The effect of Cu-doping on the corrosion behavior of NiTi alloy arch wires under simulated clinical conditions

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Abstract

Allergy to nickel based alloy arch wires, which is largely induced by corrosion behavior, can cause severe problems during the orthodontic treatment. However, no consensus has been reached in the comparison of anti-corrosion behavior between Nickel-Titanium (NiTi) and Copper Nickel-Titanium (CuNiTi) alloy arch wires. Herein, the anti-corrosion behavior of NiTi and CuNiTi arch wires was simultaneously studied in artificial saliva under loading stress to simulate clinical conditions. Scanning electron microscope (SEM) was utilized to detect the surface morphology and following x-ray diffraction (XRD), electrochemical impedance spectroscopy (EIS) as well as x-ray photoelectron spectroscopy (XPS) were used to evaluate the potential anti-corrosion tendency of the arch wires, implying that CuNiTi arch wire had more defects on the surface yet intriguingly less release of Ni compared with NiTi arch wire after test. Both groups of arch wires were more corroded when loaded with clinic-simulating stress, nevertheless, the doping of Cu element can reduce the release of Ni to some extent, which is conducive to lowering the probability of metal allergy and supplying meaningful instructions for the manuf actur es and orthodontists.

1. Introduction

Since the Nickel-Titanium (NiTi) alloy material was firstly introduced into the orthodontic clinic by Andreasen [1, 2] in 1971, numerous researches have flourished in this field due to its unique capability of shape memory and super elasticity. By reason of the NiTi alloy crystal structures are determined by temperature and mechanical pressure, a reversible transformation between dual crystal arrangements: austenite and martensite phase, as well as super elasticity can apply stress more accurately, thereby providing stable corrective force and improving the efficiency of tooth movement [7].
Though a small amount of Cu release donates slight anti-bacterial properties to CuNiTi arch wire, disadvantages including insufficient surface hardness and undesired surface roughness that may lead to unexpected fractures is hard to ignore [8–10]. Moreover, ideal corrosion resistance determined by surface morphology and composition, is a prerequisite that metal materials should meet, especially when they are used for clinical applications. Previous studies showed that the surface roughness of CuNiTi arch wire was larger than that of NiTi arch wires, whereas inconsistent results were observed in studies on the corrosion resistance of CuNiTi arch wires [9]. Deo K. Pun found that the corrosion rate of CuNiTi arch wire was higher than its NiTi counterpart [11], while other researchers reported that the Cu-doping would reduce the corrosion resistance of the NiTi arch wire [12, 13]. Moreover, Iijima and Zheng YF reported that minute amount of doped Cu can regulate the superelastic properties of the alloy, rather than its corrosion resistance in the simulated clinical environment [14, 15]. In fact, the differences in corrosion resistance and the specific corrosion mechanism between CuNiTi and NiTi arch wires have not been clear yet. Thus, Damon CuNiTi and Smart NiTi arch wires were selected as samples to determine whether surface roughness or composition weighs more in the anti-corrosion of arch wires by exploring the corrosion resistance and the release of Ni in artificial saliva under stress loading, which simulates clinical conditions during orthodontic treatments, providing experimental reference and theoretical guidance for orthodontic arch wires application and selection.

2. Experimental

2.1. Preparation of artificial saliva
Artificial saliva was prepared according to the ISO/TR10271 standard, and the composition ratio was shown in table 1. After the artificial saliva was prepared according to the above formula, the pH value was adjusted to 6.75 with lactic acid.

2.2. Stress-loading device
Damon CuNiTi (Ormco, USA) and Smart NiTi (Beijing Smart Technology Co. LTD., China) arch wires were selected as samples in this experiment and the main composition of them, according to instructions provided by
manufacturers, was listed in table2. U-shaped bending was used to simulate the stress-loading environment of the NiTi arch wire in the orthodontic practices. The stress-strain curve of the NiTi arch wire was found to be linear within a certain strain range. When the linear strain region is exceeded, the corresponding relationship between the strain and stress will change and permanent deformation may happen. In order to select the appropriate stress application value, we cut the straight parts at the end of arch wires as samples which were fixed in the holes of the resin board by adhesive with 13 mm exposed to artificial saliva and set the distance between the two holes to 10 mm (figure 1). Then, we made sure that permanent deformation did not happen on the arch wires after stress loading.

2.3. Surface morphology and composition analysis
We selected the straight ends (length, 10 mm) of the two arch wires as samples and cleaned them in ethanol (75 wt.%) and deionized water by ultrasonic for 5 min respectively, and then dried with cool air blow. Scanning Electron Microscope (SEM, Merlin compact, Germany) was used to observe the surface morphology of the arch wires, and the x-ray Energy Dispersive Spectroscopy (EDS, Merlin compact, Germany) was used to analyze the surface of the samples. X-ray diffraction (XRD, Bruker D8 ADVANCE, China) analysis was used to determine its phase structure and the element composition, valence state and chemical bond of the sample surface were analyzed by x-ray photoelectron spectroscopy (XPS, Thermo Fisher, China).

2.4. Electrochemical test
The straight ends (length, 20 mm) of the two arch wires were cut as samples and then exposed to artificial saliva with a length of 10 mm. After confirming that there was no wrong with the conductivity, we used the same steps as mentioned in 2.3 to clean them. The electrochemical test method was used to study the corrosion resistance of the material. The classic three-electrode system was applied: a 10 mm arch wire served as the working electrode with a 20 mm × 20 mm platinum auxiliary electrode; a saturated calomel electrode (SCE, 232–01, China) was used as the reference electrode. The artificial saliva served as the erosion environment and the temperature was set to be a constant 37 °C in a water bath.

At the beginning of the experiment, the open circuit potential (OCP) curve was measured for 10 min. After the OCP was stabilized, the electrochemical impedance spectroscopy (EIS, CS2350H, China) and dynamic potential polarization curve were tested. The amplitude of the excitation potential of the EIS test was 10 mV and the frequency sweep range was 100 kHz − 10 mHz. The potentiodynamic polarization curve adopted a potential scanning rate of 5 mV s⁻¹ with a scanning range of −0.5–2 V (Versus V OCP). To ensure the repeatability of the experiment, the above experiment was repeated for three times.

2.5. Immersing experiment
We divided samples of both arch wires into NiTi-stress-loading, NiTi-nonstress-loading, CuNiTi-stress-loading and CuNiTi-nonstress-loading group and briefly called them NiTi-L, NiTi-NL, CuNiTi-L and CuNiTi-NL group respectively. Then all groups were immersed in the artificial saliva at 37 °C and we used SEM to observe the surface morphology of the samples soaked for 7, 14 and 28 d respectively and XPS to test the composition of the surface of the samples soaked for 28 d. The leaching solutions were tested for Ni concentration by inductively coupled plasma mass spectrometry (ICP-MS, NexION 350D, China).
Figure 3. The micro morphology of CuNiTi arch wire before corrosion: (a) 500X; (b) 1000X (The red arrows point to the typical defects).

Table 3. The EDS result of NiTi arch wire.

| Element | wt.% | wt.% Sigma | Atom percent |
|---------|------|------------|--------------|
| O       | 1.14 | 0.53       | 3.70         |
| Ti      | 42.06| 0.93       | 45.82        |
| Ni      | 56.56| 1.08       | 50.27        |
| Cu      | 0.24 | 1.31       | 0.20         |
| Total   | 100.00| 100.00     | 100.00       |

Table 4. The EDS result of CuNiTi arch wire.

| Element | wt.% | wt.% Sigma | Atom percent |
|---------|------|------------|--------------|
| O       | 2.30 | 0.50       | 7.35         |
| Ti      | 41.09| 0.88       | 43.84        |
| Ni      | 49.62| 1.02       | 43.19        |
| Cu      | 6.99 | 1.18       | 5.62         |
| Total   | 100.00| 100.00     | 100.00       |

Figure 4. The phase Composition of the surface of the two arch wires before corrosion by XRD.
3. Results

3.1. Surface morphology and composition analysis
The pitting and point defects could be observed on the surface of the two unused arch wires (figures 2 and 3) and the pitting were unevenly distributed on the surface of the arch wires with few point defects. Compared with that of the NiTi arch wire, point defects on CuNiTi arch wire were larger and deeper.

The EDS results showed that the surface of the NiTi arch wire was mainly composed of Ni and Ti with a dominant 56.56% Ni content and a 42.06% Ti content (table 3), while that of the CuNiTi arch wire was mainly composed of Ni, Ti and Cu, with a 49.62%, 41.09% and 6.99% content respectively (table 4). There was also an oxide layer on the surface of the both two wires. The Ni content in NiTi arch wire was higher than that of CuNiTi arch wire and there was only a small amount of Cu on the NiTi arch wire (tables 3 and 4).

The XRD results of the two arch wires showed that both accorded with the characteristics of the cubic crystal NiTi alloy with no impure phases, indicating that the sample had good crystallinity and a rather single-phase composition. Despite the doping of a small amount of Cu, the alloy still mainly showed the NiTi alloy phase, indicating that Cu did not cause significant changes in the structure of the CuNiTi arch wire (figure 4).

3.2. Comparison of the corrosion resistance of two arch wires without stress loading
The OCP curve of the two arch wires that were soaked in artificial saliva for 0.5 h in advance showed that after 10 min of testing, the NiTi arch wire and CuNiTi arch wire gradually stabilized at $-0.2598 \text{ V}$ and $-0.28073 \text{ V}$.
Figure 7. The EIS results of the two arch wires in artificial saliva, Bode.

Figure 8. The equivalent circuit of the EIS results.

Figure 9. The polarization curves of the two arch wires in artificial saliva.

Table 5. The EIS result of NiTi/CuNiTi arch wires in artificial saliva.

| Arch wires types | $R_s$ (Ω·cm$^2$) | CPE-T(F) | CPE-P(F) | $R_p$ (kΩ·cm$^2$) |
|------------------|-----------------|----------|----------|-------------------|
| NiTi             | 26.31           | 2.2683E-5| 0.93986  | 2858.6            |
| CuNiTi           | 29.12           | 2.238E-5 | 0.8822   | 1452.4            |
Figure 10. The microscopic appearance of NiTi and CuNiTi arch wire of stress-loading and nonstress-loading groups after soaking in artificial saliva for 7, 14, 28d (500X) (The red arrows point to the typical defects).

Table 6. The polarization curve result of NiTi/CuNiTi arch wires in artificial saliva.

| Arch wires types | $E_{corr}$ (V) | $I_{corr}$ (μA cm$^{-2}$) |
|------------------|----------------|---------------------------|
| NiTi             | $-0.2598$      | 0.2486                    |
| CuNiTi           | $-0.2807$      | 0.2648                    |

Figure 11. The XPS diagram of NiTi arch wire before and after corrosion. A line: before corrosion; B line: soaking for 28 d in the nonstress-loading group; C line: soaking for 28 d in the stress-loading group.
(figure 5) indicating that the corrosion resistance of CuNiTi arch wire was slightly higher than that of the NiTi arch wire.

The EIS result showed that the Nyquist diagram (figure 6) of the alloy was an incomplete semicircle and CuNiTi arch wire had smaller impedance arc radius than its NiTi counterpart, indicating that it had worse corrosion resistance. Besides, Bode diagram (figure 7) showed a relatively wide phase angle, indicating that the passivation films of the two materials are relatively dense. The EIS was fitted with Z-view software and the equivalent circuit was shown in figure 8. Among parameters of the circuit, $R_s$ is the resistance of the solution, and CPE is the interfacial capacitance. Similar fitting results of these two parameters proved that the test system was basically the same. $R_p$ is the polarization resistance commonly used to evaluate the corrosion resistance of the passivation film of the alloy. In brief, the larger the $R_p$, the better the corrosion resistance of the alloy passivation film would be. The NiTi and CuNiTi arch wire’s $R_p$ were 2858.6 kΩ·cm², 1452.4 kΩ·cm² respectively, indicating that NiTi one had better corrosion resistance (table 5).

The polarization curves of the two arch wires in artificial saliva were shown in figure 9. Curve patterns of the two wires were similar and both were in line with typical passivation characteristics, indicating that both wires had the same corrosion resistance in artificial saliva. The self-corrosion potential ($E_{corr}$) and corrosion current density ($I_{corr}$) were calculated and listed in table 6. The results showed that the $I_{corr}$ of the NiTi arch wire was higher than that of the CuNiTi arch wire, indicating that the NiTi arch wire had better corrosion resistance; the $E_{corr}$ refers to the OCP in a steady state, sharing similar meanings as the OCP results mentioned above.

### 3.3. Comparison of corrosion mechanism of two arch wires under stress loading

SEM results showed that with the extension of the immersing time, the point defects on the surface of the arch wires in all NiTi groups gradually increased and became larger. The NiTi-L group showed deeper surface defects and dents at the same immersing time than that of the NiTi-NL group. The similar results also appeared in the CuNiTi groups (figure 10).

The XPS results of the NiTi arch wire were shown in figure 11. The main elements before immersing were Ti, Ni, and O, which was consistent with the EDS test results. The Ti element had two main high-resolution peaks, both of which were peaks of TiO₂. Among them, the peak appearing at 458.8 eV represented Ti2p3/2, and the latter one represented Ti2p1/2; besides, the two peaks of Ni element were Ni2O₃ (856.3 ev) and NiO (852.7 ev) which meant that the main component of the outermost oxide film of NiTi arch wire was TiO₂ with a small amount of Ni₂O₃ and NiO. After the wires soaked in artificial saliva for 28 d, XPS analysis showed that the Ti element was relatively stable in the NiTi-NL group while the obvious shift to the direction of high binding energy occurred in the NiTi-L group. The ratio of the two peaks of Ni element (Ni2p3/2: 852.7 ev, 856.3 ev) of both

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**Figure 12.** The XPS diagram of CuNiTi arch wire before and after corrosion. A line: before corrosion; B line: soaking for 28 d in the nonstress-loading group; C line: soaking for 28 d in the stress-loading group.
groups changed significantly, more obvious in the NiTi-L group than that of NiTi-NL group. Meanwhile the corresponding peak of the 529 eV metal-oxygen bond in the O1 s spectrum continuously strengthened.

The XPS results of CuNiTi arch wire were shown in figure 12. The main elements on the surface of the arch wire before immersing were Ti, Ni, Cu, O, which was consistent with the EDS test results. The main high-resolution peaks of Ti showed similar results as the NiTi wire. Only the NiO peak was observed in the Ni spectrum and the Cu element peaked at 933.6 eV representing Cu2p3/2, indicating that the main component of the outermost oxide film was TiO2 with a small amount of CuO and NiO. After the wires soaked in artificial saliva for 28 d, the Cu element signal peaks of both groups almost disappeared; the peak signal of the Ni element spectrum also weakened; the peak of the O1 s spectrum remained stable and no obvious deviation was found between CuNiTi-L and CuNiTi-NL group. The peak of the Ti element spectrum only had a small amount of deviation which was smaller than that of the NiTi-L group.

3.4. Comparison of ion release behavior of two arch wires under stress loading

With the extension of the soaking time, the Ni release of all nonstress-loading groups gradually increased and that of the NiTi-NL group was higher than that of the CuNiTi counterpart, which were statistically different for all the timepoints ($P < 0.05$; **$P < 0.01$; ***$P < 0.001$) (figure 13(a)). The similar trend of the release of Ni was also seen in stress-loading groups: the amount of the Ni release grew steadily with the corrosion time. And the statistical difference occurred for all the timepoints ($P < 0.05$) (figure 13(b)). It was also noteworthy that both arch wires had a significantly more Ni release under stress loading compared with those without. In addition, it was true that the Ni release in artificial saliva of all the groups was less than the European Union (EU) Ni release standard (table 7).

![Figure 13. The Ni release of the arch wires with different immersing time, (a) Nonstress-loading group; (b) Stress-loading group. *: $P < 0.05$; **: $P < 0.01$; ***: $P < 0.001$.](image)

![Figure 14. The Cu release of the arch wires with different immersing time. NS: no significance.](image)

Table 7. The Ni release of NiTi/CuNiTi arch wires in artificial saliva.

| Sample       | Sample area (cm²) | Nickel ion release ($\mu$g cm⁻²/week) | Used for long-term contact with skin | Used for piercing |
|--------------|-------------------|---------------------------------------|-------------------------------------|------------------|
| NiTi-NL      | 0.4355            | 0.2067 ± 0.0039                       | qualified                           | qualified        |
| NiTi-L       | 0.4355            | 0.2901 ± 0.0032                       | qualified                           | qualified        |
| CuNiTi-NL    | 0.4355            | 0.1592 ± 0.0030                       | qualified                           | qualified        |
| CuNiTi-L     | 0.4355            | 0.2470 ± 0.0132                       | qualified                           | qualified        |
In contrast, there was no significant difference between the Cu release of CuNiTi-NL group and that of CuNiTi-L group at all time points (figure 14). Besides, no obvious trend of the Cu release was observed in each group during the whole period.

4. Discussion

The effect imposed by the doping of Cu on the corrosion mechanism and surface morphology of the alloy are not clear. SEM results showed that the surface roughness of CuNiTi arch wire was greater than that of NiTi arch wire. This may be due to the doping of Cu, which requires changes in the surface processing technology. Many scholars have also found that there were more or less defects on the surface of NiTi alloy [16, 17]. These defects were prone to pitting corrosion in the complex oral environment [18, 19]. A small amount of O signal of the two samples in the EDS results showed that the oxide film on the surface of the arch wires existed. The XRD test results confirmed that the crystal structures of the two NiTi alloys were basically the same. Therefore, the same phase composition of these two arch wires suggested a good comparability of this study.

In this study, two arch wires showed similar corrosion behavior under similar testing environment and the corrosion resistance of CuNiTi was slightly worse than NiTi arch wire according to the EIS, OCP and polarization curve results, which is in accordance with some studies while contradicted other mentioned in the introduction. Some researchers [20–22] found that the Cu content of CuNiTi would lead to different phase transition behaviors and J. Briceño’s research [23] results showed that the presence of martensite phase improved corrosion resistance and significantly reduced the release of Ni other than the fact that the surface morphology would affect it too. Hence, the contradiction results may be due to the different proposition of Cu in the alloy and various alloy processing technologies [24].

The XPS and SEM results indicated that though corrosion pitting appeared on the surface of the arch wire, the corrosion intensity was low, which did not affect the stability of the Ti of the NiTi arch wire remarkably in NiTi-NL group. Ti is easily oxidized to form a dense oxide film which prevents metal from being corroded and ions from entering the solution and thus protects the alloy from corrosion, so the NiTi alloy generally has good corrosion resistance. The valence state of the Ti and O changed in the NiTi-L group, which indicated the Ti oxide film on its surface might have been greatly damaged. This change was consistent with the SEM results. In addition, after the corrosion, the ratio of Ni\(^{2+}\) and Ni\(^{3+}\) changed, which confirmed that the corrosion caused a certain change in the valence state of nickel on the surface and some Ni\(^{2+}\)/Ni\(^{3+}\) might be eluted in both NiTi groups.

It is worth noting that although the CuNiTi arch wire corroded more remarkably than the NiTi arch wire according to its morphology changes under the same conditions, XPS results showed that Ti2p and O1s remained stable in the CuNiTi-NL group. Even in the CuNiTi-L group, the binding energy of Ti only shifted slightly, indicating its good stability. Before the corrosion, the Cu2p signal on the surface of the arch wire was obvious, but there was almost no corresponding peak position after the corrosion in both CuNiTi groups. Therefore, it could be inferred that the obvious corrosion pitting on the surface of the CuNiTi arch wire were mainly caused by the preferential corrosion of Cu, because of which the stability of the CuNiTi alloy’s main structure was protected, and the release of Ni was reduced. Previous study also showed that the amount of Ni release in the NiTi alloy depended on the content of Ni in the solid solution, but it could be influenced by the presence of Cu [6, 25]. This could be explained by the higher chemical bonding energy of Cu than Ni and Ti and thus the ability of Cu to lose electrons is stronger than that of Ni and Ti. As a result, when corrosion occurs, the corrosion preferentially occurred on the Cu.

The ion release and SEM analysis revealed two facts: stress-loading condition would enhance the Ni release in both groups, indicating extra stress corrosion crack (SCC) happened; the amount of Ni release in the CuNiTi arch wire was significantly lower than that in the NiTi arch wire, indicating that the addition of Cu in the alloy imposed a certain inhibitory effect on the release of Ni. Both results were consistent with the former analysis. Firstly, Stress corrosion crack (SCC) requires three conditions to be met at the same time, namely a specific medium, a sensitive alloy and a certain stress. In this experiment, the all three necessary elements were in place and thus the differences of the corrosion behavior between the stress-loading and nonstress-loading groups could be explained by this phenomenon. Several researchers also proved that stress could increase the nickel release [26]. The density and width of the surface oxide cracks dramatically increased with decreasing radius of U-shape bending device [27]. Then, the surface of inner metal content was exposed in the corrosive medium, on which the oxide film could not be formed in time, and the stress corrosion thus happened, resulting in a faster ion release. Moreover, Jianqiu Wang proved that Ni-Ti arch wires did undergo stress corrosion by the failure analysis of deformed arch wires; high stress and acidic saliva contributed greatly to the stress related metal corrosion [28]. The rupture of the passive film may act as major cause of corrosion cracking. Secondly, the Ni release of NiTi arch wire was higher than that of CuNiTi counterpart due to the different chemical bonding.
energy mentioned above. On the other hand, the Cu release remained steady during the soaking process and no significant difference was observed between stress-loading and nonstress-loading groups. In other words, the Cu release was at similar level, whether there was the presence of the stress-loading condition or not. This is probably because the content of Cu was rather limited in the alloy and thus the Cu release reached a plateau soon after corrosion began. The experimental results showed that both arch wires were qualified for the release of Ni but it should be noted that the EN 1811:2011 standard was set for jewelry and there is no standard for the release of Ni for metallic materials in oral environment. The corrosion rate of metals and the release of Ni are bound to be affected by pH, stress, temperature, saliva conditions, mechanical loads, microorganisms, enzymes, and bacterial acidic substances and the galvanic corrosion may happen when other metal materials exist [11, 29–33]. Therefore, the actual amount of Ni released in oral environment may be higher than the amount detected in this study. In clinical practices, attention should be paid to the release of Ni.

5. Conclusions

In summary, the corrosion behavior of NiTi and CuNiTi alloy wires under stimulated clinical conditions was systematically investigated in the study. The main conclusions were listed as follows:

1. Although the corrosion resistance of CuNiTi are slightly worse than that of NiTi arch wires, both of them are within acceptable range.
2. CuNiTi arch wires releases less Ni$^{2+}$/Ni$^{3+}$ ions than NiTi arch wire in both conditions, implying that the corrosion pitting on the surface of arch wire is mainly caused by the preferential corrosion of Cu, by which way the release of Ni is reduced.
3. Stress-loading conditions can significantly enhance the Nickel release of both arch wires, while exerting little influence on Cu release.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

[1] Andreasen G F et al 1972 A use hypothesis for 55 Nitinol wire for orthodontics Angle Orthodontist 42 172
[2] Andreasen G F et al 1971 An evaluation of 55 cobalt substituted Nitinol wire for use in orthodontics Journal of the American Dental Association 82 1373–5
[3] Denkhaus E et al 2002 Nickel essentiality, toxicity, and carcinogenicity Critical Reviews in Oncology/Hematology 42 35–36
[4] Miura F 1986 The super-elastic property of the Japanese NiTi alloy wire for use in orthodontics American Journal of Orthodontics Dentofacial Orthopedics 90 1–10
[5] Sara et al 2016 Comparison of the mechanical properties of NiTi/Cu bilayer by nanoindentation and tensile test: molecular dynamics simulation Mater. Res. Express 3 126504
[6] Gil F et al 2004 Microstructural, mechanical and citotoxicity evaluation of different NiTi and NiTiCu shape memory alloys Journal of materials science Materials in Medicine 15 1181–5
[7] Taghizadeh M et al 2018 A Combined Analytic, numeric, and experimental investigation performed on NiTi/NiTiCu bi-layer composites under tensile loading Adv. Eng. Mater. 20 1700395
[8] Abdo G M et al 2013 Mechanical properties of NiTi and CuNiTi shape-memory wires used in orthodontic treatment. Part 1: stress-strain tests Dental Press Journal of Orthodontics 18 35
[9] Gravina M et al 2014 Mechanical properties of NiTi and CuNiTi wires used in orthodontic treatment. Part 2: microscopic surface appraisal and metallurgical characteristics J Dental Press Journal of Orthodontics 19 69–76
[10] Fabregat-Sanjuan A et al 2014 NiTiCu shape memory alloy characterization through microhardness tests Journal of Materials Engineering Performance 23 2498–504
[11] Pun D et al 2008 Corrosion behavior of shape memory, superelastic, and nonsuperelastic nickel–titanium-based orthodontic wires at various temperatures J dental materials : official publication of the Academy of Dental Materials 24 221–7
[12] Fragou S et al 2010 Effect of topical fluoride application on titanium alloys: a review of effects and clinical implications Pediatr Dentistry 32 99–105 https://pubmed.ncbi.nlm.nih.gov/20483011/
[13] Yi-hui X et al 2014 Corrosion resistance of 3M nickel–titanium arch wires and Damon copper–nickel–titanium arch wires in different artificial saliva with different fluoride and pH Chinese Journal of Tissue Engineering Research 18 2506–11
[14] Iijima M et al 1998 Effect of Cr and Cu addition on corrosion behavior of Ni–Ti alloys J Dental Materials Journal 17 31–40
[15] Zheng Y et al 2008 The electrochemical behavior and surface analysis of Ti49.6Ni45.1Cu5Cr0.3 alloy for orthodontic usage Journal of Biomedical Materials Research. Part B, Applied Biomaterials 86 335–40
[16] Bourauel C et al 1998 Surface roughness of orthodontic wires via atomic force microscope, laser specular reflectance, and profilometry European Journal of Orthodontics 20 79–92
[17] Višnja K et al 2014 Influence of surface layer on mechanical and corrosion properties of nickel–titanium orthodontic wires The Angle Orthodontist 84 1041–8
[18] Cissé O et al 2010 Effect of surface treatment of NiTi alloy on its corrosion behavior in Hanks’ solution Journal of Biomedical Materials Research. Part A 61 339–45
[19] Thierry B et al 2000 Effect of surface treatment and sterilization processes on the corrosion behavior of NiTi shape memory alloy J. Biomed. Mater. Res. 51 685–93
[20] Nam T H et al 1990 Cu-content dependence of shape memory characteristics in Ti–Ni–Cu alloys The Japan Institute of Metals 31 959–P
[21] Cristea C D et al 2015 Shape memory NiTi and NiTiCu alloys obtained by Spark Plasma Sintering Process Advanced Engineering Forum 13 83–90
[22] Tang W et al 2000 Experimental investigation and thermodynamic calculation of the Ti–Ni–Cu shape memory alloys Metallurgical and Materials Transactions A 31 2423–30
[23] Briceño J et al 2013 Influence of the microstructure on electrochemical corrosion and nickel release in NiTi orthodontic archwires Materials science engineering. C Materials for Biological Applications 33 4989–93
[24] Tsuji K et al 1992 Effects of Ni–Ti–Cu alloy composition and heat treatment temperature after cold working on phase transformation characteristics J. Mater. Sci. 27 2199–204
[25] Shevchenko N et al 2004 Studies of surface modified NiTi alloy Appl. Surf. Sci. 235 126–31
[26] Liu J et al 2007 Effect of load deflection on corrosion behavior of NiTi wire J. Dent. Res. 86 539–43
[27] Racek J et al 2014 Corrosion of NiTi Wires with Cracked Oxide Layer J. Mater. Eng. Perform. 23 2659–68
[28] Wang J et al 2007 Stress corrosion cracking of NiTi in artificial saliva Dent. Mater. 23 133–7
[29] Milheiro A et al 2012 Nickel release from orthodontic retention wires—the action of mechanical loading and pH Dent. Mater. 28 548–53
[30] Yanisarapan T et al 2018 Corrosion of metal orthodontic brackets and archwires caused by fluoride-containing products: Cytotoxicity, metal ion release and surface roughness Orthodontic Waves 77 79–89
[31] Nakagawa M et al 1999 Effect of fluoride concentration and pH on corrosion behavior of titanium for dental uses J. Dent. Res. 78 1568–72
[32] Lindholm-Sethson B et al 2008 Effects of pH and fluoride concentration on the corrosion of titanium Journal of Biomedical Materials Research. Part A 86 149–59 https://onlinelibrary.wiley.com/doi/full/10.1002/jbm.a.31415
[33] Kassab E et al 2016 Galvanic corrosion between CuNiTi arch wires and other metallic alloys for orthodontic applications Front. Bioeng. Biotechnol. Conference Abstract: 10th World Biomaterials Congress. 4