

# Influence of Cu Addition and Autoclave Sterilization on Corrosion Resistance and Biocompatibility of NiTi for orthodontics Applications

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Commercial archwires NiTiCu (Ormco) and NiTi (Morelli) and samples of the corresponding raw materials were tested to assess the influence of Cu addition and sterilization on the corrosion resistance and biocompatibility. Raw materials samples and commercial archwires exhibited similar corrosion resistance when compared. The addition of Cu decreased the corrosion resistance of NiTi alloy, while the sterilization process had no influence. The biocompatibility tests were carried out in different extracts of the alloys and no cytotoxicity effects were observed for the ionic concentrations used. SEM and Confocal laser analysis permitted to observe the localized corrosion morphology obtained after anodic polarization tests. Although Cu addition on NiTi can be introduced to better adjust the mechanical resistance, this third element induced detrimental effect on the corrosion resistance of raw materials and commercial archwires.

**Keywords:** *corrosion, NiTi, NiTiCu, archwire, NaCl, autoclaving, sterilization, confocal microscopy.*

## 1. Introduction

NiTi alloys are widely used in orthodontic applications, due to shape memory and superelasticity characteristics<sup>1-6</sup>. Kassab and Ponciano Gomes<sup>6</sup> and Pun and Berzins<sup>7</sup> mentions that the austenitic to martensitic transformation allows NiTi alloys to reach 8% of elastic elongation. The main advantage of using NiTi archwires in orthodontics is the release of continuous and controlled forces responsible to produce the desired teeth movement under elastic deformation<sup>8-10</sup>. This efficient tooth movement, in a short period under large deflections, is important during the alignment phase of the orthodontic therapy<sup>8,11-13</sup>, reducing the treatment time and achieving positive biological response by avoiding root resorption process<sup>5,7,8,11-13</sup>. The addition of the ternary element Cu to the composition has an impact on mechanical behavior, such as a narrowing of hysteresis, obtention of more constant superelastic stress plateau and increment of the fatigue resistance, when compared with the binary alloy<sup>1-3,5,9,13,14</sup>. Consequently, NiTiCu in orthodontic therapy<sup>1-13</sup> can exert lower forces being a good selection for the treatment of patients with periodontal disease<sup>4,8,12,15</sup>. Another advantage is the antibacterial property of copper benefiting the microflora control<sup>16</sup>.

Corrosion resistance and biocompatibility are basic requirements for a biomaterial<sup>3,4,6,12,16</sup>. Corrosion resistance is a concern since the oral cavity where are exposed the archwires contain saliva of variable pH and microflora<sup>17,18</sup>. The conjoint factors can make the archwires susceptible to corrosion degradation, promoting a continuous ions release, mainly nickel ions, and can be a major concern for a group of

patients<sup>17,18</sup>. Literature reports adverse inflammatory reactions, mutagenic, cytotoxicity, and allergic to nickel ions<sup>5,9,17,19</sup>. Furthermore, corrosion can affect the biocompatibility and, at the same time, can compromise the archwire integrity leading to loss of efficiency of the mechanical effect expected from the treatment plan by using the shape memory alloy.

There is not a consensus in the literature about the corrosion resistance of ternary NiTiCu alloys<sup>1-3,6,7,9,14,20</sup> and few studies related to corrosion resistance assessment of NiTiCu commercial archwires<sup>3,7,9,20</sup>. The lack of consensus is related to the different methodologies adopted for analysis and interpretation of the results. A group of authors<sup>2,14,20</sup> mentions a lower corrosion resistance for NiTiCu based on different parameters, such as the extension of the passive range, pitting potential and passive current density, or even corrosion rate. The controversial studies<sup>1,3,9</sup> denote similar corrosion resistance between the ternary and binary alloys considering the current density at open circuit potential estimated by Stern Geary equation ( $I_{corr}$ ) without correlating the electrochemical results with surface analysis methods.

From the knowledge of the enhancement of mechanical properties of NiTi by addition of Cu and the lack of consensus on literature concerning NiTiCu corrosion resistance, the present study aims to evaluate the influence of Cu addition on corrosion resistance and the basic aspects of biocompatibility of the alloys under investigation. The alloys were tested using raw materials samples and commercial archwires and the influence of sterilization was also considered.

The present study describes the effect of chemical composition modification and sterilization process on corrosion resistance of the alloys. The importance of selecting proper electrochemical parameters in conjoint with surface

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analyses technique to achieve a consistent corrosion resistance assessment of biomedical alloys is pointed out.

## 2. Materials and Methods

### 2.1. Materials

The raw materials were the binary Ni<sub>55</sub>Ti<sub>45</sub> (Memory Metalle, GmbH, Deutschland) and the ternary Ni<sub>45</sub>Ti<sub>50</sub>Cu<sub>5</sub> (Memry Corp., Connecticut, USA), with 0.020" and 0.040" diameters, respectively. The commercial orthodontic archwires used were the NiTiCu 27°C (Ormco Corp., Glendora, CA, USA), and NiTi 27°C (Morelli, SP, Brazil), with 0.018" and 0.020" diameters, respectively.

### 2.2. Electrochemical assessment

The working electrodes of raw materials and commercial archwires were prepared with insulation regions limiting the sample length exposed to the solution as shown in Figure 1a. The raw materials segments were cut into 50 mm and prepared with the length of 20 mm exposed to the solution, as shown in Figure 1b. The commercial archwires were prepared to expose a fixed area with a length of 50 mm (Figure 1b). The samples were used in the condition supplied by the manufacturer. All samples were cleaned with ethyl alcohol in an ultrasonic bath for 10 min, washed with distilled water and stored in a drying chamber containing silica before the tests.

The electrochemical measurements were performed in 200 mL of 0.9% NaCl solution, at room temperature, in a three-electrode electrochemical cell, connected to the potentiostat ( $\mu$ Autolab Type III), where the raw material or the commercial archwire of each alloy was the working electrode. Spiral platinum wires were used as counter electrodes and saturated calomel electrode (SCE) as the reference electrode.

The electrochemical technique used was anodic polarization performed using a scan rate of 20 mV/min from the corrosion potential ( $E_{\text{corr}}$ ) to 800 mV, or until the anodic current reached  $10^{-3}$  A, whichever happened first.

The raw materials were selected to evaluate the influence of autoclave sterilization on the corrosion resistance of NiTi and NiTiCu alloys. For the sterilized group, the raw materials were packed on sterilization envelopes and sterilized by steam under pressure using a Cristofili 21L autoclave, with

distilled water for 30 minutes after reaching the temperature of 127°C. The parameters used for sterilization were the same commonly applied at the dental clinic.

All tests were performed in triplicate, being the most representative result of each parameter presented with their average parameters. The obtained results were analyzed by one-way ANOVA and the significance was  $p < 0.05$ .

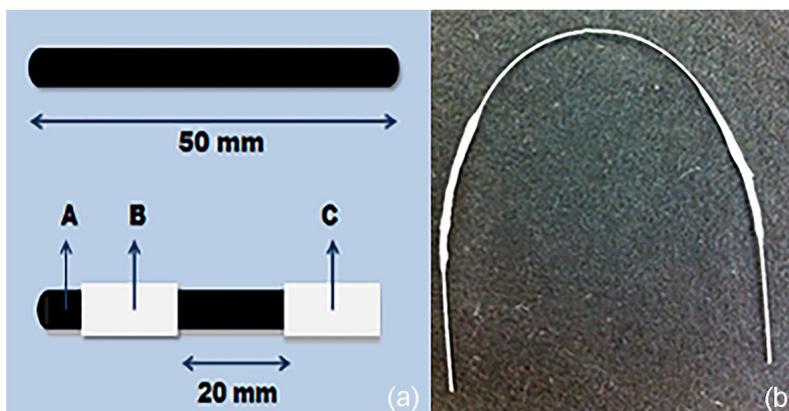
### 2.3. Surfaces characterization

The surfaces of the materials were evaluated by Scanning Electron Microscope (SEM) (Jeol, JSM-6460LV), before and after the electrochemical tests. A complementary analysis was performed by confocal laser scan microscope (Zeiss LSM 880), to characterize the surface and corrosion morphology of the materials, before and after the electrochemical tests. Roughness parameters were obtained from the average of four measurements made along the surface.

### 2.4. Biocompatibility assessment

Biocompatibility tests were based on ISO 10993-5 standard<sup>21</sup> for the choice of cell type, as well as the cytotoxicity test. The L929 cells were from the INMETRO cell bank and the test type chosen was the neutral red (NR), which marks the lysosome of the viable cells for microscopic observation. The materials were used as an extract, also based on the standard, with incubation in DMEM (Dulbecco's Modified Eagle Medium) for 24 hours at a ratio of 1g/L. After this period, the materials were removed and the extract prepared in the following concentrations: 100%, 70%, 50% and 25%. The extracts were placed in direct contact with L929 cells in the monolayer and three-dimensional culture models.

For comparison and evaluation of cell viability, a control test with SDS solution (sodiumiododecylsulfate, SIGMA) was performed. The SDS solution is a surfactant used for cell denaturation. The controls were established based on cell death. The negative control (NC) for cell death test were the cells maintained in culture medium without the presence of contaminant, viable cells. The positive control (PC) test for cell death were the cells culture in a medium with different dilutions of SDS solution (100  $\mu$ g/mL, 68.1  $\mu$ g/mL, 46.4  $\mu$ g/mL, 31.6  $\mu$ g/mL, 21.5  $\mu$ g/mL, 14.7  $\mu$ g/mL, 10  $\mu$ g/mL, 6.8  $\mu$ g/mL). The number of viable cells was estimated by neutral red (NR) assay. The controls were compared to the



**Figure 1.** Raw material (a) and commercial archwire (b) with respective work length. A: electrical contact region, B and C: insulated region. The region between B and C represents the electrode area exposed to the solution.

cells in a medium containing the extract previously prepared of different concentrations.

### 3. Results

#### 3.1. Electrochemical assessment

The anodic polarization curves are shown in Figure 2, for the raw materials (Figure 2a) and for the commercial archwires (Figure 2b), with respective parameters shown in Table 1. The parameters obtained from the anodic polarization curves and used to assess the corrosion resistance were the passive range ( $\Delta E$ ), in mV, defined as the potential difference between pitting and corrosion potential ( $E_p - E_{corr}$ ) and the passive current density ( $j_p$ ), in A/cm<sup>2</sup>. Both parameters were used to express the localized corrosion resistance of the alloys.

The polarization curves exhibited passive conditions for both NiTi and NiTiCu. However, only NiTiCu presented pitting potential in all tested conditions. For NiTiCu, the  $\Delta E$  parameter was calculated with the pitting potential as the upper limit. NiTi remained in passive range during all extent of polarization, thus no  $\Delta E$  was calculated. Raw material and commercial archwire did not presented significant differences on passive range and median current densities parameters for the binary alloy ( $p.>0.05$ ). The ternary alloy presented no significant differences on passive range comparing the samples ( $p.>0.05$ ) and slightly higher passive current densities for raw materials ( $p.<0.05$ ), but lower than  $10^{-6}$ A/cm<sup>2</sup>, which represent a similar passive condition. The NiTiCu presented a passive range limited by pitting potential and NiTi a not limited passive range. The relevant result obtained from the anodic polarization test was the localized corrosion susceptibility exhibited by NiTiCu alloy not observed for NiTi alloy.

Based on the similar corrosion resistance observed for raw materials and commercial archwires of the same alloy,

raw materials were selected to investigate the influence of autoclave sterilization. Anodic polarization curves obtained are shown in Figure 3 and the corresponding parameters ( $\Delta E$  and  $j_p$ ) in Table 2.

From the parameters obtained from the anodic polarization curves, Table 2, was observed that the sterilized condition lead to an increase of corrosion and pitting potentials and a decrease of the passive current densities for both alloys. Despite this, did not presented significant differences for the parameters, in Table 2, between the conditions sterilized or no sterilized, for both alloys ( $p.>0.05$ ). Important to point out that, after sterilization, the localized corrosion susceptibility of NiTiCu alloy and not observed for NiTi alloy was confirmed.

#### 3.2. Surface characterization

Surface characterization by SEM was obtained before and after the electrochemical tests, being disposal of in Figure 4. Once no differences on image surfaces between raw materials and commercial archwires were detected, only the images obtained for raw materials were presented.

All samples of raw materials and commercial archwires before the tests showed a surface containing manufacture marks. NiTi raw material and commercial archwire did not presented localized corrosion, or pits, on the surface after the anodic polarization, in agreement with the profile of the anodic polarization curves. NiTiCu raw material and commercial archwire presented pits on the surface after the anodic polarization, which is also in agreement with the anodic polarization curves. The sterilization process did not influence the surface condition observed before and after the electrochemical tests, for both alloys.

The Confocal 3D reconstructions were obtained from the surface of the samples before and after electrochemical corrosion tests. Once no differences on images of surfaces of

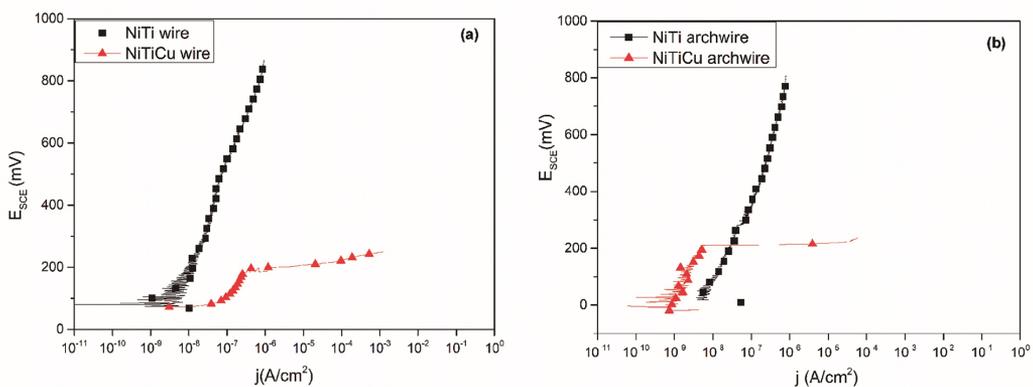
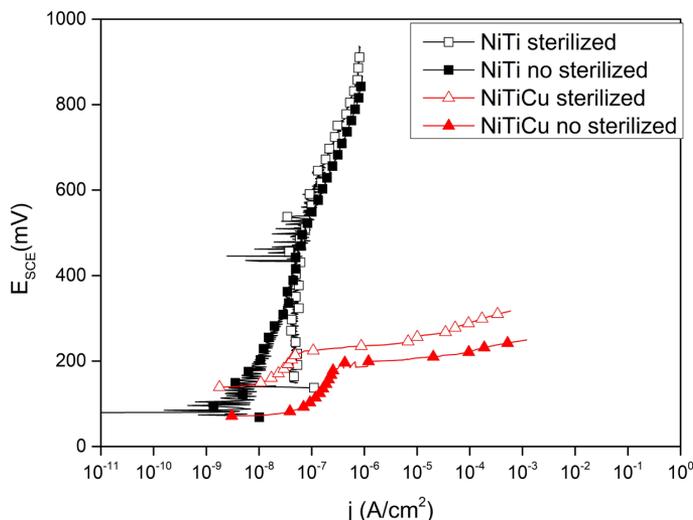


Figure 2. Anodic polarization of raw materials (a) and commercial archwires (b) in 0.9% NaCl solution.

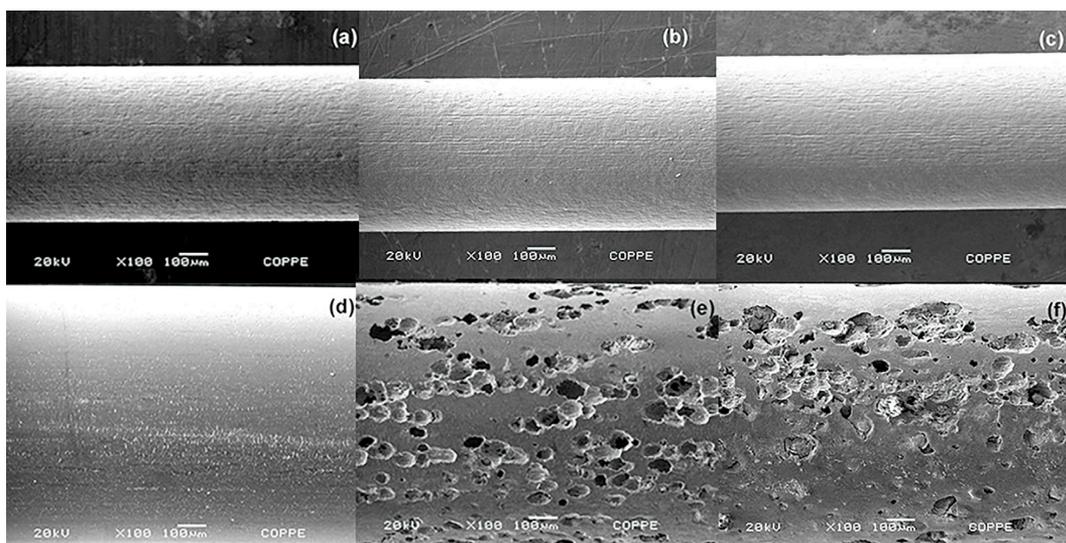
Table 1. Electrochemical parameters of raw materials and commercial archwires.

| Alloy           | $E_{corr}$ (mV <sub>ECS</sub> ) | $E_p$ (mV <sub>ECS</sub> ) | $j_p$ (A/cm <sup>2</sup> )                     | $\Delta E$ (mV <sub>ECS</sub> ) |
|-----------------|---------------------------------|----------------------------|--|---------------------------------|
| NiTi wire       | 68±32                           | -                          | $7.69 \times 10^{-8} \pm 1.12 \times 10^{-9}$  | *                               |
| NiTiCu wire     | 70±41                           | 197±30                     | $2.21 \times 10^{-7} \pm 3.16 \times 10^{-8}$  | 127                             |
| NiTi archwire   | -59±38                          | -                          | $1.69 \times 10^{-7} \pm 2.82 \times 10^{-8}$  | *                               |
| NiTiCu archwire | -40±33                          | 224±37                     | $3.11 \times 10^{-9} \pm 1.77 \times 10^{-10}$ | 264                             |

\*not calculated, no pitting potential



**Figure 3.** Polarization curves of NiTi and NiTiCu wires depending on sterilization condition in 0.9% NaCl solution.



**Figure 4.** SEM images of NiTi (a,b,c) and NiTiCu (d,e,f) raw material before (a,b) and after polarization of no sterilized group (b,e) and of sterilized group (c,f).

**Table 2.** Parameters obtained from polarization curves of wires for sterilized conditions.

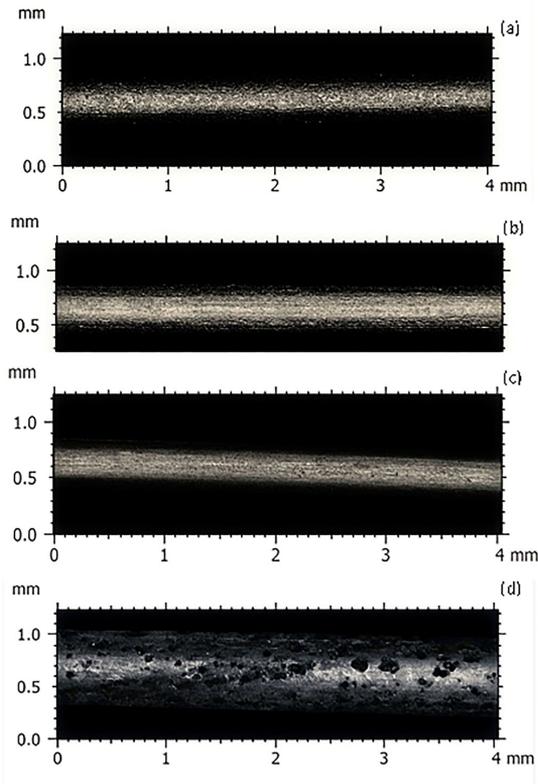
| Alloy                | $E_{corr}$ (mV <sub>ECS</sub> ) | $E_p$ (mV <sub>ECS</sub> ) | $j_p$ (A/cm <sup>2</sup> )                    | $\Delta E$ (mV <sub>ECS</sub> ) |
|----------------------|---------------------------------|----------------------------|---|---------------------------------|
| NiTi sterilized      | 96±19                           | -                          | $4.37 \times 10^{-8} \pm 3.29 \times 10^{-9}$ | *                               |
| NiTi no sterilized   | 68±32                           | -                          | $7.69 \times 10^{-8} \pm 1.12 \times 10^{-9}$ | *                               |
| NiTiCu sterilized    | 78±22                           | 224±26                     | $2.57 \times 10^{-8} \pm 3.77 \times 10^{-9}$ | 146                             |
| NiTiCu no sterilized | 70±41                           | 197±30                     | $2.21 \times 10^{-7} \pm 3.16 \times 10^{-8}$ | 127                             |

\*not calculated, no pitting potential

raw materials and commercial archwires or for the sterilized condition were observed by SEM analysis, only the images of not sterilized raw materials are shown in Figure 5. Besides that, the geometry and dimensions of the samples of raw materials were more adequate to perform the confocal microscopy analysis. This 3D reconstruction of the surface, as shown in Figure 6, allowed to observe the localized corrosion morphology with a higher microscale resolution.

The images from confocal also detected pits on the surface of NiTiCu after polarization. From this characterization was

possible to obtain profiles from the surface of the materials to characterize the pits. The obtained profile of NiTiCu surface after the polarization tests is shown in Figure 7. It was possible to observe the shape and depth of the pits – elements of localized corrosion - detected on the alloy surface. The same analysis allowed to obtain roughness parameters of  $Sa$  (square arithmetic roughness) and  $Sq$  (square quadratic roughness) presented in Table 3. The roughness increased after the electrochemical tests for all materials. The differences observed were more evident for raw materials than for



**Figure 5.** Confocal images of NiTi (a,b) and NiTiCu (c,d) raw material before (a,c) and after (b,d) polarization.

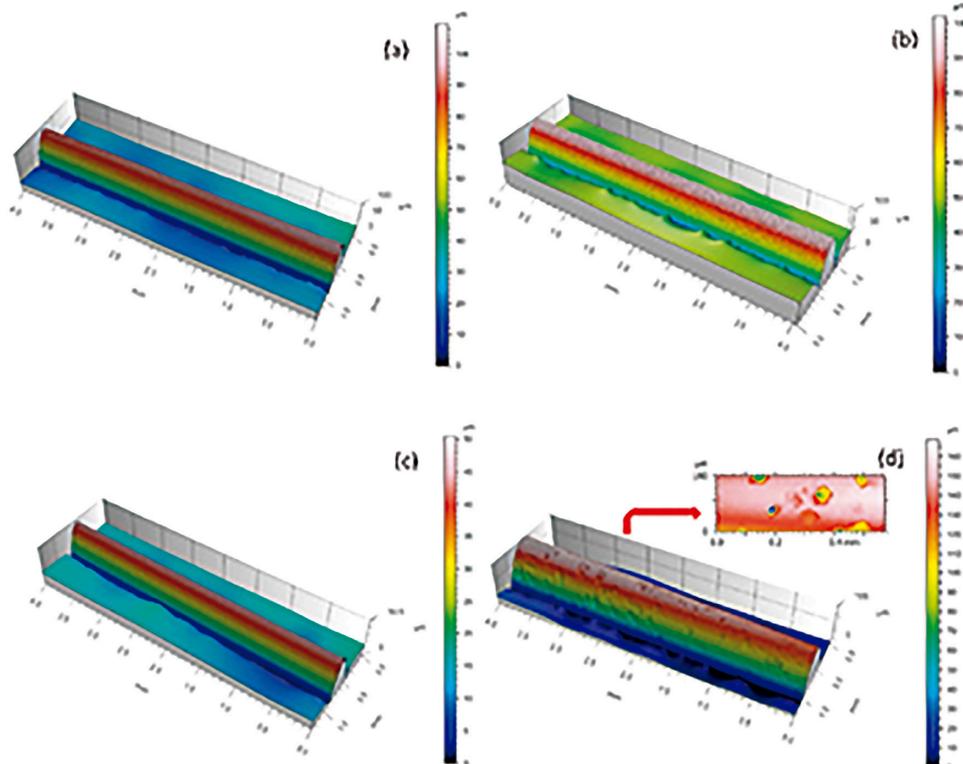
commercial archwires. NiTi presented higher roughness than NiTiCu before and after the corrosion tests.

### 3.3. Biocompatibility tests

The number of viable cells obtained through NR assay at each dilution of SDS is disposal in the SDS curve in Figure 8, being the positive control (PC) for cell death. It was possible to observe that in 100 $\mu\text{g}/\text{m}$  and 68.1 $\mu\text{g}/\text{m}$  dilutions of SDS cell death occurred, since the number of viable cells was reduced compared to other concentrations. When SDS dilution was 10  $\mu\text{g}/\text{mL}$  and 6.8  $\mu\text{g}/\text{mL}$  the number of viable cells was higher, as shown in the SDS curve in Figure 8. Figure 9 presents the number of viable cells observed in 100  $\mu\text{g}/\text{mL}$  and 10  $\mu\text{g}/\text{m}$  SDS dilutions.

Positive and negative control test conditions are important to validate the results of biocompatibility tests, being used for the comparison with the data obtained from the different extract concentrations test. The number of viable cells of negative control and of the extract of alloys obtained through NR assay is shown in Figure 10. Significant differences in the number of viable cells for the different extract concentrations were not observed. The micrograph of viable cells on the highest extract concentration was selected to be presented for NiTi and NiTiCu compared to the negative control, shown in Figure 11.

The curves referred to both alloys remained in the same range of viable cells obtained on the negative control test. Extracts of different concentrations did not reduce the number of viable cells when compared to the negative control.



**Figure 6.** 3D reconstruction obtained from confocal analysis of NiTi (a,b) and NiTiCu (c,d) raw material before (a,c) and after (b,d) polarization. An approximate view is pointed by the arrow for the NiTiCu surface after (d) polarization.

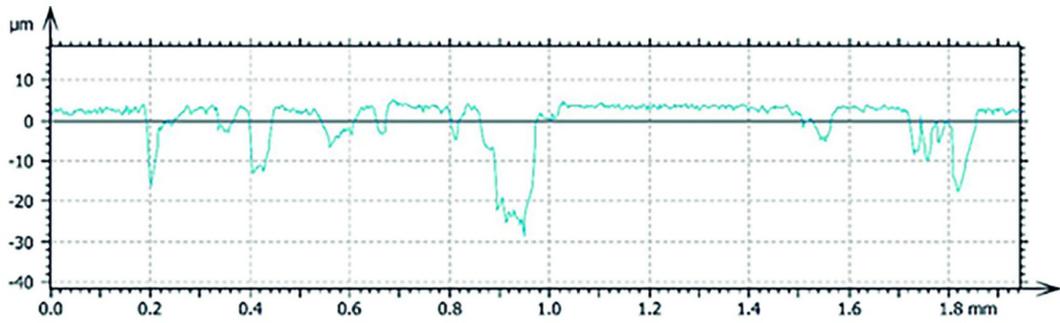


Figure 7. Profile with depths corresponding a pits obtained from NiTiCu surface after polarization.

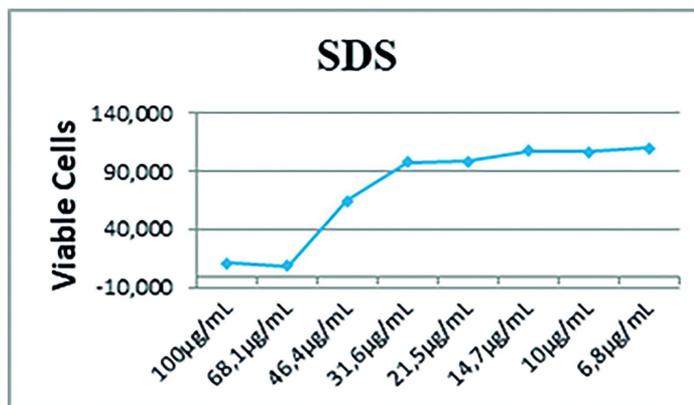


Figure 8. SDS curves on different dilutions of evaluated cells.

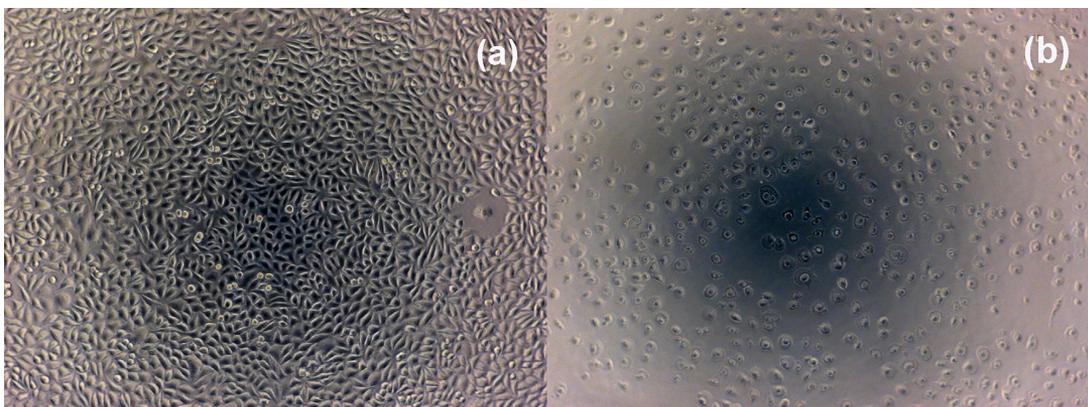


Figure 9. Viable L929 cells on SDS concentrations of 10 µg/mL (a) and 100 µg/mL (b).

Table 3. Roughness parameters obtained from confocal analysis.

| Alloy           | Sa          |            | Sq          |            |
|-----------------|-------------|------------|-------------|------------|
|                 | Before (µm) | After (µm) | Before (µm) | After (µm) |
| NiTi wire       | 3.46±0.38   | 4.95±0.31  | 4.37±0.34   | 6.32±0.50  |
| NiTiCu wire     | 2.00±0.29   | 4.42±0.22  | 2.39±0.41   | 6.26±0.46  |
| NiTi archwire   | 3.40±0.33   | 4.01±0.41  | 4.29±0.36   | 4.95±0.48  |
| NiTiCu archwire | 3.23±0.30   | 4.21±0.26  | 3.94±0.23   | 4.55±0.33  |

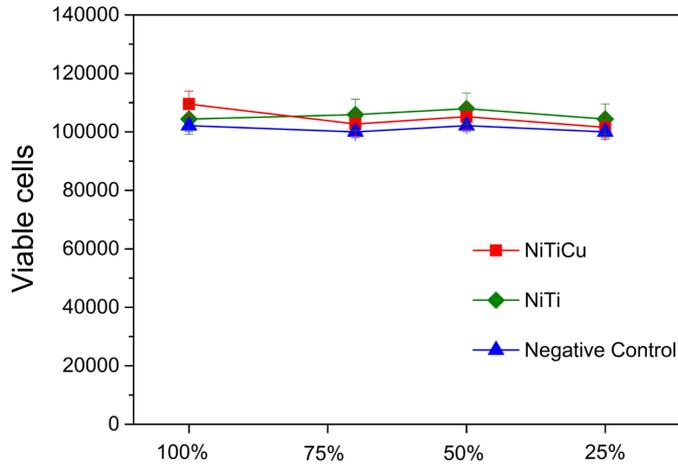


Figure 10. Viable cells in NR for NiTi and NiTiCu alloy compared to negative control (NC).

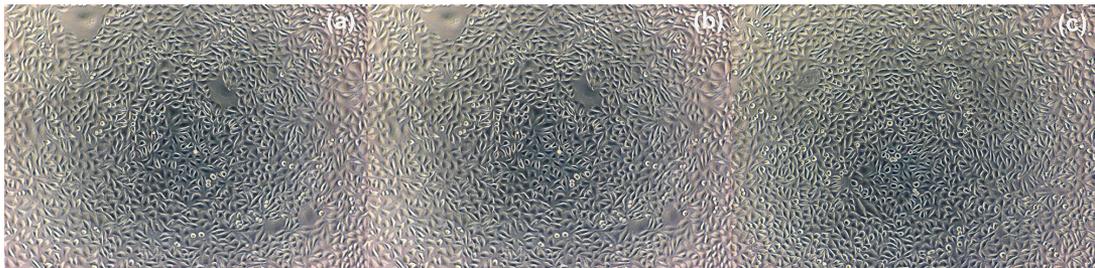


Figure 11. L929 cells in extract concentration 100% for NiTi (a), for NiTiCu (b) and negative control of L929 cells (c).

#### 4. Discussion

The results clearly indicated the negative impact of the Cu addition on the corrosion resistance of the NiTi alloy, based on the results expressed by the anodic polarization tests. NiTiCu samples, as raw material or commercial archwires, exhibited localized corrosion susceptibility, confirmed by surface analysis after the corrosion tests, which could be associated with the addition of Cu as the ternary element. The conventional binary alloy was not susceptible to localized corrosion when tested in the same solutions and conditions.

The results of the present study were in accordance with a several reports from literature<sup>2,14,20</sup> about the detrimental effect of Cu addition on corrosion resistance of NiTi based on anodic polarization curves. These studies<sup>2,14,20</sup> considered not a single parameter, but a set of parameters jointly used to analyze and interpret the results. One of the parameters was the passive range, being observed the presence of pitting potential or a lower extension of passive range ( $\Delta E$ ) when the Cu was present in the alloy. Rondelli and Vicentini<sup>14</sup> informed no pitting potential for NiTi and lower passive range with pitting potential for NiTiCu. Kassab et al.<sup>2</sup> identified pitting potential for both NiTi and NiTiCu, being the lowest passive range ( $\Delta E$ ) for the ternary alloy. Ziębowicz et al.<sup>20</sup> found lower polarisation resistance, lower pitting potential and a higher corrosion rate for NiTiCu than for NiTi.

Other studies<sup>1,9</sup> on literature did not confirm the decay of the corrosion resistance promoted by Cu addition or reported higher corrosion resistance<sup>3</sup> since these studies did not considered conjoint parameters for data analysis

or considered not adequate parameters. Zheng et al.<sup>1</sup> and Phukaoluan et al.<sup>3</sup> informed similar corrosion resistance comparing ternary NiTiCu<sup>3</sup> and quaternary NiTiCuCr<sup>1</sup> to binary alloy. The authors used the current density at open circuit potential estimated by Stern Geary equation ( $I_{corr}$ ) as a parameter to assess the corrosion resistance of the alloys. Zheng et al.<sup>1</sup> reported an  $I_{corr}$  of  $3.09 \times 10^{-6}$  A/cm<sup>2</sup> for NiTi obtained from polarization curves, six times higher than the  $I_{corr}$  obtained for NiTiCu. Phukaoluan et al.<sup>3</sup> evaluated NiTiCu raw material and commercial archwire and cited a reduction of the same parameter  $I_{corr}$ , as an indication of higher corrosion resistance of ternary alloy compared to binary alloy. However, is important to note that both studies selected the parameter  $I_{corr}$  supported by the Stern Geary equation theory. The equation mentioned can be properly used for material that undergoes active dissolution, a condition not expected for biomaterials in simulated body fluid solutions. The analysis of the electrochemical parameters passive range ( $\Delta E$ ) and passive current densities ( $j_p$ ) from anodic polarization curves on the mentioned works<sup>1,3</sup>, suggests higher corrosion resistance for the binary alloy, leading to an opposite conclusion compared to interpretation based on  $I_{corr}$ . The polarization curves reported on the cited references showed current densities on the passive range ( $j_p$ ) for modified alloys within the values  $10^{-4}$  A/cm<sup>2</sup> (Phukaoluan et al.<sup>3</sup>) to  $10^{-5}$  A/cm<sup>2</sup> (Zheng et al.<sup>1</sup>), much higher than the same values registered for binary alloy, which was  $10^{-6}$  A/cm<sup>2</sup> (Phukaoluan et al.<sup>3</sup>; Zheng et al.<sup>1</sup>). These values confirmed the decrease of the corrosion resistance of modified NiTi by Cu addition and demonstrate the importance of

using appropriate electrochemical parameters to assess the corrosion resistance. Surface characterization results were not included by the authors and, consequently, the onset of localized corrosion was not confirmed.

Another study that informs similar corrosion resistance of modified and conventional NiTi alloys was presented by Iijima et al.<sup>9</sup>. Quaternary NiTiCuCr containing 5% of Cu in partial substitution of Ni was investigated. Anodic polarization curves showed that the pitting potential of NiTiCuCr was 200 mV below the same value obtained for NiTi. SEM images showed pits and the presence of corrosion products only on the surface of the quaternary alloy. The authors considered only the equivalent values of the passive current density values to infer similar corrosion resistance between the alloys. However, considering the conjoint analysis of corrosion parameters and surface analysis, it could be suggested that NiTiCuCr clearly was more susceptible to localized corrosion than NiTi. The extension of the passive range and the surface analysis were not considered by the authors and probably are the additional parameters necessary to achieve a consistent conclusion.

In the present work, the incidence of localized corrosion was confirmed by SEM and confocal microscopy analysis carried out after the anodic polarization tests for raw materials and commercial archwires. The surface of as received archwires, before the electrochemical tests, indicated that both alloys presented similar surface morphologies, containing defects, drawing marks and slots, probably associated with the fabrication processes, characteristics also observed by Gravina et al.<sup>8</sup>. Comparing raw materials and commercial archwires after the polarization tests, significant differences, in terms of corrosion resistance, were not observed for NiTi and for NiTiCu. It is important to emphasize that NiTi did not presented pits in the surface after the anodic polarization tests, in agreement with the indications derived from the anodic polarisation curves. Localized corrosion elements, or pits, were detected on NiTiCu surface after polarization and were also detected by Pun and Berzins<sup>7</sup> using SEM analysis, corresponding to a morphology similar to the one obtained in the present study. However, the authors observed pits on NiTi and NiTiCu commercial archwires, with a lower density of pits on NiTi, and claimed that corrosion initiated at surface drawn marks of manufacturing.

Surface roughness increased after the electrochemical tests, as observed by Huang et al.<sup>22</sup> and by Huang<sup>23</sup>. Literature reported that the defects on the surface observed before electrochemical tests could act as a preferential site for the occurrence of localized corrosion, increasing roughness after the tests<sup>24</sup>. However, this correlation was not observed in our study, once NiTi presented higher roughness than NiTiCu, as raw material or commercial archwire, with no pits, and higher corrosion resistance. The chemical composition of the alloy was the determining factor of the localized corrosion resistance. A similar no correlation between roughness and corrosion resistance was detected in other studies<sup>18,22,23,25</sup>. According to the results here presented and in these other studies<sup>18,22,23,25</sup>, the roughness parameters could not be considered as a major or critical parameter to evaluate corrosion resistance. The increase in roughness was an important parameter to be correlated to bacterial or

cell adhesion, which may compromise the biocompatibility. Abraham et al.<sup>16</sup> investigated the bacterial adhesion to NiTi and NiTiCu surfaces and concluded that NiTiCu was more favorable to bacterial adherence than NiTi and explained the result as a consequence of the higher roughness of NiTiCu, despite the antibacterial property of copper.

The influence of the sterilization process, commonly used in dentistry, on the corrosion resistance of the alloys, was also evaluated in the present study. Only a slight improvement of the electrochemical parameters was detected. The temperature of the sterilization process reached 127°C and the formation of preliminary passivation of the alloys might be occurred during the process. However, the improvement of the parameters induced by sterilization was not significant, which means that the sterilization process did not influence the oxide film passivation. Some authors considered a differential oxide film formation that would reduce ions release and improve the corrosion resistance<sup>26,27</sup>. Sterilized NiTi was investigated in the literature, and the results are qualitatively coherent with those here reported. Positive effects of sterilization were explained by the reductions of defects on the passive film formed on the surface at the sterilization temperature, but this modification was not sufficient to significantly improve the corrosion resistance<sup>26,27</sup>.

Biocompatibility is a basic requirement for biomaterials. The nickel element present on orthodontic archwires is one of the known elements which may cause allergies, mutagenic and cytotoxicity<sup>5,9,14,17,19</sup>. Literature is not consistent about the correlation between ions release and immersion time. Some studies mentioned that ions release could increase with time immersion<sup>5,12,19,26</sup>, others as Zheng et al.<sup>1</sup> and Mikulewicz et al.<sup>17</sup> reported a decrease of ions release with time. The extent of the ions release process is linked to the corrosion resistance of the alloy, together with the chemical composition. Ions release could affect the biocompatibility of NiTi based alloys<sup>5,9,26</sup> due to the high nickel content. Several studies addressing the detection and quantification of Ni ions released were based on *in vitro* immersion tests of NiTi alloys for a few days<sup>1,11,19,26</sup>, but using different methodologies. Mikulewicz et al.<sup>17</sup> proposed the use of *in vitro* test under continuous solution flow to detect the amount of ions released from one fixed orthodontic appliance, initially detecting a higher concentration of metal ions that decreased with time, probably associated with the passivation of alloy. Gil and Planell<sup>12</sup> realized ICP-MS analysis to quantify ions released from NiTi and NiTiCu archwires at various immersion times and concluded that longer immersion time (120 days) leads to the highest concentration of ions, but the concentration achieved was still within the range commonly detected in drinking water. Despite the amount of Ni ions release mentioned in the cited literature, even the highest amount detected was below the Ni amount recommended in the daily diet (25-35 µg) or in blood volume (12-50 µg/L), being not sufficient to cause deleterious effects<sup>5,11,17,25,26</sup>.

Cytotoxicity tests were performed on the NiTi and NiTiCu raw materials as a primary requisite for biocompatibility, based on the effect produced in oral cells during the simulated use. The biocompatibility tests were performed using extracts of the alloys of different concentrations, obtained after the incubation period, in accordance with ISO 10993-5<sup>21</sup>. The

results of no cytotoxicity effects obtained were in agreement with the literature about the biocompatibility of NiTi based alloys. Phukaoluan et al.<sup>3</sup> also evaluated the biocompatibility of NiTi and NiTiCu alloys raw materials and commercial archwires based on ISO 10993-5<sup>21</sup> with L929 cells and the alloys presented admissible cytotoxicity, based on the number of viable cells observed.

## 5. Conclusions

The results of the present work bring a contribution to achieve a better understanding of the effect of Cu on the corrosion resistance of NiTi alloys. It was concluded that NiTiCu, commercial archwires or raw materials, exhibited lower corrosion resistance than the binary NiTi alloy. The corrosion morphology was localized and the susceptibility of the alloy containing Cu was demonstrated by the methodology based on the conjoint assessment of electrochemical parameters, obtained from corrosion tests, and surface analysis. The importance of using proper electrochemical parameters on the analysis was pointed. The most adequate electrochemical parameters were the passive range ( $\Delta E$ ) and passive current density ( $j_p$ ) considered together. Surface analysis methods were important to validate the results and consistent knowledge about the corrosion resistance of the alloys was achieved.

Autoclave sterilization presented no influence on the corrosion resistance of the alloys. The results obtained through the biocompatibility tests of the L929 cell exposition in the different concentrations extract did not indicate significant differences in terms of cytotoxic effects for both alloys investigated.

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## 7. References

- Zheng YF, Wang QY, Li L. The electrochemical behavior and surface analysis of Ti49.6Ni45.1Cu5Cr0.3 alloy for orthodontic usage. *J Biomed Mater Res B Appl Biomater*. 2008;86(2):335-40. <http://dx.doi.org/10.1002/jbm.b.31023>. PMID:18161810.
- Kassab E, Neelakantan L, Frotscher M, Swaminathan S, Maaß B, Rohwerder M, et al. Effect of ternary element addition on the corrosion behaviour of NiTi shape memory alloys. *Mater Cor*. 2014;65(1):18-22. <http://dx.doi.org/10.1002/maco.201206587>.
- Phukaoluan A, Khantachawana A, Kaewtatip P, Dechkunakorn S, Kajornchaiyakul J. Amélioration des propriétés mécaniques et biologiques des alliages NiTi par addition de Cu et de Co aux fils orthodontiques. *Int Orthod*. 2016;14(3):295-310. <http://dx.doi.org/10.1016/j.ortho.2016.07.017>.
- Gravina MA, Brunharo IHVP, Canavaro C, Elias CN, Quintão CCA. Mechanical properties of NiTi and CuNiTi shape-memory wires used in orthodontic treatment. Part 1: stress-strain tests. *Dental Press J Orthod*. 2013;18(4):35-42. <http://dx.doi.org/10.1590/S2176-94512013000400007>. PMID:24262415.
- Toker SM, Canadinc D. Evaluation of the biocompatibility of NiTi dental wires: a comparison of laboratory experiments and clinical conditions. *Mater Sci Eng C Mater Biol Appl*. 2014;40:142-7. <http://dx.doi.org/10.1016/j.msec.2014.03.060>. PMID:24857476.
- Kassab EJ, Ponciano Gomes J. Assessment of nickel titanium and beta titanium corrosion resistance behavior in fluoride and chloride environments. *Angle Orthod*. 2013;83(5):864-9. <http://dx.doi.org/10.2319/091712-740.1>. PMID:23448158.
- Pun DK, Berzins DW. Corrosion behavior of shape memory, superelastic, and nonsuperelastic nickel-titanium-based orthodontic wires at various temperatures. *Dent Mater*. 2008;24(2):221-7. <http://dx.doi.org/10.1016/j.dental.2007.05.003>. PMID:17624421.
- Gravina MA, Canavaro C, Elias CN, Chaves MDGAM, Brunharo IHVP, Quintão CCA. Mechanical properties of NiTi and CuNiTi wires used in orthodontic treatment. Part 2: microscopic surface appraisal and metallurgical characteristics. *Dental Press J Orthod*. 2014;19(1):69-76. <http://dx.doi.org/10.1590/2176-9451.19.1.069-076.oar>. PMID:24713562.
- Iijima M, Endo K, Ohno H, Mizoguchi I. Effect of Cr and Cu addition on corrosion behavior of Ni-Ti alloys. *Dent Mater J*. 1998;17(1):31-40. <http://dx.doi.org/10.4012/dmj.17.31>. PMID:9663060.
- Han S, Quick DC. Nickel-titanium spring properties in a simulated oral environment. *Angle Orthod*. 1993;63(1):67-72. [http://dx.doi.org/10.1043/0003-3219\(1993\)063<0067::NSPIA S>2.0.CO;2](http://dx.doi.org/10.1043/0003-3219(1993)063<0067::NSPIA S>2.0.CO;2). PMID:8507034.
- Phukaoluan A, Dechkunakorn S, Anuwongnukroh N, Khantachawana A, Kaewtatip P, Kajornchaiyakul J, et al. Loading and unloading forces following addition of 5% Cu in nickel-titanium alloy used for orthodontics. *Eng Mater*. 2017;730:161-6. <http://dx.doi.org/10.4028/www.scientific.net/KEM.730.161>.
- Gil FJ, Planell JA. Effect of copper addition on the superelastic behavior of Ni-Ti shape memory alloys for orthodontic applications. *J Biomed Mater Res*. 1999;48(5):682-8. [http://dx.doi.org/10.1002/\(SICI\)1097-4636\(1999\)48:5<682::AID-JBIM12>3.0.CO;2-M](http://dx.doi.org/10.1002/(SICI)1097-4636(1999)48:5<682::AID-JBIM12>3.0.CO;2-M). PMID:10490682.
- Seyyed Aghamiri SM, Nili Ahmadabadi M, Shahmir H, Naghdi F, Raygan S. Study of thermomechanical treatment on mechanical-induced phase transformation of NiTi and TiNiCu wires. *J Mech Behav Biomed Mater*. 2013;21:32-6. <http://dx.doi.org/10.1016/j.jmbmm.2013.01.014>. PMID:23454366.
- Rondelli G, Vicentini B. Effect of copper on the localized corrosion resistance of Ni-Ti shape memory alloy. *Biomaterials*. 2002;23(3):639-44. [http://dx.doi.org/10.1016/S0142-9612\(01\)00142-9](http://dx.doi.org/10.1016/S0142-9612(01)00142-9). PMID:11771683.
- Santoro M, Nicolay OF, Cangialosi TJ. Pseudoelasticity and thermoelasticity of nickel-titanium alloys: a clinically oriented review. Part I: Temperature transitional ranges. *Am J Orthod Dentofacial Orthop*. 2001;119(6):587-93. <http://dx.doi.org/10.1067/mod.2001.112446>. PMID:11395701.
- Abraham KS, Jagdish N, Kailasam V, Padmanabhan S. *Streptococcus mutans* adhesion on nickel-titanium (NiTi) and copper-NiTi archwires: A comparative prospective clinical study. *Angle Orthod*. 2017;87(3):448-54. <http://dx.doi.org/10.2319/040516-270.1>. PMID:27849122.
- Mikulewicz M, Chojnacka K, Wolowicz P. Release of metal ions from fixed orthodontic appliance: an in vitro study in continuous flow system. *Angle Orthod*. 2014;84(1):140-8. <http://dx.doi.org/10.2319/113012-911.1>. PMID:23477423.
- Krishnan M, Seema S, Kumar AV, Varthini NP, Sukumaran K, Pawar VR, et al. Corrosion resistance of surface modified nickel titanium archwires. *Angle Orthod*. 2014;84(2):358-67. <http://dx.doi.org/10.2319/021813-140.1>. PMID:24004028.
- Clarke B, Carroll W, Rochev Y, Hynes M, Bradley D, Plumley D. Influence of nitinol wire surface treatment on oxide thickness and composition and its subsequent effect on corrosion resistance and nickel ion release. *J Biomed Mater Res A*. 2006;79(1):61-70. <http://dx.doi.org/10.1002/jbm.a.30720>. PMID:16758455.
- Ziębowski A, Walke W, Barucha-Kepka A, Kiel L. Corrosion behaviour of metallic biomaterials used as orthodontic wires. *J Achiev Mater Manuf Eng*. 2018;27:151-4.

21. International Standards Organization – ISO. ISO 10993-5: 2009: biological evaluation of medical devices. Part 5: tests for in vitro cytotoxicity. Geneva: ISO.
22. Huang H, Chiu Y, Lee T, Wu S, Yang H, Su K, et al. Ion release from NiTi orthodontic wires in artificial saliva with various acidities. *Biomaterials*. 2003;24(20):3585-92. [http://dx.doi.org/10.1016/S0142-9612\(03\)00188-1](http://dx.doi.org/10.1016/S0142-9612(03)00188-1). PMID:12809787.
23. Huang H. Variation in corrosion resistance of nickel-titanium wires from different manufacturers. *Angle Orthod*. 2005;75(4):661-5. PMID:16097238.
24. Habar EH, Tatengkeng F. The difference of corrosion resistance between NiTi archwires and NiTi with additional cooper archwires in artificial saliva. *Journal of Dentomaxillofacial Science*. 2020;5(2):120-3.
25. Cissé O, Savadogo O, Wu M, Yahia LH. Effect of surface treatment of NiTi alloy on its corrosion behavior in Hanks' solution. *J Biomed Mater Res*. 2002;61(3):339-45. <http://dx.doi.org/10.1002/jbm.10114>. PMID:12115458.
26. Thierry B, Tabrizian M, Trepanier C, Savadogo O, Yahia LH. Effect of surface treatment and sterilization process on the corrosion behavior of NiTi shape memory alloy. *J Biomed Mater Res*. 2000;51(4):685-93. [http://dx.doi.org/10.1002/1097-4636\(20000915\)51:4<685::AID-JBM17>3.0.CO;2-S](http://dx.doi.org/10.1002/1097-4636(20000915)51:4<685::AID-JBM17>3.0.CO;2-S). PMID:10880117.
27. Morawiec H, Goryczka T, Lełątko J, Lekston Z, Winiarski A, Rówiński E, et al. Surface structure of NiTi alloy passivated by Autoclaving. *Mater Sci Forum*. 2010;636-637:971-6. <http://dx.doi.org/10.4028/www.scientific.net/MSF.636-637.971>.