, TiO<sub>2</sub> colloidal suspension was optimized. Then, the corrosion behavior of coatings was evaluated.

## 2. MATERIALS AND METHODS

**2. 1. Materials** In this work, TiO<sub>2</sub> powder with average size of 0.3 μm which mainly contains spherical particles was used. X-ray diffraction pattern of the TiO<sub>2</sub> powder is shown in Figure 1. To remove impurities and prevent surface contamination and also eliminate water molecules adsorbed to the surface of particles, the particles were preheated at 350°C for 3h. In order to prepare EPD suspension, a mixture of acetone and n-butanol was selected.

**2. 2. Preparation of suspension** After addition of TiO<sub>2</sub> particles to the solvent, in order to prevent agglomeration of particles, the suspensions were placed in ultrasonic bath for 30 min. TiO<sub>2</sub> concentration in the suspension was selected 40 g/l. To study the effect of solvent composition on the stability of the suspension and deposition, the ratio of acetone to n-butanol in the mixed suspension was considered in the range of 0-100%. Sedimentation test was done to characterize the optimal mixture of stable suspension. Thus, 10 ml of each mixture of acetone and n-butanol (volume fraction of acetone: 0, 30, 60, 80, 100%) was poured into a sealed and scaled glass container. During the test, in each suspension three separate regions can be seen; alcohol floated in the above, a stable suspension in the middle and sedimentation of particles in the bottom of container. Within one week, the height of each region in different suspensions was recorded at various time intervals.

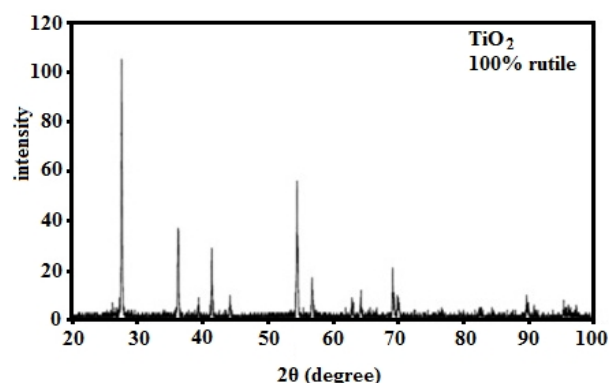
**2. 3. Electrophoretic deposition** In this work a medical grade superelastic NiTi alloy with nominal composition of 50.8 atom% Ni was used as a substrate. Surface preparation of NiTi samples was carried out by grinding up to 800 grit SiC papers followed by cleaning successively in acetone and ethanol in an ultrasonic bath for 30 min. Then, the samples were washed with distilled water and dried in air. An electrophoretic cell was designed which consisted of a 150 ml beaker, graphite electrode as anode with dimension of 30 × 20 × 10 mm, NiTi samples with 1.8 cm<sup>2</sup> surface area as cathode and a fixer (to fix the position of the

electrodes). The electrodes were set within 1 cm distance of each other. During electrophoretic deposition, constant voltage of 50 V was applied by a power supply (Mastech, DC power supply HY30001E, 9225) for 60s and change of electric current during deposition process were measured by means of Escort, 3146A Dual Display Multimeter. After deposition, the samples were dried at room temperature for 24 h. In order to increase the adhesion and density, and also reduce the porosity of coatings, the samples were sintered in a tube furnace under an atmosphere of inert gas (Argon) at 800 °C for 1 h. The heating rate was chosen to be 2°C/ min and after sintering the samples were furnace cooled under inert gas atmosphere.

**2. 4. Characterization** Phase analysis as well as surface morphology of the TiO<sub>2</sub> powder and TiO<sub>2</sub> coatings on the substrates were studied after sintering by means of XRD (Advance – D8, Bruker, Germany) and SEM (Cam Scan MV2200, Vega Tescan, Czech Republic). In order to avoid electrical charging due to low electrical conductivity of coated surfaces, they were initially covered with a very thin layer of gold. In order to evaluate the quality of TiO<sub>2</sub> coatings on the corrosion behavior of NiTi substrate, Potentiodynamic polarization test was done in physiological Ringer solution with components given in Table 1 [12]. Corrosion test was done using potentiodynamic system (models: BHP2063<sup>+</sup>, made in Behpajooh, Iran) that included, NiTi sample, platinum and Ag/AgCl as work electrode, opposite electrode and control electrode, respectively.

**TABLE 1.** Composition of Ringer solution used in corrosion tests [12]

Salts	CaCl <sub>2</sub> .2H <sub>2</sub> O	KCl	NaCl
Amount (g/l)	0.33	0.30	8.6



**Figure 1.** X-ray diffraction pattern of the TiO<sub>2</sub> powder used in this study

### 3. RESULTS AND DISCUSSIONS

SEM images of samples coated in 0%, 30% and 80% acetone are shown in Figure 2. SEM image of sample coated in 60% acetone is similar to 30% acetone. EPD in 100% acetone results in no coating on surface. As it can be shown in Figure 2-a, EPD in 0% acetone results in dense and crack-free coating that its grain size is the largest of the other surfaces but EPD in 30% acetone (Figure 2-b) contains cracks and grain size is the smallest. EPD in 80% acetone (Figure 2-c) has more porosity and non-uniform surface in comparison with two other coating surfaces.

The Ti present in NiTi substrate tends to oxidize. The oxidation can be increased with temperature so that substrate can easily absorb oxygen from the  $TiO_2$  coating. Also, defect and oxygen vacancies in the coating can be developed. Presence of oxygen vacancies in the  $TiO_2$  network provides required space for grain growth so porosity of the coating can be reduced. When the thickness of coating is large, the outer and visible surface on the SEM images of coating is located further from substrate so that grain growth and condensation of coating are invisible [13].

The stability of suspensions used in this study was evaluated using sedimentation test and the results are shown in Figure 3. As shown in Figure 3, stability of 0% acetone suspension (100% n-butanol) is higher than the other suspensions and with increasing acetone from 30 to 80%, the stability of the suspension decreases and 100% acetone suspension deposits in the first minute. Due to more difference between viscosity of n-butanol (3 cP at 25°C) and acetone (0.32 cP at 25°C), more stability of n-butanol suspension can be justified. Curves of Current density-time during the EPD process is shown in Figure 4. It can be observed that current density drops to lower values with increasing n-butanol.

Electrical resistance of suspension ( $R_s$ ) is obtained by using Equation (1) [5]:

$$R_d = \frac{v}{i} - R_s \quad (1)$$

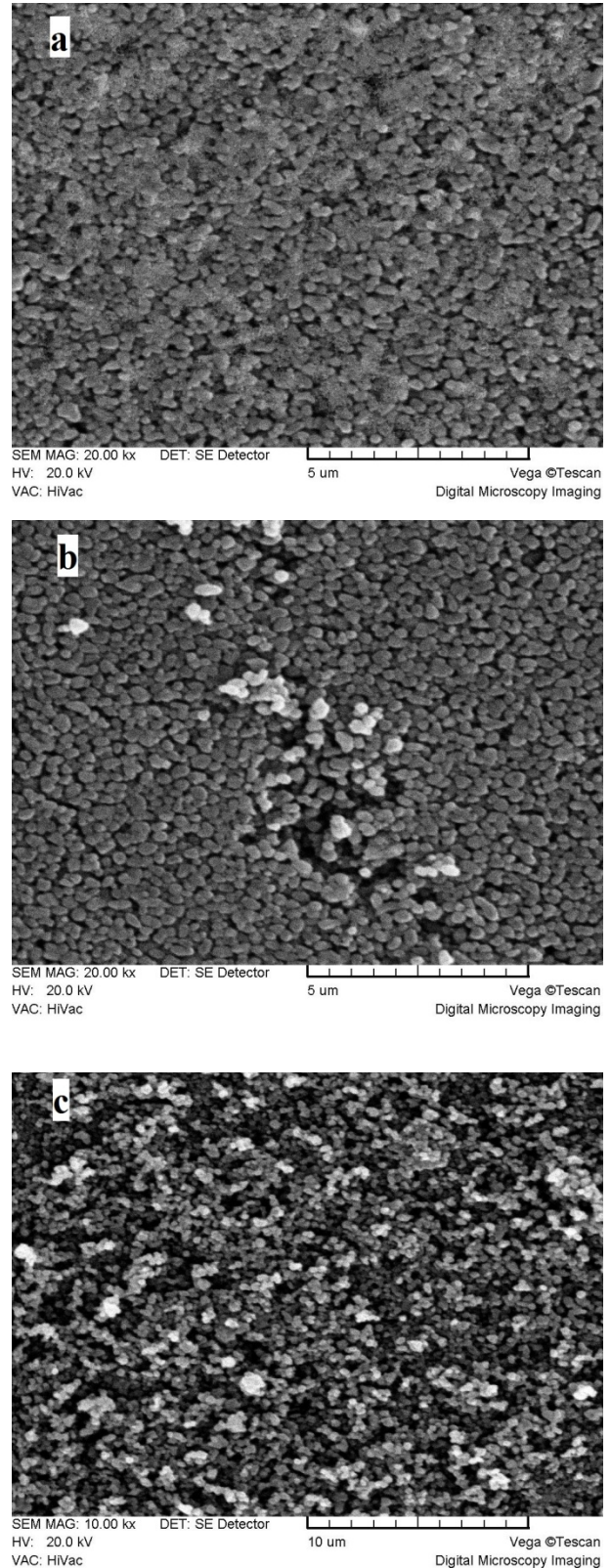
where,  $v$  is applied voltage,  $i$  is current flow in the circuit of electrophoretic process (Figure 5) and  $R_d$  is resistance of deposition. Due to deposit of insulating  $TiO_2$  particles and high values of  $R_d$ , current density values are low (about 0.015-0.04 A/cm<sup>2</sup>).

The reason of drop in current density with time can be justified by considering electrical resistance of suspension from Equation (2) [5].

$$R_{sUS} = \left[ \frac{1}{R_{p,sus}} + \frac{1}{R_{l,sus}} \right]^{-1} \quad (2)$$

$$R_{l,sus} = \rho_{l,sus} \frac{(L-d)}{A}$$

$$R_{p,sus} = \frac{(L-d)}{\mu Ac Q_{eff}}$$



**Figure 2.** SEM images of a)  $TiO_2$  coating in a 0% suspension, b) 30% and c) 80% acetone after sintering at 800°C for 2 hours with heating rate 2°C / min

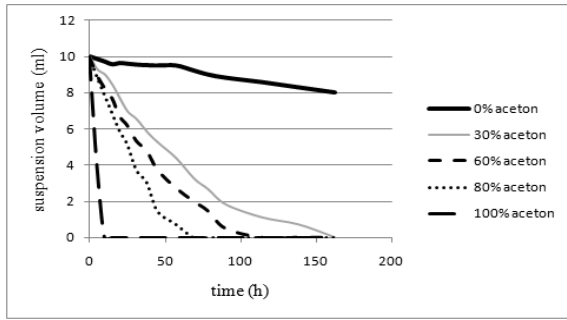


Figure 3. Curves of stable suspension volume with time

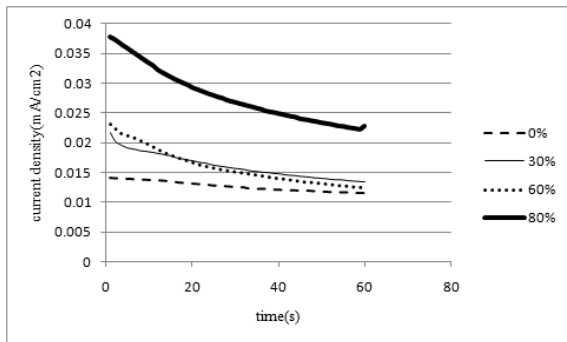


Figure 4. Curves of I-t during the EPD process

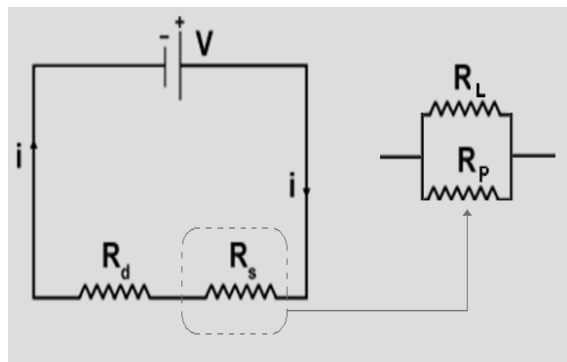


Figure 5. Circuit of Electrophoretic process

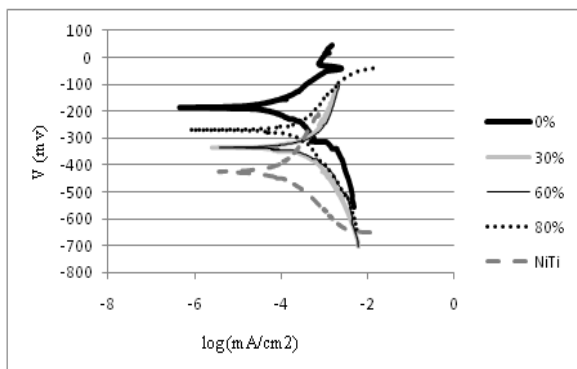


Figure 6. Polarization curves of uncoated and TiO<sub>2</sub> coated samples

where,  $R_{l,sus}$  is the resistance of liquid phase in the suspension,  $R_{p,sus}$  the resistance of charged particles in the suspension,  $L$  the distance between the electrodes,  $A$  the electrode surface area,  $d$  the thickness of deposition,  $\rho_{l,sus}$  resistivity of liquid phase in the suspension,  $\mu$  electrophoretic mobility of charged particles,  $Q_{eff}$  the effective charge on the particle surface and  $c$  particle concentration in suspension. According to Equation (2),  $R_{p,sus}$  and  $R_{l,sus}$  must be considered for calculating of  $R_{sus}$ .  $R_{p,sus}$  is the same for all suspensions used in this study, but  $R_{l,sus}$  which depends on density of liquid phase in suspension, varies. Density of acetone and n-butanol are  $0.79 \text{ g/cm}^3$  and  $0.81 \text{ g/cm}^3$  respectively, hence,  $R_{l,sus}$  acetone is lower than n-butanol.  $R_{l,sus}$  can be increased by increasing n-butanol in the suspension so that  $R_{sus}$  can be maximized and current density minimized in 100% n-butanol. Increasing deposition with time results in reducing the number of charged particles in the suspension and drop of current density with time in all suspensions. According to Equation (3), the more current density, the more increasing conductivity of suspension and with increasing of suspension conductivity, the coating thickness can be increased, at the same time.

$$\Lambda = \frac{I}{ES} \tag{3}$$

where,  $\Lambda$  ( $\text{Sm}^{-1}$ ) is suspension conductivity,  $I$  (A) is electric current,  $E$  ( $\text{Vm}^{-1}$ ) is electric field and  $S$  ( $\text{m}^2$ ) is the surface of electrode.

Polarization curves of uncoated and TiO<sub>2</sub> coated samples achieved in Ringer's solution at 37°C are shown in Figure 6. As it is shown in Figure 6, the curve for dense and uniform surface coated in 0% acetone is above the curves of other surfaces. Numerical results obtained using linear extrapolation of the results of polarization tests, are shown in Table 2. Corrosion current density ( $i_{corr}$ ) of samples coated in 0% acetone reduces in comparison with other samples and the corrosion potential ( $E_{corr}$ ) is the most positive. Decreasing  $i_{corr}$  indicates decreasing corrosion rate (Kinetic factor). Increasing  $E_{corr}$  indicates reduced tendency to corrosion (thermodynamic factor).

$$i_{corr} = \frac{b_a \times b_c}{2.3 R_p (b_a + b_c)} *$$

TABLE 2. Numerical results obtained from the polarization test

Samples	EPD in 80% acetone	EPD in 60% acetone	EPD in 30% acetone	EPD in 0% acetone	NiTi
$b_a$ (mV/Decade)	205.17	297.13	250.38	99.919	263.01
$b_c$ (mV/Decade)-	190.86	227.72	194.31	104.38	147.16
$E_{corr}$ (V)	-270	-342	-336	-188	-424
$i_{corr}$ (mA/cm <sup>2</sup> )*	$E^{-4} 3.90$	$E^{-4} 7.59$	$E^{-4} 4.91$	$E^{-5} 7.29$	$E^{-4} 1.43$
$R_p$ (k $\Omega$ .cm <sup>2</sup> )	110.346	74.873	96.913	304.360	284.583

#### 4. CONCLUSION

1. Due to higher viscosity of n-butanol compared to acetone, with increasing amount of acetone, stability of suspension reduces.
2. Electrophoretic deposition of TiO<sub>2</sub> in 0% acetone suspension renders crack-free, dense coating surface that its grain size is the largest of the other surfaces coated in 30, 60 and 80% acetone.
3. Corrosion current density ( $i_{\text{corr}}$ ) of samples coated in 0% acetone reduces in comparison with other samples and the corrosion potential ( $E_{\text{corr}}$ ) is the most positive.

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V. Khalili, J. Khalil-Allafi, H. Maleki-Ghaleh

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هدف پژوهش حاضر، تبدیل سطح ختای زیستی NiTi به سطح زیست فعال و زیست سازگار است. به منظور ایجاد لایه‌ی زیست فعال و مقاوم به خوردگی بر روی NiTi، از روش رسوب‌گذاری الکتروفوریتیک استفاده شد و ذرات TiO<sub>2</sub> بر روی سطح رسوب داده شدند. سوسپانسیون ذرات TiO<sub>2</sub> با استفاده از مخلوط استون و n-پوتانول (۰٪، ۳۰٪، ۶۰٪، ۸۰٪ و ۱۰۰٪ استون) و بدون استفاده از هیچ گونه پراکنده سازی آماده شد و آزمایش ته‌نشینی برای مشخصه‌یابی آن مورد استفاده قرار گرفت. مطالعه‌ی مورفولوژی سطحی پوشش‌ها با استفاده از SEM نشان داد که رسوب‌گذاری الکتروفوریتیک از سوسپانسیون ۰٪ استون باعث ایجاد پوششی عاری از ترک، متراکم، دارای دانه بندی نسبتاً درشت و مقاومت به خوردگی بالا می‌شود

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