

Influence of fluoride and chloride on corrosion behavior of NiTi orthodontic wires

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Abstract

The influence of fluoride and chloride ions on the corrosion behavior of nearly equiatomic nickel–titanium orthodontic wires was studied using conventional electrochemical measurement methods, including corrosion potential, potentiodynamic and cyclic potentiodynamic polarization measurements. In addition, scanning electron microscopy was employed to observe the surface morphology before and after the test. All the electrochemical parameters are analyzed based on the sample standard deviations. The results indicated that NiTi alloy is primarily susceptible to localized corrosion when exposed to a solution containing chloride, while it is susceptible to general corrosion when subjected to a solution containing fluoride. Furthermore, the synergistic interaction of fluoride and chloride on corrosion of NiTi alloy is associated with their respective molar concentrations.

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1. Introduction

In the last few decades, nearly equiatomic NiTi alloys (nitinol) have been considered as excellent biomaterials for use in biomedical implant devices since they possess unique properties, such as shape memory effect, superelasticity and good biocompatibility [1–7]. Currently, they are widely and successfully used as orthodontic wires, self-expanding cardiovascular and urological stents, bone fracture fixation plates and staples, etc. [5–9].

Like other metallic implant biomaterials, the corrosion resistance of NiTi alloys affects their biocompatibility and biofunctionality, which are two absolute requirements for ideal implant biomaterials [10]. It has been clearly shown that Ni ion release, due to the corrosion process, can lead to allergenicity, toxicity and carcinogenicity [10–13]. Also, there have been reports with regard to corrosion failure of NiTi implant biomaterials in human physiological solution [14–18].

For the purpose of hygienic health of the oral cavity, especially for the prevention of tooth decay, fluorides are widely introduced into the oral environment by means of toothpastes, mouth rinses, orthodontic gels and other therapeutic dental products [11,19]. Additionally, systemic fluorides may be ingested orally through tea, dietary supplements and fluoridated bottled water. Therefore, NiTi orthodontic wires are readily exposed to fluoride medium.

To date, there have been two main schemes used to evaluate the corrosion resistance of NiTi alloys in vitro. The first method is to use atomic absorption spectrometry [18,20,21] to analyze the Ni ion release. The second method is to use electrochemical tests [3,11,22–25] in artificial saliva to assay the electrochemical properties, such as the corrosion potential, IR drop, polarization resistance, passive current density and pitting potential (E_b), which are closely linked to biocompatibility.

There is a wealth of published studies on the corrosion resistance of NiTi alloys in simulated physiological solutions, particularly in both fluoridated and non-fluoridated Fusayama–Meyer artificial saliva [11,19,20,26–28]. It has also been well documented that fluoride exhibits a negative effect on the

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corrosion resistance of NiTi alloys [19,27]. However, there is little information to interpret the detailed aggravative effect of fluoride and no specific work has clarified whether different mechanisms exist regarding the corrosion behavior of NiTi orthodontic wires in fluoride- and chloride-containing media. Consequently, it is of importance to identify the mechanism(s), in order to provide an indepth understanding of the biocompatibility of NiTi orthodontic wires in complex physiological solutions and offer significant guidance for clinical applications of NiTi alloys.

The present work aimed to investigate the distinct corrosion characteristics of NiTi orthodontic wires in individual chloride and fluoride solutions, and quantitatively compare their different effects on the corrosion resistance of NiTi alloys. In order to achieve this objective, potentiodynamic and cyclic potentiodynamic polarization measurements were performed in a series of defined solutions which exhibited equivalent molar concentrations of chloride and fluoride ions. The corresponding corrosion morphologies before and after the test were also observed using scanning electron microscopy (SEM).

2. Materials and methods

2.1. Test materials

The material used was a commercial superelastic NiTi orthodontic straight wire (Shenzhen Superline Technology Co. Ltd., China). It consisted of 52 at.% Ni and 48 at.% Ti. The as-received NiTi orthodontic wire, with a nominal diameter of 0.02 in., exhibited an electropolished shiny surface and was not modified by other surface treatments.

For the electrochemical measurements, a series of NiTi orthodontic wires were coated at both ends using silicon gel with a bare length of 30 mm as the working electrode exposed to solution. The precise diameter and exposed length of each individual wire were measured prior to the experiment in order to obtain the actual area of the working electrode.

2.2. Test solutions

As documented in a large number of publications, chloride and fluoride are assumed to be the most corrosive agents in human saliva, and so are of the most interest to this work. Accordingly, two groups of control solutions were designated with characteristic concentration series specified based on identical molar concentrations of anions, as presented in Table 1. As stated previously, fluo-

ride has seen wide application in dentistry. Of the fluorides used, sodium fluoride is the most prevalent, rather than $\text{SnF}_2/\text{Na}_2\text{FPO}_4/\text{amine}$ fluorides or acidulated phosphate fluoride (APF) [29,30]. In many available published works, saliva solutions containing 0.1–0.3 (wt.%) sodium fluoride [19,29], and sometimes even up to 2% [31], were prepared. Consequently, NaF solutions of 0.1, 0.2, 0.3 and 0.646 (wt.%) were designed, where 0.646% NaF solution is equivalent to the common physiological solution of 0.9% NaCl in terms of the same molar concentration of the anion. Hence, the corresponding control solution group of sodium chloride was prepared based on the same molar concentration (Table 1). Moreover, it should be noted that the equivalent concentration of chloride in Fusayama–Meyer artificial saliva [19,20,31] is equal to $0.01837 \text{ mol l}^{-1}$, close to the molar concentration of 0.1% NaF solution ($0.0238 \text{ mol l}^{-1}$). Therefore, the respective influence of chloride and fluoride on the corrosion behavior of NiTi orthodontic wires can be characterized quantitatively.

In addition, three mixed solutions of equivalent molar chloride and fluoride were prepared to study the interaction, containing 0.05, 0.1 and 0.3 (wt.%) NaF, respectively.

In the electrochemical measurements, all the solutions, prepared from reagent grade agents and distilled water, were maintained at $37 \pm 0.1 \text{ }^\circ\text{C}$ (the normal temperature of the oral cavity) through a controlled-temperature water bath. It is reported that the pH value of the saliva is main in the range of 2–5 [20]. In this work, the pH value of the test solutions was adjusted to 4 [32] through the addition of an appropriate amount of lactic acid. It is well known that lactic acid exists naturally in the human oral cavity as a product of the oral cell tissues and of the bacteria [33] that reside in the dental plaque on the surface of the teeth, and is also present in various foods, such as sour milk and yogurt [34]. The pH value was measured via a digital pH meter (Type PHS-25, Wei Ye Instruments, Shanghai, China).

2.3. Electrochemical measurements

All the electrochemical measurements were performed using a potentiostat (model 273A, EG&G Instruments, Princeton Applied Research), according to the ASTM standard G5 [35]. The standard three-electrode system was adopted. The working electrode was a NiTi orthodontic wire with 0.5 mm diameter and 30 mm length exposed to solution; the counter electrode was a rectangular platinum plate ($20 \text{ mm} \times 10 \text{ mm}$); and the reference electrode was a saturated calomel electrode (SCE), which was connected to the working electrode via a salt bridge and Lug-

Table 1
Test solutions (with conversion of molar and weight concentration)

| Solution type | Concentration | | | | | | | | | |
|-----------------|---------------|---------------------|-------|---------------------|-------|---------------------|-------|---------------------|-------|---------------------|
| | wt.% | Mol l ⁻¹ | wt.% | Mol l ⁻¹ | wt.% | Mol l ⁻¹ | wt.% | Mol l ⁻¹ | wt.% | Mol l ⁻¹ |
| Sodium fluoride | 0.05 | 0.0119 | 0.1 | 0.0238 | 0.2 | 0.0476 | 0.3 | 0.0714 | 0.646 | 0.1538 |
| Sodium chloride | 0.069 | | 0.139 | | 0.279 | | 0.418 | | 0.9 | |

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