Effect of Fluoride on Nickel-Titanium and Stainless Steel Orthodontic Archwires: An In-Vitro Study

Farzin Heravi[1], Mohamad Hadi Moayed[2], Nima Mokhber[3]✉

[1]Department of Orthodontics,School of Dentistry Mashad University of Medical Sciences, Mashhad, Iran
[2]Department of Materials and Metallurgical Engineering, Ferdowsy University , Mashhad, Iran
[3]Department of Orthodontics, Academic Center of Education, Culture and Research (ACECR), Mashhad, Iran

✉ Corresponding author:
N. Mokhber, Department of Orthodontics, Academic Center of Education, Culture and Research (ACECR), Mashhad, Iran

nimamokhber@yahoo.com

Abstract
Objectives: The commonly used Nickel-Titanium (NiTi) archwires in orthodontic treatment are often exposed to fluoride-containing mouthwashes. The aim of this in-vitro study was to evaluate and compare the corrosion resistance of three commercially available NiTi archwires exposed to 0.05 wt% and 0.2 wt% fluoride mouthwashes.
Materials and Methods: Three different types of NiTi archwires, 0.016" in diameter, from Dentaurum, Global, and GAC, and a stainless steel archwire from Dentaurum were examined to assess their corrosion resistance in Fusayama-Meyer artificial saliva and in two other artificial saliva containing 0.05 wt% and 0.2 wt% sodium fluoride (NaF). After the primary setup of wires, they were tested by potentiodynamic and potentiostatic polarization and corrosion potential/time analyses. Their surfaces were evaluated using a scanning electronic microscope (SEM).
Results: The results showed that all the wires were passive in artificial saliva. In contrast, by adding fluoride ions to the solution, the decrease in the archwires' corrosion resistance was in direct proportion to the increase in fluoride concentration.
Conclusion: The NiTi wires experienced deterioration of their corrosion properties under the effect of fluoride but not as much as the stainless steel archwires.
Keywords: Corrosion; Fluoride; Nickel-titanium alloy; Scanning electron microscopy

INTRODUCTION

Titanium-based alloys have high corrosion resistance because they form a thin, stable oxide layer. Nevertheless, fluoride-containing prophylactic agents can cause corrosion and associated discoloration of titanium-based orthodontic wires [1]. Resistance to corrosion, superelastic properties, and permanent shape memory, make the orthodontic treatment more efficient for clinicians by decreasing the number of wire changes required for each patient [2].

Furthermore, Ni–Ti wires, thanks to their pseudoelastic properties, allow the orthodontists to apply light and continuous forces to the teeth, reducing the risk of patient discomfort, tissue hyalinization and undermining resorption [3].

It is important to recommend the regular use of fluoride- containing products, in particular gels and mouthwashes, during the course of orthodontic treatment to help prevent dental caries [4]. Additionally, systemic fluoride may be ingested orally by drinking tea and fluoridated bottled water and also taking dietary supplements. Therefore, NiTi orthodontic wires are readily exposed to fluoride [5]. Fluoride mouthwashes, available in 0.05% and 0.2% fluoride concentrations, are frequently prescribed by orthodontists for weekly and even daily use to prevent caries.

It has been clearly shown that Ni ion release, due to the corrosion, can cause allergenicity, toxicity and carcinogenicity [5-8]. It can also cause allergic contact dermatitis, the incidence of which is as high as 20–30% [9-11]. The corrosion phenomenon not only may influence the mechanical properties of the metal appliances, but also may affect the body due to leached metal ions [12-14].

Because of the ionic, thermal, microbiological, and enzymatic properties of the oral environment, patients are often exposed to corrosion products [15].

Atomic absorption spectrometry has been used to analyze the Ni ion release [16-18]. The second method is to use electrochemical tests [7,19–21] in artificial saliva to assess the electrochemical properties in order to evaluate the corrosion resistance of NiTi alloys in vitro.

There are many published studies on the corrosion resistance of NiTi alloys in physiological solutions, particularly in both fluoridated and non-fluoridated Fusayama–Meyer artificial saliva [7, 17, 22, 23]. Moreover, NiTi archwires are significantly more stable and resistant to corrosion than stainless steel archwires [23-25]. Furthermore, it has been well documented that fluoride has a negative effect on the corrosion resistance of NiTi alloys [22, 23]. However, there is little information to interpret and compare the adverse effects of different concentrations of fluoride available in typical mouthwashes.

The purpose of the present study was to investigate and compare the electrochemical corrosion characteristics of three different types of NiTi and one stainless steel archwires in fluoride mouthwashes with two different concentrations. In order to achieve this objective, open circuit potential measurements and potentiodynamic and potentiostatic polarization tests were performed in non-fluoridated and 0.05 wt% and 0.2 wt% fluoridated Fusayama–Meyer artificial saliva. The corresponding corrosion morphologies were also observed using SEM.

MATERIALS AND METHODS
For the comparison purposes, three types of commercially available NiTi wires and a stainless steel wire were selected. The media for corrosion tests were the artificial saliva used as the control and the artificial saliva containing 0.05wt% and 0.2wt% sodium fluoride.

Wires: The selected NiTi orthodontic wires were divided into three groups: NiTi-1 Rematitan (Dentaurum, Germany), NiTi-2 Sentalloy (GAC, USA), and NiTi-3 Global (Global, Canada). The last group consisted of SS archwires (Dentaurum, Germany). All of the wires were 0.016 inches (0.41 mm) in diameter and shaped as preformed lower arches. Each test sample contained three pieces of wire 6 mm in length (12 specimens for each test solution).

Artificial saliva: The reference electrolyte used was Fusayama − Meyer artificial saliva. Table-1 exhibits the composition of the artificial saliva, which closely resembles natural saliva.

Table 1. Contents of the Fusayama-Meyer artificial saliva

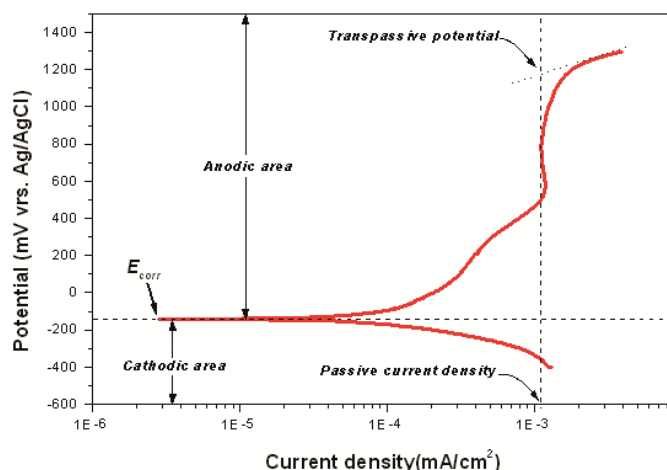| Ingredient	Amount (g/l)
KCl	0.400
NaCl	0.400
$CaCl_2.2H_2O$	0.906
$NaH_2PO_4.2H_2O$	0.690
$Na_2S.9H_2O$	0.005
Urea	1.000

Fig 1. Depicting various parameters in a polarization plot

All the constituents were provided from Merck Chemical Company, Germany. The pH was measured with a pH-meter (WTW, D82362, Weilheim, Germany). The pH of this reference saliva, corresponding to the first test solution, was 5.35. To evaluate the effect of fluoride concentration on the corrosion resistance of commercial NiTi archwires, different amounts of NaF were added to the artificial saliva to prepare 0.05% and 0.2% NaF concentrations, simulating the fluoride concentrations in commercially available fluoridated mouthwashes. The pH of both these media was maintained at 5.3.

Electrochemical set-up: Each group was tested in 250 mL glass jars. Their covers were made of Teflon plates having two openings to allow the insertion of electrodes (Azarteb, Urmia, Iran) and two smaller holes for the tips/ends of the archwires.

The jars filled with artificial saliva containing 0.05 wt% and 0.2 wt% NaF were stored at 37±1°C in a bain-marie bath (Pars Azma type 1400, Iran).

Before each test, the wires were degreased ultrasonically with acetone for 15 minutes at ambient temperature, then washed with distilled water and dried with a hairdryer.

A 6 mm portion of each wire was marked and immersed in the media.

The reference electrode was Ag/AgCl, and the auxiliary electrode was made of platinum (Azarteb corp., Iran). The whole system was connected to a potentiostat (Gill AC, England). Corrosion resistance analyses: The corrosion resistance analyses comprised of polarization tests (potentiostatic and potentiodynamic), the corrosion potential monitoring and evaluation of the surface topography of wires.

The corrosion potential was measured over time by plotting the polarization curves once the potential was stabilized, to determine the corrosion resistance of the titanium alloys in different media. The potential for all the wires in each media was recorded every 10 seconds for a period of 24 hours.

To determine the corrosion current density (icorr) in the potentiodynamic polarization tests, the archwires were polarized both anodic and cathodic (-300mV to 1500mV) relative to the reference electrode. The corrosion current density values are given in mA/cm2. The experiments were performed three times for each orthodontic wire in each test solution. Each curve represents one of the three experiments of each material in each medium and all the curves were obtained from reproducible individual measurements. The Ecorr, icorr values are the mean values of the three experiments with a maximum error of 10–15% (Figure 1).
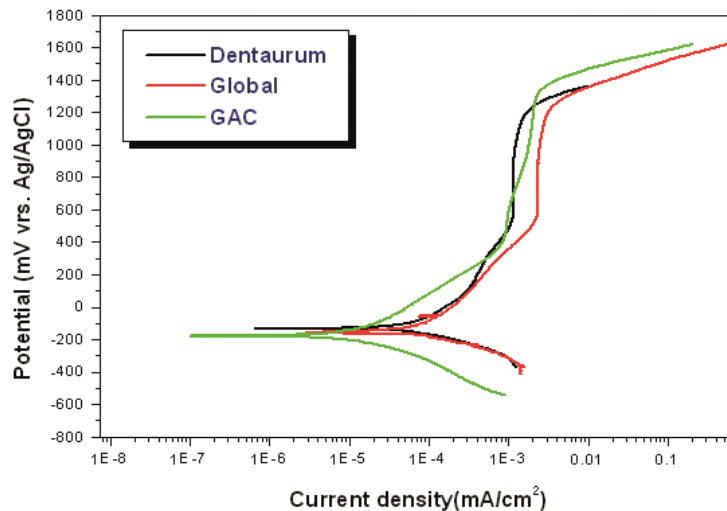
Fig 2. Comparison of NiTi archwires' polarization plots in artificial saliva

The potentiostatic polarization tests were also performed in a stable anodic potential of 200mV. The changes in corrosion current density were recorded as dependent of time. In the end, the topographic evaluation of working electrodes (the wires) was done using SEM (Cambridge, S-360, England).

RESULTS

The corrosion potential of the different alloys was measured after 24 hours in the four test solutions.

As shown in Table 2, the potentials decreased as the concentration of NaF increased. This finding suggested that the corrosion resistance of archwires diminished by increasing the NaF concentration.

The polarization curves were plotted in the potential range of -300 mV to $+1500$ mV at a scanning rate of 0.5mV/s.

The corrosion current increased and the potential of breakdown decreased (the potential at which the alloys started to corrode) as the fluoride concentration increased (Tables 3 and 4).

Table 2. Corrosion potentials (mV/SCE) of the samples in different media after 24 hours

E_{corr}(mV/SCE)	NiTi-1	NiTi-2	NiTi-3	Stainless steel
Fusayama-Meyer Saliva	75	19	115	147
Artificial saliva & 0.05wt% NaF	-210	-305	-170	11
Artificial saliva & 0.02wt% NaF	-218	--380	-353	-110

Table 3. The corrosion current densities (10^{-6} A/cm^2) of the samples in different media

I_{corr}(10^6A/cm^2)	NiTi-1	NiTi-2	NiTi-3	Stainless steel
Fusayama-Meyer Saliva	0.13	0.02	0.11	0.07
Artificial saliva & 0.05wt% NaF	0.92	0.13	0.26	0.19
Artificial saliva & 0.2wt% NaF	1.4	0.36	0.51	0.23

Table 4. Potential of breakdown (mV) of the samples in different media

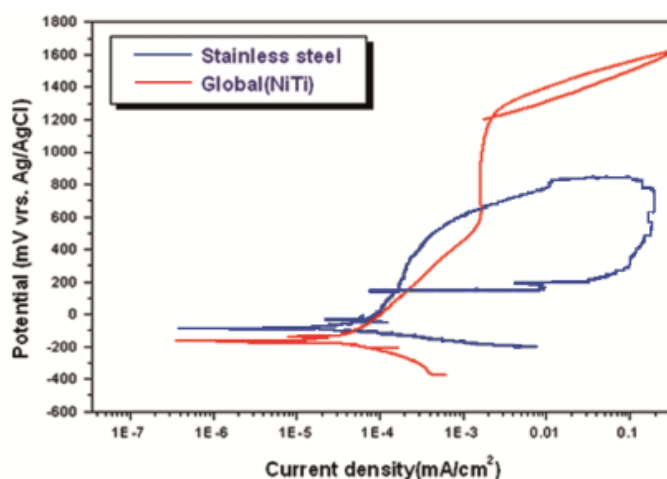| Potential of breakdown (mV)	NiTi-1	NiTi-2	NiTi-3	Stainless steel
Fusayama-Meyer Saliva	1300	1280	1250	630
Artificial saliva & 0.05wt% NaF	400	1180	1100	580
Artificial saliva & 0.2wt% NaF	300	1100	1070	550

Fig 3. Potentiodynamic polarization plot for stainless steel and NiTi-3 (Global) archwires in artificial saliva
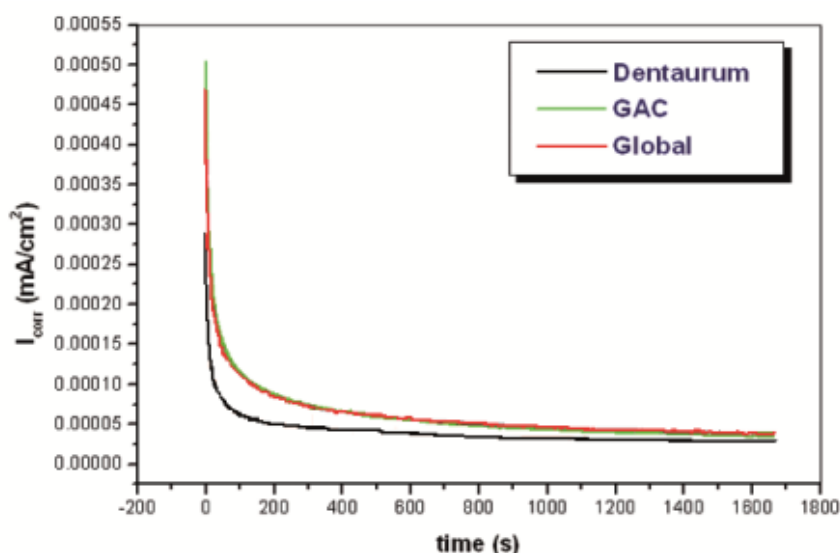

Fig 4. Comparison of NiTi archwires' potentiiostatic plots in artificial saliva

In artificial saliva, there was a little difference between NiTi-2 and the two other wires in cathodic area.

In the anodic area, the plots showed a large range of passivity: beyond this area, a transpassivity phenomenon occurred.

Passivity area continued from 500 to 1200mV of anodic area (Figure 2).

In contrast, stainless steel wires showed a pitting corrosion registered at 630mV while NiTi-3 as the representative of NiTi alloys revealed the pits in a potential roughly over 1100 mV (Figure 3).

Since the anodic reactions are responsible for metal dissolution during polarization of an alloy, studying the anodic branch of polarization curves obtained from potentiodynamic experiments is of interest.

Since the corrosion current density of stainless steel archwires in potentiostatic tests was far more than that of NiTi alloys, it was not possible to chart it in Figure 4 next to other NiTi wires. Both the potentiostatic tests and the corrosion potential (Ecorr) over time confirmed the passivity of NiTi wire in neutral environment (Figures 4 and 5).
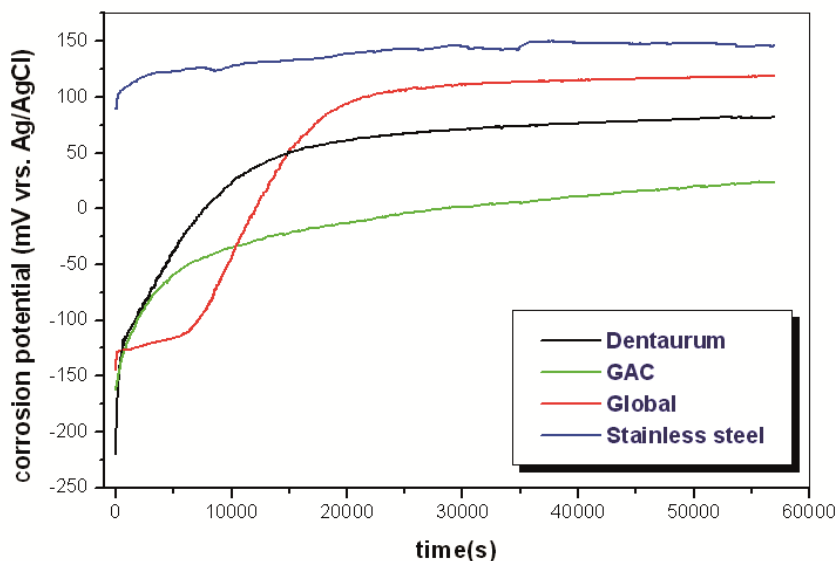
Fig 5. Comparison of NiTI archwires' corrosion potential over time in artificial saliva

Figure 5 shows the changes in corrosion potential of Nitinol and stainless steel archwires in simulated saliva solution. For Nitinol archwires, the corrosion potential simultaneously increased due to polarization of anodic branch of corrosion system.

This polarization of anodic reaction is due to the integration of the passive layer on the surface in the form of TiO_2. After about 200 seconds, the corrosion potential became almost constant and stable.

However, the variation of corrosion potential for stainless steel wire was different. The initial corrosion potential of stainless steel was almost 200 mV more positive than Nitinol archwires and it was stable for the course of experiment at about 125 mV. This behavior may be attributed to the stability of passive film; mainly Cr_2O_3, on stainless steel. However variation of corrosion potential for about 60,000 seconds indicated that the alloy showed passivity.

Potentiostatic results of Nitinol archwires at 200 mV potential above the corrosion potential are shown in Figure 4. As seen, the current densities of all three NiTi alloys when applied above 200 mV showed a sharp decrease and reached a stable condition.

This behavior proves that all alloys are in passive state at 200mV applied anodic potential. The only marginal difference mentionable is the greater tendency of NiTi-1 (Dentaurum) archwire that showed a sharper drop in passive current density for the first 100 seconds of the experiment and a lower stable passive current density at the end of the course of experiment in comparison with the other two NiTi archwires. However, the passive current density of the three alloys at the end of the experiment was about 50 nA/cm2. This negligible passive current density proves the stability of these alloys in artificial saliva environment due to the formation of a corrosion resistant passive film.

The addition of fluoride ions resulted in reduction of corrosion resistance. An increase in the corrosion current density was observed as the concentration of fluoride increased.

The corrosion current densities in the saliva containing 0.05 wt% fluoride were 0.92 µA/cm2 for NiTi-1, 0.13 µA/cm2 for NiTi-2 and 0.26 µA/cm2 for NiTi-3 wires. In 0.2wt% fluoridated saliva, Icorr were 1.4 µA/cm2, 0.36 µA/cm2 and 0.51 µA/cm2 for NiTi-1, NiTi-2 and NiTi-3 archwires, respectively (Figures 6 and 7).

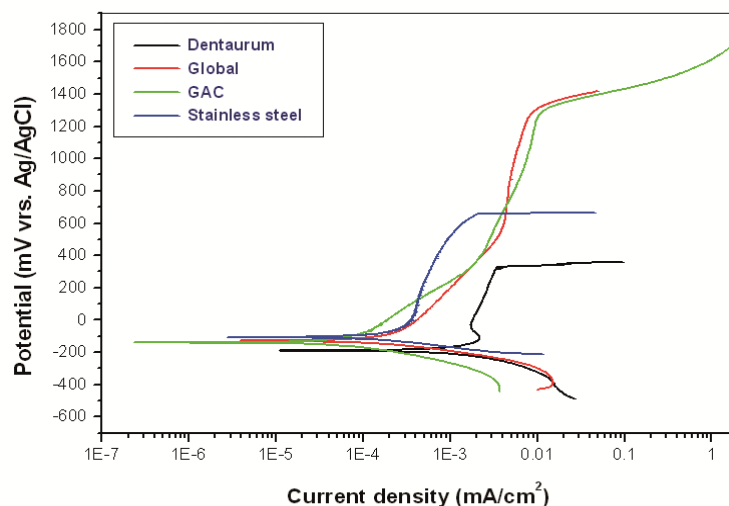**Fig 6.** Comparison of NiTi archwires' polarization plots in artificial saliva with 0.05wt% NaF
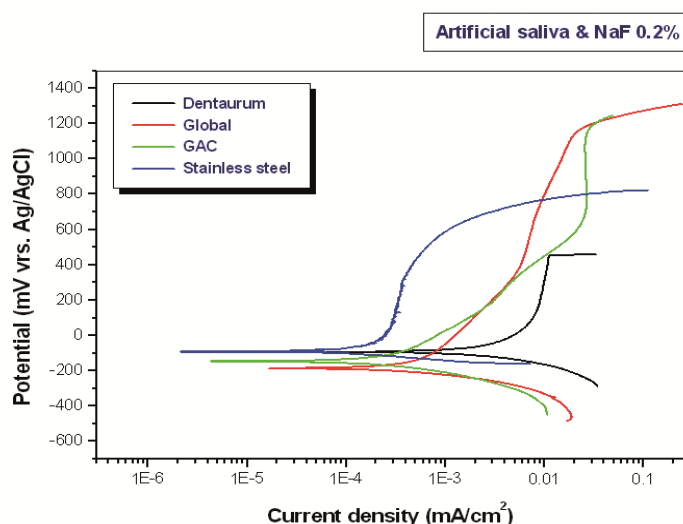

Fig 7. Comparison of NiTi archwires' polarization plots in artificial saliva with 0.2wt% NaF

The increase in corrosion currents in response to increased concentration of NaF confirmed that the corrosion resistance had a reverse correlation with NaF concentration.

Topographic assessment by SEM showed a pitting corrosion in different shapes in all the wires tested. In both stainless steel and NiTi-1 wires, the shape of pits was well-defined; whereas, in the other wires, the pits were accompanied by fissures and porous surfaces (Figure 8).

DISCUSSION

Results of the polarization test in the artificial saliva revealed that all NiTi wires showed passive behavior, no pitting corrosion and transpassivity due to water oxidation. NiTi-1 group showed the highest resistance while the stainless steel wires exhibited passivity in corrosion potential. Pitting corrosion was seen when the anodic potential increased. The passive oxide layer is mainly TiO_2 for NiTi and Cr_2O_3 for stainless steel.
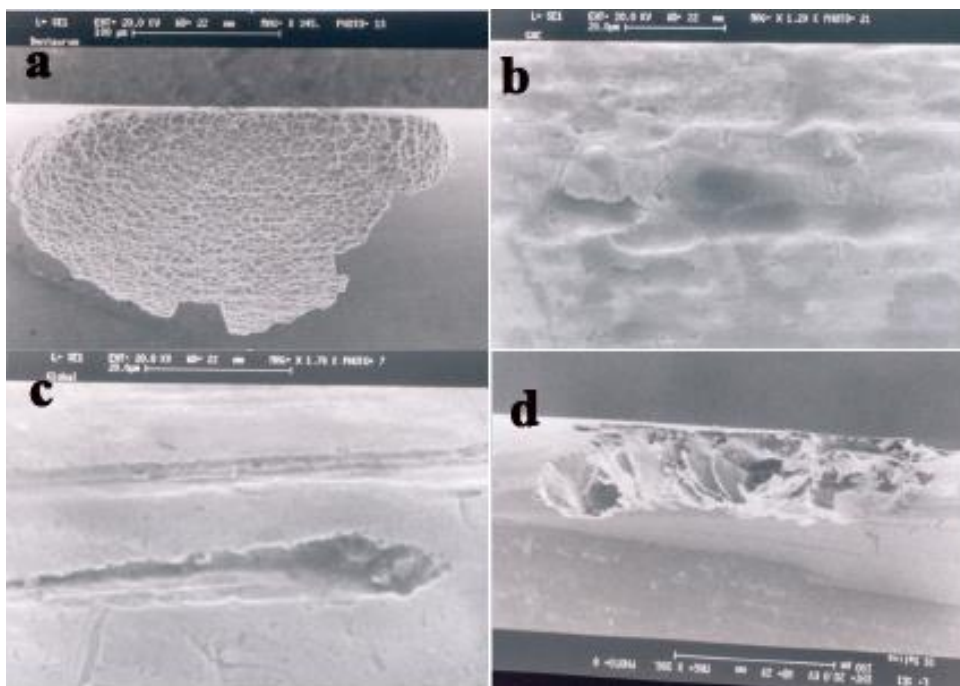
Fig 8. SEM images of pitting corrosion in a)Dentaurum NiTi-1 archwires b)GAC NiTi-2 archwires c)Global NiTi-3 archwires d)Dentaurum stainless steel archwires

As seen in Figure 3, steel wires showed pitting corrosion current density in lower potentials.

This indicated that the stainless steel passive film was more protective than that of NiTi in this saliva solution. However, the resistance of this alloy to pitting corrosion was much lower than that of NiTi due to surface inclusions. Potentiostatic results of Nitinol and stainless steel wires at 200mV above the corrosion potential are shown in Figure 4 indicating that Nitinol wires were passive.

Additionally, the passivity current density continuously decreased with time and after 15 minutes, it reached around 500 nA/cm2 for the three NiTi wires. The experiments demonstrated that the corrosion potential of NiTi alloys experienced a pronounced decline by adding fluoride, which suggested that the corrosion resistance of NiTi orthodontic archwires decreased in presence of fluoride in an acidic environment.

Potentiodynamic tests revealed that NiTi-2 group showed pitting corrosion in higher anodic potentials (around 1200 mV) by adding fluoride ions to the media in comparison with the other two NiTi wires. This behavior is due to the local dissolution of TiO2 oxide layer in the presence of fluoride ions at higher potentials. In presence of fluoride ions, the corrosion potential decreased, the corrosion current density increased and the passivity current density increased as well. These indicate that the anodic reaction was depolarized. Therefore, dissolution of TiO2 increased in presence of fluoride.

A similar decrease in corrosion potential of NiTi alloys created by fluoride has also been reported in the literature [7, 22, 27]. Fluoride ions attacked the protective oxide layer on all the alloys tested. In artificial saliva, a chemical attack characterized by localized pitting was clearly visible under SEM.

It can be concluded from these observations that the TiO2 protective layer on the surface of NiTi wires is much more resistant than the Cr2O3 layer on stainless steel wires, confirming the findings of Rondelli and Schiff [22, 26].

The acceleration in corrosion behavior of Nitinol wire in the saliva solution in presence of fluoride can be attributed to either the increase in aggressive ion concentration or the nature of fluoride as an accelerator ion.

There are few studies discussing the effect of fluoride ions on the orthodontic NiTi wires using potentiostatic tests in different anodic potentials and the evolution of the corrosion current density in time as an addition to the traditional potentiodynamic tests.

Potentiostatic tests confirmed that the corrosion resistance of NiTi wires decreased by adding NaF to artificial saliva, but the polarization plot of NiTi-1 group was different from that of the other NiTi wires as the increase of current density was pronounced and parallel to the X axis. In contrast, the increase of current density in the other NiTi groups led to a slight curve approximately parallel to Y-axis.

SEM demonstrated that the shape of corrosion pits was also different for the NiTi-1 group when compared with the others and its smoother surface contrasted the rough surface of other wires. Probably, the cold working/ manufacturing of these wires is responsible for the differences seen in the corrosion behavior and polarization plot of these wires. The pictures show a well-defined saucer-shaped pits with a honeycomb form in depth for NiTi-1 but fissures and cracks along the archwires' length for NiTi-2 and NiTi-3. It may explain the different breakdown potentials of NiTi-1 and the shape of its corrosion pits in presence of NaF. Consequently, it could be pointed out that the pitting potential of NiTi orthodontic wires in fluoride can be significantly influenced by their surface topography. Although the corrosion resistance decreased in artificial saliva with 0.05wt% NaF, the corrosion pits were created in high potentials (approximately +200mV). In addition, the corrosion potentials in all three groups of NiTi archwires and stainless steel group were the same in the mentioned electr lytes in spite of their difference in shape of corrosion pits.

Though our results may seem to differ from those of Lee et al, [28] suggesting that different NiTi archwires had dissimilar corrosion resistance in acidic fluoride-containing artificial saliva. This controversy may be due to the difference in the concentration of fluoride ions in the two studies. They used the maximum 0.5wt% fluoride in their experiment, which was 10 times more than the concentration used in our study. In the solution containing 0.2wt% NaF, the attack was more intense than in the other solutions. The corrosion resistance decreased as the concentration of fluoride increased.

Our finding is consistent with that of previous studies [4,7], which have shown that a NiTi orthodontic archwire may corrode in commercially available fluoride mouthwashes. Furthermore, our results confirm the studies reporting that [29] the protective role of TiO_2 formed on Ti alloy is compromised by fluoride ions when the NaF concentration exceeds 0.1wt%. Aggressive behavior of fluoride ions on titanium alloys in aqueous environment has been attributed to the chemical reaction of fluoride ions with the TiO_2 passive film and destruction of the TiO_2 passive film by the formation of soluble TiF_6^{2-} ion (following reaction). This reaction leads to deterioration of passivity by thinning of TiO_2 passive film leading to the depolarization of the anodic branch of polarization curve. It means that higher passive current density can be reached in presence of fluoride due to the depolarization of passive film.

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O \qquad (1)$$
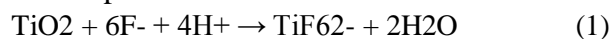
The increase of passivity current density may also be attributed to the increase in TiO_2 oxide layer defects in presence of F^- ions and its oxide chemical dissolution by the abovementioned reaction [30]. Therefore, it is wise to use fluoride mouthwashes with lower weight percentage of fluoride when their consumption seems necessary, especially during long-term orthodontic treatments as these incur the risk of poorer physical and electro-

chemical characteristics of the wires. Moreover, the nickel ions released from alloys attacked by fluoride may cause toxic and allergic reactions.This study only assessed the pitting corrosion. The oral cavity conditions are, however, more complex and some other types of corrosions such as crevice corrosion or galvanic corrosion also need to be considered, as well as food debris accumulation, diet and differences in oxygen concentrations. All these are factors that contribute to the corrosion of orthodontic archwires.

CONCLUSION
1) In the artificial saliva, all the NiTi archwires were found to be passive, in contrast to the stainless steel wire, which showed pitting corrosion.
2) The addition of fluoride to artificial saliva decreased the corrosion resistance of all the archwires tested.
3) As the fluoride concentration in saliva increased, the corrosion resistance of wires decreased. This may be due to the destructive effect of fluoride on the protective oxide coating.
4) The shape of pits depended on the surface properties of archwires.

ACKNOWLEDGMENTS

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