Can people clipped with orthodontic wire made of Ni-Ti alloy take Ecosprin tablet orally?-YES

V.Agnes Brigitta*[1] & C.Thangavelu[2] & S.Rajendran [3]

*[1]Department of Chemistry, SBM college of Engineering and Technology, Thamaraipadi, Dindigul-624005, Tamil Nadu, India.

[2] P.G& Research department of chemistry,Periyar E.V.R.College(Autonomous),Trichirappalli -620023 , Tamil Nadu, India.

[3] Research Center, Department of Chemistry, St. Antony's College of Arts and Science For Women, Thamaraipadi, Dindigul-5,Tamil Nadu, India

Received: January 30, 2019 Accepted: March 10, 2019

ABSTRACT: *People are implanted or clipped with orthodontic wires made of different materials in order to regulate the growth of teeth,. When these orthodontic wires are exposed to the oral environment, by the influence of food intake, toothpastes, mouthwash, some tablets like vitamin, used as pain killer and antibiotics. During this process, the orthodontic wires may undergo corrosion. Hence, the main objective of this study was to evaluate Can people clipped with orthodontic wire made of Ni-Ti alloy take Ecosprin tablet (500 ppm) orally?- by electrochemical study and surface morphological study. Scanning Electron Microscopy imaging gave the morphological data for the sample; however, by using Scanning Electron Microscopy and Energy Dispersive Analysis of X-rays the elemental composition was determined. Further, the analysis of the protective film formed on the metal surface was done using Polarization Study and AC impedance spectra. The corrosion resistance of the Ni-Ti alloy system in various solutions decreases in the following order: Artificial Saliva + Ecosprin tablet > Artificial Saliva.This is Evidenced by increases of Linear Polarization Resistance (LPR), decreases of Corrosion Current (Icorr) in polarization study, and increases of charge transfer Resistance (Rct) , decreases of double layer Capacitance (Cdl) in AC impedance spectra. The high corrosion resistance offered by the tablet is due to the formation of a protective film. It confirmed that the active principles of the tablet ingredients have co-ordinated with the Ni-Ti metal ions through their polar atoms to form a complex. Hence these electro chemical studies conclude that people clip with orthodontic wire made of Ni-Ti alloy can take Ecosprin tablet orally without any hesitation.*

Key Words: *Corrosion resistance, Scanning electron microscopy, Energy Dispersive Analysis of X-rays, polarization study, AC impedance spectra, orthodontic wire, Ni-Ti alloy and Ecosprin tablet.*

1. INTRODUCTION

On the dental market there are a variety of dental alloys used in dentistry for manufacturing of fixed and removable prostheses. In the oral cavity, these structures are exposed to a chemically adverse environment, with saliva being the most corrosive agent, due to the high concentration of chloride ions that are causing localized corrosion. One of the most important factors determining the use of a metal alloy for making prosthesis is its resistance to corrosion.[1,2] To resist corrosion, SS, CoCr, and titanium alloys depend on the formation of a passive surface oxide film. However, even though these protective oxide films are present on the metal surface, metal ions can still be released.[3]Non-precious metal alloys are being used due to their low cost and adequate mechanical properties. Nitinol is regarded as alloy with excellent corrosion resistant, but its corrosion and electrochemical behaviour requires careful examination. The excellent corrosion of Ni-Ti results from the formation resistance of very stable, continuous adherent and protective oxide film on its surface.[4] As titanium has high affinity for oxygen, TiO2 based oxides form spontaneously by exposing the fresh metal surface to the air or moisture. Various types of metal alloys are being used for the orthodontic treatment, which undergo chemical or electrochemical reaction with the oral environment. The oral environment is highly aggressive under several situations and leads to corrosion. various metals and alloys such as Ti-Co alloy,[5] Ti30Ta alloy,[6] Ti-6Al-4V alloy,[7] Ti-6Al-7Nb alloy,[8] Co-Cr alloy,[9-13] CP-Ti and Ni-Cr-Ti alloy,[14] Co-Cr-Mo alloy,[15,16] Ni-Cr alloy,[13,17,18] Ti-Cu,[19] Ti-20Zr alloy,[20] Ti12Mo and Ti60Ta,[21] Ni-Ti shape memory alloy and stainless steel wire,[22] and Ti-Mo,[23] were used for many studies. The present work is undertaken to study Can people clipped with orthodontic wire made of Ni-Ti alloy take Ecosprin tablet (500 ppm) orally?, the answer has been evaluated by electrochemical studies such as Polarization study, AC impedance Spectra, SEM and EDAX.

2. EXPERIMENTAL

2.1. Materials

The metal specimens, namely, Ni-Ti, were chosen for the present study. The study was carried out in the presence of artificial saliva (AS) using Ecosprin tablet. The composition of Ni-Ti alloy is Ni-55.2% and Ti- 44.8%. The composition of artificial saliva in g/L-1 is KCl (0.4), NaCl (0.4), $CaCl_2.2H_2O$ (0.906), $NaH_2PO_4.2H_2O$ (0.690), $Na_2S.9H_2O$ (0.005) and urea (1.0) [16-18].The ingredients of the Ecosprin tablet is Aspirin lP–75mg,Titanium Dioxide Lp.

2.2. Methods

2.3. Electrochemical studies

2.3. i. Potentiodynamic polarization study

Polarization analysis has been used for detection of the formation of protective film on the metal surface during corrosion resistance process. Polarization Studies were carried out in a CHI-Electrochemical work station with impedance. A three electrode cell assemblies were used. The working electrode was the Ni-Ti alloy. A saturated Calomel electrode (SCE) was the reference electrode and platinum electrode was the counter electrode. From the polarization study corrosion parameters such as Corrosion Potential (E_{Corr}),Linear PolarizationResistance (LPR), Corrosion Current(I_{Corr}) and Tafel slopes (anodic= b_a and cathodic= bc) were calculated.

2.3. ii. AC impedance measurements

The measure of the ability of a circuit to resist the flow of electrical current is known as impedance. By applying an AC potential to an electrochemical cell and then measuring the current through the cell, the electrochemical impedance is usually measured using a small excitation signal. The instrument used for the polarization study was also used to record AC impedance spectra. The cell setup was also the same. The real part (Z') and imaginary part (Z") of the cell impedance were measured in Ohms at various frequencies. Values of the charge transfer resistance (Rt) and double layer capacitance (Cdl) were calculated from the Nyquist plot and the impedance; log (z/Ohm) value was calculated from Bode plots. During AC, impedance spectra were recorded: the scan rate (V/s) was 0.005; hold time at Ef(s) was zero and quite time (s) was 2. The value of charge transfer resistance (Rt) and double layer capacitance (Cdl) were calculated from Nyquist plot.

$$Rt = (Rs + Rt) - Rs$$

(where Rs = solution resistance, Rt =charge transfer resistance)

$$Cdl = \frac{1}{2 \times 3.14 \times Rt \times fmax}$$

where fmax= frequency at maximum imaginary impedance.

2.3. iii. Scanning Electron Microscopic studies (SEM)

The surface morphology measurements of the thin wire metal (Ni-Ti) specimen were examined using scanning electron microscope. The surface morphology was examined for the thin wire (Ni-Ti) metal specimen in absence and in presence of the Ecosprin tablet system. The specimen immersed in the best system for a period of one day was removed,rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology.

2.3. iv.Energy Dispersive Analysis of X-rays (EDAX)

SEM imaging gives the morphological data for a sample;The elements present in a material are determined by an EDAX spectrum. An energy dispersive X-ray analyzer (EDAX) [Brucker, Nano,GMBH, Germany] unit attached to the SEM machine was used to carry out the elemental analysis of the metal surface.

3. RESULTS AND DISCUSSION

3.1. Analysis of Potentiodynamic polarization curves

Corrosion Resistance of Ni-Ti alloy immersed in various test solutions are given in Table 1. The potentiodynamic polarization curves are shown in Figure1.When corrosion resistance increases Linear Polarization Resistance (LPR) increases, Corrosion current(I_{corr}) decreases.

Table 1: Corrosion parameters of orthodontic wires immersed in Artificial Saliva (AS) in the absence and presence Ecosprin tablets (500ppm) obtained by polarization study

Metals	System	E_{corr} mVvs SCE	b_c mV/ decade	b_a mV/decade	LPR Ohm cm^2	I_{corr} A/ cm^2
Ni-Ti alloy	Artificial Saliva (AS)	-477	0.165	0.232	15381385.0	2.729X10^{-9}
	Artificial Saliva + Ecosprin tablet	-514	0.138	0.266	32861806.0	1.205 X10^{-9}

It is observed from the table that in presence of Ecosprin tablet in artificial saliva corrosion resistance of Ni-Ti alloy is increases. This is evident from the fact that there is an increases in LPR value (from 15381385.0 to 32861806.0 Ohm cm^2) and decreases in Corrosion Current (I_{corr}) value (from 2.729X10^{-9} to1.205X10^{-9}). The Corrosion Potential (E_{corr}) value shifts to cathodic side. This indicates that in the presence of the tablet cathodic reaction is controlled predominantly. These reveal that, there is an effective protective film formed on the metal surface, This protective film prevents further corrosion by blocking oxygen diffusion to the metal surface and stops corrosion from spreading into the bulk of the metal[24].These protective film probably consist of complexes formed between the active principle of the ingredients of the tablets and metal ion present on the metal surface. It is observed from the table that the corrosion resistance of Ni-Ti alloy decreases in the following order:

Artificial Saliva (AS) + Ecosprin tablet > Artificial Saliva (AS)

This study implies that people having orthodontic wire made of Ni-Ti alloy can take Ecosprin tablet orally without any hesitation.

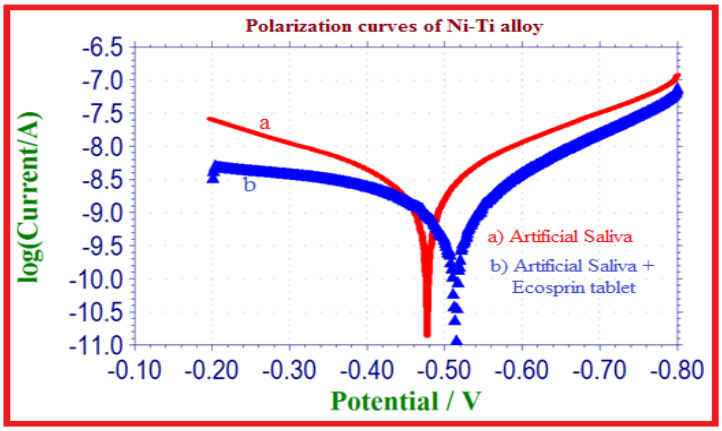


Figure 1. Polarization curves of Ni-Ti alloy immersed in various test solutions
a) Artificial Saliva b) Artificial Saliva + Ecosprin tablet

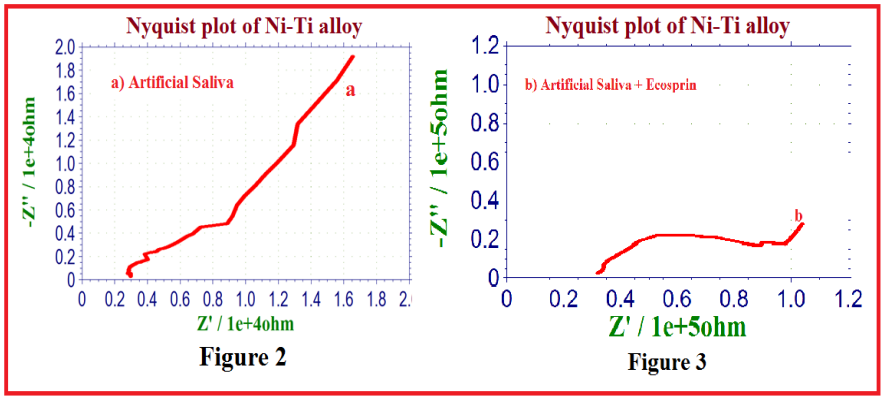
3.2. Analysis of AC Impedance spectra

AC impedance spectra has been used for detection of the formation of protective film on the metal surface during Corrosion Resistance process. AC impedance parameters such as charge transfer Resistance (R_t), double layer Capacitance (C_{dl}) (derived from Nyquist plots), and impedance value log(z/ohm) (derived from Bode plots) of various alloys immersed in artificial saliva and artificial saliva containing Ecosprin tablet are given in Table 2. Nyquist plots are shown in Figures 2 and 3, Bode plots in Figures 4 and 5. When corrosion resistance increases, the charge transfer resistance (R_t) value increases, impedance value increases and double layer capacitance value decreases.

Table 2: Corrosion parameters of alloys immersed in artificial saliva (AS) in the absence and presence of Ecosprin tablet 500 mg obtained by AC impedance Spectra.

Metal	System	Nyquist plot		Bode plot
		R_t ohm cm^2	C_{dl} F/cm^2	Impedance log(z/ohm)
Ni-Ti alloy	Artificial Saliva (AS)	13547	3.76 x 10 $^{-10}$	4.397
	Artificial Saliva + Ecosprin tablet	75840	6.72 x 10 $^{-11}$	5.030

The AC impedance spectra of Ni-Ti alloy immersed in various test solutions are shown in Figure 2 and 3.The corrosion parameters are given in table 2. It is observed from the table 2 that in presence of Ecosprin tablet in artificial saliva the corrosion resistance of Ni-Ti alloy increases. This is evident by increases of the charge transfer Resistance (R_t) (from 13547 to 75840 ohmcm^2) and decreases of the double layer Capacitance (C_{dl}) (3.76 x 10 $^{-10}$ to 6.72 x 10 $^{-11}$ F/cm^2) and increases of impedance value (4.397 to5.030 log(z/ohm)). These observations indicate that a protective film is formed on the metal surface when Ni-Ti alloy is immersed in artificial Saliva in presence of Ecosprin tablet. The protective film prevents the transfer of electrons from the metal surface to the bulk of the solutions.[24] The protective film probably consists of Ni-Ti ions, and the active principle of the Ecosprin tablet ingredients. Hence people clipped with orthodontic wire made of Ni-Ti alloy can take Ecosprin tablet orally without any hesitation.



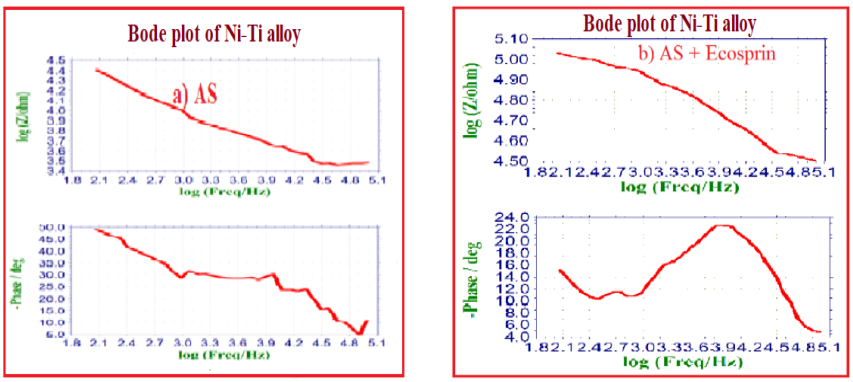


Figure 2: AC impedance spectra (Nyquistplot) of Ni-Ti alloy immersed in various test solutions
a) Artificial Saliva (AS)

Figure 3: AC impedance spectra (Nyquistplot) of Ni-Ti alloy immersed in various test solutions
b) Artificial Saliva (AS) + Ecosprin

Figure 4: AC impedance spectra (Bode plot) of Ni-Ti alloy immersed in various test solutions.
a) Artificial Saliva (AS)

Figure 5: AC impedance spectra (Bode plot) of Ni-Ti alloy immersed in various test solution
b) Artificial Saliva (AS) + Ecosprin

3.3. Analysis of Scanning Electron Microscopy (SEM)

SEM images for Ni-Ti alloy in absence and presence of the system are shown in Fig.6(a,b and c). The surface is found to be smooth only for pure polished metal. Pure Titanium and Titanium alloys are highly reactive. Therefore, when they are exposed to oral cavity (Artificial saliva) they quickly developed a passive film (TiO_2), act as protective interface between the metal structure and biological medium that is saliva[25,26], due to the combination of chemical reaction and mechanical action the passive film undergo complex degradation process can ultimately lead to surface corrosion[27].Therefore the surface is looking more rough (Figure 69(b)) than pure polished metal(Figure 69(a)). In presence of Ecosprin tablet the roughness of the

metal surface is less (Figure 6 (c)) than the artificial saliva alone. This is because of the presence of a film deposited on the metal surface. This protective film is due to the deposition of the active principles of the ingredients present in the Ecosprin tablet.

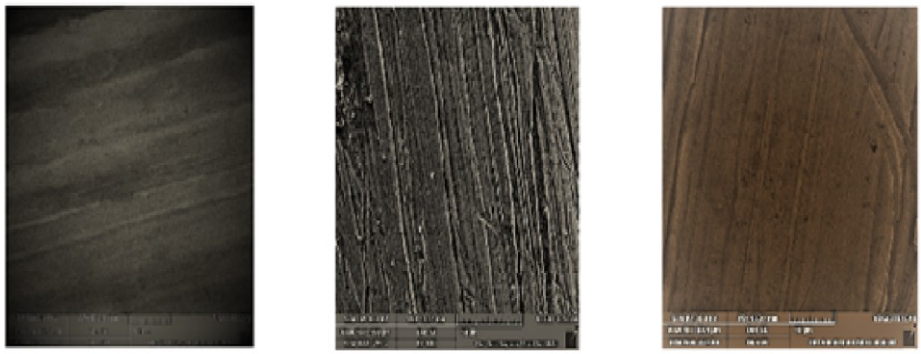


Figure 6 (a) Figure 6 (b) Figure 6 (c)

Figure 6. SEM images for Ni-Ti alloy in absence and presence of the system (Artificial Saliva + Ecosprin tablet). (a) Polished Ni-Ti alloy. (b) Polished Ni-Ti alloy immersed in Artificial Saliva. (c) Polished Ni-Ti alloy immersed in artificial saliva containing Ecosprin.

3.4. Energy Dispersive Analysis of X-rays (EDAX)

The EDAX spectra are shown in Fig. 7 (a), (b) and (c). It is seen from the EDAX spectra that C, Ti and Ni are present in pure polished Ni-Ti alloy and both absence and presence of the inhibitor (Table 3 and 4 and 5). But the weight percentage of these elements has changed after immersion in the Artificial Saliva containing Ecosprin tablet. The weight percentage of Ti and Ni has increased as weight percentage of C decreases. The intensity of the peak of Ti is reduced as the active principles of the Ecosprin tablet ingredients form a protective film on the metal surface, thus preventing the corrosion of the Ni-Ti alloy.

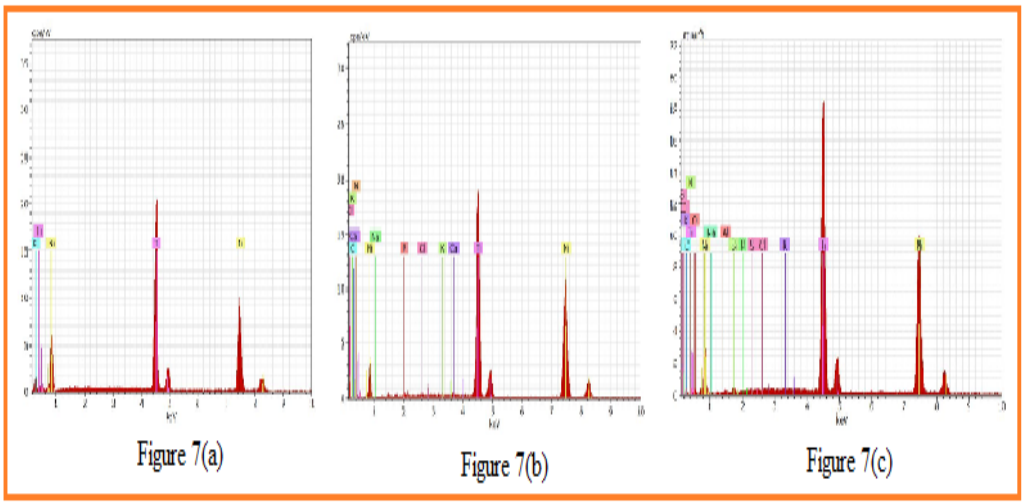


Figure 7(a) Figure 7(b) Figure 7(c)

Figure 7: EDAX Spectra of Ni-Ti alloy in absence and presence of the system (Artificial Saliva + Ecosprin tablet). (a) Polished Ni-Ti alloy. (b) Polished Ni-Ti alloy immersed in Artificial Saliva. (c) Polished Ni-Ti alloy immersed in artificial saliva containing Ecosprin tablet.

Table 4: Spectrum of Ni-Ti alloy

E1	AN Series unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error (1 Sigma) [wt.%]
C 6 K-series	19.74	20.74	53.69	5.34
Ti 22 K-series	34.53	36.29	23.56	1.02
Ni 28 K-series	40.89	42.97	22.76	1.12
Total	95.16	100.00	100.00	

Table 5: Spectrum of Ni-Ti immersed in artificial saliva

E1	AN Series unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error (1 Sigma) [wt.%]
C 6 K-series	10.20	10.66	34.37	3.58
Ti 22 K-series	38.52	40.26	32.55	1.13
Ni 28 K-series	45.93	48.00	31.66	1.25

Table 6: Spectrum of Ni-Ti immersed in artificial saliva containing Ecosprin tablet

E1	AN Series unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error (1 Sigma) [wt.%]
C 6 K-series	6.54	6.77	22.31	2.69
Ti 22 K-series	38.39	39.80	32.88	1.13
Ni 28 K-series	46.42	48.12	32.43	1.26

4. CONCLUSIONS

In presence of Ecosprin tablet in Artificial Saliva, the corrosion resistance of Ni-Ti alloy increases. Hence, it is recommended that people clipped with orthodontic wire made of Ni-Ti alloy can take Ecosprin tablet orally without any hesitation. So, dentists can recommend this tablet (Ecosprin 500 ppm) to their patients while they are clipping with Ni-Ti orthodontic wire on their teeth.

5. ACKNOWLEDGEMENTS

The authors are thankful to their respective departments for the help and encouragement to carry out this research.

6. REFERENCES

1. A. C. Fraker, "Corrosion of Metallic Implants and Pros-Thesis Devices," In: ASTM International, Ed.,ASTM Metals Handbook, Metals Park,Ohio, Vol.13, pp.1324-1335, (1987).
2. M. F. Leclerc, "Surgical Implants," In: ASTM Interna-tional, Ed., ASTM Metals Handbook,Metals Park, Ohio, Vol. 02, pp.164-180,(1987).
3. H.H. Huang, Y.H Chiu, T.H Lee, et al. Ion release from NiTi orthodontic wires in artificial saliva with various acidities. Biomaterials 24:3585-92,(2003).
4. L. Tan, R.A. Dodd, W.C. Crone, Corrosion and wear-corrosion behavior of Ni-Ti modified by plasma source ion implementation, Biomaterials 24, 3931-3939, (2003).
5. I. Mutlu, Synthesis and characterization of Ti-Co alloy foam for biomedical applications, Transactions of Nonferrous Metals Society of China (English Edition), 26(1): 126-137, (2016).
6. R. Chelariu, D. Mareci, C. Munteanu, C. Crimu, I. Zetu, Electrochemical behavior of experimental Ti30ta alloy in the presence of fluoride and albumin protein, Digest Journal of Nanomaterials and Biostructures, 9(4): 1349-1358, (2014).
7. E. M. Anwar, L. S. Kheiralla, R. H. Tammam, Effect of fluoride on the corrosion behavior of Ti and ti6al4v dental implants coupled with different superstructures, Journal of Oral Implantology, 37(3): 309-317, (2011).
8. F. Rosalbino, S. Delsante, G. Borzone, G. Scavino, Influence of noble metals alloying additions on the corrosion behavior of titanium in a fluoride-containing environment, Journal of Materials Science: Materials in Medicine, 23(5): 1129-1137, (2012).
9. W. Cheng, H. Yu, X. Lin, T. Ding, P. Ji, The effect of fluoride on dental alloys in different concentrations of fluoride artificial saliva, West China Journal of Stomatology,30(1):18-21, (2012).
10. D. I. Baila, C. V. Doicin, C. M. Cotrut, I. G. Ghionea, C. I. Tarba, Sintering the beaks of the elevator manufactured by direct metal laser sintering (DMLS) process from Co-Cr alloy, Metalurgija (Open Access), 55(4): 663-666, (2016).
11. X. Z. Xin, J. Chen, N. Xiang, Y. Gong, B. Wei, Surface characteristics and corrosion properties of selective laser melted Co-Cr dental alloy after porcelain firing, Dental Materials, 30(3): 263-270, (2014).
12. F. Alifui-segbaya, P. Foley, R. J. Williams, The corrosive effects of artificial saliva on cast and rapid manufacture-produced cobalt chromium alloys, Rapid Prototyping Journal, 19(2): 95-99, (2013).
13. Y. Ge, X. He, F. L. Zhang, Z. Y. Chen, X. Wang, Evaluation on corrosion resistance of dental prosthetic materials Ni-Cr alloy, Co-Cr alloy and pure Ti in Cola, Journal of Jilin University Medicine Edition, 39(2): 335-338, (2013).
14. B. G. Liang, X. T. Shen, L. Liu, Y. X. Lu, Z. D. Yu, C. X. Yang, Y. Z. Zhang, Effect of pH value and fluoride ions on

corrosion resistance of pure Ti and Ni-Cr-Ti alloy in artificial saliva, Journal of Zhejiang University Medical Sciences, 39(4): 399-403,(2010).

15. S. R. M. De Aguiar, M. Nicoai, M. Almeida, A. Gomes, Electrochemical behaviour of a cobalt-chromium-molybdenum dental alloy in artificial salivas, Bio- Medical Materials and Engineering, 25(1): 53-56, (2015).
16. T. Puskar, D. Jevremovic, R. J. Williams, D. Vukelic, I. Budak, A comparative analysis of the corrosive effect of artificial saliva of variable pH on DMLS and cast Co- Cr-Mo, Dental Alloy Materials (Open Access), 6(9): 6486-6501, (2014).
17. I. C. Matos, I. N. Bastos, M. G. Diniz, M. S. De Miranda,Corrosion in artificial saliva of a Ni-Cr-based dental alloy joined by TIG welding and conventional brazing, Journal of Prosthetic Dentistry, 114(2): 278-285, (2015).
18. J. Wan,G. Qiao,The effect of hydrogen peroxide on the electrochemical corrosion properties and metal ions release of nickel-chromium dental alloys, Shanghai Journal of Stomatology, 22(2): 137-141, (2013).
19. I. Mutlu, Electrochemical corrosion behavior of TiN-coated biomedical Ti-Cu alloy foam in fluoride containing artificial saliva, Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science, 45(8): 3640-3644, (2014).
20. J. M. Calderon Moreno, M. Popa, S. Ivanescu, E. I. Neacsu, M. V. Popa, Microstructure, mechanical properties, and corrosion resistance of Ti-20Zr alloy in undoped and NaF doped artificial saliva, Metals and Materials International, 20(1): 177-187, (2014).
21. D. Mareci, R. Chelariu, G. Bolat, V. Grancea, D. Sutiman, Electrochemical behavior of Ti alloys containing Mo and Ta as β-stabilizer elements for dental application, Transactions of Nonferrous Metals Society of China (English Edition), 23(12): 3829- 3836, (2013).
22. C. Zhang, X. Sun, X. Hou, H. Li, D. Sun, The corrosion resistance of composite arch wire laser-welded by NiTi shape memory alloy and stainless steel wires with Cu interlayer in artificial saliva with protein, International Journal of Medical Sciences Open Access, 10(8): Indian Journal of Advances in Chemical Science 4(4) (2016) 478-483 482 1068- 1072, (2013).
23. D. Mareci, R. Chelariu, D. M. Gordin, D. Sutiman, T. Gloriant, Effect of Mo content on electrochemical behavior of TiMo alloys for dental applications, Materials and Corrosion,61(10): 829-837, (2010).
24. Jianhai Qiu. "Stainless Steels and Alloys: Why They Resist Corrosion and How They Fail", Corrosionclinic.com, (2012).
25. Olmedo DG, Tasat DR, Duffo G,Guglielmotti MB,Cabrini RL. The issue of corrosion in dental implants: Acta Odontol Latinoam 3-9, (2009).
26. Chaturvedi TP,An overview of the corrosion aspect of dental implants (titanium and its alloy). Indian J Dent Res. (2009), 20: 91-98.
27. Savithri Abey, Mathew T. Mathew,Damian J.Lee,Kent L. Knoernschild, Markus A. Wimmer, Cortino Sukotjo, Electrochemical Behaviour of Titanium in Artificial Saliva: Influence of pH,Journal of Oral Implantology, Vol.XL, No.One, (2014).