



Comparative study on corrosion behaviour of Nitinol and stainless steel orthodontic wires in simulated saliva solution in presence of fluoride ions

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ARTICLE INFO

Article history:

Received 17 June 2012

Received in revised form 10 December 2012

Accepted 14 January 2013

Available online 20 January 2013

Keywords:

Stainless steel

Nitinol

Pitting corrosion

Crevice corrosion

Passivity

ABSTRACT

Localized corrosion and effects of pre-passivation treatment of Nitinol and SS304 orthodontic wires in simulated saliva solution in the presence and absence of fluoride ions were investigated by means of potentiodynamic and potentiostatic polarisations. Results revealed that Nitinol does not show pitting corrosion in saliva solution however, SS304 shows pitting corrosion. Meanwhile fluoride ion has deteriorative effect on pitting corrosion of Nitinol, while its effect on SS304 was marginally constructive. Additionally, the presence of artificial crevice has no effect on corrosion behaviour in the presence of fluoride. Pre-passivation treatment has positive influence on pitting corrosion of both alloys in the presence of F^- ions.

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1. Introduction

The orthodontic metal wire has been progressed from cobalt–chromium–nickel (Co–Cr–Ni) and stainless steel (SS) alloys to nickel–titanium (NiTi) alloy. In clinical orthodontic treatment, different alloys have a wide range of applications. These applications relate to NiTi alloy properties including superelasticity, thermal shape memory, good corrosion resistance and good biocompatibility [1]. The characteristics of NiTi wire alloy can reduce chair time and shorten treatment times. The biocompatibility of NiTi relies on the tendency of its surface to be covered by TiO_2 based oxides in natural conditions [2,3]. Oxide films present on the surface of alloys such as stainless steel and titanium based alloys are responsible for their corrosion resistance.

To achieve good oral hygiene care during orthodontic treatment, practitioners recommend that their patients use fluoride mouthwashes. In particular, most patients are adolescents who do not always follow a satisfactory oral hygiene regime and are subjected to high risk of dental decay. Fluoride mouthwashes which are typically available in 0.05% and 0.2% concentrations of fluoride ions are frequently prescribed by orthodontists daily or weekly to reduce prevalence of cavities [4]. Because of ionic, thermal, microbiological and enzymatic properties of oral environment, it is favourable for the biodegradation of metal. Therefore, it can be presumed that patients are exposed to a certain extent of corrosion processes [2,5,6]. Fluoride promotes the formation of calcium fluoride globules that adhere to the teeth and stimulate remineralisation

while protecting against acid attack. Thus, fluoride mouthwashes help prevent the development of caries and protect dental enamel.

Much research have been conducted on the effect of chloride containing fluoride ions on localized corrosion of NiTi orthodontic arch wires and indicate the destructive influence of fluoride on corrosion behaviour of NiTi orthodontic wire. Research by Schill et al. [2,6] on NiTi alloy in artificial saliva with different pH and fluoride content showed a remarkable localized corrosion phenomenon of this alloys in fluoride and acid–fluoride saliva solutions. Li et al. [7] proposed a conversion of corrosion on NiTi orthodontic wire from localized to general corrosion when they were exposed to the chloride solution and solution containing chloride and fluoride. Examining various Ti containing dental orthodontic wire in solution containing chloride and fluoride ions, Lee et al. [8] found that the corrosion rate of all alloys in the presence of fluoride ions increases up to 1000 times and a remarkable decrease in passive film breakdown potential was also recorded.

Stainless steels as well as NiTi alloy are applied for the dental applications especially as the brackets and screws. Kocijan et al. [9] have studied the evolution of the passive films on 2205 duplex stainless steel (2205 DSS) and AISI 316L stainless steel in artificial saliva in the presence and absence of fluoride ions. According to their findings, the extent of the passive range increased for the 2205 DSS compared to the AISI 316L in both solutions and the passive films on both materials predominantly contained Cr-oxides. Wiegman-Ho and Ketelaar [10] have studied the corrosion of stainless steels in saliva solution quantitatively. Nie et al. [11] have investigated the effect of crystalline size on the corrosion behaviour of SS304 in an artificial saliva solution. They found that nanocrystalline structure is more resistant to corrosion than microcrystalline one. Mahato et al. [12] have illustrated that pitting

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corrosion of SS304 in saliva solution can happen in the absence of chloride ions by some commonly used dietary spices such as red chilli. There are also some other works that deal with the corrosion of stainless steels in human body [13–17].

Exposing stainless steel alloys in nitric acid solution for improving their corrosion resistance has been already investigated in detail. Hong et al. [18] examined the effect of nitric acid passivation on type 430 ferritic stainless steel using potentiodynamic polarisation, EIS, and Auger electron spectroscopy (AES). Pitting potential and total impedance magnitude were positively correlated to surface Cr concentration. In response to this study, Crolet [19] remarked that causality does not always follow from correlation of results from electrochemical tests and results from surface analysis. Strictly speaking, the effect of inclusion removal on pitting potential cannot be distinguished from the effects of Cr surface enrichment.

Noh et al. [20] characterized pitting potentials and metastable pitting transients of pre-passivated SS316 in HNO₃ solutions ranging in concentration up to 50 wt.% immersed in deaerated 1 M NaCl solution at 70 °C. MnS inclusions were removed to certain extents at all concentrations. Furthermore, an optimum concentration for HNO₃ based on Cr/Fe ratio of passive layer was introduced in which maximum E_{pit} was achieved. Additionally, correlation between E_{pit} and Cr/Fe ratio was not a linear one, suggesting the influence of other factors, such as inclusions, in determining E_{pit} .

The effect of pre-passivation in HNO₃ on improving corrosion behaviour of heat treated NiTi wire at 500 °C was also reported by O'Brien et al. [21]. Improvements of corrosion behaviour after passivation are primarily attributed to a reduction of Ni or NiO

content in surface and an increase of TiO₂ content in surface, rather than being related to oxide thickness.

Present study intends to investigate pitting and crevice corrosion behaviour of NiTi orthodontic arch wire in artificial saliva solution containing fluoride ions. Further investigation was conducted on the effect of pre-passivation of wires in HNO₃ on pitting and crevice corrosion in the same solution.

2. Materials and methods

2.1. Materials

In this study two types of orthodontic wires are used; Nitinol (purchased from Dentaaurum, Germany) and SS304 (purchased from Tiger Ortho, USA). The wire diameters are 0.4 mm. First, to characterize the chemical composition of the wires, energy dispersive X-ray (EDX) was used and the type of elements which form the wire was identified. Then, quantitative chemical compositions of major elements were measured by atomic adsorption spectroscopy (AAS). Fig. 1 shows the results of EDX analysis of Nitinol and SS304 surfaces. As it can be seen, Nitinol wire contains only nickel (Ni) and titanium (Ti) peaks in its EDX result and the oxygen (O) appears due to surface oxide layer. SS304 results show iron (Fe), chromium (Cr), nickel (Ni) and molybdenum (Mo) peaks in addition to silicon (Si), sulphur (S), phosphorus (P) and manganese (Mn) which exist in all types of steels. The AAS results of these two wires are presented in Table 1 showing that the chemical composition of these materials is in agreement with the Nitinol and SS304.

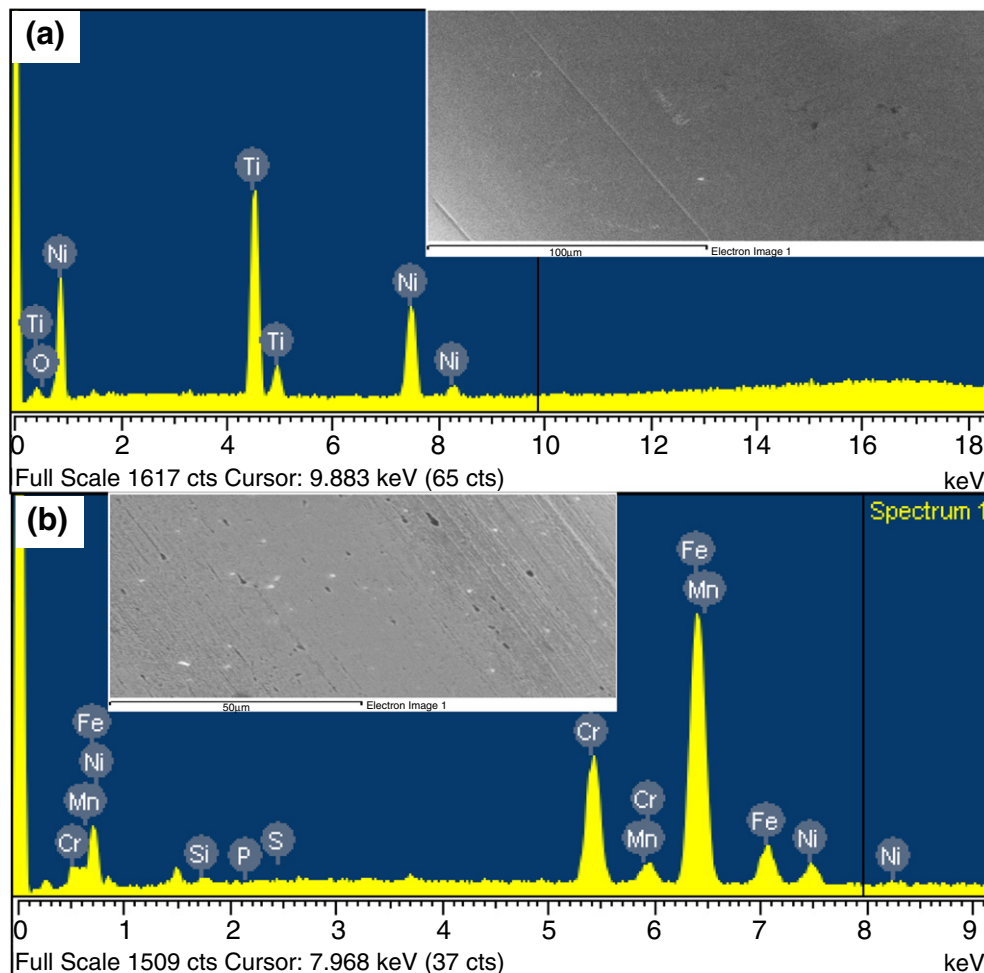


Fig. 1. Results of EDX analysis for (a) Nitinol and (b) SS304 orthodontic wires.

Table 1
AAS result of two purchased orthodontic wires (wt.%).

	Ni%	Ti%	Cr%	Mo%	C%	S%	Mn%
Nitinol	52.65	47.30	–	–	–	–	–
SS304	7.88	–	18.42	0.58	0.075	0.02	1.54%

Before each experiment, the wires are cleaned ultrasonically with acetone for 15 min at ambient temperature and then washed with distilled water. The wires were then stored in acetone to avoid any types of contamination prior to testing. Before corrosion examinations, the wire was elicited from acetone and washed with distilled water. In order to simulate the saliva solution, the Fusayama-Meyer solution has been used [2,6]. Chemical composition of this solution is close to the natural saliva and contains different types of salts which are shown in Table 2. All the salts have been purchased from Merck, Germany.

To investigate the effect of fluoride ions, the simulated saliva solution has been prepared with addition of 0.05 M sodium fluoride salt (NaF). The pH of simulated saliva solution in body temperature (37 °C) was 5.09 and in the presence of fluoride ions, it was 5.21.

2.2. Corrosion and microstructural examinations

Open circuit potential (OCP) measurement, potentiodynamic and potentiostatic polarisations have been used to study the electrochemical behaviour of orthodontic wires. All measurements were carried out at human body temperature (37 ± 1 °C). The temperature has been controlled using water bath. Potentiodynamic polarisation with the scan rate of 0.5 mV/s was selected from 50 mV below the corrosion potential to anodic potentials in which passivity breakdown occurs. Potentiostatic polarisation measurements were performed at different anodic potentials for 900 s with the frequency of measurement of 2 Hz. All the measurements were recorded by automated ACM Instrument potentiostat (Gill AC) and standard three electrode cell. In this cell, orthodontic wire was working electrode and saturated calomel electrode (SCE) and a foil of platinum with 2 cm² area were used as reference and auxiliary electrodes, respectively.

The schematic of test cell is shown in Fig. 2. The area of working electrode was measured after the tests base on the length of exposed wire in the solution and the obtained results were normalized by the working electrode surface area.

The effect of crevice on corrosion behaviour of orthodontic wires in simulated saliva solution and also the solution with additional fluoride ions has been studied by inserting 5 O-rings on wires. The purpose of this investigation was to simulate the crevice corrosion caused by fixing the wires on teeth. The wire with O-rings was immersed in the test solution and when its corrosion potential become stable, crevice corrosion has been studied using potentiodynamic measurements as described above.

Furthermore, the effect of pre-passivation treatment on corrosion behaviour was investigated. After cleaning treatment, some of the wires were pre-passivated using different nitric acid concentrations at room temperature for 60 min. The wires were then taken out of the acid solution and washed with distilled water several times before electrochemical measurements. The nitric acid concentrations and their pH used for pre-passivation treatment are shown in Table 3.

Table 2
Fusayama-Meyer artificial saliva solution composition.

Chemical compound	KCl	NaCl	CaCl ₂ ·2H ₂ O	NaH ₂ PO ₄ ·2H ₂ O	Na ₂ S·9H ₂ O	CO(NH ₂) ₂
Concentration (g/l)	0.4	0.4	0.906	0.690	0.005	1

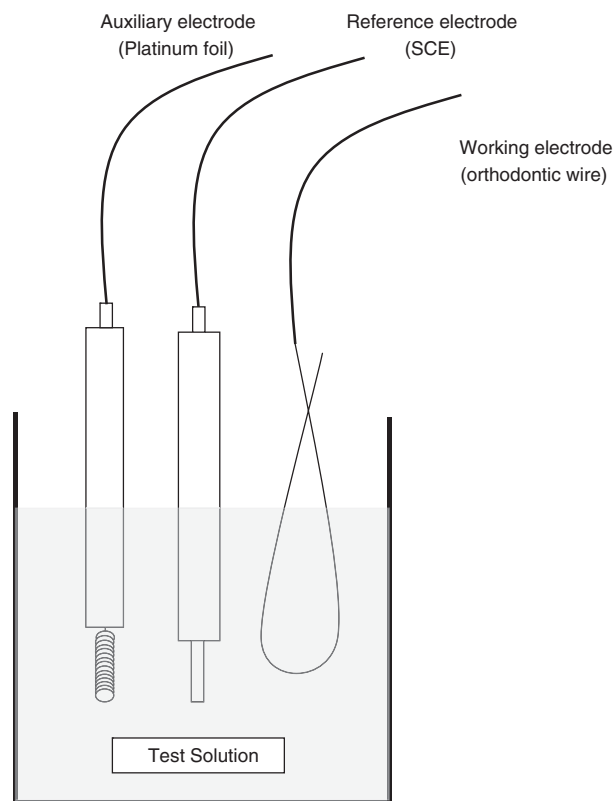


Fig. 2. Schematic of electrochemical test cell.

The surface of wires after electrochemical tests has been studied using scanning electron microscopy (SEM-EDX) model LEO 1450 VP. For this investigation, the wires after corrosion test were taken out from the test solution and ultrasonically cleaned in acetone.

3. Results and discussion

3.1. Effect of fluoride ions

Potentiodynamic results of Nitinol and SS304 orthodontic wires are shown in Fig. 3. In simulated saliva solution, Nitinol wires show passive behaviour. While, this solution contains chloride ions, this specimen shows no pitting corrosion and has transpassivity due to water oxidation. The SS304 orthodontic wire is passive in corrosion potential, however, at higher potentials it shows pitting corrosion due to existing of chloride ions. The oxide passive layer is mainly TiO₂ for Nitinol [22,23] and is M₂O₃ oxide type (M=Cr, Fe, Mo) for SS304 [24]. As it can be seen, SS304 wire shows higher corrosion potential and lower passivity current density. This indicates that SS304 passive film is more protective than that of NiTi in this saliva solution. However, the resistance of this alloy against pitting corrosion is much lower than NiTi due to surface inclusions. It is remarkable that the EDX results of SS304 (see Fig. 1) show existence of both Mn and S elements (Fig. 1) that can form MnS inclusions and are believed to be responsible for pitting corrosion of stainless steels. This type of metallurgical heterogeneities could not be observed in NiTi wires.

Table 3
Nitric acid concentration and their pH for pre-passivation of NiTi and SS304 orthodontic wires.

Nitric acid concentration (vol.%)	10	25	40	50
pH	–1.1	–1.65	–1.96	<–2

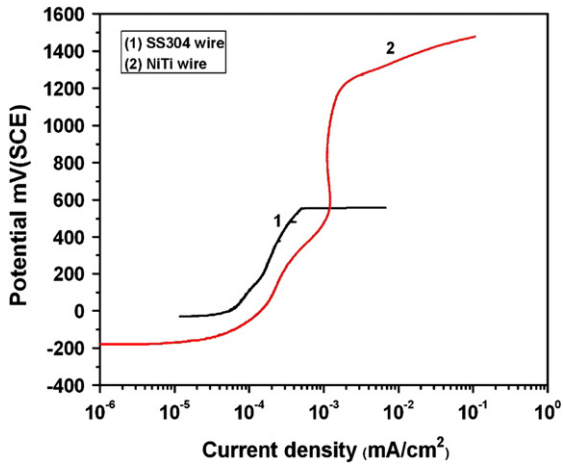


Fig. 3. Anodic polarisation of (1) SS304 and (2) Nitinol orthodontic wires in simulated saliva solution at 37 ± 1 °C with scan rate of 30 mV/min.

Potentiostatic results of Nitinol and SS304 wires at different anodic potentials above the corrosion potential are shown in Fig. 4. As it can be seen, in Nitinol wires, at anodic potentials of 300 mV and 550 mV above corrosion potentials, the wire is passive. Additionally, the passivity current density continuously decreases with time and after 15 min, it is lower than 500 nA/cm² for both potentials. The results also revealed that the passivity current density increases by an increase in anodic potential. However, at potential of 1000 mV higher than corrosion

potential, the current increases gradually. Based on the result obtained by potentiodynamic polarisation, this increase in current density is probably due to the water oxidation and not pitting corrosion.

The potentiostatic results of SS304 wire at different anodic potentials above corrosion potential shows that the pitting occurs at 400 mV above corrosion potential. As it is clear, by increasing the potential, background passivity current density increases, however, it is still lower than 100 nA/cm² up to 350 mV above corrosion potential. This observation confirms the obtained results from potentiodynamic polarisation in which passivity current density of SS304 was well below that of NiTi. At 300 mV above the corrosion potential, the metastable pitting occurrence can be observed. It is noticeable that metastable pitting occurrence could be occurred in lower potentials, but, it is not detectable because of the value of the background passivity current density. At the potential of 300 mV higher than corrosion potential, the magnitude of these metastable pitting occurrences increased and makes them distinguishable from the background passivity current density. Although the background passivity current density increases at 350 mV higher than corrosion potential, the frequency of occurrence of metastable pitting and also their magnitude increased. By further increasing the potential to 400 mV, the pitting occurs on the wire surface and the metastable pits become stable. This increase in current density of SS304 at 400 mV above E_{corr} is due to the stable pitting occurrence.

Fig. 5 shows the changes in corrosion potential of Nitinol wire in simulated saliva solution and saliva solution with addition of 0.05 M fluoride ion. In simulated saliva solution, at first minutes, corrosion potential decreases which is due to nickel dissolution. After that, corrosion potential simultaneously increases due to polarisation of anodic branch

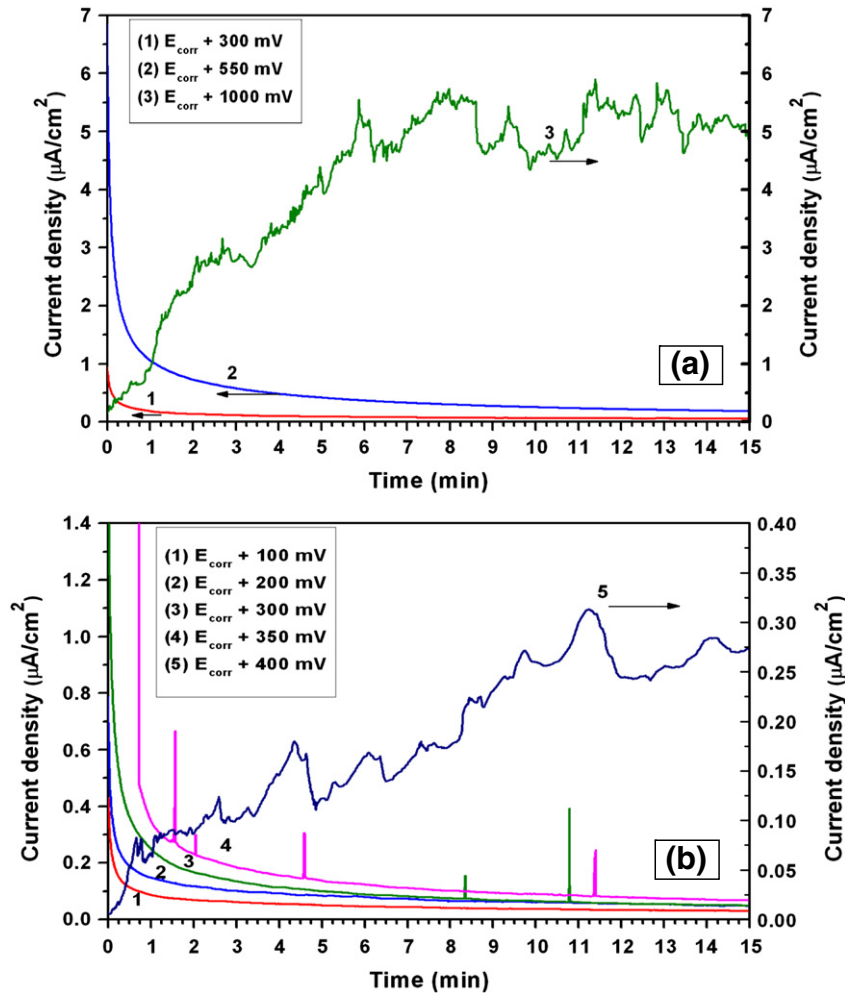


Fig. 4. Potentiostatic polarisation of (a) Nitinol and (b) SS304 orthodontic wires at different potentials above corrosion potential in simulated saliva solution at 37 ± 1 °C.

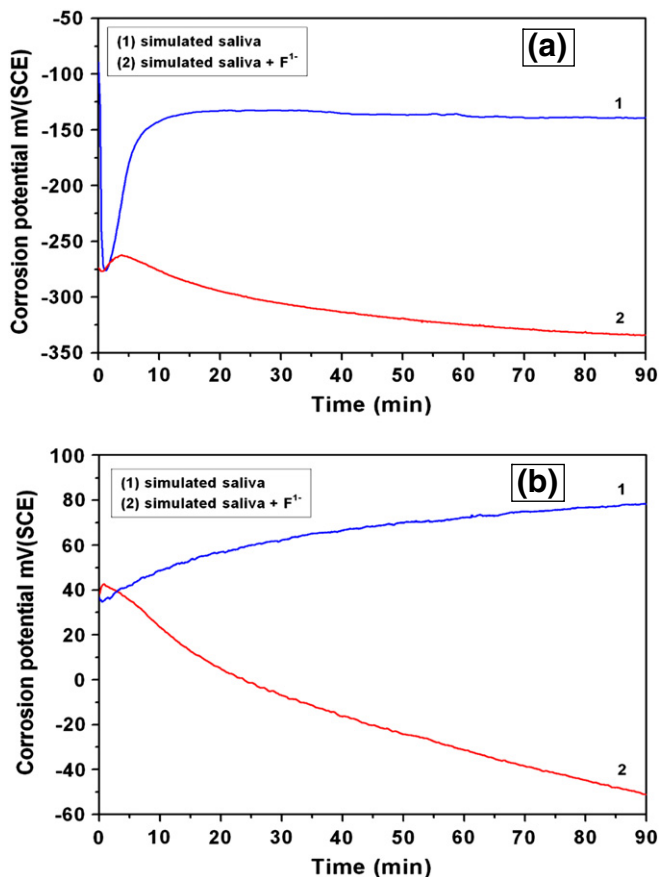


Fig. 5. Corrosion potential of (a) Nitinol and (b) SS304 orthodontic wires in simulated saliva solution and solution containing fluoride ions at 37 ± 1 °C.

of corrosion system. This polarisation of anodic reaction is due to the formation of passive layer on surface in the form of TiO_2 , as described above. After about 10 min, the corrosion potential becomes constant and stable. However, the corrosion potential in solution containing the fluoride ions is lower than that of pure saliva solution. In addition, after a slight increase in potential after about 5 min of immersion, the corrosion potential continuously decreases. This continuous decrease of corrosion potential may be attributed to continuous dissolution of surface as a result of fluoride ions existence.

Similar results were obtained for SS304 alloy. These results also confirm the potentiodynamic results in which higher corrosion potential was detected for SS304 compared to NiTi alloy. It is definitely clear that the presence of F^- ions has destructive effect on the corrosion behaviour of these two alloys.

Fig. 6 shows anodic polarisation results of Nitinol wires in the presence and absence of 0.05 M fluoride ion and also 0.05 M chloride ion in addition to chloride ions of simulated saliva solution. It should be noticed that the value of Cl^- concentration of simulated saliva solution is 0.0183 M. As it can be seen, in the saliva solution containing F^- and additional Cl^- ions, Nitinol wire shows pitting corrosion. This behaviour is due to the local dissolution of TiO_2 oxide layer in the presence of fluoride and chloride ions at higher potentials. In the presence of fluoride ions the corrosion potential has decreased and the corrosion current density increased and also passivity current density increased for a decade. These indicate that the anodic reaction has been depolarised. Therefore, dissolution of Ti oxide is raised in the presence of fluoride according to the following pH-dependent chemical reaction.

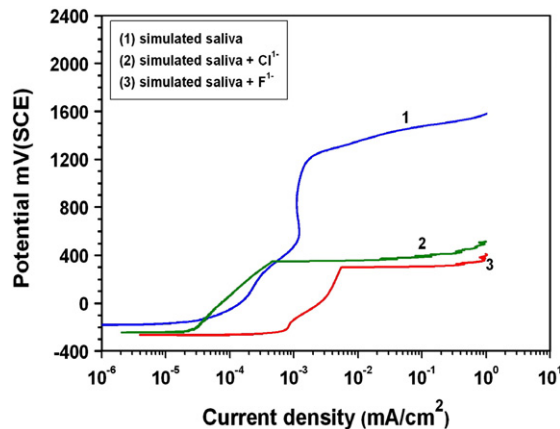


Fig. 6. Anodic polarisation of Nitinol orthodontic wire in simulated saliva solution and solution containing fluoride and chloride ions at 37 ± 1 °C and scan rate of 30 mV/min.

The increase of passivity current density can be attributed to the increase in oxide layer defects in the presence of F^- ions and its oxide chemical dissolution (see reaction 1).

As a result of this, at higher potentials, this oxide layer breaks locally and pits nucleate on the surface [22,23]. By further increase in potential, metastable pits tend to become stable. Since the value of current associated to metastable pit initiation on titanium alloys surface is too much lower than background passive current density [23], no metastable pit occurrence can be seen in potentials lower than pitting potential.

The acceleration in corrosion behaviour of Nitinol wire in saliva solution in the presence of fluoride ions can be attributed to either increase in aggressive ion concentration or nature of fluoride as an accelerator ion. To investigate this phenomenon, during corrosion potential measurement, 0.05 M fluoride and chloride ion were added to saliva solution. The results are presented in Fig. 7. As it can be observed, after addition of fluoride ions at about 175 min, corrosion potential decreases abruptly. This means that as soon as fluoride ions are added to the solution, surface chemical dissolution happens and continues. However, addition of chloride ions has almost no effect on corrosion potential. Regarding Fig. 6, it can be seen that in simulated saliva solution with additional 0.05 M Cl^- ion, corrosion potential has been decreased (like effect of F^- ions). However, corrosion and passivity current densities are similar to the simulated saliva solution. In other word, fluoride ions increase the Ti dissolution by creating a complex species between F^- ions from solution and Ti atoms of passive layer (TiF_6^{2-}). As a result, passivity current density increases. Consequently, the higher passivity current density and also higher corrosion current density of Nitinol

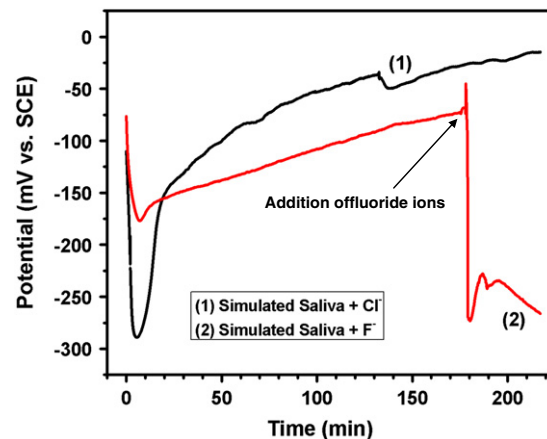


Fig. 7. Corrosion potential of Nitinol orthodontic wire in simulated saliva solution containing (1) 0.05 M additional chloride and (2) 0.05 M fluoride ions.

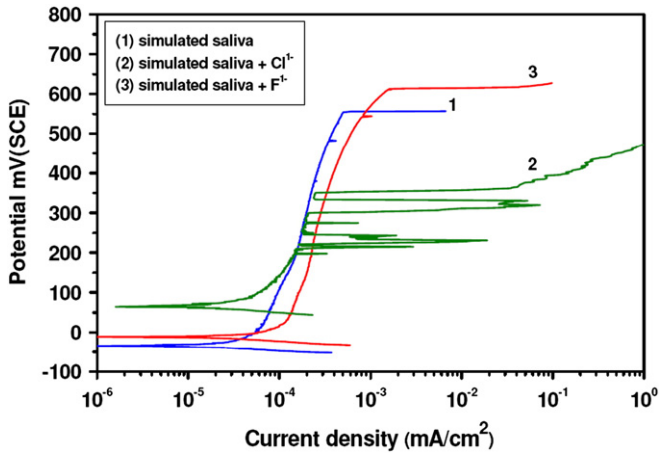


Fig. 8. Potentiodynamic polarisation of SS304 orthodontic wire in simulated saliva solution and solution containing fluoride and chloride ions at 37 ± 2 °C and scan rate of 30 mV/min.

wire in the presence of fluoride ions are due to aggressive nature of fluoride ion.

It is reported that initiation sites for pitting corrosion on titanium alloys are not inclusions and they arise from passive film itself [23].

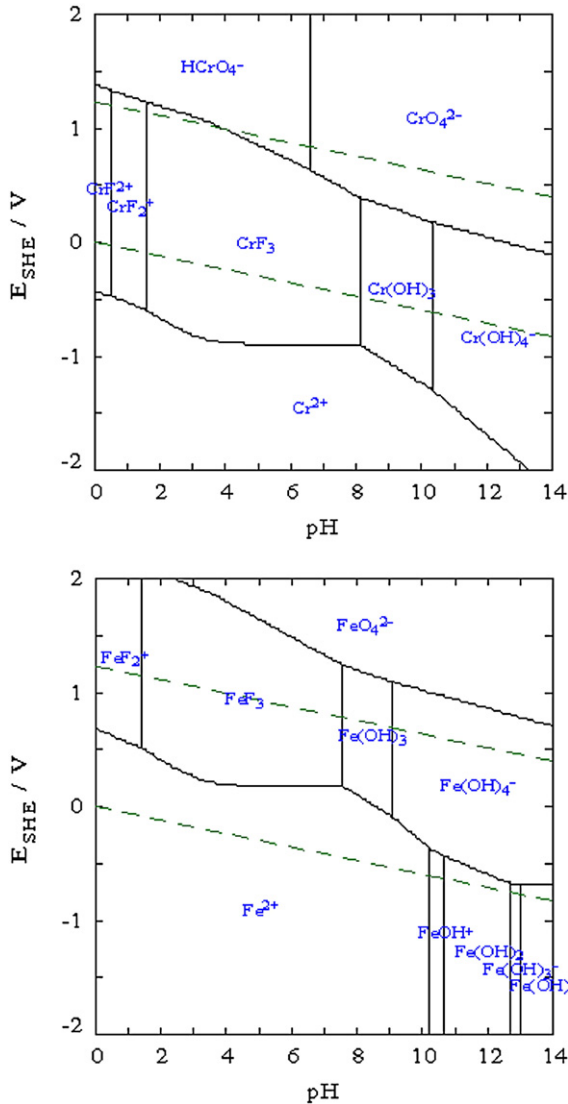


Fig. 9. Pourbaix diagram of Cr and Fe in simulated saliva solution containing fluoride ions.

According to this proposed model, the passive film ruptures explosively on a microscopic scale because aggressive ions accumulate at the metal/film interface. Passive film on titanium alloys is provided by the oxide film of titanium not by a relatively low-concentration alloying element like that of stainless steels and breakdown must occur in this oxide. This notion of pit nucleation arises from the fact that the nucleation events do not disappear with time of exposure [23], and therefore, they cannot eliminate sites by repetitive pit nucleation. According to this model proposed by Burstein et al. [23] growth of the titanium oxide film involves migration of oxide ions through oxide vacancies at the metal/film interface. It is noted that in the presence of fluoride ions, oxide vacancies increase by oxide dissolution according to Eq. 1. In the presence of aggressive ions such as chloride and fluoride, Cl^- and F^- can migrate in parallel across the oxide film. Thus, if Cl^- and F^- reach the metal/oxide interface, they would form the metal chloride or metal fluoride and accumulate there. The oxide would then rupture explosively and reveal a bare metal surface and form a microscopically saturated chloride/fluoride solution. The origin of the explosive oxide film rupture is the fact that metal chlorides/fluorides generally have greater molar volumes than the corresponding oxides, and formation of the chloride/fluoride salt at the metal/oxide interface produces stresses which would tend to cause blistering in the passive film. This notion is true of the titanium chlorides and fluorides, for which the molar volume is calculated as 38, 58.4, 110, 30.84 and $44.26 \text{ cm}^3/\text{mol}$ respectively for TiCl_2 , TiCl_3 , TiCl_4 , TiF_3 and TiF_4 compared

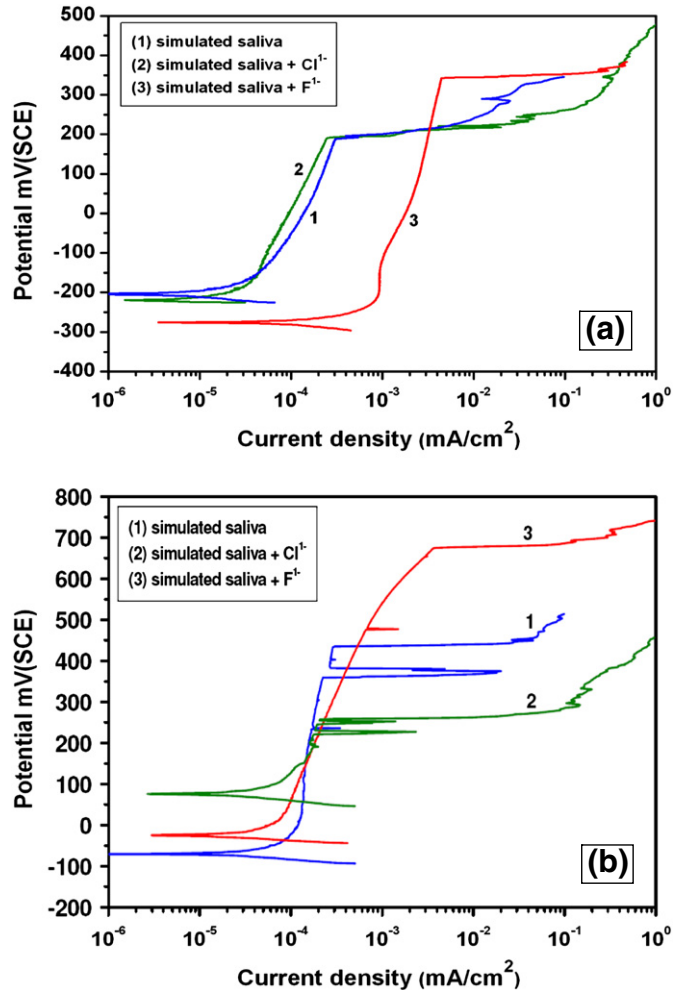


Fig. 10. Effect of crevice condition on potentiodynamic polarisation of (a) Nitinol and (b) SS304 orthodontic wires in (1) simulated saliva solution and solution containing (2) additional chloride and (3) fluoride ions at 37 ± 1 °C and scan rate of 30 mV/min.

to oxide molar volume which is $18.8 \text{ cm}^3/\text{mol}$ for TiO_2 (rutile form) [23,25].

Fig. 8, shows anodic polarisation results of SS304 wire in the presence and absence of 0.05 M fluoride and chloride ions. It is obvious that the existing fluoride ions increase corrosion potential, corrosion current density and also passivity current density. Interesting behaviour of SS304 wires in the presence of fluoride ions is that the pitting potential increases. By adding equal molar fraction of chloride ions, pitting potential decrease significantly and it is in agreement with previous investigations [26]. The difference between corrosion potential and pitting potential (passivity domain) of SS304 wire in simulated saliva solution was $510 \pm 100 \text{ mV}$ and for solution containing additional fluoride ions it is $650 \pm 70 \text{ mV}$. It is clear that fluoride acts as an accelerator ion and similar to the results of Nitinol wire, passivity current density in the presence of fluoride is higher than its absence. This can be confirmed by looking into the saliva solution with additional chloride ions where passivity current density is similar to the simulated saliva solution.

In order to investigate the reason of higher pitting potential in the presence of fluoride ions, Pourbaix diagrams of chromium and iron in simulated saliva solution in the absence and presence of fluoride are

helpful. These diagrams are shown in Fig. 9 (plotted by open source Medusa software). It is obvious that in the presence of fluoride, iron and chromium fluorides (FeF_3 and CrF_3) may be precipitated in pits and as a result the pitting potential increases.

3.2. Effect of crevice

The effect of crevice on anodic dissolution of Nitinol wires is shown in Fig. 10(a). As it can be seen, in crevice condition, breakdown potential of Nitinol wires in simulated saliva solution has been decreased significantly. It means that the transpassivity behaviour changes from water oxidation to crevice corrosion. As it is reported elsewhere [27], crevice corrosion of orthodontic wires depends strongly on chemical composition of alloy and also the surface condition of wire. The anodic Tafel polarisation of Nitinol wire in the presence of additional Cl^- ions is similar to the simulated saliva solution. This means that the additional chloride ions have no effect on the crevice behaviour. However, similar to the non-crevice condition, in the presence of F^- ions, passivity current density is higher than simulated saliva solution. Interestingly, crevice has almost no effect and even positive effect on breakdown potential in the

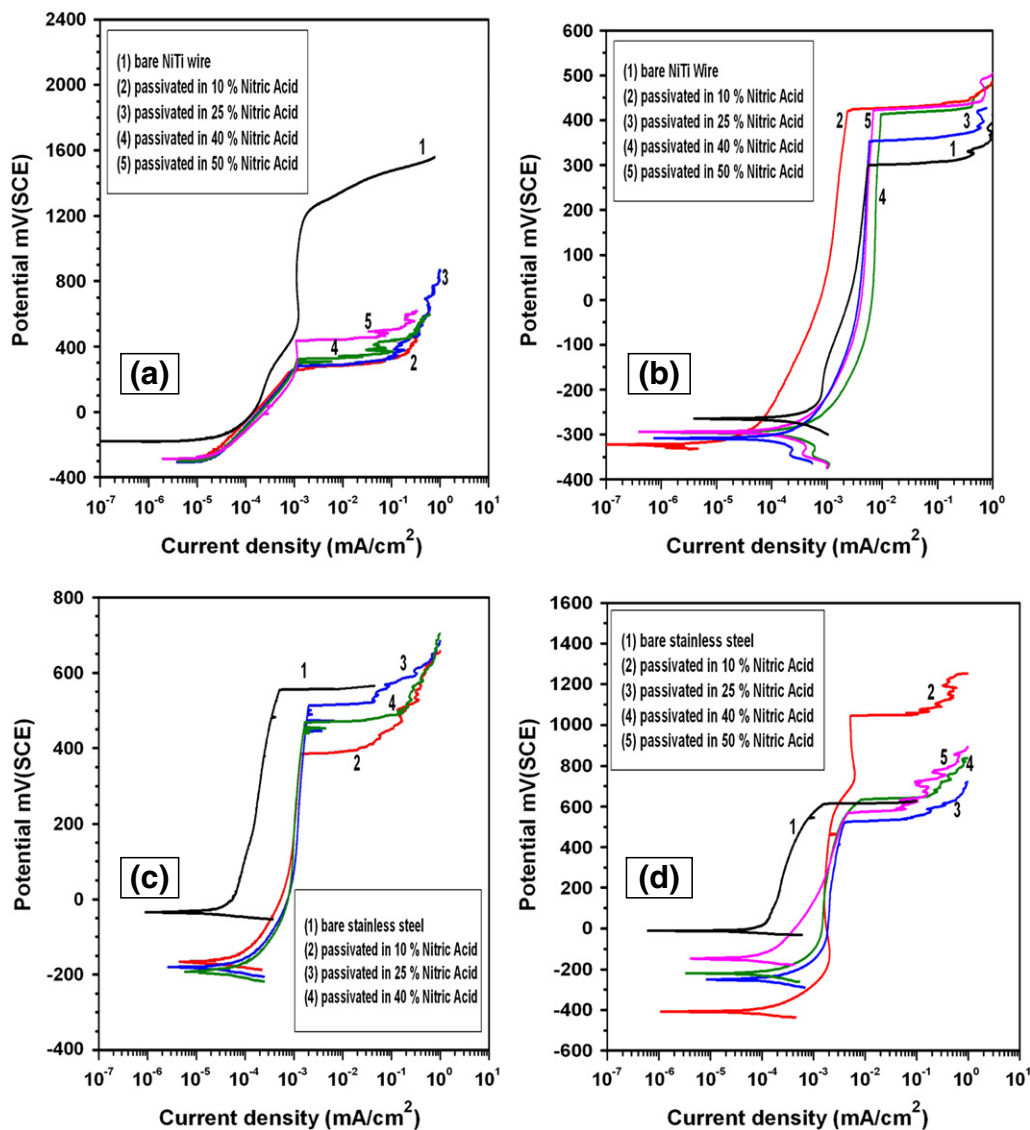


Fig. 11. Potentiodynamic polarisation of prepassivated by different nitride acid concentrations (a) Nitinol wire and simulated saliva solution (b) Nitinol wire and simulated saliva solution containing fluoride ions (c) SS304 wires in simulated saliva solution and (d) SS304 wires in solution containing fluoride ions at $37 \pm 1 \text{ }^\circ\text{C}$.

presence of fluoride ions. The dissolution of titanium in crevice condition is reported to be in the form of Ti^{3+} ions [28]. This means that in the presence of fluoride ions, TiF_3 salt can precipitate. Furthermore, this behaviour can be explained by Eq. 1 in which dissolution of each mol TiO_2 consumes 4 mol of H^+ in the presence of fluoride ion to form TiF_6^{2-} . Therefore the required acidity condition for further crevice corrosion is diminished.

Fig. 10(b) shows the results of anodic polarisation of SS304 wire in simulated saliva solution in the presence of 0.05 M fluoride and additional chloride ion in crevice condition. By comparing this figure with the non-crevice condition results presented in Fig. 8, it is clear that breakdown potential in simulated saliva solution and the solution with additional chloride ions has been significantly decreased. In addition, passivity current density increases and is analogous to the solution with additional fluoride ions. As it is reported elsewhere [29], by increasing chloride concentration, passivity breakdown potential in crevice condition has been decreased. Like the results of Nitinol wire, crevice has no or even positive effect on breakdown potential of solution containing fluoride ions. As it was explained above, similar to the results of pitting corrosion in the presence of fluoride ions, this increase is due to the formation of iron and chromium fluorides.

3.3. Effect of pre-passivation

Fig. 11 shows the effect of pre-passivation in different nitric acid concentrations on anodic dissolution of Nitinol and SS304 wires. As it can be seen, for both materials, pre-passivation decreases the corrosion potential and increases the passivity current density. According to O'Brien et al. [21] this increase in current density in Nitinol alloy can be attributed to the existence of Ni and NiO in the passive layer and future dissolution of this element. In addition, passivity breakdown potential in pre-passivated condition is lower than in non-pre-passivation one. This can be especially observed in Nitinol potentiodynamic results. As it is stated above, the Nitinol wires

in simulated saliva solution do not show pitting corrosion. While by pre-passivation treatment the thickness of oxide layer increases, as it is indicated above, dissolution of Ni and NiO of oxide layer makes the passive layer more defective and susceptible to pitting corrosion. It is previously reported that surface treatment can change the passive layer composition and hence affect the passivity condition [30]. Furthermore, normally, the pre-passivation treatment increases the corrosion potential by decreasing the passivity current density [20,31]. However, in this case, pre-passivation treatment increases the passivity current density in simulated saliva solution and also decreases the corrosion potential. This can be attributed to the Cr/Fe ratio of passive film. According to Noh et al. [20] there is an optimum acid concentration in which the Cr/Fe ratio is maximum. By further increasing the acid concentration, this ratio decreases and results in increasing the passivity current density and decreasing the pitting potential. The same condition may be considered for NiTi alloy in which the ratio of Ti/Ni is the critical criterion for passivity current density and pitting potential. It seems that by increasing the acid concentration this ratio decreases. According to O'Brien et al. [21] by increasing the Ni and NiO contents of passive layer of NiTi alloy the passivity current density increases and pitting potential decreases. The decrease in corrosion potential by pre-passivation was previously reported [31]. This decrease in corrosion potential is explained in Fig. 12. As it is illustrated, the anodic current has raised in pre-passivated state while the cathodic branch has not almost changed. As a result, the cathodic branch crosses the anodic one in lower potential leading to a decrease in corrosion potential.

These results show that the pre-passivation has deteriorative effect on corrosion behaviour of Nitinol and SS304 wires in the bare simulated saliva solution. However, pre-passivation has positive effect on corrosion of these orthodontic wires in the presence of 0.05 M fluoride ion. Fig. 11(b–d) shows the results of anodic polarisation of Nitinol and SS304 orthodontic wires in the simulated saliva solution with 0.05 M fluoride ions. As it could be observed, by pre-passivation treatment, the passivity domain in the presence of

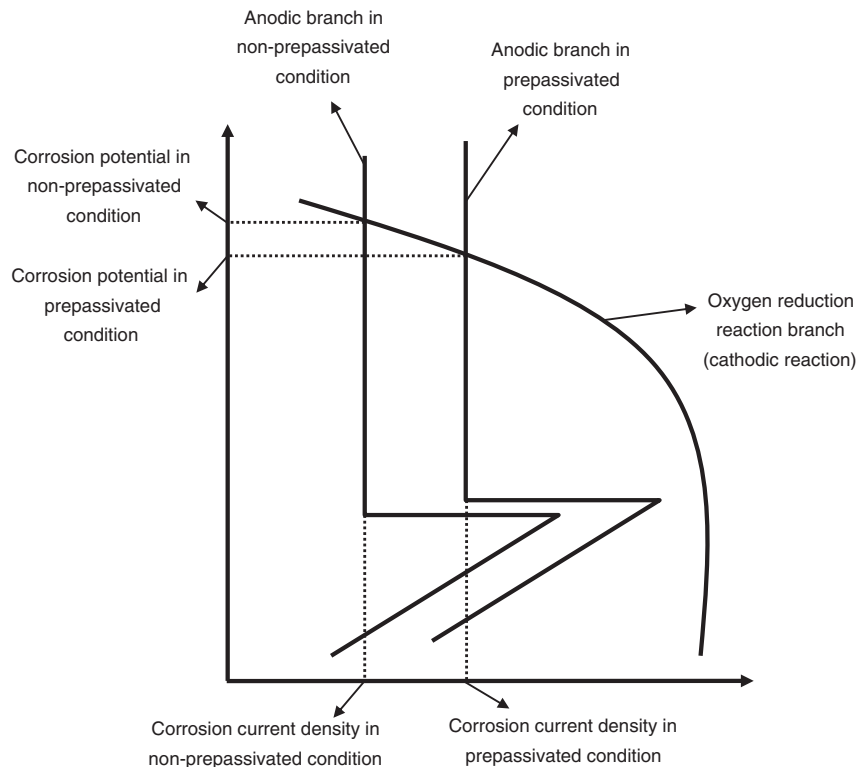


Fig. 12. Schematic of the effect of pre-passivation treatment in this study of the anodic and cathodic branches. Clearly the decrease in corrosion potential comes from the acceleration of anodic dissolution and as a result higher anodic current density in pre-passivated condition.

fluoride ions has been increased significantly for both materials. This shows that the driving force for pitting corrosion in the presence of fluoride ions is significantly higher in pre-passivated specimens than the in non-pre-passivated condition. This behaviour can be explained by the fact that pre-passivation treatment increases the passive film thickness and defects. In the absence of fluoride ions, higher defects of passive film make it more susceptible to pitting corrosion. However, in the presence of this aggressive ion, the thicker film on the surface delayed the film breakdown and increased the pitting potential and passivity domain as well.

These figures show that the most beneficial pre-passivation solution is 10% nitric acid for both materials and by further increase in nitric acid concentration the corrosion behaviour has been deteriorated.

3.4. Corrosion attack morphology

The SEM depicts of Nitinol and SS304 wires are shown in Fig. 13. As it can be seen, the corrosion type of both wires in simulated saliva solution containing fluoride ions is pitting corrosion. As it was reported elsewhere [32–34], in stainless steel materials, the pitting is more likely to be initiated from inclusions and also from interfaces of inclusion and metal. Therefore, in Fig. 13(a) the pitting of SS304 is initiated from the surface groove or from interface of precipitates and inclusions which are the weakest points on the surface.

In addition to the pitting corrosion mechanism reported above for titanium alloys, other authors reported that the pitting is more likely to initiate from weaker regions of the surface [35]. The pits on Nitinol surface could be initiated from surface grooves or small amount of inclusions and it may also be the result of local dissolution of surface in

segregation sections. Since Nitinol has crystalline structure, the pits can initiate from grain boundary regions which are weaker sites. Because the oxide thickness on surface is not homogenous over the surface, the thinner oxide regions are more susceptible to pitting corrosion [35,36].

4. Conclusion

1. Nitinol wire shows passive behaviour in simulated saliva solution while, SS304 wire shows pitting corrosion in this solution.
2. Fluoride ions increase the passivity current density in both wires and it causes the breakdown potential of Nitinol to decrease while, it has an inverted effect on breakdown potential of SS304. The same molar fraction of chloride has no considerable effect on the passivity current density of both wires, however, it decrease the breakdown potential significantly.
3. While the crevice condition accelerates corrosion behaviour in simulated saliva solution and the solution containing chloride, crevice has no effect on breakdown potential of solution containing fluoride ions.
4. Pre-passivation of Nitinol and SS304 wires in nitric acid has a deteriorative effect in simulated saliva solution however, in the presence of fluoride ions, pre-passivation has a positive effect of pitting corrosion and the best results were obtained when pre-passivation was performed in 10% nitric acid.
5. The SEM results revealed that pits are initiated from surface non-homogeneities such as grooves, inclusions and even thinner oxide parts on Nitinol surface.

Acknowledgements

The authors would like to appreciate the financial support from Ferdowsi University of Mashhad provision of laboratory facilities during the period that this research was conducted.

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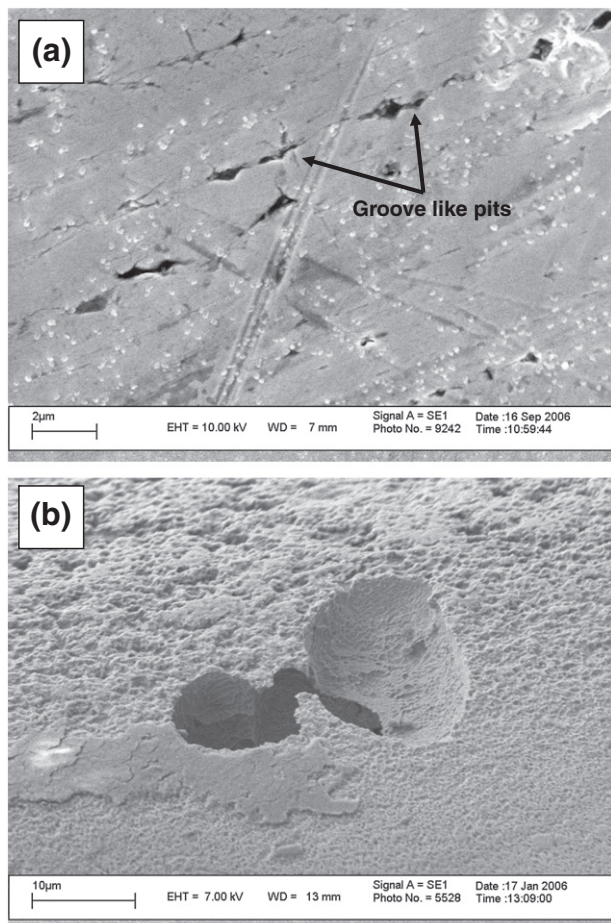


Fig. 13. SEM micrograph of (a) SS304 and (b) Nitinol wires after corrosion test in simulated saliva solution containing fluoride ions.

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