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Corrosion resistance of titanium-containing dental orthodontic wires in fluoride-containing artificial saliva

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ABSTRACT

This study was to investigate the corrosion resistance of different Ti-containing dental orthodontic wires (including Ni–Ti, Ni–Ti–Cu, Ti–Mo–Zr–Sn, and Ti–Nb alloys) in acidic fluoride-containing artificial saliva using cyclic potentiodynamic polarization curve measurements. Different NaF concentrations (0%, 0.2%, and 0.5%), simulating the fluoride contents in commercial toothpastes, were added to the artificial saliva. Surface characterization was analyzed using X-ray photoelectron spectrometry. Cyclic potentiodynamic polarization curves showed that the presence of fluoride ions, especially 0.5% NaF, was detrimental to the protective ability of the TiO_2-based film on the Ti-containing wires. This might lead to a decrease in the corrosion resistance of the tested alloys, *i.e.* an increase in the corrosion rate and anodic current density and a decrease in the passive film breakdown potential. Among the tested Ti-containing wires, the Ni–Ti and Ni–Ti–Cu wires containing mainly TiO_2 on surface film were more susceptible to fluoride-enhanced corrosion, while the Ti–Mo–Zr–Sn and Ti–Nb wires containing $MoO_3/ZrO_2/SnO$ and Nb_2O_5, respectively, along with TiO_2 on surface film were pitting corrosion resistant and showed a lower susceptibility to fluoride-enhanced corrosion. The difference in corrosion resistance of the tested commercial Ti-containing dental orthodontic wires was significantly dependent on the passive film characteristics on wires' surface.

1. Introduction

Titanium (Ti) and its alloys are used for many dental applications. The popularity of Ti and Ti alloys is primarily due to their good mechanical properties, high corrosion resistance, and excellent biocompatibility. However, Ti may also cause chemical–biological interactions. Tissue discoloration and allergic reactions in patients who have come in contact with Ti have also been reported [1]. On the other hand, nickel–titanium (Ni–Ti) wires are widely used for dental orthodontic applications due to their good working, mechanical [2–4], and anticorrosion [2,5–8] properties. Although Ni–Ti wire has a protective TiO_2-based passive film which is also formed on Ti and Ti alloys, Ni and/or Ti ions may still be released from the Ni–Ti alloy surface into the oral environment through corrosion processes [8].

It is well known that the corrosion resistance of orthodontic wire is an important factor determining its biocompatibility, because the corrosion process may have negative consequences on its biocompatibility. Furthermore, the release of metal ions from orthodontic wires via corrosion process may also stain the enamel surface, and then leads to a negative aesthetic outcome. Therefore, extensive studies on the corrosion resistance of Ni–Ti orthodontic wires have been reported [5,9–14]. However, the dissimilarity in corrosion resistance, in terms of different corrosion parameters, between Ni–Ti and other Ti-containing orthodontic wires (*e.g.*, nickel–titanium–copper (Ni–Ti–Cu), titanium–molybdenum–zirconium–tin (Ti–Mo–Zr–Sn), and titanium–niobium (Ti–Nb) alloys) in simulated oral environments is relatively limited in published literature.

In oral environments, fluoride-containing commercial mouthwashes, toothpastes, and prophylactic gels are widely used to

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Table 1
Chemical composition (wt%), provided by the manufacturer (a) and identified using energy dispersive spectrometry (b), and dimension of the as-received Ti-containing wires used in this study.

Materials	Chemical composition (wt%)	Dimension (in)
Ni–Ti	(a) 54.90% Ni, 0.2% Cr, 0.06% C, balance Ti (b) 52.5–56.2% Ni, 0.2–0.4% Cr, balance Ti	ϕ 0.016
Ni–Ti–Cu	(a) 49.10% Ni, 5.0% Cu, 0.2% Cr, 0.06% C, balance Ti (b) 46.5–50.7% Ni, 4.4–4.6% Cu, 0.3–0.5% Cr, balance Ti	ϕ 0.016
Ti–Mo–Zr–Sn	(a) 10.0–13.0% Mo, 4.5–7.5% Zr, 3.75–5.25% Sn, 0.10% C, balance Ti (b) 10.2–15.0% Mo, 5.2–6.3% Zr, 4.2–5.1% Sn, balance Ti	ϕ 0.016
Ti–Nb	(b) 42.1–46.8% Nb, balance Ti	0.017 × 0.025

prevent dental caries and relieve dental sensitivity. A fluoride mouth rinse is an effective adjunct to mechanical cleaning. Its topical effect reduces enamel decalcification and gingival inflammation, and enhances the remineralization of enamel adjacent to orthodontic brackets [15–17]. The use of topical fluorides in addition to fluoride toothpaste reduces the incidence of decalcification in populations with both fluoridated and nonfluoridated water supplies [18]. However, the detrimental effects of fluoride ions on the corrosion resistance of Ti and Ti alloys have been reported in the past decade [19–26]. Fluoride ions are very aggressive toward the protective TiO_2 film formed on pure Ti and Ni–Ti alloy [25–27]. Because the outermost surface of the commercial Ti-containing dental orthodontic wires (*e.g.*, Ni–Ti–Cu, Ti–Mo–Zr–Sn, and Ti–Nb alloys) may contain a TiO_2 film with other oxides [28], the fluoride-enhanced corrosion of these Ti-containing orthodontic wires is expected to occur. However, to the present, research on this issue is still not well known.

The hypothesis is that the fluoride ions have a negative effect on the corrosion resistance of commercial Ti-containing dental orthodontic wires. The purpose of this study was to investigate the difference in corrosion resistance among commercial Ni–Ti, Ni–Ti–Cu, Ti–Mo–Zr–Sn, and Ti–Nb dental orthodontic wires in acidic artificial saliva with different NaF concentrations, simulating the fluoride contents in commercial toothpastes. The corrosion resistance of the Ti-containing wires was correlated to the surface film characters of wires.

2. Materials and methods

2.1. Specimen preparations

Four different kinds of commercial Ti-containing dental orthodontic wires (NI-TI®, COPPER NI-TI®, TMA®, and TITANIUM NIOBIUM FA^{TM}) from Ormco Corporation, Glendora, USA, were used in this study. These wires were designated as Ni–Ti, Ni–Ti–Cu, Ti–Mo–Zr–Sn, and Ti–Nb, respectively. The chemical compositions (wt%), provided by the manufacturer and identified using energy dispersive spectrometry (EDS) (EX-200, Horiba, Kyoto, Japan), and dimension of the as-received commercial Ti-containing wires are listed in Table 1. Surface chemical compositions and surface morphology of the tested Ti-containing wires before and after corrosion tests were analyzed using X-ray photoelectron spectroscopy (XPS) (Sigma Probe, Thermo VG Scientific, East Grinstead, UK) and scanning electron microscope (SEM) (ABT-150S, Topcon Co., Tokyo, Japan), respectively.

2.2. Cyclic potentiodynamic polarization test

A potentiostat (AUTOLAB PGSTAT 30, Eco Chemie BV, Utrecht, The Netherlands) was used to perform the cyclic potentiodynamic polarization curve measurements. The as-received commercial Ti-containing wires with a length of 3 cm were used as the working electrode. The cross-sectional dimension of the tested wires was listed in Table 1. The test wire specimens were rinsed with alcohol followed by deionized water before the corrosion test. A saturated calomel electrode (SCE) and platinum sheet were used as the reference electrode and counter electrode, respectively. Modified Fusayama artificial saliva [8,10,14] was used as the corrosion test electrolyte. This artificial saliva contained 400 mg/L NaCl, 400 mg/L KCl, 795 mg/L $CaCl_2{\cdot}2H_2O$, 690 mg/L $NaH_2PO_4{\cdot}H_2O$, 300 mg/L KSCN, 5 mg/L $Na_2S{\cdot}9H_2O$, and 1000 mg/L urea (pH 5). To evaluate the fluoride concentration effect on the corrosion resistance of the Ti-containing wires, different NaF contents were added to the artificial saliva to prepare the 0.2% and 0.5% NaF concentrations, simulating fluoride concentrations contained in commercial fluorinated toothpastes. The fluoride ion concentrations in the artificial saliva containing 0.2% and 0.5% NaF were measured using a fluoride electrode (No. 27502-19, Cole-Parmer Instrument Co., Vernon Hills, USA) which revealed about 950 and 2300 ppm, respectively. Before the corrosion tests, all electrolytes (both with and without NaF addition) were adjusted to pH 5.0 using lactic acid, and were maintained at 37 °C.

The electrolyte was deaerated with argon gas for 1 h before the corrosion test. The cyclic potentiodynamic polarization curves of the test wires were measured from cathodic potential in the anodic direction with a scan rate of 1 mV/s after the wires had dipped in the electrolyte for 1 h. The reverse of the applied anodic potential was scanned when the anodic current density reached 10^{-3} A/cm^2 or the applied anodic potential reached 2 V (SCE). At least six wires were used for each corrosion test group. The corrosion test results showed good similarities.

3. Results and discussion

3.1. Surface analysis

As shown in Table 1, the chemical composition (wt%), identified using EDS, of the tested wires were as follows: Ni–Ti contained 52.5–56.2% Ni, 0.2–0.4% Cr, and balance Ti; Ni–Ti–Cu contained 46.5–50.7% Ni, 4.4–4.6% Cu, 0.3–0.5% Cr, and balance Ti; Ti–Mo–Zr–Sn contained 10.2–15% Mo, 5.2-6.3% Zr, 4.2–5.1% Sn, and balance Ti; Ti–Nb contained 42.1–46.8% Nb and balance Ti. The above-mentioned chemical compositions were close to those provided by the manufacturer, except the very minor content of 0.06% C in Ni–Ti and Ni–Ti–Cu wires.

The XPS surface film analysis results, in terms of main oxides, for the tested Ti-containing wires before (as-received condition) and after corrosion tests in 0.5% NaF-containing solution are shown in Fig. 1. The quantitatively elemental contents (in atomic percentage) corresponding to XPS surface film analysis results for the tested wires before corrosion tests are shown in Table 2. As shown in Fig. 1 and Table 2, the main oxides formed on the outermost surface film of the as-received Ti-containing wires were as follows: TiO_2 and trace NiO for the NiTi wire; TiO_2, trace NiO, and trace CuO for the Ni–Ti–Cu wire; TiO_2 and small amount of $MoO_3/ZrO_2/SnO$ for the Ti–Mo–Zr–Sn wire; similar amount of TiO_2 and Nb_2O_5 for the Ti–Nb wire. It was obvious that TiO_2 was formed on the outermost surface of all as-received Ti-containing wires. After corrosion tests in 0.5% NaF-containing solution, the presence of Ti-F complex compound (Na_2TiF_6) could be detected on all tested Ti-containing wires along with those oxides detected on the as-received wires. Huang [25,26] reported that the protectiveness of TiO_2 formed on Ti and Ti–6Al–4V alloy can be destroyed by fluoride ions when the NaF concentration exceeds 0.1% (fluoride close to 500 ppm) via the formation of a Ti–F complex compound. Note that the quan-

Table 2
Quantitatively elemental contents (in atomic percentage) corresponding to XPS surface film analysis results for the tested Ti-containing wires before corrosion tests.

Ti-containing wires	Ti	Ni	Nb	Mo	Zr	Sn	Cu	O
Ni–Ti	35	<1						[a]
Ni–Ti–Cu	33	<1					< 1	[a]
Ti–Mo–Zr–Sn	28			3	4	1		[a]
Ti–Nb	18		17					[a]

[a] *Note*: represented the balanced element.

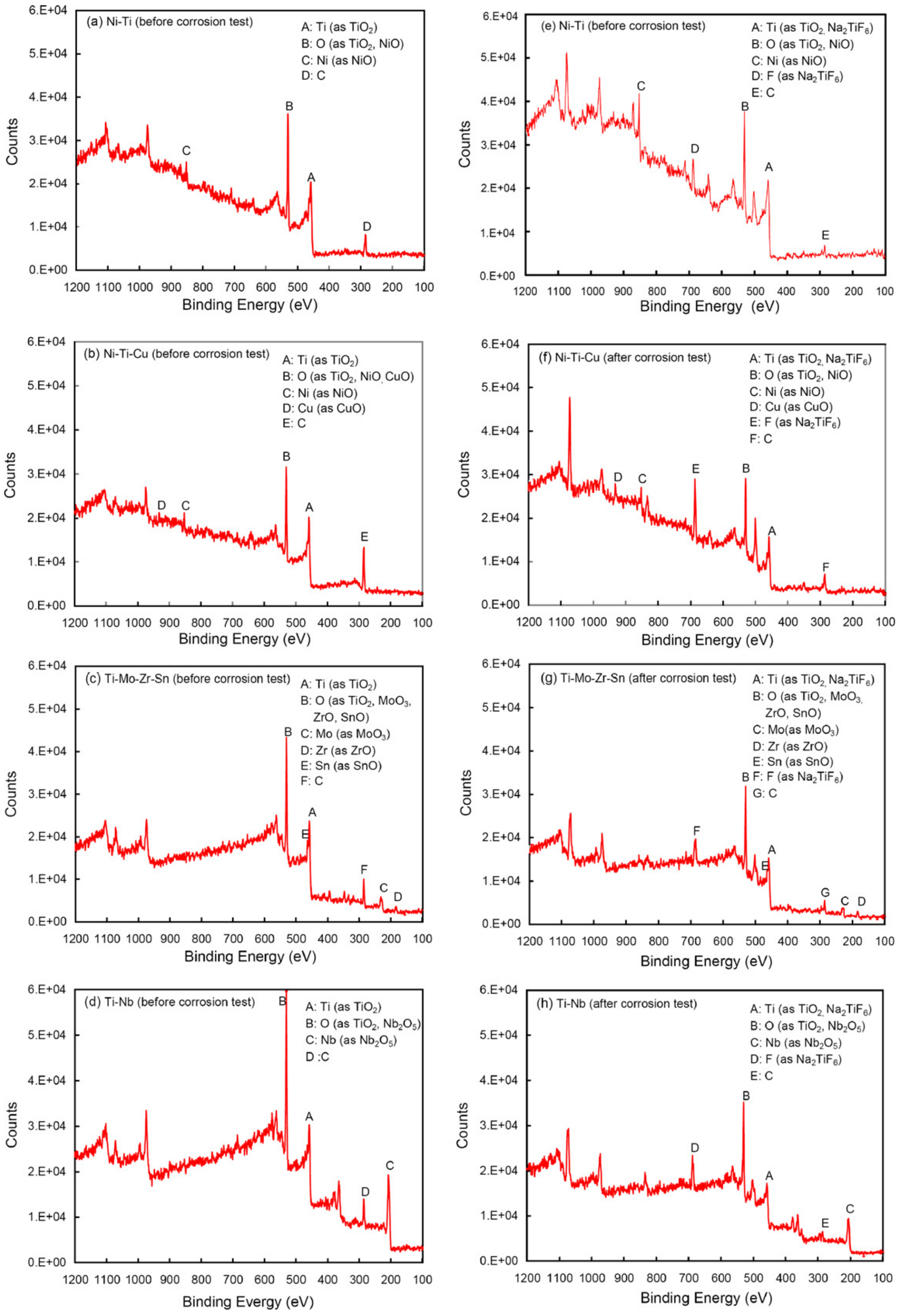


Fig. 1. X-ray photoelectron spectrometric analysis, in terms of main oxides, for the surface film on the tested Ti-containing wires (a)–(d) before (as-received condition) and (e)–(h) after corrosion tests in 0.5% NaF-containing artificial saliva.

Table 3
Corrosion parameters obtained from the polarization curves of Ti-containing wires (Ni–Ti, Ni–Ti–Cu, Ti–Mo–Zr–Sn, and Ti–Nb wires) in artificial saliva with and without NaF addition.

Materials	Artificial saliva with		
	0% NaF	0.2% NaF	0.5% NaF
(a) Corrosion rate (μA/cm^2)			
Ni–Ti	0.9 (0.2)	3.2 (0.5)	57.5 (13)
Ni–Ti–Cu	0.3 (0.1)	1.1 (0.3)	19.4 (9)
Ti–Mo–Zr–Sn	0.3 (0.1)	0.7 (0.4)	23.1 (8)
Ti–Nb	0.4 (0.2)	0.6 (0.3)	17.5 (11)
(b) Anodic current density at 0 V (μA/cm^2)			
Ni–Ti	0.6 (0.1)	16.0 (3.1)	>1000.0
Ni–Ti–Cu	0.4 (0.1)	10.1 (1.5)	495.7 (94)
Ti–Mo–Zr–Sn	0.5 (0.1)	13.3 (2.8)	311.6 (62)
Ti–Nb	0.6 (0.2)	4.5 (1.1)	163.5 (34)
(c) Passive film breakdown potential (mV)			
Ni–Ti	1302 (92)	1107 (195)	[a]
Ni–Ti–Cu	1370 (177)	1100 (214)	[a]
Ti–Mo–Zr–Sn	>2000	>2000	>2000
Ti–Nb	>2000	>2000	>2000

Note: standard deviations are given in parentheses.

[a] Indicates no protective film was present.

titatively elemental contents corresponding to XPS surface film analysis results for the tested wires after corrosion tests in 0.5% NaF-containing artificial saliva are not shown in Table 2, because the complexity in the species of artificial saliva led to a difficulty in precisely quantitative analysis.

3.2. Cyclic potentiodynamic polarization curve

Fig. 2 shows the cyclic potentiodynamic polarization curves of the as-received Ti-containing wires in acidic artificial saliva with different NaF concentrations (0%, 0.2%, and 0.5%). The corresponding corrosion parameters obtained from the polarization curves of the tested wires are listed in Table 3. Increasing the NaF concentration in artificial saliva increased the corrosion rate and the anodic current density, and decreased the passive film breakdown potential of all tested Ti-containing wires, especially for Ni–Ti and Ni–Ti–Cu wires. Among the wires tested in the NaF-containing environments, Ni–Ti wire had the highest corrosion rate and anodic current density but the lowest passive film breakdown potential; while Ti–Nb wire had the lowest corrosion rate and anodic current density. Furthermore, the passive film breakdown potential of Ti–Mo–Zr–Sn and Ti–Nb wires in artificial saliva with and without NaF addition was over 2 V (SCE) which was much higher than that of Ni–Ti and Ni–Ti–Cu wires.

The properties of surface passive film on metals play an important role in the corrosion resistance of metals. A higher passive film breakdown potential represents better passive film stability. The anodic current density at the passive region of a metal in electrolyte is related to the charge transfer resistance through the surface passive film which may form spontaneously on corrosion resistant metal. A lower anodic current density represents higher charge transfer resistance through the passive film. Basically, a protective passive film should have higher passive film breakdown potential and lower anodic current density at the passive region.

As shown in Fig. 2 and Table 3, since decreasing the passive film breakdown potential and significantly increasing the corrosion rate and anodic current density (a few to thousands of times higher) of the tested wires, increasing the NaF concentration in acidic artificial saliva led to a decrease in corrosion resistance of commercial Ni–Ti, Ni–Ti–Cu, Ti–Mo–Zr–Sn, and Ti–Nb orthodontic wires. However, the corrosion rate and anodic current density (at 0 V) of the tested commercial Ti-containing orthodontic wires in 0.2% and 0.5% NaF-containing artificial saliva (Table 3) were still lower than those of the Ti–6Al–4V alloy in 0.25% and 0.5% NaF-containing artificial saliva, respectively [26].

Previous studies have shown that the Ni–Ti and Ni–Ti–Cu orthodontic wires in commercially available fluoride (250 ppm) mouthwashes, can corrode [29,30]; the Ti–Mo–Zr–Sn orthodontic wire strongly corrodes in commercial mouthwash with lower fluoride concentration (<250 ppm) [29]. On the contrary, it has been reported that a single application of fluoride prophylactic agents in 1 month may not change the surface roughness of Ti-containing orthodontic wires (as used in this study), but a few applications of acidulated phosphate fluoride agents (estimated F ions > 10,000 ppm) may change the surface color of Ti–Mo–Zr–Sn wire which contains a large amount (about 80 wt%) of Ti [24]. In this study, we further investigated the corrosion resistance of the Ti-containing alloys in an intermediate fluoride-containing (950 and 2300 ppm) artificial saliva, simulating the commercial fluorinated toothpastes, and then correlated the results to the surface passive film characters on wires.

It has been reported that few ten ppm F ions is not enough to corrode the Ni–Ti and Ni–Ti–Cu wires in acidic artificial saliva for 10-day immersion [31]. In this study, the presence of 0.2% NaF (F ions = 950 ppm) in artificial saliva increased the corrosion rates (about 1.5–4 times) and anodic currents at 0 V (about 7.5–27 times) of the test Ti-containing wires, as compared to those obtained in fluoride-free artificial saliva (Table 3). On the other hand, the corrosion rates of the test Ti-containing wires in artificial saliva with and without 0.2% NaF (F ions = 950 ppm) were under 3.2 μm/cm^2. This value was close to or about 10 times lower than that obtained in the previous report which investigated the corrosion rate of the Ti-containing wires (as used in this study) in either aerated artificial saliva or commercial mouthwashes with F ions <150 ppm [29].

The corrosion resistance of Ti–10% Mo and Ti–15% Mo alloy in fluoride-containing solution has been investigated [32–34]. It has been reported that the anodic current at 0 V of Ti–10% Mo alloys in 0.126% NaF-containing NaCl solution is in the range of 3–7 μA/cm^2 [32], which is some less than that for Ti–Mo–Zr–Sn wire in 0.2% NaF-containing artificial saliva obtained in this study. By comparing with the previous study [33], it showed that the anodic current at 0 V of Ti–10% Mo alloy in 0.05% NaF-containing solution (estimated F ions <250 ppm) is about few times lower than that of Ti–Mo–Zr–Sn wire in fluoride-free artificial saliva obtained in this study. However, the corrosion rate and average anodic passive current of Ti–15% Mo alloy in 0.15 M NaCl + 1140 ppm F ions are 1.77 and 930 μA/cm^2, respectively [34], which are few times and few hundred times higher than those for Ti–Mo–Zr–Sn wire in 0.2% NaF-containing (F ions = 950 ppm) artificial saliva obtained in this study.

In the artificial saliva with the highest 0.5% NaF concentration, a significant anodic dissolution was observed for the Ni–Ti and Ni–Ti–Cu wires (Fig. 2 (a) and (b)), while a passive region still existed for the Ti–Mo–Zr–Sn and Ti–Nb wires (Fig. 2(c) and (d)). This indicated that no passivation occurred on the Ni–Ti and Ni–Ti–Cu wires in 0.5% NaF-containing solution. In addition, the anodic current density of the Ni–Ti and Ni–Ti–Cu wires increased with increasing the applied anodic potential and could reach 10^{-3} A/cm^2 under the tested conditions. Therefore, under such high fluoride (0.5% NaF) conditions, the protectiveness of passive film (mainly as TiO_2) on the Ni–Ti and Ni–Ti–Cu wires decayed significantly at higher anodic potentials. On the contrary, the surface film passivation still occurred on the Ti–Mo–Zr–Sn and Ti–Nb wires, even though the presence of 0.5% NaF in the test solution. This indicated that the presence of MoO_3/SnO/ZrO_2 and Nb_2O_5 in the TiO_2-containing surface film on Ti–Mo–Zr–Sn and Ti–Nb wires, respectively, was more resistance to fluoride-enhanced corrosion as compared to mainly TiO_2-based surface film on Ni–Ti and

Ni–Ti–Cu wires. Recently, the effects of Mo [35,36], Zr [37,38], Sn [39], or Nb [40] addition on the corrosion resistance of Ti metal have been investigated, which mostly focused on the individual influence of oxide (MoO_3, SnO, ZrO_2, or Nb_2O_5) on the various corrosion parameters of Ti in simulated physiological media. The effect of MoO_3/ZrO_2/SnO or Nb_2O_5 on the improvement of fluoride-enhanced corrosion resistance of Ti metal needs, however, further detailed investigations.

According to the descriptions in the International Organization for Standardization (ISO) 10271 [41], the hysteresis loop in the cyclic polarization curve can be used to obtain information on pitting corrosion. In this study, the Ti–Mo–Zr–Sn and Ti–Nb wires showed no hysteresis loop in the cyclic polarization curves in artificial saliva with and without NaF (0.2% and 0.5%) (Fig. 2(c) and (d)), indicating that these two Ti-containing wires were resistant to pitting corrosion in the above-mentioned test solutions. After corrosion tests, no pitting corrosion morphology was observed for Ti–Mo–Zr–Sn and Ti–Nb wires under scanning electron microscope investigation (not shown). On the other hand, the Ni–Ti and Ni–Ti–Cu wires, showing a hysteresis loop in the cyclic polarization curves in fluoride-free artificial saliva (as indicated by arrows in Fig. 2(a) and (b)), were susceptible to pitting corrosion. Fig. 3 shows the SEM micrographs of the tested Ti-containing wires before (as-received condition) and after corrosion test in fluoride-free artificial saliva. It revealed that the pitting corrosion occurred on Ni–Ti and Ni–Ti–Cu wires after corrosion test in fluoride-free solution (as indicated by arrows in Fig. 3(e) and (f)), which supported the results shown in Fig. 2(a) and (b). In our previous studies, pits are observed on commercial Ni–Ti dental orthodontic wires (the same as used in this study) after corrosion tests in acidic artificial saliva [10,14]. In this study, the Ti–Mo–Zr–Sn and Ti–Nb wires were more pitting corrosion resistant than the Ni–Ti and Ni–Ti–Cu wires in the acidic fluoride-free artificial saliva. This implied that the presence of MoO_3/SnO/ZrO_2 or Nb_2O_5 in the TiO_2-containing surface film improved the pitting corrosion resistance of TiO_2-based surface film in acidic artificial saliva. Although the mechanism of pitting corrosion resistance for Ti–Mo–Zr–Sn and Ti–Nb wires still needs further investigations, the above results can provide dentists with useful information on choosing pitting corrosion resistant orthodontic wires for clinical application.

It should be noted that the presence of fluoride ions in artificial saliva was detrimental to the protectiveness of TiO_2 surface film on Ni–Ti and Ni–Ti–Cu wires. As a result, the uniformly anodic

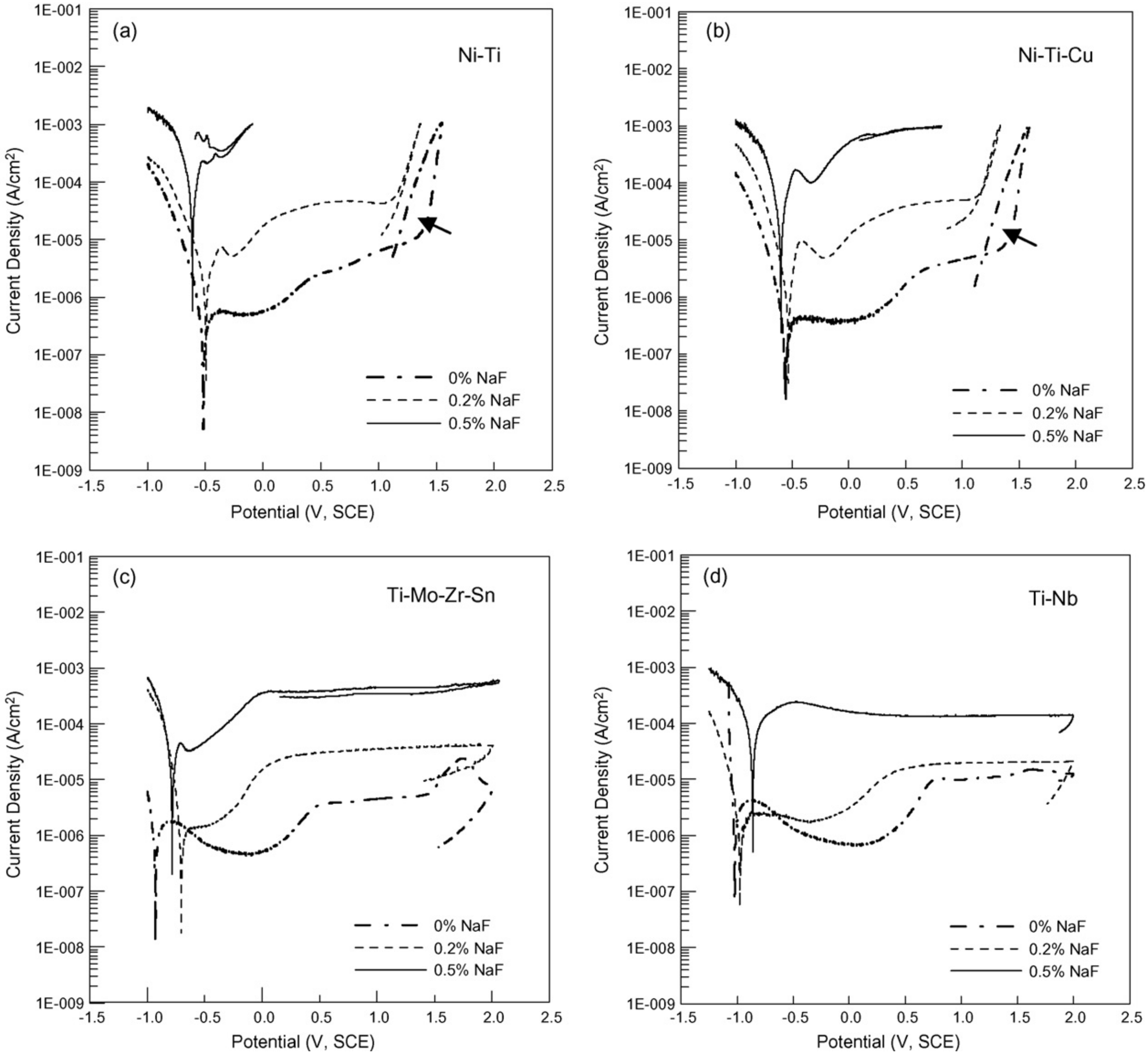
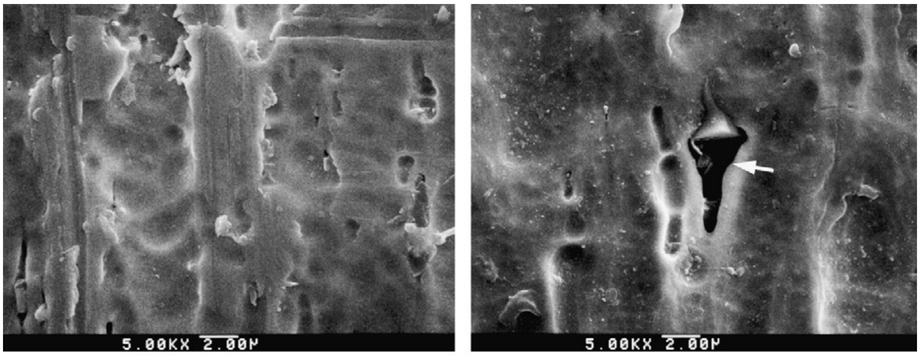


Fig. 2. Cyclic potentiodynamic polarization curves of Ti-containing wires (Ni–Ti, Ni–Ti–Cu, Ti–Mo–Zr–Sn, and Ti–Nb wires) in acidic artificial saliva with different NaF concentrations (arrows in (a) and (b) indicated hysteresis loop).

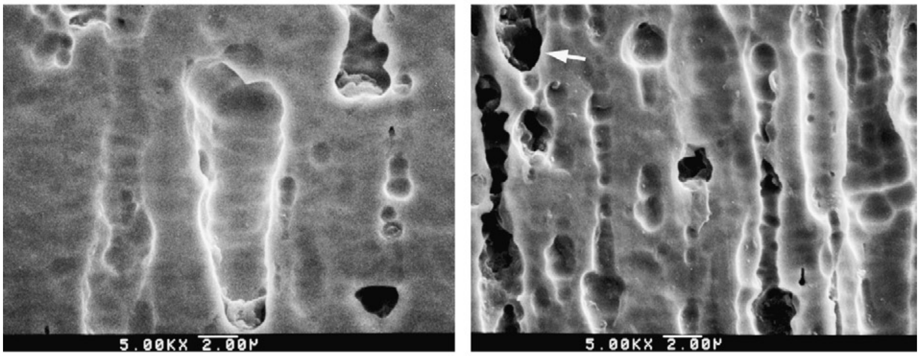
dissolution on the whole wire's surface was enhanced in high fluoride ions-containing solution, and thus the local pitting corrosion sensitivity would be relatively depressed. This might partially explain the disappearance of hysteresis loop in the cyclic polarization curves for the Ni–Ti and Ni–Ti–Cu wires when tested in NaF-containing artificial saliva (Fig. 2(a) and (b)).

The species NaF in acidic solution can induce hydrofluoric acid (HF) [42]. Then, the HF acts in response with Ti-oxide on Ti surface and destroys the protectiveness of Ti-oxide through forming Ti–F complex compound [43,44]. Namely, F ions can develop a soluble complex compound with Ti ions released from the protective Ti-oxide surface film. If the protective Ti-oxide film is



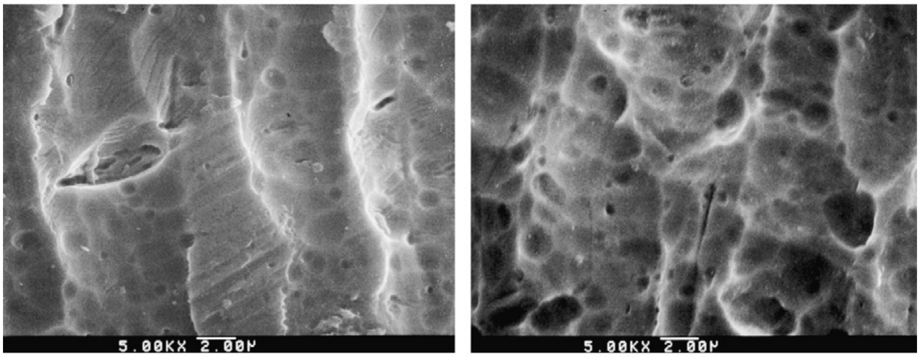
(a) Ni-Ti (as-received)

(e) Ni-Ti (after corrosion test)



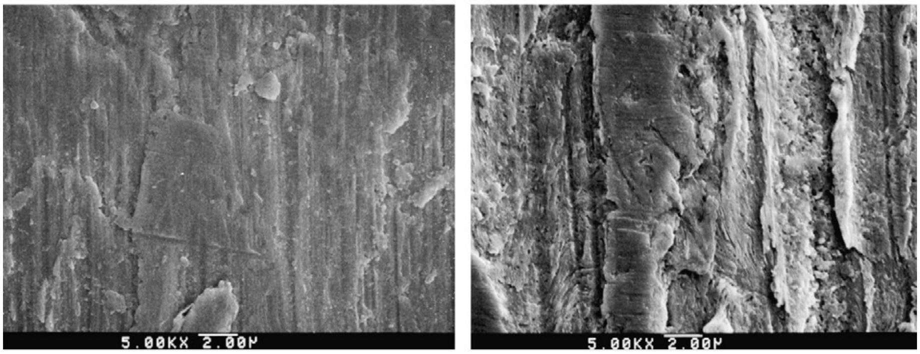
(b) Ni-Ti-Cu (as-received)

(f) Ni-Ti-Cu (after corrosion test)



(c) Ti-Mo-Zr-Sn (as-received)

(g) Ti-Mo-Zr-Sn (after corrosion test)



(d) Ti-Nb (as-received)

(h) Ti-Nb (after corrosion test)

Fig. 3. SEM micrographs of the tested Ti-containing wires before (as-received condition) and after corrosion test in fluoride-free artificial saliva.

destroyed, acidic corrosion process can occur and Ti surface will be attacked. This results in the decrease in the corrosion resistance of Ti-containing alloys in acidic fluoride-containing solution. In this study, the protectiveness of the TiO_2-containing passive film on the tested Ti-containing wires would be negatively affected by the presence of NaF in the acidic artificial saliva through the formation of complex compound Na_2TiF_6 (Fig. 1). Consequently, the corrosion resistance of Ti-containing wires decreased as the NaF concentration increased (Fig. 2 and Table 3). It was clear that the corrosion resistance of the tested commercial Ti-containing dental orthodontic wires depended on the presence of fluoride ions in acidic artificial saliva.

It is known that the release of metal ions from orthodontic wires *via* corrosion process in oral environment may stain the enamel surface, and have negative consequences on wires' biocompatibility, especially the toxicity and hypersensitivity of Ni ions [45–47]. In our previous study, if a full-mouth appliance is considered, the total released ions (mainly as Ni and/or Ti ions) from the four different kinds of commercial Ti-containing orthodontic wires (as used in this study) in fluoride-free artificial saliva are lower than 4 μg per day; the release ions of Mo, Zr, Sn, or Nb element are lower than 0.1 μg per day or negligible [28]. Therefore, it can be expected that the released Ni ions per day from the test Ti-containing wires in fluoride-free artificial saliva should be under 4 μg which is well below the critical value necessary to induce allergy (600–2500 μg) [48]. Note that Ti, a main component of the test Ti-containing wires, is not cytotoxic [49–51]. As shown in Table 3, the corrosion rate of the test Ti-containing wires in NaF-containing artificial saliva was under 100 times larger than that as tested in fluoride-free artificial saliva. Therefore, the released metal ions, especially Ni ions, from the tested Ti-containing wires in NaF-containing artificial saliva should be under 400 μg per day, which was still below the critical value necessary to induce allergy. Furthermore, it has been reported that the content of the released metal elements of Ni–Ti and Ni–Ti–Cu orthodontic wires (as used in this study) during 3-day immersion in F-containing (<500 ppm) acidic (pH 6) solution is negligible [52].

It was clear that the protective TiO_2-based passive film on the Ni–Ti and Ni–Ti–Cu wires was fully destroyed in the 0.5% NaF-containing artificial saliva. However, the TiO_2-containing passive film on the Ti–Mo–Zr–Sn and Ti–Nb wires was not seriously attacked by the fluoride ions, which was related to the presence of some other oxides (except TiO_2) in the surface passive film. In other words, with respect to the amount of TiO_2, the presence of small amount of $MoO_3/ZrO_2/SnO$ or similar amount of Nb_2O_5 in the TiO_2-containing surface film should play an effective role in improving the fluoride-enhanced corrosion resistance of the Ti–Mo–Zr–Sn and Ti–Nb wires, respectively. The mechanisms of the above-mentioned statements still need further investigations, although the corrosion resistance of Ti metal in simulated physiological media can be improved by the presence of MoO_3 [35,36], ZrO_2 [37,38], SnO [39] or Nb_2O_5 [40]. The optimal amount of $MoO_3/ZrO_2/SnO$ or Nb_2O_5 in the TiO_2-based surface film for improving the fluoride-enhanced corrosion resistance should be analyzed in the near future.

4. Conclusions

The presence of fluoride ions in artificial saliva was detrimental to the corrosion resistance of the tested commercial Ti-containing dental orthodontic wires, including Ni–Ti, Ni–Ti–Cu, Ti–Mo–Zr–Sn, and Ti–Nb alloys, especially at the higher fluoride concentration (0.5% NaF). This led to an increase in the corrosion rate and anodic current density (a few to thousands of times higher), and a decrease in the passive film breakdown potential for Ti-containing wires, especially for Ni–Ti and Ni–Ti–Cu wires. Among the tested wires, the TiO_2-based surface film with trace amount of NiO on the Ni–Ti and Ni–Ti–Cu wires was more susceptible to fluoride-enhanced corrosion, while the TiO_2-containing surface film with either $MoO_3/ZrO_2/SnO$ on the Ti–Mo–Zr–Sn wire or Nb_2O_5 on the Ti–Nb wire showed pitting corrosion resistant and lower susceptibility to fluoride-enhanced corrosion. In terms of corrosion resistance in fluoride-containing oral environments, the Ti–Mo–Zr–Sn and Ti–Nb wires would be the good candidates for orthodontic treatments among the tested commercial Ti-containing wires.

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References

[1] H. Tschernitschek, L. Borchers, W. Geurtsen, Quintessence Int. 36 (2005) 523–530.
[2] W.V. Moorleghem, M. Chandrasekaran, D. Reynaerts, J. Peirs, H.V. Brussel, Biomed. Mater. Eng. 8 (1998) 55–60.
[3] L. Torrisi, Biomed. Mater. Eng. 9 (1999) 39–47.
[4] W.A. Brantley, T. Eliades, Orthodontic Materials: Scientific and Clinical Aspects, Thieme, Stuttgart, Germany, 2001, pp. 77–104.
[5] G. Rondelli, B. Vicentini, J. Biomed. Mater. Res. 51 (2000) 47–54.
[6] B. Thierry, M. Tabrizian, C. Trepanier, O. Savadogo, L'H. Yahia, J. Biomed. Mater. Res. 51 (2000) 685–693.
[7] S.A. Shabalovskaya, Int. Mater. Rev. 46 (2001) 1–18.
[8] H.H. Huang, Y.H. Chiu, T.H. Lee, S.C. Wu, H.W. Yang, K.H. Su, C.C. Hsu, Biomaterials 24 (2003) 3585–3592.
[9] A.G. Veldhuizen, D.J. Wever, J. de Vries, H.J. Busscher, D.R.A. Uges, J.R. van Horn, Biomaterials 19 (1998) 761–769.
[10] H.H. Huang, J. Biomed. Mater. Res. A 66A (2003) 829–839.
[11] J.S. Shin, K.T. Oh, C.J. Hwang, Aust. Orthod. J. 19 (2003) 13–18.
[12] H. Kim, J.W. Johnson, Angle Orthod. 69 (1999) 39–44.
[13] N.P. Hunt, S.J. Cunningham, C.G. Golden, M. Sheriff, Angle Orthod. 69 (1999) 433–440.
[14] H.H. Huang, J. Biomed. Mater. Res. A 74A (2005) 629–639.
[15] J. Denes, K. Gabris, Eur. J. Orthodont. 13 (1991) 129–133.
[16] R.L. Boyd, J. Clin. Dent. 3 (1992) 83–87.
[17] R.L. Boyd, Angle Orthod. 63 (1993) 25–30.
[18] B.L. Chadwick, J. Roy, J. Knox, E.T. Treasure, Am. J. Orthod. Dentofacial Orthop. 128 (2005) 601–606.
[19] F. di Carlo, L.F. Ronconi, G. Gambarini, M. Andreasi Bassi, M. Quaranta, J. Dent. Res. 80 (2001) 663 (abstract #1096).
[20] E. Watanabe, I. Watanabe, T. Okabe, G. Goto, J. Dent. Res. 80 (2001) 663 (abstract #1092).
[21] N. Horasawa, M. Marek, J. Dent. Res. 80 (2001) 546 (abstract #0153).
[22] M. Nakagawa, S. Matsuya, K. Udoh, Dent. Mater. J. 20 (2001) 305–314.
[23] M. Nakagawa, S. Matsuya, K. Udoh, Dent. Mater. J. 21 (2002) 83–92.
[24] I. Watanabe, E. Watanabe, Am. J. Orthod. Dentofacial Orthop. 123 (2003) 653–656.
[25] H.H. Huang, Biomaterials 23 (2002) 59–63.
[26] H.H. Huang, Biomaterials 24 (2003) 275–282.
[27] H.H. Huang, Dent. Mater. 23 (2007) 24–33.
[28] K.L. Tung, Y.Y. Lin, H.H. Huang, Proceedings of International Corrosion Engineering Conference, Seoul, Korea, 2007, paper no. RLM-K-2.
[29] N. Schiff, B. Grosgogeat, M. Lissac, F. Dalard, Biomaterials 25 (2004) 4535–4542.
[30] N. Schiff, M. Boinet, L. Morgon, M. Lissac, F. Dalard, B. Grosgogeat, Eur. J. Orthodont. 28 (2006) 298–304.
[31] Y.H. Kwon, C.M. Jang, J.H. Jang, J.H. Park, T.H. Kim, H.I. Kim, Dent. Mater. J. 27 (2008) 133–138.
[32] A.P.R. Alves, F.A. Santana, L.A.A. Rosa, S.A. Cursino, E.N. Codaro, Mater. Sci. Eng. C 24 (2004) 693–696.
[33] M.C.R.A. Rezende, A.P.R. Alves, E.N.C.C.A.M. Dutra, J. Mater. Sci.: Mater. Med. 18 (2007) 149–154.
[34] S. Kumar, T.S.N.S. Narayanan, J. Dent. 36 (2008) 500–507.
[35] N.T.C. Oliveira, A.C. Guastaldi, Corros. Sci. 50 (2008) 938–945.
[36] N.T.C. Oliveira, A.C. Guastaldi, Acta Biomater. 5 (2009) 399–405.
[37] F.C. Giacomelli, C. Giacomelli, A.G. De Oliveira, A. Spinelli, Mater. Lett. 59 (2005) 754–758.
[38] W.G. Kim, H.C. Choe, Trans. Nonferrous Met. Soc. Chin. 19 (2009) 1005–1008.
[39] Y.F. Zheng, B.L. Wang, J.G. Wang, C. Li, L.C. Zhao, Mater. Sci. Eng. A 438–440 (2006) 891–895.
[40] Y.B. Wang, Y.F. Zheng, Mater. Lett. 63 (2009) 1293–1295.

[41] International Organization for Standardization (ISO) 10271, Dental Metallic Materials—Corrosion Test Methods, 2001, pp. 1–18.

[42] A.J. Bard, Encyclopedia of Electrochemistry of the Elements, Marcel Dekker, New York, 1976, pp. 305–395.

[43] G. Boere, J. Appl. Biomater. 6 (1995) 283–288.

[44] Y. Oda, E. Kawada, M. Yoshinari, K. Hasegawa, T. Okabe, Jpn. J. Dent. Mater. Dev. 15 (1996) 317–322.

[45] H. Kerosuo, A. Kullaa, E. Kerosuo, L. Kanerva, A. Hensten-Petterson, Am. J. Orthod. Dentofacial Orthop. 109 (1996) 148–154.

[46] M. Berger-Gorbet, B. Broxup, C. Rivard, L.H. Yahia, J. Biomed. Mater. Res. 32 (1996) 243–248.

[47] J.K. Bass, H. Fine, G.J. Cisnero, Am. J. Orthod. Dentofacial Orthop. 103 (1993) 280–285.

[48] K. Kaaber, N.K. Veien, J.C. Tjell, Br. J. Dermatol. 98 (1978) 197–201.

[49] A.M. Maurer, K. Merritt, S.A. Brown, J. Biomed. Mater. Res. 28 (1994) 241–246.

[50] P. Locci, E. Becchetti, M. Pugliese, L. Rossi, C. Lilli, M. Calvitti, N. Staffolani, J. Periodont. 67 (1996) 1260–1266.

[51] J.L. Putters, D.M. Kaulesar Sukul, G.R. Zeeuw, A. Bijma, P.A. Besselink, Eur. Surg. Res. 24 (1992) 378–382.

[52] H.S. Ahn, M.J. Kim, H.J. Seol, J.H. Lee, H.I. Kim, Y.H. Kwon, J. Biomed. Mater. Res. 79B (2006) 7–15.