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Reduction of Ni release and improvement of the friction behaviour of NiTi orthodontic archwires by oxidation treatments

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Abstract This work studies NiTi orthodontic archwires that have been treated using a new oxidation treatment for obtaining Ni-free surfaces. The titanium oxide on the surface significantly improves corrosion resistance and decreases nickel ion release, while barely affecting transformation temperatures. This oxidation treatment avoids the allergic reactions or toxicity in the surrounding tissues produced by the chemical degradation of the NiTi. In the other hand, the lack of low friction coefficient for the NiTi superelastic archwires makes difficult the optimal use of these materials in Orthodontic applications. In this study, the decrease of this friction coefficient has been achieved by means of oxidation treatment. Transformation temperatures, friction coefficient and ion release have been determined.

1 Introduction

NiTi shape-memory alloys can be used in a wide range of biomedical applications. However, despite their unique and attractive shape-memory properties, superelasticity and excellent damping characteristics, they are still controversial because of the potentially toxic, allergic and carcinogenic effects of releasing Ni into the exterior medium [1–4].

To prevent adverse reactions to implants, researchers have studied surface treatments using a variety of approaches. The oxidation of NiTi material has been used to obtain surfaces with a low Ni content. This work focuses on surface oxidation treatments. NiTi alloys are highly biocompatible due to an inert protective TiO_2 layer that forms on the surface of the material [5]. However, depending on the thickness, composition and morphology of the layer, corrosion and ion release may vary [6, 7]. In this work, we studied the oxidation treatment in a low oxygen pressure atmosphere, which provides a very low Ni surface concentration and a thick oxide layer.

It is generally assumed that the optimal tooth movement is achieved by applying forces that are low in magnitude and continuous in nature. Such forces minimise tissue destruction and produce a relatively constant stress in the periodontal ligament during tooth movement [8–10]. The pseudoelasticity of NiTi archwires allows the orthodontist to apply an almost continuous light force with larger activations that results in the reduction of tissue trauma and the patient discomfort, thus facilitating enhanced tooth movement [11].

In contrast, forces that are high in magnitude encourage hyalinisation of the periodontal ligament and may cause irreversible tissue damage such as root resorption. The NiTi archwires produce teeth movement with greater efficiency and in a shorter time when compared to other orthodontic alloys and they are especially adequate in situations requiring large deflections, such as the preliminary bracket alignment stage in load deflection stage in orthodontic therapy [12, 13].

In orthodontic applications superelasticity is especially useful since constant forces can be transmitted to the dentition over a long activation period resulting in a desirable biological response. Despite of these advantages,

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the lack of low friction coefficient makes difficult the optimal use of these materials in Orthodontic applications. In this study, the decrease of this friction coefficient has also been developed by means the oxidation treatments.

2 Materials and methods

2.1 Samples preparation

The chemical composition of the NiTi alloy studied was 44% Ti and 56% Ni in weight percentage. The transformation temperatures of the alloy studied without diffusion treatment were: $M_s = 29.2°C$, $M_f = -10.5°C$, $A_s = -7.5°C$ and $A_f = 34.2°C$. The samples showed an austenitic phase at room temperature.

Ten NiTi archwires (scheme showed in Fig. 1) were treated in order to form a nickel-depleted surface layer. The samples were homogenized in a tubular furnace (ST16, Hobersal, Spain) in an argon atmosphere at 1,100°C for 6 h, with a heating ramp of 6°C/min. They were then subjected to a thermal treatment in order to stabilize the β phase and activate the shape-memory properties. This treatment consisted of a 10-min heating phase at 800°C, a cold-water quench, and a 1-h annealing at 500°C. In order to produce the titanium oxide coating, the archwires were thermally treated for 2 h and 30 min at a pressure of 3×10^{-2} mbar and a temperature of 400°C [14, 15].

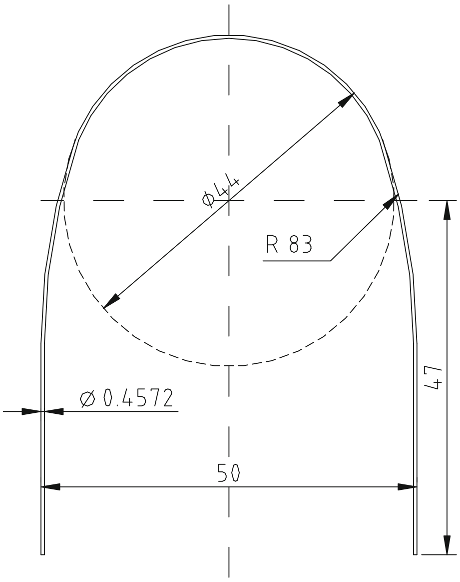

Fig. 1 Scheme of the orthodontic wires studied

2.2 Surface chemical composition

The surface chemical composition of the samples after treatment was determined by means of X-ray photoelectron spectroscopy (XPS) (PHI5500, Physical Electronics, USA). The nickel concentration profile of the samples was determined by means of argon sputtering.

The surface of the samples was analysed by means of X-ray photoelectron spectrometry (XPS). The XPS experiments were performed in a PHI 5500 Multitechnique System (Physical Electronics) with a monochromatic X-ray source (Aluminium Kα line with 1,486.6 eV and 350 W), placed perpendicular to the analyser axis (takeoff angle: 45°) and calibrated using the 3d5/2 line of Ag with a full width at half maximum (FWHM) of 0.8 eV. The analysed area was a circle with a diameter of 0.8 mm. The selected resolution for the fitted spectra was 23.5 eV of pass energy and 0.1 eV/step. In-depth measurements and chemical composition depth profiles were obtained by sputtering the surface with an Ar^+ ion source (4 keV energy). In these conditions, a 6 nm/min sputtering rate was determined as calibrated against a TiO_2 standard. These measurements were taken in an ultra-high vacuum chamber.

Multiplex (narrow-scan) spectra were obtained for C1s, O1s, $Ti2p_{3/2}$, $Ti2p_{1/2}$, $Ni2p_{3/2}$, $Ni2p_{1/2}$ and Ar1s photopeaks. The obtained spectra were analysed using Multipak software (Physical Electronics, USA). All binding energies were referenced to the C1s peak at 284.8 eV, corresponding to adsorbed hydrocarbon (C–H) contamination at the surface. The atomic sensitivity factors included in the instrument data system were used to calculate the atomic concentration of the elements. The curve-fitting analysis was performed using a Gaussian–Lorentzian fitting. The oxide thickness was estimated based on the depth at which the oxygen signal had decreased to 50% of its maximum value [14, 15]. One, two or three samples were analysed per group, depending on the surface treatment.

2.3 Transformation temperatures and stresses

The transformation temperatures were measured by means of a calorimeter. The calorimetric system used has already been described in previous papers [16, 17] and it is based on a flow calorimeter which measures differential signals (ΔT) by means of thermobatteries. Temperature was measured by means of a standard Pt-100 probe. All signals were digitalized through a multichannel recorder and linked to a microcomputer. M_s and A_s transformation temperatures occur when there is a sudden increment in calorimetric signal. In the same way, the final temperatures, M_f and A_f, are determined when the calorimetric signal returns to the base line. The transformation temperatures were measured during the first heating and cooling cycle after heat treatments. The sensitivity of this calorimetric technique is approximately 100 times higher than other conventional methods such as Differential Thermal Analysis (DTA) or Differential Scanning Calorimetry (DSC).

The transformation stresses were measured by an electromechanical testing machine MTS-Adamel equipped with an environmental chamber which contained artificial saliva at 37°C. The specimens tested were cylinders of 2.5 mm in diameter and of 150 mm of height. The gauge length of the specimens or the distance between the grips was 77 mm and the cross-head speed used was 10 mm/min.

2.4 Friction coefficients

The friction coefficients (the proportionality constant between the friction force and the normal force) for the as received and the heat treated NiTi alloy were determined against the material commonly used for the brackets manufacture the 316 Stainless steel.

These coefficients were measured by an electromechanical testing machine MTS-Bionix equipped with an environmental chamber which contained artificial saliva at 37°C. The chemical composition of the artificial saliva is shown in Table 1.

The test method used to determine the friction coefficient between the archwires and the brackets was the dynamic method using a cell load of 250 N with a sensitivity of 1 g-force with a high precision dynamometer. The cross-head speed used was 1 mm/min and the frequency of the acquisition dates was 30 values/s. The archwires roughness R_a were 0.13 µm (as received material) and 0.17 µm (sample treated), and that of the stainless steel brackets was 0.13 µm. The scheme of the test can be observed in Fig. 2.

Table 1 Chemical composition of artificial saliva

Chemical product	Concentration (g/dm^3)
K_2HPO_4	0.20
KCl	1.20
KSCN	0.33
Na_2HPO_4	0.26
NaCl	0.70
$NaHCO_3$	1.50
Urea	1.50
Lactic acid	Until pH = 6.7

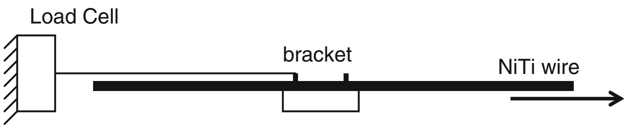

Fig. 2 Scheme of the test method to determine the friction coefficient

2.5 Ion release

The ion release test was performed by immersing the samples (treated and untreated) in 6 ml of artificial saliva (Table 1), at pH = 7.4, 37°C, for 30 days. At day 5, the SBF was changed to avoid saturation of the medium. The released Ni was measured by means of graphite furnace atomic absorption spectroscopy (GFAAS) (AAS Solar 989, Unicam, Germany) at 1 and 5 h and at 1, 2, 5 and 15 days. The results are mean values of three measurements.

2.6 Statistical analysis

The data were statistically analysed using Student's *t* tests, one-way ANOVA tables and Turkey's multiple comparison tests in order to evaluate statistically significant differences between the sample groups. The differences were considered significant when *P* value <0.05. All statistical analyses were performed with Minitab^{TM} software (Minitab release 13.0, Minitab Inc., USA).

3 Results and discussion

Oxygen diffusion in NiTi superelastic archwires produces a growth of a titanium oxide film, as can be seen in Fig. 3. The thickness of this titanium oxide film increases with the temperature and time of the heat treatment, since both parameters favour the oxygen diffusion. The film is homogeneous on the whole surface and it shows a good adherence, since it is not produced by means of a projection method, but by a chemical reaction between the substrate and the oxygen gas.

3.1 Surface chemical composition

Using XPS and argon sputtering, we detected a nearly 20-nm-thick layer that was practically nickel-free, followed by a progressive increase in nickel concentration in the treated samples (Fig. 4). The absence of nickel on the surface is essential to preventing the release of this ion, which produces an allergic reaction in a large percentage of the population.

The new heat treatment combines a very low surface Ni concentration with a thick protective oxide. This treatment is performed in a low oxygen pressure atmosphere and

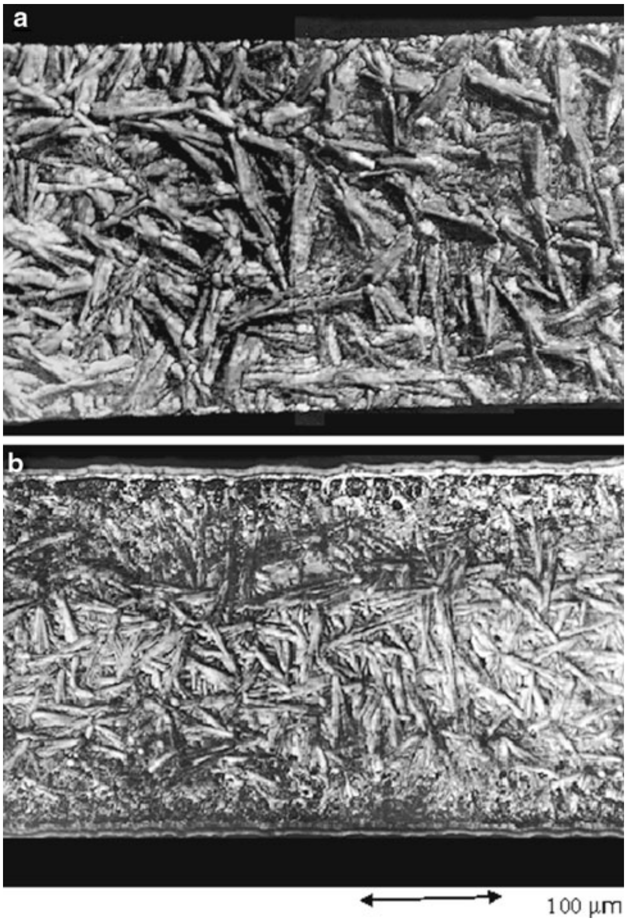

Fig. 3 Archwire microstructure before and after the oxidation treatment. **a** Original sample and **b** archwire with oxidation treatment, it can be observed the TiO_2 film on the surface

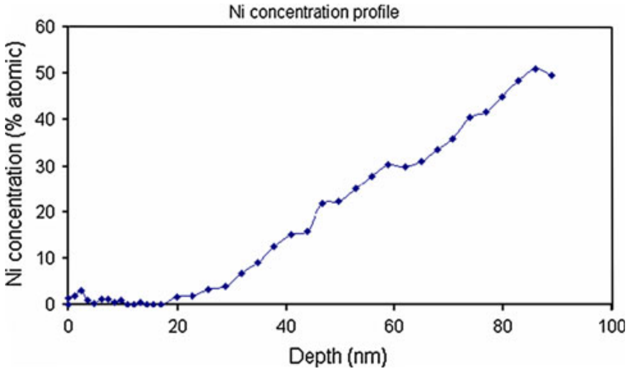

Fig. 4 Nickel concentration profile of oxidized samples

leads to specific Ti oxidation, as explained by Chan et al. [16]. We detected no Ni oxides with TiO_2, unlike with thermal treatments carried out at atmospheric pressure [16–18]. A low-Ni zone formed beneath the surface. Based on studies published in the literature, an oxidation pathway could to explain these results. According to Armitage et al. [18], at 400°C, the oxide layer is predominantly formed by the inward diffusion of O ions inside the NiTi lattice. Because $\Delta G_{\text{formation (298 K)}}$ for TiO_2 and NiO are -212.6 and -50.6 kcal mol^{-1}, respectively [19–22], there is a preferential oxidation of Ti. Ni remains in its metallic state. The formation of stoichiometric TiO_2 is progressive and TiO_x ($x < 4$) may be present underneath [23] at the TiO_2–NiTi interface. Espinos et al. [24] showed that, under these conditions, NiO° interacts with Ti^{n+} ions ($n < 4$) and diffuses through TiO_x. NiO disappears from the surface due to a migration in deeper layers.

3.2 Transformation temperatures and stresses

According to the transformation temperatures presented in Table 2, the alloy studied is in its austenitic phase at room temperature.

From these results it can be noticed that small chemical composition changes produce variations in the transformation temperatures for NiTi alloys: a variation of 0.1% in Ni produces a change in the M_s temperature of 29.2–26.7°C. The decrease of the titanium content is due to the formation of titanium oxide on the surface. The decrease of the titanium content produces an austenitic stabilization and consequently the transformation temperatures M_s and M_f of the thermally oxidized samples are lower than the samples without heat treatment. However, the A_s and A_f of the samples oxidized are higher than the originals. The variations in the transformation temperatures are according to the different studies about the influence on the chemical composition of NiTi on the transformation temperatures [25, 26]. Very Long treatments could cause the loss of superelasticity and shape memory effect [27].

From the stress–strain curves it can be deduced that the treated samples have a stress induced martensitic transformation. The transformation stresses are low and constant, being adequate for orthodontic therapy. The oxygen content in the orthodontic archwire produces small changes in the transformation temperatures and consequently in stresses about 10 MPa, as can be observed in Table 2. These changes are not critical for the orthodontic therapy.

3.3 Friction coefficients

The friction coefficient varies from 1.35 for the NiTi without oxidation treatment to 0.40 for the NiTi with titanium oxide on the surface when disks of austenitic stainless steel were used. Figure 5 shows the variation of the friction coefficients with the wear distance, respectively.

The NiTi archwires treated will produce tooth movement with greater efficiency and in a shorter time when compared to NiTi without treatment. This improvement in

Table 2 Martensitic and austenitic transformation temperatures and stresses (austenitic to stress induced martensite, A → SIM and reverse transformation, SIM → A) of the NiTi alloy studied (standard deviation)

	Temperature (°C)				Stress (MPa)	
	A_s	A_f	M_s	M_f	σ^{A-SIM}	σ^{SIM-A}
Non-treated	−7.5 (0.8)	34.2 (0.6)	29.2 (1.0)	−10.5 (0.9)	320 (15)	150 (7)
Thermally oxidized	−6.0 (0.3)	36.1 (0.9)	26.7 (0.7)	−10.7 (1.1)	331 (17)	161 (10)

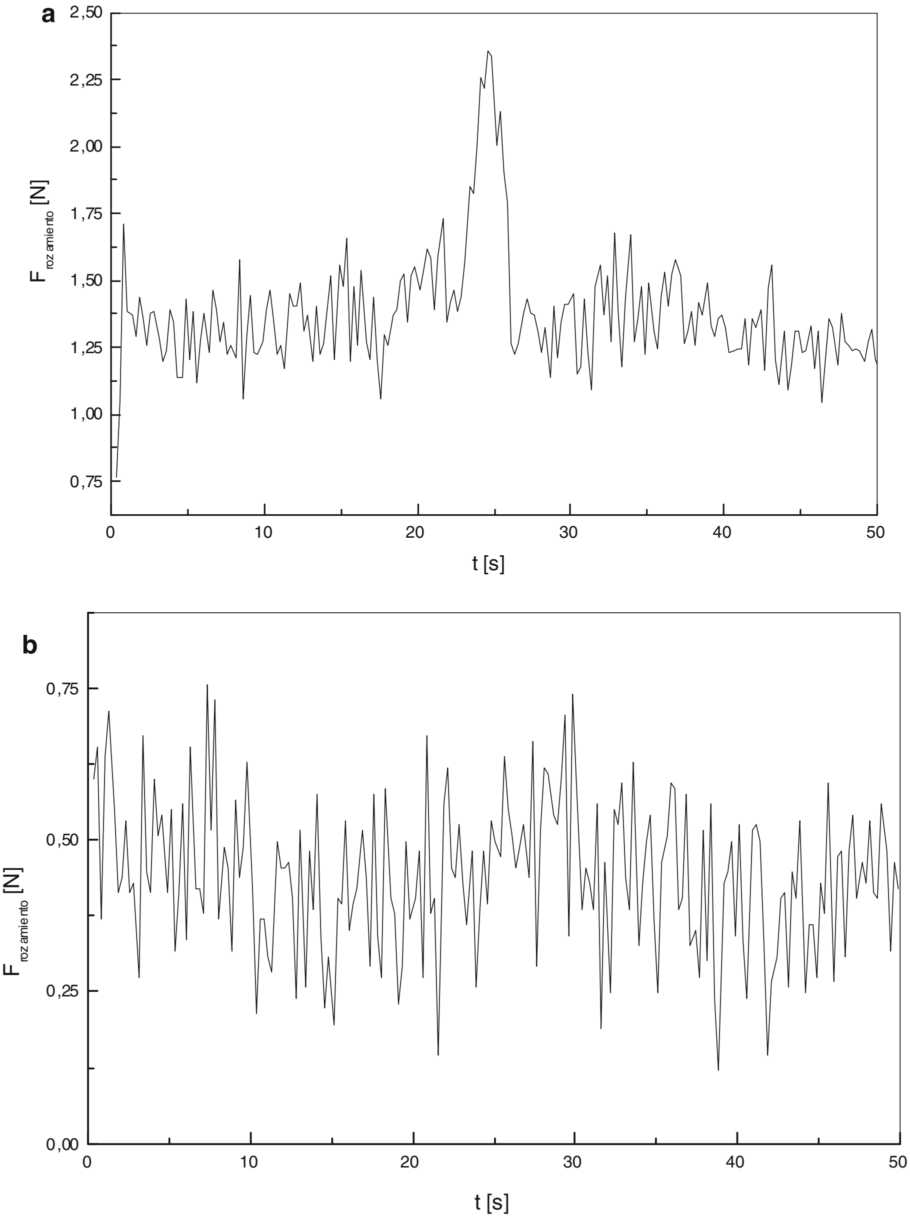

Fig. 5 Friction coefficients **a** without oxidation treatment **b** with oxidation treatment

the friction coefficient is especially useful in situations requiring large deflections of an orthodontic archwire such as the preliminary bracket alignment stage of the load deflection stage in orthodontic therapy [28–30]. Consequently, the NiTi oxidized wires are preferred in the early stages of orthodontic therapy because of its high slip capacity. The resulting high deflections and low forces are favourable for the large misalignments in the early stages. However, at the intermediate and end stages of treatment most clinicians switch to higher modulus, larger cross section wires, when the high deflections are no longer necessary [31, 32].

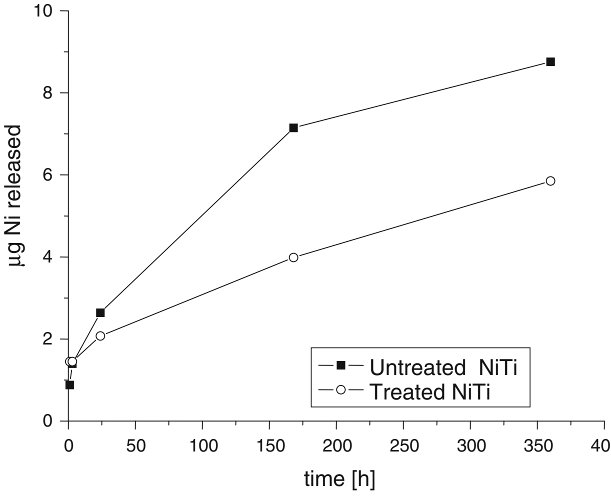

Fig. 6 Mass of nickel released in the simulated body fluid over time

3.4 Ion release

The inert film of titanium oxide reduces the release of the metallic ion into the environment and acts as an obstacle to biodegradation. Figure 6 shows the release of ions. In both cases, the concentration of ions released into the medium initially increases very sharply and later reaches a saturation level [33].

This oxide is protective and reduces Ni release into the medium. Although the quantity of Ni ions released is well below 300–500 µg (the critical concentration for inducing allergy [34]), this quantity might be enough to induce long-term inflammatory responses or alter cell behaviour, even in untreated surfaces. Sun et al. [35] showed that metal ions can alter osteoblast behaviour even at subtoxic concentrations. Some studies have shown a significant decrease in alkaline phosphatase activity (ALP) and DNA synthesis with Ni ions. Other works have shown that Ni ions could be responsible for inducing the secretion of different cytokines involved in the inflammatory process. Wataha et al. [36] observed an increase in IL1β secretion by macrophages at Ni concentrations known to be released by NiTi dental materials. Another study [37] demonstrated that the quantity of IL1β secreted from monocytes due to the release of Ni ions (7.2 µg/ml) was large enough to indirectly induce the secretion of ICAM1 (intracellular adhesion molecules involved in the recruitment of other inflammatory cells) on endothelial cells. Finally, Cederbrant et al. [38] showed that a quantity of Ni even as small as 1.2 µg/ml could induce an increase in the proliferation of lymphocytes and the secretion of IL10 in subjects allergic to Ni. Thus, the results obtained for oxidized surfaces may help improve the long-term biocompatibility properties of materials and reduce sensitization to Ni and allergies.

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