THE INFLUENCE OF ARTIFICIAL SALIVA ON NiTi ORTHODONTIC WIRES: A STUDY ON SURFACE CHARACTERIZATION

İ. ÜNAL [2], *S. ZOR* [1], *H. ATAPEK* [2]

[1] *Kocaeli University, Department of Chemistry, Umuttepe Campus, Turkey;*

[2] *Kocaeli University, Metallurgical & Materials Engineering, Umuttepe Campus, Turkey*

Ni and Ti based alloys are prospective materials for dental orthodontic wires because of their superior mechanical properties and corrosion resistance. The studies on the corrosion resistance of these materials according to their surface characterization in artificial saliva are limited. In this study, the changes on the surface of NiTi alloy based orthodontic wires in F^- and PO_4^{3-} added or not added artificial saliva after a period of time were investigated by SEM and EDS studies.

Keywords: *orthodontic materials, corrosion, scanning electron microscopy, energy-dispersive spectroscopy.*

Several metals and metal alloys are used in dentistry and orthodontic applications. The corrosion on the surface of metal used in any application can be formed after a period of time depending on the environment of mouth [1]. The corrosion occurs from either loss of metal ions directly into solution or progressive dissolution of a surface film, usually an oxide or a sulphide.

The stainless steel, cobalt-chromium, and titanium alloys used in orthodontic appliances rely on the formation of a passive surface oxide film to resist corrosion. This protective layer is not infallible; it is susceptible to both mechanical and chemical disruption. Even without disruption, oxide films often slowly dissolve only to reform as the metal surface is exposed to oxygen from the air or the surrounding medium [1].

The acidic drinks and foods containing sodium chloride are corrosive materials. The aggressive media such as chloride ions and acidic conditions accelerate the corrosion. Also, the fluoride ions in toothpaste and products used as mouthwash are an important factor which accelerates the corrosion. Several studies reported that the fluoride based acidic solutions increase the titanium corrosion [1–5]. Therefore, clinically, the role of fluoride in the corrosion of orthodontic appliances might not be as important as suggested by the in vitro studies.

Schiff et al. compared the corrosion resistance of 3 types of orthodontic brackets (stainless steel, cobalt-chromium, titanium) when placed in a reference solution of artificial saliva and 3 commercially available fluoride mouthwashes. According to electrochemical results, all 3 mouth washes had little effect on the cobalt-chromium brackets, but the stannous flouride in 1 mouth wash caused considerable corrosion of the stainless steel and titanium brackets [2].

Ni and Ti alloys have been developed as orthodontic materials. The studies on the corrosion resistance of these materials in artificial salivas are very popular. In this study, the changes on the surface of NiTi alloy based orthodontic wires in F^- and PO_4^{3-} added or not added artificial salivas after a period of time were investigated by SEM (Scanning Electron Microscopy) and EDS (Energy-Dispersive Spectroscopy) studies.

Experimental study. ***Material and method.*** The nickel-titanium (NiTi) alloy as orthodontic wire has been used in this experimental study and its composition has been

Corresponding author: S. ZOR, e-mail: szor2001@yahoo.com

chosen among the materials which are commonly used and frequently mentioned in [6]. The chemical composition of the alloy used in this study is as follows: NiTi alloy – Ni/55Ti/45.

The orthodontic wires were cut of a length of 1.5 cm and then all wires were immersed into artificial salivas at a temperature range of 22...37°C. All solutions, listed in the Table, were numbered as I, II and III for easy notation. The changes on the surfaces of metals after the 10th day were examined by SEM and EDS studies.

The compositions of artificial salivas used in experimental study

Modified fusuyama solution (I) (normal oral environment)	1 g/L NaF added modified fusuyama solution (II) (toothpaste effective oral environment)	1.7% H_3PO_4 added modified fusuyama solution (III) (acidic nutrient effective oral environment)
KCl (0.4 g/L) NaCl (0.4 g/L) $NaH_2PO_4.2H_2O$ (0.69 g/L) $CaCl_2.2H_2O$ (0.906 g/L) $Na_2S.9H_2O$ (0.005 g/L)	KCl (0.4 g/L) NaCl (0.4 g/L) $NaH_2PO_4.2H_2O$ (0.69 g/L) $CaCl_2.2H_2O$ (0.906 g/L) $Na_2S.9H_2O$ (0.005 g/L) + NaF (1 g/L) pH 4.8	KCl (0.4 g/L) NaCl (0.4 g/L) $NaH_2PO_4.2H_2O$ (0.69 g/L) $CaCl_2.2H_2O$ (0.906 g/L) $Na_2S.9H_2O$ (0.005 g/L) + 1.7% H_3PO_4 pH 2.5

The NiTi alloy is commonly used as a prospective material for dental orthodontic wires because of its superior mechanical properties and also corrosion resistance. It is possible that a protective passive film exists on the NiTi alloy due to electrochemical reactions, Ni or Ti ions may be released from the metal surface in the source of oral environment through the corrosion processes [7]. On the other hand, NiTi alloys consist of a certain amount and dispersed Ni_xTi_y type intermetallic precipitations in Ni-rich matrix depending on chemical composition of the alloy and applied heat treatment. The coherence between precipitation and matrix is very important for mechanical properties and corrosion resistance. Microcracks or microvoids occur due to the incoherent interface and also corrosion will be aggressive around these precipitation having incoherent interface in the matrix [8].

Results and discussions. ***The effect of fusuyama artificial saliva and surface examinations.*** The artificial saliva based solutions have a corrosive effect due to having chloride ions. If the environment has a certain ratio of chloride ions, these ions cause the formation of pitting corrosion. Pitting corrosion due to the existence of chloride ions in the saliva solutions are clearly observed in experimental study after SEM examinations on the NiTi alloy surface.

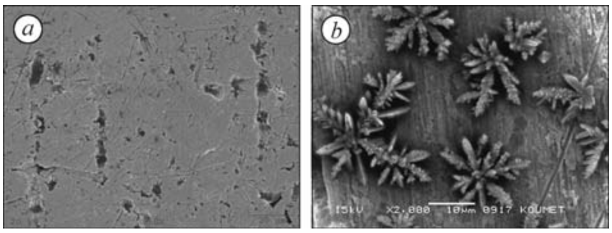
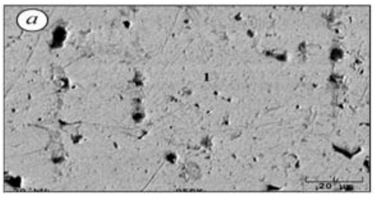


Fig. 1. A general view of NiTi alloy after the 10th day in artificial saliva (*a*), Ti based oxide in crystalline form (*b*).

Fig. 1 shows the surfaces of NiTi orthodontic wire which is immersed into solution I during 10 days. There are many voids formed due to corrosion and many particles in dark-gray contrast, which are the formed corrosion products as several oxides, on the surface (Fig. 1*a*). The formation of voids is inevitable because of chemical interaction between a metal and a solution and this results in dissolving of matrix under corrosion. In artificial saliva, Ti ions are released from the metal surface due to lower affinity of nickel to oxygen and Ti based oxide in a crystalline form may occur as a result of corrosion (Fig. 1*b*). The oxide formation on the surface commonly appears in the crystalline form due to nucleation [9].



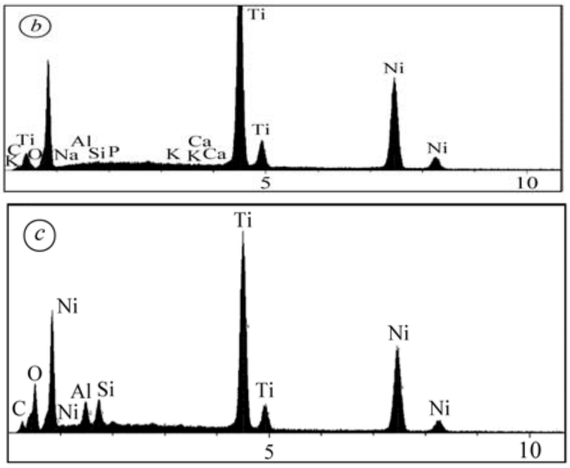


Fig. 2. A general view of the surface of NiTi alloy in artificial saliva (*a*), the results of EDS analysis for numbers marked on the surface (*b*, *c*).

The EDS studies will be very useful to determine the formed components on the surface of the metal because of the corrosion in artificial saliva in a period of time. A general view of the NiTi alloy surface is presented in Fig. 2*a* and two points on the image are marked to show where EDS analysis is done. Number 1 refers to the matrix and Number 2 refers to the formed corrosion product in Fig. 2*a*. Ni and Ti are the base metals in matrix and the concentrations of these metals are very high and also close to the original composition of the alloy mentioned above.

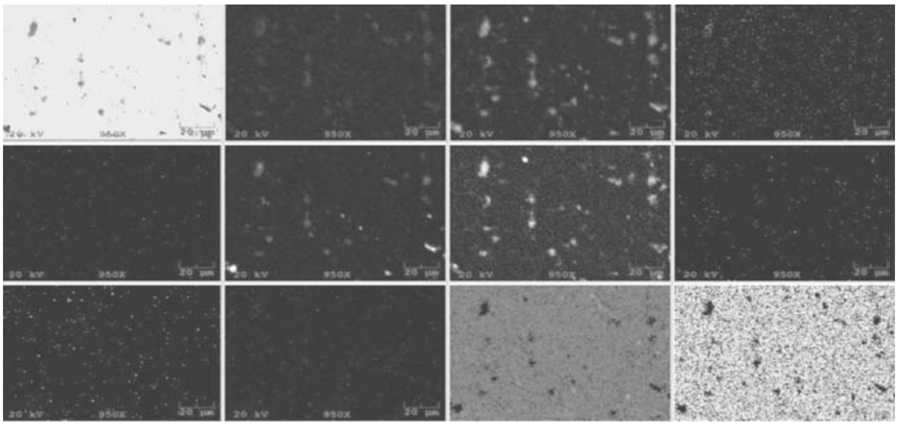


Fig. 3. EDS mapping of selected region of NiTi alloy immersed into solution I during 10 days.

The EDS results shown in Fig. 2*b* indicate that there is a clear decrease in the amount of Ni and Ti due to dissolution of metals. From a clinical point of view, the final result of orthodontic treatment may be compromised by corrosion and metal ions as corrosion products (Ni^{2+}) can result in symptoms of toxicity and allergic reactions [10]. The concentration of oxygen in the region marked as Number 1 is very low and its existence is a proof of a thin oxide film on the metal surface. The oxide film layer behaves as a protective layer during corrosion in an aggressive environment [11]. On the other hand, there are several impurities such as C, Al, Si because of the alloy composition and Na, P, K, Ca exist in artificial saliva. The formed oxide based particles appear in a dark-gray contrast under SEM examination (Fig. 2*c*). It is clearly seen that the concentration of oxygen is higher than of the matrix. This indicates that Ti based oxide is formed because of a strong interaction between the metal and the solution. The dissolution of nickel from the matrix to the solution is very high. All effects can be followed by considering the concentration differences in EDS analysis in Fig. 2*b* and *c*. EDS mapping will be very useful to understand the elemental distribution for given materials. Fig. 3 represents the EDS mapping of the studied NiTi alloy surface. Ni and Ti are the dominant elements on the surface and oxide based particle can be easily separated from the matrix due to their oxygen level.

The effect of F^- added fusuyama solution. For the purpose of tooth protection, fluorides are widely used to provide oral health by means of toothpastes, mouth rinses, orthodontic gels and other therapeutic dental products. Additionally, systemic fluorides may be ingested orally through tea, dietary supplements and fluoridated bottled water. Therefore, the NiTi orthodontic wires are readily exposed to fluoride medium [12].

Fluoride ions have an abrasive effect. The corrosion resistance of NiTi and β-Ti alloy decreases due to increasing of the hydrogen embrittlement in the environments having fluorine ions. Walker et al. reported that fluoride ions in tooth-gels increase the corrosion behavior of orthodontic wires [13].

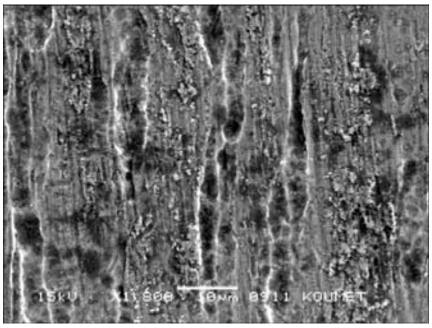


Fig. 4. A general view of the surface of NiTi alloy immersed into solution II during 10 days.

It is clearly observed that the degradation of the NiTi alloy surface is more drastic than that of metal which is affected by artificial saliva (Fig. 4). This is a result of the fluoride effect on the surface. Several EDS analysis marked as Number 3–5 are done on the metal surface to understand the effect of fluoride and also formed corrosion products (Fig. 5*a*). At first, the matrix is characterized and the EDS result shows a similar elemental distribution on the surface compared to other analysis done before (Fig. 5*b*). The region numbered as 3 refers to the matrix and the EDS results denote that the amounts of Ni and Ti are very high, while the concentration of oxygen is very low, therefore, nickel and titanium exist in marked region as the fine oxide phase.

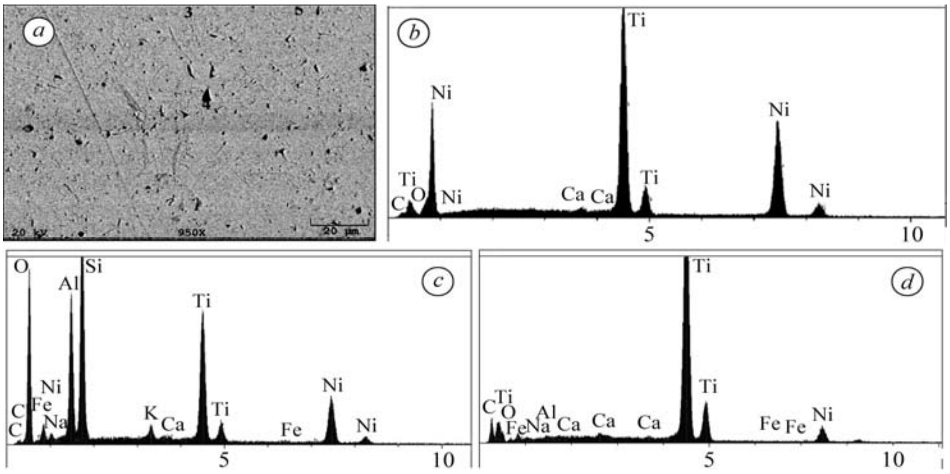


Fig. 5. The regions where EDS analysis were done on the surface of NiTi alloy immersed into F^- added artificial saliva (*a*); the elemental peaks of matrix numbered as 3 in the microstructure (*b*); the results of EDS analysis for numbers marked as 4 and 5 on the surface (*c*, *d*), respectively.

These oxide phases occur due to the interaction between the metal and the water molecules. The particles in dark/gray contrasts are obtained during SEM examinations and Fig. 5*c*–*d* show that the particles formed on the surface of metal are the corrosion products consisting of a high level of oxygen concentration. The formed intensive oxide layer can be mentioned for the particle marked as number 4. EDS result (Fig. 5*c*) displays that the particle include both impurities existing in the composition of metal and also elements existing in the composition of artificial saliva. In Fig. 5*d*, there is a certain peak according to EDS analysis referring a strong Ti based oxide particle. Titanium exists in the solution as TiO_2 having a more stable form.

The effect of PO_4^{3-} added fusuyama solution. Phosphate added fusuyama solution has a more acidic characteristic compared to other artificial salivas. Huang et al. concluded that the manufacturer, pH value, and also immersion period had a significantly statistical influence on the release amount of Ni and Ti ions. In their experimental study, the NiTi orthodontic wires in artificial saliva with various acidities were examined. The amount of Ti ions released in a certain level of pH, was mostly not detectable. It was indicated that the TiO_2 film on NiTi wires exhibited a good protection against corrosion. The NiTi wire with the highest release of the metal ions showed the maximal increase in the surface roughness after immersion test, while a rougher surface did not correspond to a higher metal ion release [14].

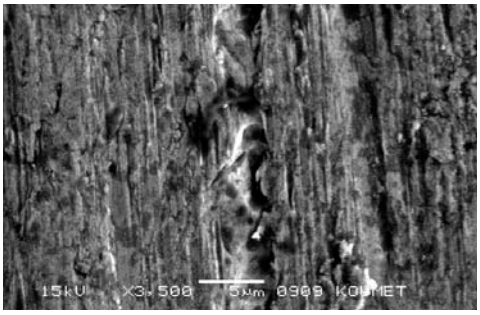


Fig. 6. A SEM image showing the effect of PO_4^{3-} added artificial saliva on NiTi wire.

The effect of solution III on NiTi wire is illustrated by a SEM image in Fig. 6. As seen, there are much more dimples and particles as corrosion product on the surface of experimental alloy wire.

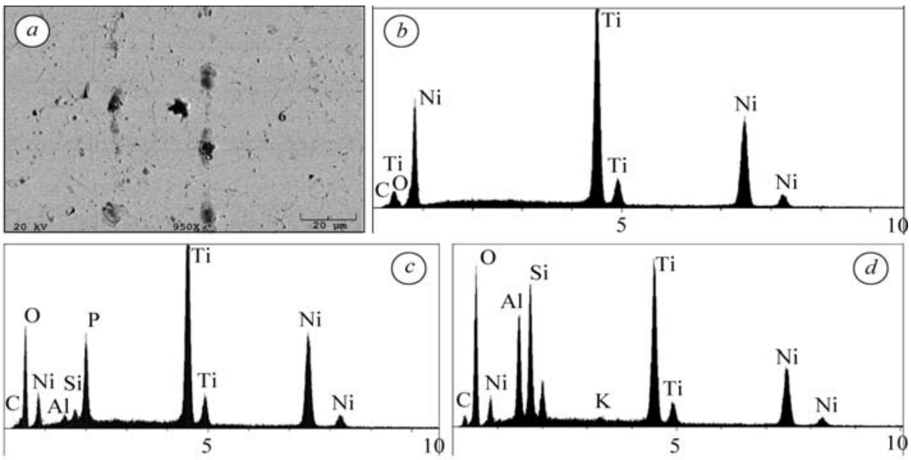


Fig. 7. The regions where EDS analysis was done on the surface of NiTi alloy immersed into PO_4^{3-} added artificial saliva (*a*); the elemental peaks of matrix numbered as 6 in the microstructure (*b*); the results of EDS analysis for numbers marked as 7 and 8 on the surface (*c*, *d*), respectively.

The EDS analysis is necessary to understand the effect of the solution on the metal surface similar to the studies done above in this study (Fig. 7). Fig. 7*a* shows where the analysis was done by marking the points as Numbers 6–8. The peaks belonging to the elemental distribution on the matrix surface are shown in Fig. 7*b* and it is obvious that there is an oxide film layer on the surface. On the other hand, the results for particles on the surface are presented in Fig. 7*c*–*d* and formed corrosion products due to high oxygen level can be clearly observed. There is a certain amount of phosphorus indicating the environment.

CONCLUSIONS

In this study, the influence of artificial saliva solution on NiTi orthodontic wire was investigated. Several artificial salivas were prepared to determine the effect of different environments depending on the composition of saliva solution. The conclusions are the following: the formation of corrosion is determined by examining the surfaces immersed into all artificial saliva solutions (Solution I–II–III) in a period of 10 days. SEM examinations reveal the matrix having a fine oxide film layer and particles as corrosion product on the surface. The EDS analysis is useful to support the formation of a thin oxide film on the surface and to determine the type of particles. The elemental distribution differs depending on the dissimilarities in the environment of corrosion; pitting corrosion due to chloride ions is observed on the metals surfaces; fluoride and phosphate added fusuyama solutions are more effective on the formation of corrosion than the fusuyama solution with no additive.

РЕЗЮМЕ. Сплави на основі Ni та Ti – перспективні для виготовлення ортодонтичних дротів завдяки своїм високим механічним характеристикам та корозійній тривкості, яка у синтетичній слині методами поверхневого аналізу досліджена недостатньо. Вивчено зміни властивостей поверхні ортодонтичних дротів із нікельтитанового сплаву під час витримки в синтетичній слині з додаванням F^- та PO_4^{3-} та без них за допомогою сканівної електронної мікроскопії (SEM) та енергодисперсійного мікроаналізу (EDS).

РЕЗЮМЕ. Сплавы на основе Ni и Ti – перспективные для изготовления ортодонтичных проводов благодаря своим высоким механическим характеристикам и коррозионной стойкости, которая в синтетической слюне методами поверхностного анализа исследована недостаточно. Изучены изменения свойств поверхности ортодонтичных проводов из никельтитанового сплава во время выдержки в синтетической слюне с добавлением F^- и PO_4^{3-} и без них с помощью сканирующей электронной микроскопии (SEM) и энергодисперсионного микроанализа (EDS).

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