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Corrosion resistance properties of 304 stainless steel and nickel-titanium orthodontic wires in artificial saliva solution

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The most commonly used alloys in orthodontic wires are stainless steel and titanium due to their corrosion-resistant properties. While these alloys generally exhibit good corrosion behavior in mildly aggressive environments, unexpected breakages and allergic reactions can sometimes occur. This is mainly due to the degradation of the passive film of orthodontic wires, which is caused by the complex and variable conditions within the oral cavity. The composition of human saliva and the duration of exposure can differ significantly depending on the patient. This study evaluated the corrosion resistance properties of two commercially available orthodontic wires: 304 steel and a nickel-titanium alloy. Their electrochemical behavior was investigated using cyclic potentiodynamic polarization curves recorded in artificial saliva at 37 °C and a pH of 5.5. The results showed that 304 stainless steel orthodontic wires exhibit variable corrosion resistance properties, ranging from excellent to poor. Furthermore, when the passive film on 304 stainless steel breaks down, the repassivation potential is lower than the corrosion potential. This indicates that damage can easily propagate, leading to significant failure and the release of metal ions. This poses risk of allergies. On the other hand, the nickel-titanium orthodontic wires never showed localized corrosion behavior, demonstrating superior corrosion resistance properties compared to 304.

KEYWORDS: LOCALIZED CORROSION, ORTHODONTIC WIRES, ARTIFICIAL SALIVA, CYCLIC POTENTIODYNAMIC POLARIZATION;

INTRODUCTION

Stainless steel and nickel-titanium (NiTi) alloys are among the most commonly used materials for orthodontic wires due to their combination of mechanical strength, formability, and corrosion resistance. However, despite their widespread use and general reliability, failures and allergic reactions have been reported in clinical practice, often associated with corrosion-induced degradation. These failures can compromise the mechanical integrity of the wire, leading to fracture or premature loss of functionality, and can also result in the release of metallic ions, such as nickel, iron, and chromium, which may cause biological complications, including local irritation or allergic responses [1, 2].

The corrosion behavior of orthodontic alloys is strongly influenced by the oral environment, which is highly variable and chemically complex. The composition of saliva differs among individuals and can fluctuate with diet, medication, or pathological conditions. These conditions create an aggressive environment in the oral cavity, capable of

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promoting localized corrosion phenomena, such as pitting or crevice corrosion, particularly in stainless steels.

To reproduce such complex in vivo conditions, laboratory investigations typically employ artificial saliva (AS) solutions with controlled composition, temperature, and pH. These tests enable the evaluation of corrosion resistance under reproducible and clinically relevant conditions. Nevertheless, before assessing the electrochemical performance of orthodontic materials, it is essential to verify that both the electrolyte and the experimental setup are appropriate and reliable.

In this context, the present study aimed to verify the suitability of the selected artificial saliva solution as a representative electrolyte for corrosion testing. Subsequently, the experimental setup was validated to ensure that it could effectively evaluate the corrosion resistance of wire-shaped metallic samples. Once these preliminary steps were established, the research focused on investigating the localized corrosion resistance of commercial and orthodontic wires in artificial saliva at 37 °C and pH 5.5.

By following this approach, the study intends to provide a more reliable framework for the electrochemical evaluation of orthodontic alloys, linking methodological accuracy with clinically relevant insights into corrosion behavior.

MATERIALS AND METHODS

The corrosion behavior of different stainless steel and NiTi wires was investigated through electrochemical testing in AS at 37 °C and pH 5.5. The AS composition shown in table 1 was derived from previous studies aimed at reproducing the ionic environment of the human oral cavity [3].

Tab.1 - Composizione chimica della saliva artificiale in % in peso / *Chemical composition of the AS in wt.%.*

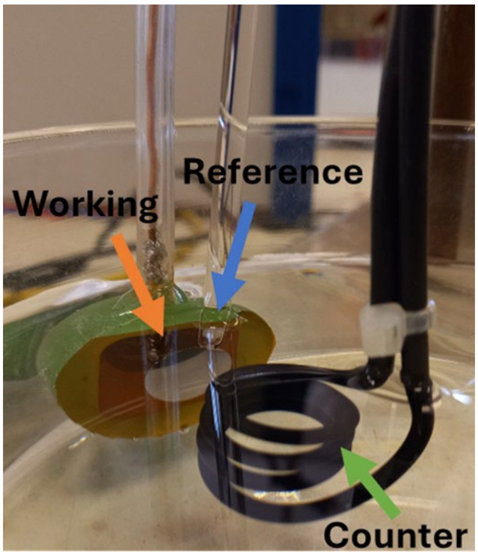
NaCl	KCl	KSCN	$Na_2HPO_4 \cdot 12H_2O$	KH_2PO_4	$CaCl_2 \cdot 2H_2O$	$KHCO_3$	Citric acid
0.060	0.072	0.006	0.086	0.068	0.022	0.150	0.145

Five different metallic materials were investigated in this study: wrought AISI 304 stainless steel (wrought 304), commercial AISI 304 stainless steel wire (wire 304), orthodontic AISI 304 stainless steel wire (orthodontic 304), commercial NiTi wire (nitinol), and orthodontic NiTi wire (orthodontic nitinol).

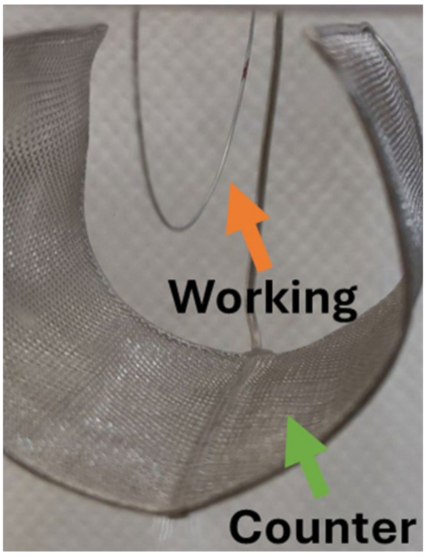
Two electrochemical cell configurations were employed depending on the geometry of the samples.

A conventional three-electrode cell was used for the plain surface of wrought 304, equipped with a saturated calomel electrode (SCE) as reference and a platinum wire as counter electrode. The exposed area of the wrought 304 specimen was 2 cm^2, and its surface roughness was the result of grinding using emery papers (1200 grit). This setup, shown in figure 1a and inspired by previously published works [4,5], was employed to validate the electrochemical measurements conducted in the AS solution (table 1), specifically formulated for testing the wire samples, ensuring that the modified wire cell configuration produced reliable and interpretable data for the 304 stainless steel.

For wire samples, a modified cell setup was adopted from previously published works [6,7] for studying pitting corrosion and avoiding crevice corrosion: a bent wire, used as the working electrode, is immersed in the testing solution without using any specific sample holders or polymer coating to define the exposed surface. More specifically, this last parameter is defined considering the length of the wire portion immersed in the solution and its cross-section geometry. In this configuration, the counter electrode consisted of a platinum mesh surrounding the metallic wire to ensure a uniform current distribution along the cylindrical geometry (figure 1b), while the reference electrode (SCE) was the same as in the conventional setup. From this electrochemical cell configuration, the exposed areas were 1 cm^2 for wire 304, 0.8 cm^2 for orthodontic 304, 0.8 cm^2 for nitinol, and 0.64 cm^2 for orthodontic nitinol.



(a)



(b)

Fig.1 - Setup della cella: convenzionale per superfici piane (a) e per campioni di filo (b) /
Cell setup: conventional plain samples (a) and wire samples (b).

Before testing, all samples were ultrasonically cleaned in n-hexane and deionized water to remove surface contaminants.
Electrochemical Impedance Spectroscopy (EIS) was carried out before Cyclic Potentiodynamic Polarization (CPP) measurements to determine the solution resistance and correct the polarization curves for the ohmic drop. The EIS spectra were collected in the frequency range from 100 kHz to 1 Hz, with 10 points per decade and a sinusoidal perturbation amplitude of 10 mV.
After EIS, CPP tests were performed to assess the localized corrosion resistance. The Open-Circuit Potential (OCP) was monitored for 30 minutes to ensure stabilization, after which the polarization scan was initiated 15 mV below the stationary OCP. The potential was swept in the anodic direction at a scan rate of 0.166 mV · s^{-1}, and then reversed using the same scan rate once the current density reached 0.01 mA · cm^{-2}. Each test was repeated at least five times to verify the reproducibility of the measurements.
All electrochemical tests were conducted at 37 °C using a thermostatic bath to maintain a constant temperature during the experiments. The wrought 304 specimen was also tested at room temperature (RT).

RESULTS AND DISCUSSION

The stability of the artificial saliva was preliminarily verified by monitoring its pH over several days. The pH remained constant at approximately 5.5, ensuring the stability of the electrolyte and thus the reliability of the CPP measurements.
Figure 2 shows the CPP curves for the wrought 304 stainless steel tested at RT and at 37 °C, as well as for the wire 304 tested at 37 °C. The comparison between the wrought 304 curves at the two temperatures highlights the expected effect of temperature on the electrochemical behavior of stainless steels: the pitting and repassivation potentials decrease as the temperature increases, whereas the corrosion potential shifts slightly toward more positive values. This confirms that the electrolyte simulating the saliva supplies an expected anodic behavior of the material as typically occurs, thus validating the experimental setup.
Additionally, figure 2 illustrates the comparison of the anodic curves of the wire 304 and the wrought 304 sample. The CPP curve of the wire 304 exhibits markedly different characteristic potentials: a significantly higher corrosion potential (around +0.1 V), a lower repassivation potential, and a higher pitting potential compared to the wrought 304. Moreover, the curve is shifted leftward by nearly two orders of magnitude in current density relative to the wrought sample, corresponding to a lower passivation current density and indicating a more protective passive film present on the wire. This result agrees with the significantly higher pitting potential of the wire 304, suggesting a less susceptibility to localized corrosion with

respect to wrought 304. Such differences can be partially attributed to the different geometry of the electrochemical cells (figure 1), but most likely to the smoother surface of the wire as a result of the drawing process compared to the wrought 304, ground at 1200 grit. A low roughness improves the protective characteristic of the passive film.

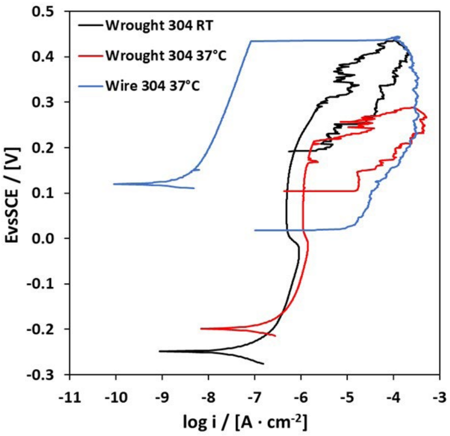


Fig.2 - Curve CPP più rappresentative dell'acciaio Wrought 304 e del filo 304 a temperatura ambiente e a 37 °C / *Most representative CPP curves of Wrought 304 and wire 304 at RT and 37°C.*

Representative CPP curves for the orthodontic 304 wires are shown in figure 3. The corrosion potential and the passivation current density are highly reproducible and close to that observed for the wire 304 in figure 2; in particular, the purple curve in figure 3 is comparable to that reported by other authors [7], who tested similar orthodontic wires in an AS solution with a composition close to that used in this work. However, the pitting potential exhibits significant variability: in some specimens, it exhibits low values (around +0.45 V), in others, it is higher (up to +0.95 V), and in certain cases, the anodic branch exhibits only an increase of current density, most likely associated with oxygen evolution from water. Most of the orthodontic 304 wire curves recorded in this work fall into the "higher potential" category (blue curve in figure 3). Assuming this anodic behavior as the most representative of the orthodontic 304 wires examined, the corresponding pitting potential is considerably higher than that of the commercial wire (see blue curve in figure 2). This result can be attributed to the better surface finish of the orthodontic wires, which is deliberately diamond drawn to obtain a very smooth surface that reduces the adhesion of bacteria present in the oral cavity [8].

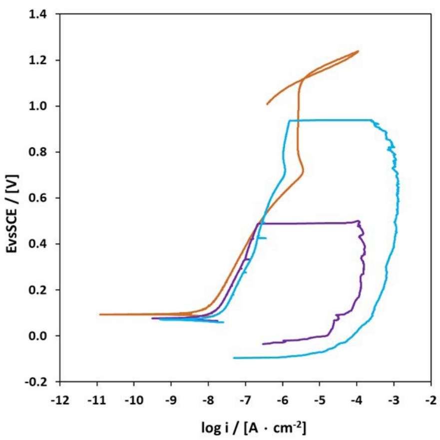


Fig.3 - Curve CPP più rappresentative del filo ortodontico in acciaio 304 a 37 °C / *Most representative CPP curves of orthodontic 304 wire at 37°C.*

The repassivation potential is found below the corrosion potential, indicating imperfect passive behavior of the tested orthodontic wires. This suggests that when these wires undergo localized corrosion, the process tends to propagate, potentially leading to mechanical failure and the release of significant amounts of metal ions. In several cases, the localized corrosion damage observed on orthodontic 304 wires was extensive. In the most severe instances, corrosion attack was so pronounced that it led to the complete fracture of the orthodontic wire, confirming that the wires operate in the critical condition of the absence of the perfect passive behavior in the solution simulating the saliva.

Figure 4 displays the representative CPP curves of the NiTi commercial and orthodontic wires. Both materials exhibit very similar electrochemical behavior, showing no evidence of localized corrosion phenomena under the present test conditions. These results confirm the superior resistance to localized corrosion of NiTi alloys compared with the 304 stainless steel samples when exposed to this artificial saliva environment [7, 9, 10].

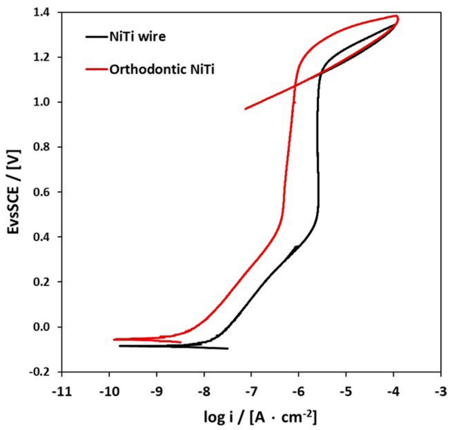


Fig.4 - Curve CPP più rappresentative del filo commerciale e ortodontico in NiTi a 37 °C / *Most representative CPP curves of NiTi commercial and orthodontic NiTi wire at 37°C.*

Finally, figure 5 summarizes the characteristic potentials (corrosion, pitting, and repassivation) for the 304-based samples. The reported values represent the average and standard deviation for each characteristic potential obtained from the CPP curves. For the orthodontic 304 wires, only the specimens that exhibited measurable pitting potentials were considered in this analysis.

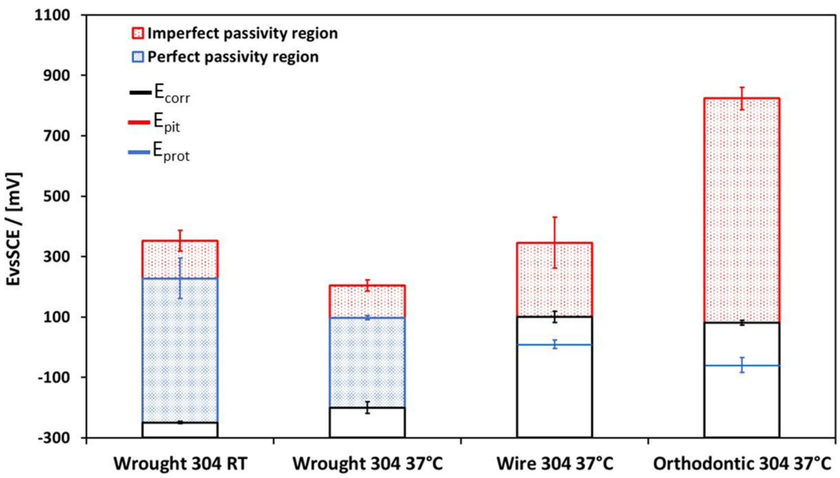


Fig.5 - Medie e deviazioni standard dei potenziali caratteristici delle curve CPP / *Averages and standard deviations of characteristic potentials of the CPP curves.*

CONCLUSION

This study examined the corrosion behavior of stainless steel and nickel-titanium orthodontic wires in artificial saliva at 37 °C and pH 5.5, assessing the electrolyte stability, cell setup reliability, and localized corrosion resistance. The artificial saliva remained stable over time, ensuring reproducible CPP measurements.

The comparison between wrought and wire 304 stainless steel confirmed that temperature, geometry of the electrochemical cell and the surface finish of metal significantly affect corrosion behavior. Orthodontic 304 wires showed variable resistance to localized corrosion, with most samples exhibiting high pitting potentials (up to +0.95 V) and imperfect passivity. In severe cases, localized attack was significant and even caused wire fractures, indicating a potential risk of mechanical failure and metal ion release.

In contrast, NiTi and orthodontic NiTi wires showed no evidence of localized corrosion, confirming the superior stability of their passive film. Overall, while 304 stainless steel may be suitable for short-term orthodontic applications, NiTi wires represent a more reliable and durable option for long-term use.

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Proprietà di resistenza a corrosione di archi ortodontici in acciaio inossidabile 304 e nichel-titanio in soluzione di saliva artificiale

Le leghe più comunemente utilizzate negli archi ortodontici sono l'acciaio inossidabile e le leghe di titanio per via delle loro proprietà di resistenza alla corrosione. Queste leghe sono generalmente caratterizzate da un buon comportamento alla corrosione in ambienti debolmente aggressivi, sebbene talvolta si verifichino rotture impreviste e reazioni allergiche. Le principali cause possono essere attribuite al degrado del film passivo degli archi ortodontici, dovuto alle condizioni complesse e variabili che si verificano all'interno del cavo orale, poiché la composizione della saliva umana e la durata dell'esposizione possono differire significativamente a seconda del paziente. In questo studio è stata considerata la valutazione delle proprietà di resistenza alla corrosione per due archi ortodontici disponibili in commercio: acciaio 304 e una lega nichel-titanio. Il comportamento elettrochimico è stato indagato mediante curve di polarizzazione potenziodinamica ciclica registrate in saliva artificiale a 37 °C e pH 5,5. I risultati hanno dimostrato che gli archi ortodontici in acciaio 304 presentano proprietà di resistenza alla corrosione variabili, da eccellenti a scarse. Inoltre, quando si verifica la rottura del film passivo nell'acciaio 304, il potenziale di ripassivazione risulta inferiore al potenziale di corrosione, indicando che i danni possono propagarsi facilmente, portando a guasti significativi e al rilascio di ioni metallici, con conseguente rischio di allergie. Al contrario, gli archi ortodontici in nichel-titanio non hanno mai mostrato corrosione localizzata, dimostrando proprietà di resistenza alla corrosione superiori rispetto al 304.

PAROLE CHIAVE: CORROSIONE LOCALIZZATA; FILI ORTODONTICI; SALIVA ARTIFICIALE; POLARIZZAZIONE CICLICA POTENZIODINAMICA;