Effects of temperature and pH on the corrosion behavior of NiTi orthodontic arch wire in artificial saliva

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Abstract:
There are few studies on the electrochemical corrosion behavior of Nitinol at various pH and temperature. Considering the pH of mouth can alter at a wide range, the present study investigated the effects of various pH and temperature of artificial saliva on the electrochemical stability of commercial equiatomic Ni-Ti orthodontic wire. In this manner, cyclic polarization tests were performed at different temperatures and pH. Surface conditions of wires were evaluated with Scanning-Electron Microscopy. Decreasing of pH to the acidic pHs and increasing of temperature in these pHs cause to increasing of I_{corr} and C.R. and decreasing of E_{corr} and E_{pit}. The SEM micrographs indicate that the surface of sample become smoother after cyclic potentiodynamic tests. In fact, cyclic potentiodynamic tests cause to a general corrosion on the surface of sample. Corrosion behaviour of NiTi completely relies on the characteristics of its passive layer. Decreasing of pH causes to partly dissolution of the passive layer of NiTi in the acidic pHs. Influence of temperature on the corrosion behaviour of NiTi, related to the pH of solution. It appears that pitting critical temperature of NiTi in the artificial saliva is higher than 42°C.

Keywords: Nitinol, Orthodontic wire, Corrosion, Artificial Saliva

In conventional orthodontic treatment, NiTi alloy, which contains about equiatomic Ni and Ti, is one of the most common orthodontic wires applied clinically due to its good working and mechanical properties. Since it has been assumed that a satisfactory corrosion resistance represents a necessary requirement for good biocompatibilty [1,2], several studies have been carried out on this subject. In particular, since the Ni-Ti alloy, like other implant metallic biomaterials, relies on the presence of a passive film on its surface to develop good corrosion resistance, importance was given to the methods of evaluation of the passive film breakdown resistance.

In the oral cavity, dental plaque, this includes organic acids such as lactic acid, precipitate on the metal surface[3]. pH of dental plaque after consuming sugar is about 4.0 [4], but it can range from 2.0 to 11.0 depending on the foods and beverages consumed [5]. Thus, it is necessary to investigate the corrosion properties of nitinol for clinical use, especially under various conditions in the mouth. The present study investigated the effects of pH and temperature on the electrochemical behaviour of nitinol by potentiodynamic tests.

Materials and methods

One kind of commercial round NiTi alloy orthodontic arch wire (produced by Ortho technology) with diameter of 0.018 in was used in this study. The chemical analysis of arch wire was determined by atomic adsorption spectrometer and it is shown in table [1].

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Ti (%)	Ni (%)	Fe (%)
49.5	49.5	≈1

Table 1. Chemical analysis of NiTi orthodontic arch wire.

Artificial saliva was used as the potentiodynamic test electrolyte, which consisted of KCl 1.47 g/l, NaHCO3 1.25 g/l, KSCN 0.52 g/l, KH2PO4.H2O 0.19 g/l [6]; pH of this solution was about 8.9 and then The electrolyte was adjusted to pH 8, 6.8, 5.4, and 3.5, respectively by lactic acid.

The as-received orthodontic wires were rinsed with alcohol in ultrasonic cleaning bath before the following Potentiodynamic tests. The cell apparatus was similar to that described in the G 5 standard reference test method [7] and except for the specimen holder, the potentiodynamic measurements were performed according to the G 61 standard reference test method [8] and a scanning rate of 600 mVh^{-1}, starting from -800 mV versus SCE, was adopted. The scanning of voltage was reversed at 1600 mV versus SCE and the test was ended at -800 mV versus SCE. Controlling of Temperature in experiments was conducted by the warm water bath. The conditions tested in this work are shown in table 2.

		pH				
		3.5	5.4	6.8	8	8.9
Temperature	25°C		✓	✓		✓
	37°C	✓	✓	✓		✓
	42°C		✓	✓		✓

Table2. Conditions that were tested in this investigation

A graphite-furnace Atomic Absorption Spectrometer (AAS) was used to determine the amount of Ni and Ti ions released after different Potentiodynamic tests.

Results

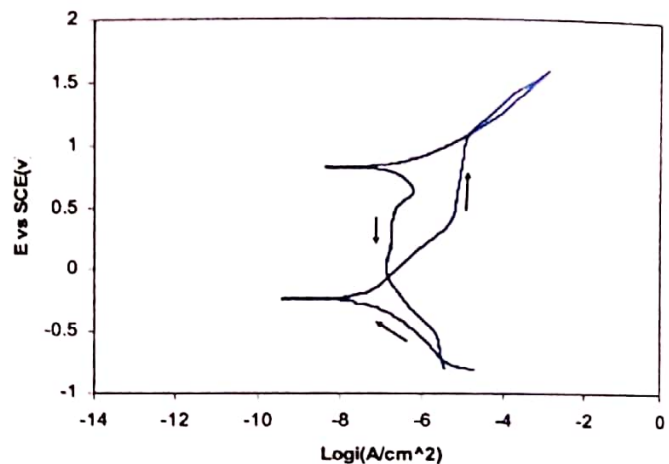Representative Potentiodynamic polarization plot for NiTi is presented in Figure1.

Figure1. Representative Cyclic Potentiodynamic polarization plot for NiTi in artificial saliva at 37°C and pH 6.8.

This figure shows that NiTi exhibits instantaneous repassivation on the reverse scan and the current density reduces rapidly.

Stern-Geary relation was used to calculate the corrosion current density (Icorr) in nAcm-2.The corrosion rate in (mpy) was calculated based on equivalent weight and density values included in the experimental set up for the M352 software. The calculated Icorr, CR and Epit and measured Ecorr, values are shown in table 3.

pH	Conditions Temperature (°C)	E_{corr} (mv)	I_{corr} (nA/cm^2)	E_{pit} (mv)	C.R. (mpy)
8.9	25	-204	15.9	1130	0.006
	37	-131	20.5	1032	0.008
	42	-283	26.2	1024	0.010
8	37	-281	15.3	1150	0.007
6.8	25	-236	21.5	1246	0.008
	37	-300	22.7	1058	0.008
	42	-319	31.2	1170	0.012
5.4	25	-345	21.7	952	0.008
	37	-407	38.6	920	0.015
	42	-487	76.2	980	0.030
3.5	37	-500	58.5	932	0.023

Table 3. The calculated Ecorr, Icorr, CR and Epit values which are obtained in different conditions

In this research, after cyclic potentiodynamic tests, all test solutions showed a little amount of Ni, confirming its removal from the surface of wires. This data is presented in table 4, which shows no amount of Ti may be because its amount is under detection limit of atomic adsorption spectrometer

element	pH=8.9	pH=8	pH=6.8	pH=5.4	pH=3.5
Ni (ppm)	-	0.1	0.18	0.22	0.28

Figure 2 and 3 show SEM micrographs the surface morphology of the NiTi orthodontic arch wire before and after cyclic potentiodynamic tests.
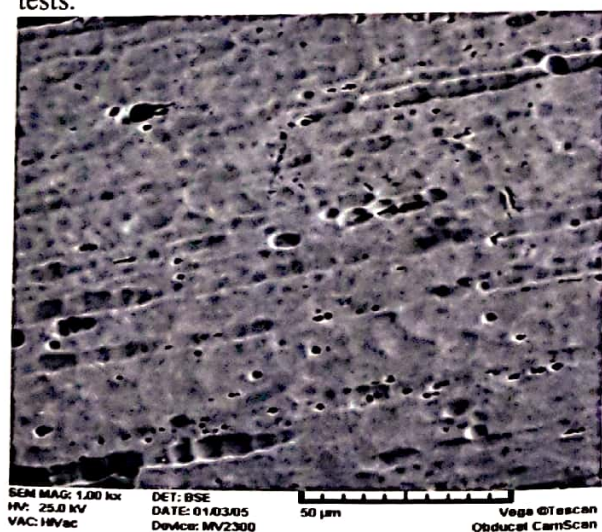

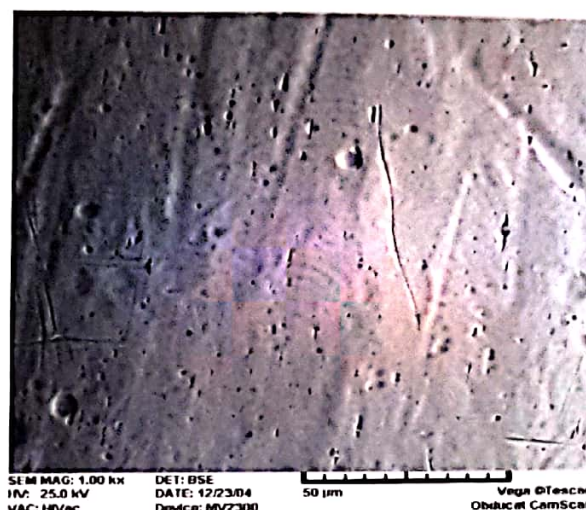**Fig.2. SEM micrograph of the NiTi surface before cyclic potentiodynamic test**

Fig.3. SEM micrograph of the NiTi surface after cyclic potentiodynamic test at 37°C and pH 6.8.

As shown in Fig.2, the surface topography of the NiTi orthodontic arch wire exhibits longitudinal grooves over the whole length of the wire and round craters in some places. Fig.3 indicates smooth surface of arch wire after cyclic potentiodynamic test.

Discussion

Figure1 shows that NiTi exhibits instantaneous repassivation on the reverse scan and the current density reduces rapidly. This phenomenon suggests two hypotheses. first one is that the NiTi was less susceptible to propagation of existing surface damage and the second one is that increasing of current density in the positive scan part of the anodic polarization curve, had another reasons such as oxidation of water near the surface of the working electrode or occurrence of anodic dissolution in the region of transpassivity.

Assessing the influence of pH on the corrosion behaviour of NiTi in artificial saliva irrespective of the role of cathodic reactions is impossible. Two important cathodic reactions in this system are the reduction of Hydrogen and Oxygen. Increasing of pH decreases the equilibrium half-cell potentials of Hydrogen and Oxygen [9].

Because of this decreasing, corrosion potential of NiTi in artificial saliva decreases. However, as can be seen in figure 5, corrosion potential of NiTi is decreased because of pH decreasing. This phenomenon may have various reasons. Dissolution of oxide layers such as Ni3O4, Ni2O3, NiO and probably TiO2 as a result of pH decreasing can cause to activation of NiTi surface and decreasing of corrosion potential [10]. In addition, formation of soluble complexes in lower pHs can be culminate to decrease of corrosion potential [9]. As it is pointed before, artificial saliva contains $SCN^-, HCO_3^-, H_2PO_4^-$ anions. If supposed that the solution be acidic, predominant species of HCO_3^- anion would be carbonic acid and that of $H_2PO_4^-$ anion would be phosphoric acid. Considering to the equilibrium constants of these acids [11], it is noticed that equilibrium constant of $HSCN$ is greater than that of above tow acids. Consequently, the amount of SCN^- anion is greater than the other anions.

With regard to the formation constants of various complexes of SCN^- and Ni^{2+} [12], it appears that Ni mostly in the form of complexes such as $NiSCN^+, Ni(SCN)_2$ exists in the test solution. In consequence of the formation of these soluble complexes, effective concentration of metallic ions decreases and it causes to decreasing of electrode potential. Furthermore, it can be assumed complexes as a chemical species, which its bonding energy to metallic ions is less than the bonding energy of metallic ions to the water molecules. So more metal ions can exist in the solution before attain the equilibrium state and this means decreasing of electrode potential [9].

Decreasing of pH causes to slightly decreasing of pitting potential and this is because of instability of oxide layers exist on the surface of NiTi arch wire.

Figure 4 and 5 show the plots of corrosion current density (Icorr) and corrosion rate (C.R.) versus solution pH at 37°C. In spite of Ecorr, Icorr and C.R. show an ascending trend in effect of pH decreasing. This phenomenon has several reasons. In the first place, pH-decreasing causes

to oxide layers exist on the surface of NiTi become instable and its protective properties decrease. Secondly, pH-decreasing leads to increase of equilibrium half-cell potentials of Hydrogen and Oxygen and in other words, it causes to cathodic branches of polarization curves moving up. Furthermore, increasing of H+ ions cause to increasing of reaction rate of hydrogen reduction and also increasing of corrosion current density and corrosion rate.
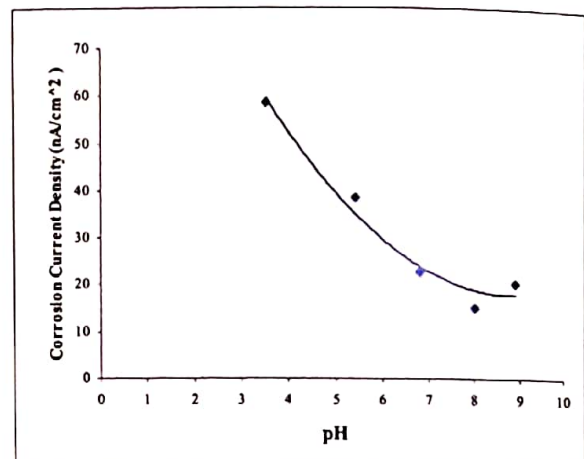

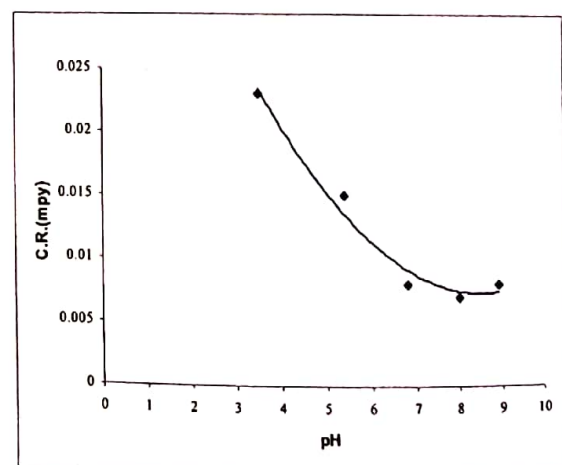**Figure 4. plot of Icorr versus pH of solution at 37°C**

Figure 5. plot of C.R. versus pH of solution at 37°C

As can be seen in table 3, in pH= 8.9 and 6.8, increasing of temperature has not so much effect

on the amount of E_{corr}, but in acidic pH= 5.4, increasing of temperature leads to decrease of E_{corr}. In assessing the effect of temperature on the corrosion potential, it must be considered that increasing of temperature causes to increase of exchange current density of hydrogen reduction and this leads to increase of corrosion potential. Because cathodic branch of polarization curve interrupt the anodic branch at the higher point. Increasing of temperature decreases charge transfer polarization and diffusion polarization in the cathodic reactions. Consequently, this depolarization of cathodic reactions leads to increase of E_{corr}. Considering in table 3, increasing of temperature most of the time, causes to decrease in E_{corr}. The reason of this decreasing can be increasing of anodic current density in the effect of temperature increasing. With increasing of current density, anodic branch of polarization curve interrupts the cathodic branch at the lower potential. Perceptible falling of corrosion potential in effect of temperature increasing in pH=5.4 are noticed clearly. This decreasing of corrosion potential is because of firstly, instability of oxide layers in effect of temperature increasing and secondly, increasing the formation kinetics of above mentioned complexes.

Table 3 shows that, increasing of temperature in pH= 8.9, 6.8 and 5.4 has not so much effect on the E_{pit} and it causes to slight decreasing occasionally. Increasing of temperature causes to an increase in activation of Cl^- ions exist in artificial saliva and consequently a decrease in pitting potential. However, table 3 shows that, increasing of temperature has no significant effect on the E_{pit} because the tested temperatures may be below the pitting critical temperature.

It has been shown that passive layer of nitinol contains not only TiO_2 but also a very thin NiO layer on top of the main oxide layer [13]. Increasing of entered Ni ions in solution (table 4) as the result of pH decreasing can confirm the existence of a nickel oxide layer on top of the sample, which is instable as the result of pH decreasing and its Ni enters in the test solution.

Fig. 2 shows longitudinal grooves over the whole length of the wire and round craters in some places. This kind of surface topography is like the surface topography of treated wire. A treatment such as chemically etching of wire reveals a micrograph like Fig. 2 [14]. Round craters and long grooves are, in fact, pits induced during selective etching around particles. These pits, induced by chemical etching, have smooth walls. The surface morphology induced by chemical etching was not altered after corrosion testing, though the surface became generally smoother [15]. As shown in figs. 2 and 3, the surface of sample became smoother after cyclic potentiodynamic tests. In fact, cyclic potentiodynamic tests cause to a general corrosion on the surface of sample. With regard to analyses of solutions which was used in the cyclic potentiodynamic tests and taking place of general corrosion, it can be said that a nickel oxide layer such as NiO exists on the top of NiTi orthodontic arch wire according to findings of O'Brien [13].

Conclusion

Corrosion behaviour of NiTi completely relies on the characteristics of its passive layer. Decreasing of pH cause to partly dissolution of the passive layer of NiTi in the acidic pHs. Influence of temperature on the corrosion behaviour of NiTi, related to the pH of solution. Partly dissolution of NiTi contains the dissolution of top layer of its passive layer that maybe it is NiO. This dissolution causes to decreasing of E_{corr}. Decreasing of pH to the acidic pHs and increasing of temperature in these pHs cause to increasing of I_{corr} and C.R. and decreasing of E_{corr} and E_{pit}. It appears that pitting critical temperature of NiTi in the artificial saliva is higher than 42°C.

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