The corrosion of nickel-titanium rotary endodontic instruments in sodium hypochlorite

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Abstract

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Aim To evaluate the corrosion resistance of nickeltitanium (NiTi) endodontic rotary instruments immersed in 5.25% sodium hypochlorite (NaOCl) solution.

Methodology The corrosion performance of NiTi instruments (S1 25 mm, ProTaper Dentsplay Maillefer, Ballaigues, Switzerland) was evaluated using commercial 5.25% NaOCl solution (pH = 12.3), and the same solution partially neutralized adding H_2SO_4 to reach pH = 10.1. Electrochemical measurements were carried out using a potentiostat equipped with a five-channel zero resistance ammeter (ZRA) for galvanic current measurements. The instruments were sectioned into three parts (cutting part, noncutting part and shank) and degreased with acetone and rinsing with demineralized water prior to being immersed in NaOCl solution for testing. Each set of the three parts

constituted one 'virtual' instrument through the ZRA, giving access to the galvanic currents that circulate between the three parts. Nine instruments were employed to check the reproducibility of the electro-chemical measurements.

Results The corrosion potential (E_{corr}) of the NiTi alloy reached the passive domain in approximately 20 s of immersion in the solution having a pH 10.1. After this initial period the potential remained steady, indicating that stable passivation was achieved. However, at pH 12.3 no stationary state was achieved even after 6000 s of immersion time. Thus, the alloy was not stable in this medium from a corrosion point of view.

Conclusions The corrosion resistance of NiTi alloy was enhanced by lowering the pH of NaOCl solution to 10.1, which allows the system to reach the stability domain of the passivating species TiO_2 and NiO_2 .

Keywords: corrosion resistance, rotary endodontic instrument, sodium hypochlorite.

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Introduction

The potential risk of nickel–titanium (NiTi) endodontic rotary instruments to fracture during root canal shaping is of concern. NiTi endodontic rotary instruments usually fracture through two mechanisms: torsion or through metal fatigue caused by flexure. Fracture due to torsion occurs when the tip of the file or any part of the instrument becomes locked in the root canal, whilst the shank continues to rotate in the handpiece (Martin *et al.* 2003). When this occurs, the elastic limit of the metal is surpassed; the metal becomes deformed and finally fractures. The other type of fracture is caused by stress, and by the fatigue of the metal itself (cyclical fatigue) (Luebke *et al.* 2005). The smaller the radius of curvature, the more critical the cyclical fatigue becomes (Lopes *et al.* 1994, Zelada *et al.* 2002, Varela-Patiño *et al.* 2005). Those instruments considered to be most resistant to cyclical stress are

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weakened when they undergo torsional stress. Stress caused by cyclical fatigue is reduced when the instruments are more flexible and have smaller diameters (Sattapan *et al.* 2000, Yared *et al.* 2000, Gambarini 2001).

The chemical mechanisms that occur, either prior to or during instrumentation (the disinfection of the material, sterilization, irrigation) may cause corrosion and/or deterioration of the instruments, leading to early failure. These mechanisms have received limited attention, and the results which have been made available by various authors are contradictory (Busslinger et al. 1998, Haikel et al. 1998a, b, Kim & Johnson 1999, Stokes et al. 1999, Kuphasuk et al. 2001, O'Hoy et al. 2003, Darabara et al. 2004a,b). As far as the effect of exposure to sodium hypochlorite (NaOCl) solutions is concerned, discrepancies are due mainly to misinterpretations of the experimental data. For instance, whilst the study performed by O'Hoy et al. (2003) shows clear evidence of corrosion after overnight immersion in diluted bleach, the study by Darabara et al. (2004b) concluded the contrary based on electrochemical data which my have been misinterpreted as the electrochemistry of the NaOCl solution itself was disregarded.

Nickel-titanium instruments experience severe corrosion after a certain time immersed in diluted NaOCl solution (O'Hoy *et al.* 2003). Moreover, time to fracture below a critical applied stress is highly dependent on NaOCl concentration (Yokoyama *et al.* 2004). Typical corrosion damage following exposure to 5.25% NaOCl solution can be seen in Fig. 1a. The corrosion reveals the grain boundaries of the alloy (Fig. 1b), and leaves white deposits of NaCl (Fig. 1c). The aim of the present paper was to investigate corrosion-related degradation of NiTi rotary instruments in NaOCl solutions.

Materials and methods

A commercial endodontic solution of 5.25% sodium hypochlorite (Dentaflux Lab, Madrid, Spain) was used. Two versions of the solution were employed: as received (pH = 12.3) and partially neutralized, using 1 mol L^{-1} H₂SO₄, to obtain the desired pH value of 10.1. H₂SO₄ was used as a neutralizing agent to prevent modification of the initial chloride concentration of the medium, as chloride ions are more corrosive than sulphates.

Nine rotary endodontic instruments (ProTaper S1 25 mm, Dentsply Maillefer, Ballaigues, Switzerland) were tested. The instruments were sectioned into three



Figure 1 Scanning electron microscope images showing: (a) corroded end of the instrument, (b) detail of the corrosion attack: grain boundaries are visible below NaCl deposits, (c) detail of NaCl deposits outside the corroded area. Instrument immersed in NaOCl 5.25% overnight (about 15 h).

parts (cutting part, noncutting and shank). Each set of the three parts constituted one 'virtual' instrument through a zero resistance ammeter (ZRA), giving access



Figure 2 Experimental set-up devised for measuring galvanic currents. The three sections of the tested instrument (working electrodes WE_1 , WE_2 and WE_3) are short-circuited externally through the zero resistance ammeter (ZRA). The potentiostat drives the current through platinum gauze acting as counter electrode (CE), and measures the potential of the galvanic system with respect to the reference electrode (RE). The bottom end of the noncutting section is masked by an epoxy resin in order to avoid contact of the solution with the cross section of the instrument.

to the galvanic currents that circulate between the three parts (Fig. 2).

Surface morphology was observed using a JEOL 5410 Scanning Electron Microscope (SEM) (JEOL, Akishima, Tokyo, Japan) equipped with energy dispersive X-ray microanalysis (EDX). EDX microanalysis showed that the cutting and noncutting sections of the instrument were made of a NiTi alloy, whilst the shank was made of gold-plated brass. The rotary instruments were used in the electrochemical tests as received. A degreasing procedure with acetone followed by rinsing with demineralized water was applied prior to testing.

Electrochemical measurements were performed using a potentiostat (Applied Corrosion Monitoring, Cark-in-Cartmel, UK) equipped with a 5-channel ZRA for galvanic current measurements. A large surface platinum gauze was employed as a counter electrode. The reference electrode employed was an Ag/AgCl electrode with an electrochemical potential of -16 mV with respect to the saturated calomel electrode (SCE). All potentials in the text refer to the SCE, which is +242 mV with respect to the normal hydrogen electrode (NHE). The working electrodes were the three sections of the rotary instrument (as described above), either individually or galvanically coupled through the potentiostat's ZRA. All electrochemical tests were performed at room temperature $(22 \pm 2 \text{ °C})$.

One potential problem that was foreseen was the risk of corrosion because of galvanic coupling; that is, when two dissimilar metals (here gold-plated brass plus the NiTi alloy) are in electrical contact and immersed in the same solution. This hypothesis of galvanic coupling was analysed using an experimental set-up designed to measure the galvanic currents circulating between the different sections of the instrument: the shank (Au, noble component), the noncutting section (the cylindrical part of the instrument, with low conformational stress, and then showing only the intrinsic activity of the alloy, and the cutting part. As the cutting section of the instrument accumulates mechanical stress during canal shaping, it was expected to be anodic with respect to the remainder of the instrument.

The measurement of galvanic currents between multiple elements is a well-documented procedure (Nóvoa *et al.* 1987, Alonso *et al.* 1993, 1995, 1998a,b, Collazo *et al.* 1999, Abreu *et al.* 2002) and involves the use of multiple ZRA which are wired to the elements being tested. Figure 2 provides a description of the experimental set-up devised for those measurements.

Results

Bulk solution, pH = 12.3

Figure 3 summarizes the initial behaviour of the unused electrodes. The corrosion potential fluctuates between +300 and +400 mV (Fig. 3b), the galvanic current between the instrument body and the shank was high, and the polarity was as expected: the shank (Au) is the cathode (negative current) and the body demonstrated anodic behaviour (positive current) as Fig. 3a shows. The cutting section of the instrument presented unexpected cathodic behaviour, although some discrete anodic periods were observed (at about 20, 80 and 100 s).

Figure 4a,b correspond to the cyclic voltammograms (from +200 to 1000 mV) performed on the threeelement galvanic system (cutting section, noncutting and shank).

The behaviour of the most active (tip of cutting section) and most noble (shank) parts of the instrument is presented in Fig. 5, where substantial current values were recorded. At the end of this polarization, galvanic



Figure 3 Evolution with immersion time of galvanic current densities (a), and corrosion potential (b).

measurements were performed again in order to analyse the reactivity of the newly formed surfaces. The results are given in Fig. 6 where it can be seen that, initially, the tip behaved as a cathode with respect to the shank. Nevertheless, after 140 s the shank became more noble and the situation persisted over time, as shown in Fig. 6b.

Bulk solution + H_2SO_4 , pH = 10.1

The behaviour of the samples was also investigated when immersed in a solution of lower pH. Figure 7 corresponds to the galvanic test performed in the pH 10.1 solution with and without the shank galvanically coupled to the system. In Fig. 8 the evolution of the corrosion potential, E_{corr} , with immersion time for the galvanic system (cutting section, noncutting and shank) in pH 10.1 and pH 12.3 solutions, are compared.

Discussion

Figure 3 corresponds to a highly unstable galvanic system where the shank behaves in a cathodic manner and the noncutting section in an anodic manner, whilst the cutting section supports a small cathodic current.

Sodium chloride deposits were identified over the surface of the instruments (see Fig. 1c); hence the cathodic process shall involve Cl⁻ formation. Moreover,



Figure 4 Cyclic voltammetry for the galvanic couple elements. Scan rate was 1 mV s⁻¹. Potential range: from -200 mV to +1000 V (vs. saturated calomel electrode) in 5.25% NaOCl solution.

both the anodic and cathodic reactions occurred with gas evolution, which suggests that both processes involve gaseous species. Equations 1 to 3 correspond to the possible cathodic reactions in this medium. Reactions 1 and 3 will lead to high corrosion potential values together with the formation of Cl.

$$ClO^{-}+H_2O+2e^{-} \rightleftharpoons Cl^{-}+2OH^{-} E^{0}=+0.84V_{vs.NHE}$$
 (1)

$$ClO^{-}+H_2O+e^{-} \rightleftharpoons \frac{1}{2}Cl_2+2OH^{-} E^{0}=+0.32V_{vs.NHE}$$
 (2)

$$\frac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^- \quad E^o = +1.36V_{vs.NHE} \tag{3}$$

Gas evolution at anodic sites is more difficult to interpret because, in principle, the anodic reaction corresponds to alloy dissolution (corrosion). Neverthe-



Figure 5 Cyclic voltammetry for the galvanic couple rotary instrument tip + shank. Scan rate 1 mV s⁻¹. Potential range: from -200 mV to +1000 V in 5.25% NaOCl solution. The estimated active surface of the rotary instrument tip is (S = 0.005 cm^2).

less, one possibility is that water oxidation is occurring (Equation 4). The required conditions for this process to happen will be discussed later.

$$H_2O \rightarrow \frac{1}{2}O_2^{\uparrow} + 2H^+ + 2e^- \quad E^o = +1.23V_{vs.NHE}$$
 (4)

The processes developing on the three sections of the tested galvanic coupling is given in Fig. 4. The electrochemical potential of the system was scanned from -200 to +1000 mV and back again to -200 mV (cyclic voltammetry). It can be seen in Fig. 4 that whilst the cathodic branch (between -200 and about +600 mV) is similar for the three elements, the anodic current for the cutting section is about two orders of magnitude higher, which indicates higher activity, probably due to accumulated mechanical stress.

The limiting behaviour of the galvanic system is analysed in Fig. 5. The good reversibility of the redox process developing on the gold surface can be seen in Fig. 5 because of the lack of hystereses between the forward and reverse curves. Nevertheless, the accumulation of corrosion products at the arrow makes the zero current potential to shift anodically by about 200 mV in the reverse curve (about +600 mV abscissa) with respect to the forward one (about +400 mV abscissa). The situation is typical for the formation of higher valence oxides, as occurs for iron oxides (Andrade *et al.* 1995, 2001, Alonso *et al.* 1998b).

The accumulation of corrosion products at the rotary instrument tip due to polarization should contribute to



Figure 6 Galvanic currents and corrosion potential for the galvanic couple rotary instrument tip + shank. (a) Immediately after cyclic voltammetry. (b) 10 min later.

Figure 7 Corrosion potential, E_{corr} (b) and galvanic current (a) for the studied system in pH 10.1 solution.

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Figure 8 Corrosion potential evolution with immersion time (6000 s) of the rotary instrument (shank not immersed) in both test solutions: pH = 12.3 (5.25% NaOCl solution) and pH = 10.1 (NaOCl solution neutralized with H₂SO₄).

surface passivation, i.e. the surface becomes less reactive. In order to verify this hypothesis, galvanic measurements were performed after polarization. The results are given in Fig. 6 where it can be seen that, initially, the tip exhibited cathodic behaviour with respect to the shank. Thus, the electrochemically formed oxide ennobles the tip. Nevertheless, these oxides were not stable and dissolved, so that after 140 s the shank became more noble again. The corrosion potential increases as the shank becomes more cathodic, probably due to its higher active surface available for Cl_2 and ClO^- reduction.

The transients in potential and current observed in Fig. 6a,b should correspond to events of oxide formation (thus surface passivation) and dissolution (activation). Figure 1b is the image of that instability. In summary, the system's instability described in Fig. 3 is because of the poor corrosion behaviour of the NiTi alloy in this solution. The passivating properties of the nickel and titanium oxides in this hypochlorite medium seem to be insufficient to maintain the chemical stability of the alloy.

Figure 9 illustrates the situation from the thermodynamic perspective. The oxidizing power of the environment (due to the oxidants present, ClO^- and Cl_2) shifts the corrosion potential in the anodic direction to values depicted in Figs 3 and 6. That potential range is depicted in Fig. 9a,b as a double arrow located on the pH 12.3 vertical dotted line. The E_{corr} potential range is located above line (b) in the diagram. This line is the equilibrium line for water oxidation (Equation 4). Thus, oxygen evolution will take place along with alloy corrosion. Figure 9b demonstrates also that the measured potential range comprises several nickel oxide phases: from the reduced form Ni_3O_4 , to the highest oxidation state NiO_2 and, in between, the Ni_2O_3 form. All those valence changes involve:

1. Density changes that induce film breakdown and hence poor protecting properties of the oxide layer.

2. Changes in the noble character of the alloy that can make it more noble than gold (see Fig. 6a) when covered by NiO_2 .

Moreover, Fig. 9a shows that at pH 12.3 the possible TiO_2 passive film is not stable and tends to dissolve chemically as HTiO_3^- for pH > 12. These results show that the alloy does not reach a stable passive state because of chemical (pH) or electrochemical (redox potential) factors. One possible mechanism to overcome these effects is lowering the solution's pH in order to:

1. Give chemical stability to TiO_2 passive film.

2. Give chemical stability to Ni oxides in the passive film. Lowering pH will shift the equilibrium in Equation 2 towards Cl_2 production, which, according to Equation 3 will increase the electrolyte's oxidizing power and thus E_{corr} will be shifted towards the NiO₂ stability domain, as depicted in Fig. 9b.

In order to verify this hypothesis, tests were carried out in a pH = 10.1 solution, prepared by addition of H_2SO_4 to the as-received NaOCl solution The resulting solution was yellowish in colour that indicates higher Cl_2 content, in agreement with Equation 2 and the increasing reactivity of the solution reported in the literature (Greenwood & Earnshaw 1990).

The corrosion potential depicted in Fig. 7 (galvanic test performed at pH 10.1) is more anodic than that depicted in Fig. 3 (galvanic test performed at pH 12.3), which confirms the previous hypothesis concerning to oxidizing power of the solution. Moreover, potential fluctuations occur at higher frequency levels and no visible damage is observed neither on the shank, nor on the cutting section, although the measured current was high. Thus, probably most current from the anodic areas (noncutting section) is because of water oxidation (Equation 4) and current at cathodic areas from Cl_2 (Equation 3) and ClO^- (Equation 2) reduction, the latter one being highly favoured on gold (Xia & Kelly 2001).

When the gold shank is electrically isolated ('shank out' in Fig. 7), the galvanic current falls to the small value existing between the cutting and noncutting sections whilst the potential decreases by 0.5 V. The



Figure 9 Pourbaix diagrams for titanium (a) and nickel (b), showing the domain of existence (pH and potential) of the studied system. The thick double arrows represent the range of corrosion potentials, E_{corr} , measured.

lack of evidence of corrosion suggests that the anodic reaction occurring on the alloy is mainly water oxidation (Equation 4), which generates a local acidic pH. Thus, the alloy will be free of oxides, which explains the observed potential decreasing. As the local pH increases because of the end of proton production, the alloy begins to passivate and E_{corr} tends to increase. If the shank is switched on again, the situation returns to the original state.

Hence, the alloy seems to be stable at pH 10.1 and represents only a support of water oxidation. The stability of the NiTi alloy in NaOCl solutions at pH 10.6 has been reported in the literature (Darabara *et al.* 2004a,b) with a corrosion current close to $0.3 \ \mu A \ cm^{-2}$, a value that certainly is an overestimation of the real corrosion rate because water oxidation was not taken into account.

The passivation rate of the NiTi alloy in both solutions (pH 12.3 and 10.1) is compared in Fig. 8, which shows the evolution of E_{corr} with immersion time. It can be seen that at pH 10.1 the alloy reaches its passive state in about 20 s, and after that the potential remains steady indicating stable passivation. Nevertheless, at pH 12.3, a steady state is not reached even after 6000 s, which proves that the alloy is not stable in this medium.

Conclusions

The kinetic and thermodynamic data suggests that the NiTi alloy corrodes at pH 12.3, mainly when galvanically coupled to gold-plated shank, because gold catalyses hypochlorite reduction. Corrosion performance can be increased by lowering the solution's pH to about 10, because the system enters the stability domain of the passivating species TiO_2 and NiO_2 .

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