Digest Journal of Nanomaterials and Biostructures Vol. 19, No. 4, October-December 2024, p. 1825-1834

Surface properties and metal ions leaching behaviors of nickel-titanium orthodontic archwires modified by oxidation

S. H. Chang*, J. X. Lin, C. H. Chiang
Department of Chemical and Materials Engineering, National I-Lan University, I-Lan 260, Taiwan

This study examined the metal ions released from nickel-titanium (TiNi) orthodontic archwires, which had been surface-modified by oxidation at various temperatures. The Ni ion was more easily leached from the TiNi orthodontic archwires than Ti ion, because the Ti atoms were readily to form passive TiO_2 films on the surface. TiNi orthodontic archwires should be heat-treated at an appropriate temperature, such as 300 and 400 °C, to possess a smooth and intact TiO_2 film on the surface, better corrosion-resistance properties, and fewer selectively leached Ni ions to ensure the long-term safety of the implantation. TiNi orthodontic archwires heat-treated at a higher temperature, such as 500 °C, may lead to poor corrosion-resistance properties and risk the increase of selectively leached Ni ions.

(Received September 21, 2024; Accepted November 28, 2024)

Keywords: Nickel-titanium, Surface modification, Heat treatment, Selective leaching, Electrochemical property

1. Introduction

TiNi shape memory alloys (SMAs) are extensively utilized as modern biomedical materials due to their distinctive shape memory effect and superelasticity [1-3]. Many biocompatibility studies suggested that TiNi SMAs are low cytotoxicity and low genotoxicity [4]. However, TiNi SMAs implanted in the human body potentially result in allergic reactions and an increased risk of cancer because of the leaching of Ni ion [5]. Shih et al. [6] reported that the corrosion products of TiNi SMAs stent were cytotoxic to rat aortic smooth muscle cells. When the concentration of released nickel ion was higher than nine ppm, growth inhibition became significant. Hahn et al. [7] demonstrated that replacing Ni atoms in TiNi SMAs by Nb can reduce the ion release of the alloys and improve their cytocompatibility for certain biomedical applications.

* Corresponding author: shchang@niu.edu.tw
https://doi.org/10.15251/DJNB.2024.194.1825

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Implant materials are often modified by surface treatments due to the degradation of biocompatibility that can arise from implant damage or interactions with surrounding tissues. Various methods have been examined to protect implants from typical corrosion damages and the deterioration of surface properties [8-10]. Many studies have investigated the corrosion characteristics of TiNi SMA surfaces modified by heat treatments [11-13]. These studies showed that the formation of TiO_2 films through heat treatment enhanced the ability of TiNi SMAs to withstand corrosion.

Firstov et al. [14] observed that NiTi alloys exhibit distinct oxidation behaviors depending on whether the temperature is above or below 500°C. At lower temperatures, a layer of TiO and metallic nickel forms beneath a TiO_2 layer containing $NiTiO_3$. This oxide layer is smooth and protective, with a relatively low oxidation rate. When the temperature reaches 600 °C or higher, rutile forms at the oxide interface, and at 800°C, an underlying layer containing $NiTiO_3$ develops. Consequently, oxidizing NiTi in air at temperatures close to 500 °C produces a smooth, nickel-free protective oxide layer that improves the biocompatibility of NiTi implants.

Chu et al. [15] investigated the surface characteristics of oxidized TiNi SMAs treated with an H_2O_2 solution and an advanced UV/H_2O_2 photocatalytic system. They found that nickel levels on the upper surface of the modified TiNi SMAs were nearly undetectable and significantly reduced throughout the titanium oxide film, which could enhance the biocompatibility of NiTi SMAs. Chang et al. [16-19] reported that the leaching behaviors of metal ions are strongly influenced by the surface properties of SMAs. Gil et al. [20] systemically studied the Ni release, friction behavior, superelastic properties, and topographical features of TiNi orthodontic archwires. They reported that the TiO_2 layer on the surface of TiNi orthodontic archwires significantly improves the corrosion resistance, but barely affecting their transformation temperatures. In this study, we aim to study the leaching behaviors of the TiNi orthodontic archwires modified by oxidation using various heat treatments.

2. Experimental

The TiNi orthodontic archwires (Ortho Organizers, Inc., USA) had a diameter of 0.4 mm and were cut into 30 mm segments. These wire samples were heat-treated individually at 300 °C, 400 °C, and 500 °C for 60 minutes and then quenched in water. Ten TiNi orthodontic archwires for each heat treatment were immersed in a beaker filled with 500 ml of Ringer's solution (Tai Yu Chemical & Pharmaceutical Co., Ltd., Taiwan) and maintained at 37 °C in an orbital shaker incubator for 60 days to obtain the leaching behaviors. Metal ion concentrations after selective leaching from the various heat-treated TiNi orthodontic archwires were measured using an Agilent 7500ce inductively coupled plasma-mass spectrometer (ICP-MS). The surface morphologies of the heat-treated TiNi orthodontic archwires were determined with a Tescan 5136 MM SEM. Chemical compositions of the surface of TiNi orthodontic archwires were analyzed by X-ray photoelectron spectroscopy (XPS) (K-Alpha, Thermo Scientific (VGS)) with 1468.6 eV Al Kα radiation source. The corrosion resistance of the heat-treated TiNi orthodontic archwires was conducted using an electrochemical workstation (ECW-5600, Jiehan). A platinum plate served as the counter electrode, a saturated calomel electrode (SCE) was used as the reference electrode.

3. Results

Figures 1(a) and 1(b) show the concentrations of Ti and Ni ions, respectively, released from the untreated, 300 °C, 400 °C, and 500 °C heat-treated TiNi orthodontic archwires. Figure 1(a) reveals that the concentrations of Ti ion after selective leaching from each specimen were deficient (below 5 ppb), including the TiNi orthodontic archwires immersed in Ringer's solution for 60 days. Figure 1(b) reveals that the Ni ion selective leaching from the untreated TiNi orthodontic archwires was above 5 ppb during the first 5 days and approached a steady value of approximately 10 ppb after 30 days. In addition, the concentrations of Ni ions released from the 300 °C and 400 °C heat-treated TiNi orthodontic archwires determined at the same immersion time were both slightly lower than those of the untreated TiNi orthodontic archwires. This indicates that oxidation at 300 °C and 400 °C reduced the selective leaching rate of Ni ions from TiNi orthodontic archwires. However, the concentration of Ni ions after selective leaching from the 500 °C heat-treated TiNi orthodontic archwires approached 43.5 ppb after 60 days. This indicates that the Ni ion leaching rate from TiNi orthodontic archwires heat-treated at 500 °C was considerably higher than that of the other treatments. According to Figure 1(b), the concentration of Ni ion after selective leaching from each specimen was much higher than that of Ti ion. This indicates that Ni ion was more easily released from the TiNi orthodontic archwires than Ti ion.

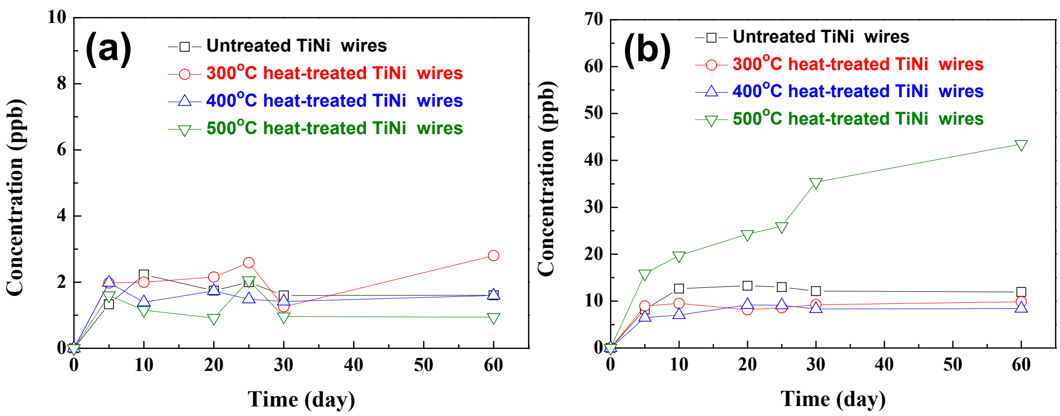

Fig. 1. The concentrations of (a) Ti and (b) Ni ion selectively leached from untreated, 300 °C, 400 °C, and 500 °C heat-treated TiNi orthodontic archwires.

Figures 2(a) to 2(d) show the surface morphologies of the untreated, 300 °C, 400 °C, and 500 °C heat-treated TiNi orthodontic archwires, respectively, using SEM observations. Figure 2(a) shows that the TiO_2 film on the untreated TiNi orthodontic archwire exhibited some scratches on the surface. These scratches were caused by the high levels of deformation caused by the wire drawing process during manufacture. Compared with the untreated TiNi orthodontic archwire, the TiO_2 films on the surfaces of the 300 °C and 400 °C heat-treated TiNi orthodontic archwires were smoother without obvious scratches or defects. Figure 2(d) shows that the TiNi orthodontic archwires after the 500 °C heat treatment also exhibited some scratches on the surface, which might be produced during manufacture process.

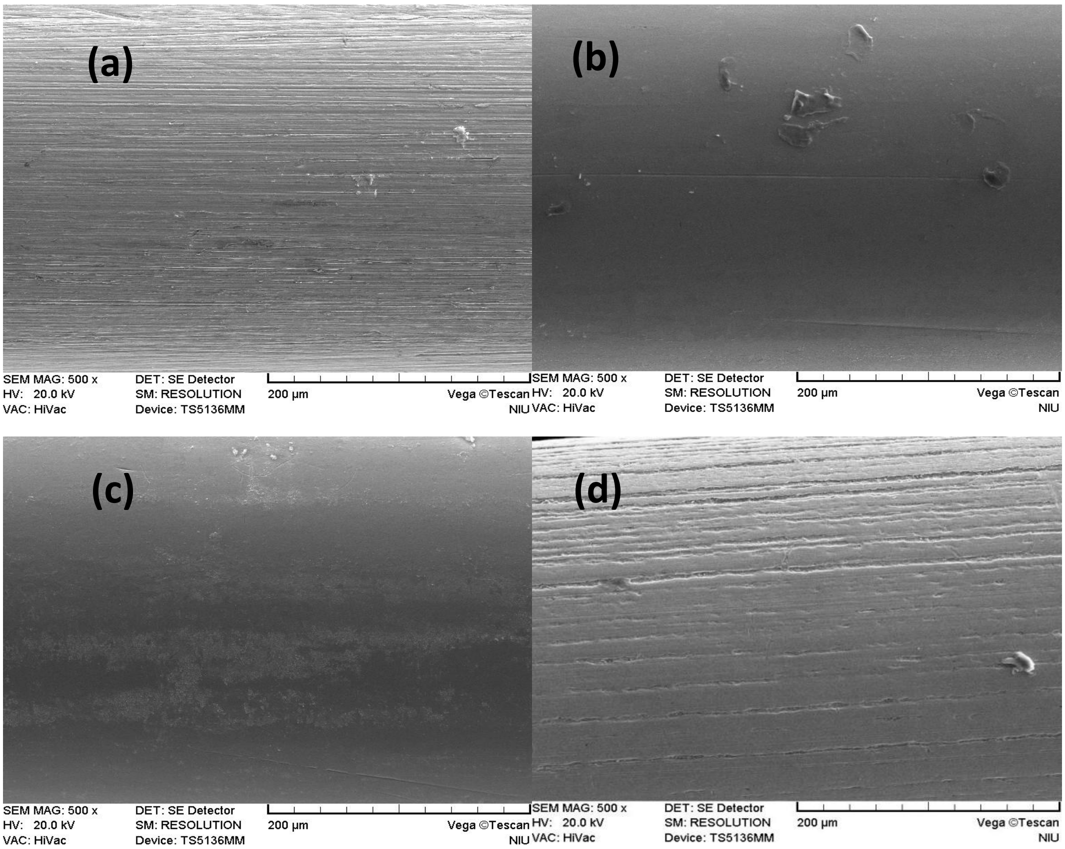

Fig. 2. SEM micrographs (500×) of (a) untreated, (b) 300 °C, (c) 400 °C, and (d) 500 °C heat-treated TiNi orthodontic archwires.

Figures 3(a) to 3(d) show the XPS survey spectra of the untreated, 300 °C, 400 °C, and 500 °C heat-treated TiNi orthodontic archwires, respectively. Figure 3(a) shows that the XPS spectrum of the untreated TiNi orthodontic archwires displays prominent peaks for Ti, O, and contaminant C, but only a relatively weak peak for Ni. This suggests that TiO2 films predominantly formed on the surface of the untreated TiNi orthodontic archwires. Figures 3(b) and 3(c) show that the XPS spectra of the 300 °C and 400 °C heat-treated TiNi orthodontic archwires were almost identical of that of the untreated TiNi orthodontic archwires, suggesting that these TiNi orthodontic archwires should also possess TiO_2 fims on their surface. However, as shown in Figure 3(d), the XPS spectrum of the 500 °C heat-treated TiNi orthodontic archwire exhibited not only the characteristic peaks of Ti, O, and C, but also showed significant characteristic peaks of Ni. Table 1 presents the elemental compositions of the TiNi orthodontic archwires calculated from Figure 3 (extruding contamination carbon). Table 1 shows that the untreated, 300 °C, and 400 °C heat-treated TiNi orthodontic archwires only possess a low Ni content below 4 at.%. However, the Ni content increased significantly to approximately 30 at.% after 500 °C heat-treatment.

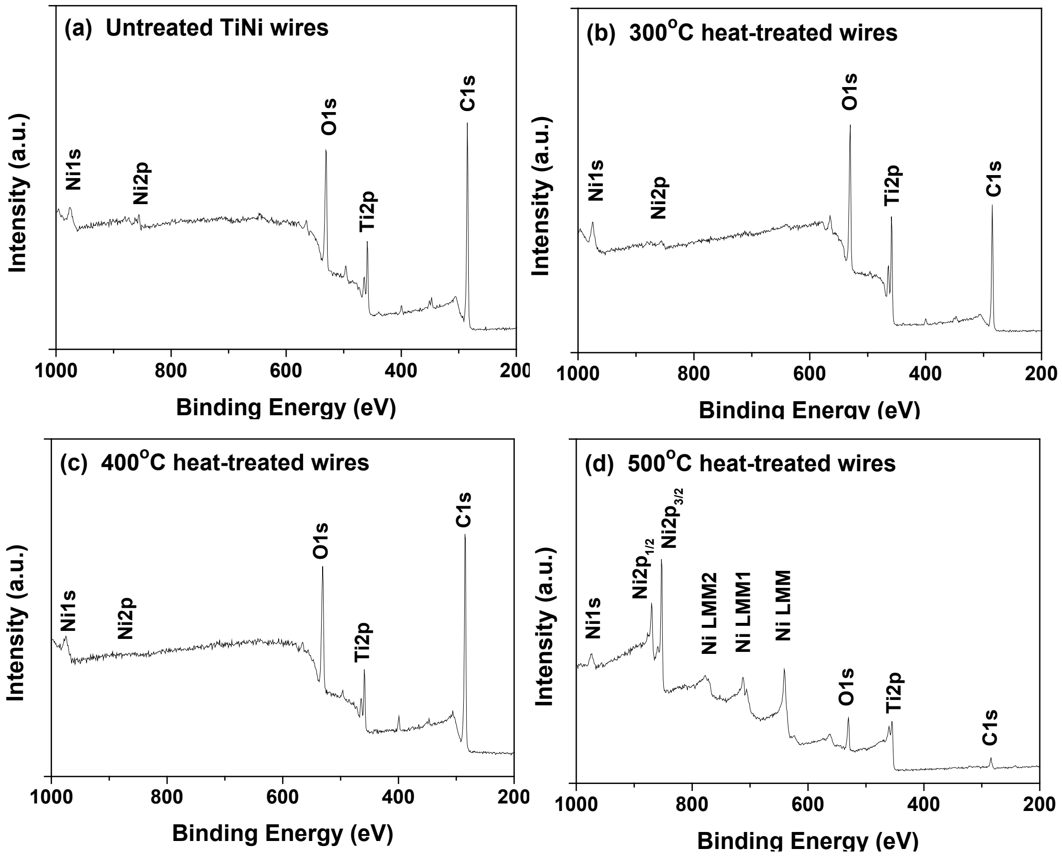

Fig. 3. XPS survey spectra of (a) untreated, (b) 300 °C, (c) 400 °C, and (d) 500 °C heat-treated TiNi orthodontic archwires.

Table 1. The elemental compositions of the TiNi orthodontic archwires calculated from Fig. 3.

	Chemical composition (at. %)		
	Ti	Ni	O
Untreated TiNi wires	19.25	3.92	76.83
300 °C heat-treated TiNi wires	24.10	2.75	73.15
400 °C heat-treated TiNi wires	16.58	1.76	81.66
500 °C heat-treated TiNi wires	27.38	30.81	41.81

Figure 4(a) shows the selected Tafel curves of the untreated, 300 °C, 400 °C, and 500 °C heat-treated TiNi orthodontic archwires measured in Ringer's solution at 37 °C. To determine the average corrosion potential (E_{corr}) and corrosion current density (i_{corr}) of each sample, five Tafel curves were measured per sample and the results are summarized in Table 2. As shown in Table 2, the untreated, 300 °C, and 400 °C °C heat-treated TiNi orthodontic archwires exhibited an E_{corr} of –0.80 V, whereas the 500 °C heat-treated TiNi orthodontic archwires exhibited an E_{corr} value of –0.84 V. These results indicate that the surface of the TiNi orthodontic archwires became more susceptible to corrosion after the 500 °C heat treatment. Table 2 also reveals that the 300 °C and 400 °C heat-treated TiNi orthodontic archwires exhibited an i_{corr} value of approximately 5.6 × 10^{-7} A/cm^2, which is lower than that of the untreated TiNi orthodontic archwire of (6.26 ± 0.02) × 10^{-7}. The i_{corr} values of the 300 °C and 400 °C heat-treated TiNi orthodontic archwires were lower than that of the untreated TiNi orthodontic archwires, suggesting a decrease in the corrosion rate of the heat-treated TiNi orthodontic archwires. However, the 500 °C heat-treated TiNi orthodontic archwires exhibited the highest i_{corr} values of (6.59 ± 0.09) × 10^{-7} A/cm^2, indicating that they showed the highest corrosion rate in the Ringer's solution.

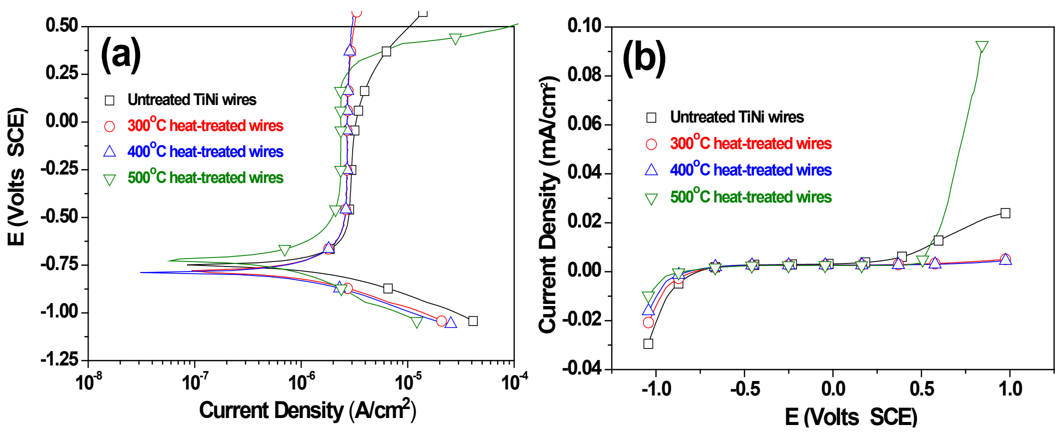

Fig. 4. (a) Cathodic and anodic polarization Tafel curves for untreated, 300 °C, 400 °C, and 500 °C heat-treated TiNi orthodontic archwires. (b) The polarization curves plotted on linear axes.

Table 2. The average E_{corr}, E_{br}, and i_{corr} values determined according to the Tafel curves in Fig. 4.

	E_{corr} (V)	i_{corr} (A/cm^2)	E_{br} (V)
Untreated TiNi wires	-0.764±0.006	(6.26±0.02)×10^{-7}	0.515±0.039
300 °C heat-treated TiNi wires	-0.787±0.003	(5.72±0.02)×10^{-7}	0.753±0.008
400 °C heat-treated TiNi wires	-0.804±0.013	(5.59±0.02)×10^{-7}	0.864±0.013
500 °C heat-treated TiNi wires	-0.842±0.031	(6.59±0.09)×10^{-7}	0.529±0.015

Figure 4(b) replots the polarization curves from Figure 4(a) on linear axes to determine breakdown potential (E_{br}). E_{br} denotes the potential at which a significant increase in anodic current is observed. Table 2 also presents the E_{br} values of the untreated, 300 °C, 400 °C, and 500 °C heat-treated TiNi orthodontic archwires determined from Figure 4(b). According to Table 2, the average E_{br} value of the untreated TiNi orthodontic archwires was determined to be 0.515 ± 0.039 V. The average E_{br} values of the 300 °C, and 400 °C heat-treated TiNi orthodontic archwires increased to 0.753 ± 0.008 V and 0.864 ± 0.013 V, respectively. However, the average E_{br} value of the 500 °C heat-treated TiNi orthodontic archwires was only 0.529 ± 0.015 V. The E_{br} is the potential at which the surface's passive film breaks down. Consequently, the 300 °C and 400 °C heat-treated TiNi orthodontic archwires possessed higher E_{br} values, indicating that the TiNi orthodontic archwires were less susceptible to initiation of pitting corrosion after surface modifications by 300 °C and 400 °C heat treatments.

4. Discussion

As depicted in Figure 1, selective leaching results reveal substantially higher concentrations of Ni ions compared to Ti ions. This phenomenon is attributable to the high thermodynamic stability of TiO_2, which facilitates the oxidation of Ti atoms near the surface [13]. The formation of the highly corrosion-resistant passive TiO_2 film on the TiNi SMA surface inhibited Ti leaching. Nevertheless, the Ni ions are more readily released from the TiNi orthodontic archwires. Figure 1 also reveals that the concentration of Ni ions after selective leaching from TiNi orthodontic archwires can be reduced after being heat-treated at 300 °C and 400 °C. This feature is associated with the fact that the Ni contents determined on the surfaces of 300 °C and 400 °C heat-treated TiNi orthodontic archwires were slightly lower than that of the untreated TiNi orthodontic archwires, as shown in Table 1. Besides, as depicted in Figure 1(b), the Ni ion concentrations for untreated and 300 °C and 400 °C heat-treated archwires reached a constant value after 10 days. This suggests that the rate at which Ni ions were being leached from these archwires reached a constant rate after 10 days. However, the concentration of the Ni ion after selective leaching from the 500 °C heat-treated TiNi orthodontic archwires was approximately 4 times higher than those selective leaching from the 300 °C and 400 °C heat-treated TiNi orthodontic archwires. This phenomenon is corresponding to the fact that the Ni content determined on the surface of the 500 °C heat-treated TiNi orthodontic archwires was much higher than those of other TiNi orthodontic archwires, as shown in Figure 3 and Table 1. According to the E_{corr}, E_{br}, and i_{corr} results shown in Table 2, the 300 °C and 400 °C heat-treated TiNi orthodontic archwires exhibited the most favorable corrosion properties. This is because the 300 °C and 400 °C heat-treated TiNi orthodontic archwires both possessed a smooth and intact TiO_2 film on the surface, as shown in Figure 2. Consequently, the 300 °C and 400 °C heat-treated TiNi orthodontic archwires exhibited the least selectively leached Ni ions, because of the protection of the intact TiO_2 films. However, as shown in Table 2, the 500 °C heat-treated TiNi orthodontic archwires exhibited the poorest corrosion resistance properties.

The 500 °C heat-treated TiNi orthodontic archwires exhibited the highest Ni content on the surface, highest Ni ion leached concentration, and poorest corrosion resistance properties are corresponding to the deteriorated surface conditions of the TiNi orthodontic archwires after 500 °C heat-treatment. Gu et al. [11] and Vojtěch et al. [13] both have reported that the Ni content increased significantly with the depth beneath the TiO_2 films of TiNi SMA. Figure 2(d) reveals that the damaged or scaled off of TiO_2 films may lead to the exposure of the abundant nickel atoms beneath the TiO_2 films, causing the high Ni content of the 500 °C heat-treated TiNi orthodontic archwires in XPS tests. Similar results have also been reported by Firstov et al. [14]. According to their SEM images, the surface morphology of the oxidized TiNi SMAs plates changes from smooth to rough with visible porous when the heat-treated temperature was increased from 300 °C to 800 °C. This is because the surface oxide layer was changed from a thin smooth TiO_2 film to a thick rough rutile layer and visible porous structure with the increasing heat-treated temperature.[14] Therefore, the TiO_2 films that are formed on the surface of TiNi orthodontic archwires can improve the corrosion and selective leaching properties of the TiNi orthodontic archwires only by oxidation at suitable heat treatment temperatures. According to our studies, we suggest that TiNi orthodontic archwires should be heat-treated at a lower temperature to possess a smooth and intact TiO_2 film on the surface, better corrosion-resistance properties, and fewer selectively leached Ni ions to ensure the long-term safety of the implantation. On the other hand, TiNi orthodontic archwires heat-treated at a higher temperature may lead to poor corrosion-resistance properties and risk the increase of selectively leached Ni ions.

5. Conclusions

This study examined the effects of surface modification by oxidation at various temperatures on the selective leaching behaviors, surface morphologies, and electrochemical properties of TiNi orthodontic archwires were investigated. Ni ions were more easily released from the surface of the

TiNi orthodontic archwires than Ti ions because the Ti atoms near the surface rapidly oxidized to form a protective TiO_2 layer. The 300 °C and 400 °C heat-treated TiNi orthodontic archwires exhibited less selective leaching of Ni ions because the intact TiO_2 films on the surfaces provided protection from corrosion. The 500 °C heat-treated TiNi orthodontic archwires exhibited the highest concentration of selective leaching of Ni ions because the TiO_2 film on the surface was damaged and caused corrosion resistance to deteriorate. Surface modification of TiNi orthodontic archwires by forming passive TiO_2 films on the surface can improve the corrosion and selective leaching resistance of the TiNi orthodontic archwires if oxidation is performed at suitable temperatures.

Acknowledgments

The authors gratefully acknowledge the financial support for this research provided by the National Science and Technology Council (NSTC), Taiwan, under Grant NSTC 112-2221-E-197-014-MY2.

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