Int. J. Electrochem. Sci., 10 **(2015)** 7453 - 7464

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Effect of Fluorine Ion on the Corrosion of Ti-6Al-4V Alloy in Artificial Saliva

Qing Qu[1,*], *Yue He*[1], *Lei Li*[2], *Min Yang*[2], *Benshan Lai*[1], *Ying Chen*[2]

[1] School of Chemical Science and Technology, Yunnan University, Kunming 650091, China
[2] Laboratory for Conservation and Utilization of Bio-Resources, Yunnan University, Kunming 650091, China
[*]E-mail: quqing@ynu.edu.cn; quqing58@126.com

Received: 8 June 2015 / *Accepted:* 30 June 2015 / *Published:* 28 July 2015

The corrosion behavior of Ti-6Al-4V alloys after 5 d immersion in artificial saliva solutions with and withou fluorine ion were studied by electrochemical methods. In addition, the morphologies of materials were observed by scanning electron microscopy. The results showed that the presence of fluorine ion posed a serious threat for Ti-6Al-4V alloy in artificial saliva. Obvious increase in OCP was observed in solutions with fluorine ion compared with that without fluorine ion. The presence of fluorine ion was also associated with decreases in R_{ct} and increase in i_{corr} values, indicating the corrosion rate was clearly accelerated in the presence of fluorine ion. And it is clear that the corrosion increased with increasing the concentration of fluorine ion. Scanning electron microscopy indicated that pitting occurred on the surface of Ti-6Al-4V alloy after immersion in artificial saliva containing fluorine ion. The Ti-F complex was suggested as the viable pitting corrosion mechanism.

Keywords: Ti-6Al-4V alloy; fluoride ion; artificial saliva; corrosion

1. INTRODUCTION

Metallic materials are being increasingly used in medical applications as implants to restore lost functions or replace organs functioning below acceptable levels. Titanium alloys (such as Ti-6Al-4V alloy) are among the most used metallic biomaterials, particularly for orthopedic applications [1-4]. However, titanium and its alloys are often damaged in some complicated environments, such as oral environments[2-4]. The release of titanium can lead to undesirable effects ranging from discoloration of tissues to severe inflammatory reaction, Al and V release in the organism was also shown to induce cytotoxic effects and neurological disorders [2]. Several researches have described patients who did not fit dentures made by titanium metal [3,4] or patients allergic to titanium ion [5,6], which cause a severe problem to resolve. Oral cavity is a complicated environment; various factors may affect the application of materials in oral cavity (e.g., the concentration of fluoride, pH, concentration of dissolved oxygen, and temperature). Fluorine ion has been considered as one of the most important factors in oral cavity [7,8]. Fluorine ion can strengthen tooth enamel structure and resistance to acid of teeth, fluoride therapy has been recognized as one of the principal methods in preventing dental caries [9]. It not only brings convenience to people's life but also triggers a series of problems with the toothpaste, gel and mouthwash containing fluoride, [10]. Thus, many studies about the effect of fluoride ion on the corrosion of titanium and its alloys were reported [11-13], but the results are different, some results showed that the presence of the fluorine ion accelerated the corrosion rate of metals, some results confirmed that certain type of titanium alloys was unaffected by fluoride. For example, Li et al. [11] studied the influence of fluoride and chloride on the corrosion behavior of NiTi orthodontic wires after 10 h immersion, they found there was a synergistic interaction of the fluoride and chloride on the corrosion of NiTi alloy, but no interpretation was attempted to explain the role of fluoride ion. Mabilleau et al. [12] studied the corrosion of CP-Ti immersed in artificial saliva with F^-, H_2O_2 and lactic acid was studied, their results indicated that the solution containing F^-, H_2O_2 and lactic acid can increase the surface roughness obviously. Takemoto et al. [13] studied the corrosion mechanism of Ti-Cr alloys in solutions containing fluoride; they pointed out that the formation of a chromium oxide-rich surface film improved corrosion resistance to fluoride in Ti-Cr alloys. As a result, it is clear that the effect of fluoride ions on the corrosion of different titanium and its alloys is different. As one of the main metallic biomaterials, Ti-6Al-4V alloy is widely used in dental implantology fields due to its good corrosion resistance, suitable mechanical properties and good biocompatibility [14]. However, the role of fluoride ions on the corrosion of Ti-6Al-4V alloy has not been extensively reported up to now, and the mechanism of Ti-6Al-4V alloy in the presence of fluorine ions also is unclear. The corrosion of Ti-6Al-4V alloy begins with the alteration of passivation oxide film and lead to the leaching of V and Al. Leaching of V and Al from this alloy may cause long-term health problems, such as, peripheral, neuropathy, osteomalacia and alzheimer diseases [2,15,16]. So making the corrosion mechanism of Ti-6Al-4V alloy clear is very important.

For the sake of providing an in-depth understanding of the corrosion behavior of Ti-6Al-4V alloy, and to provide efficient guidance for clinical applications of Ti-6Al-4V alloy, it is of significance to find out the mechanism of Ti-6Al-4V alloy corrosion in saliva containing fluorine ion. In order to achieve this objective, electrochemical measurements were performed in a series of defined solutions. The corresponding corrosion morphologies were also observed using scanning electron microscopy (SEM). And a possible mechanism also was suggested to explain the results.

2. EXPERIMENTAL

2.1 Preparation of the Specimens

The experiments were carried out with Ti-6Al-4V alloys with the following chemical composition (Wt %): Fe $\leq$ 0.30, C $\leq$ 0.10, N $\leq$ 0.05, H $\leq$ 0.015, O $\leq$ 0.20, Al: 5.5～6.8, V: 3.5～4.5, Ti remainder. The specimens were embedded in epoxy resin disks with an exposed area of (10mm×10 mm). Then they were abraded with emery papers from 100# to 2000#, and rinsed by distilled water, degreased with CH_3COCH_3, then dried with a warm air stream, sterilized with 2% glutaraldehyde solution and rinsed with sterile distilled water.

2.2 Preparation of the solutions

All the experiments were carried out in artificial saliva containing Na_2HPO_4: 0.26 g/l, NaCl: 6.7 g/l, KSCN: 0.33 g/l, KH_2PO_4: 0.2 g/l, $NaHCO_3$: 1.5 g/l, KCl: 1.2 g/l, carbamide: 1.5 g/l. The pH of the medium was adjusted to 6.7 using 0.1 M hydrochloric acid (HCl) solution and sterilized by autoclaving at 121 ºC for 20 min and at 100 kPa. Different concentrations of fluorine ion were added into the artificial saliva to produce a series of test solutions. And the concentration of fluorine ion in this study was 0, 500, 1000 and 2000 ppm, respectively.

2.3 Electrochemical procedures

A potentiostat of PARSTAT 2263 electrochemical tester was used to test the electrochemical behavior of Ti-6Al-4V alloy. In the experiment, the Ti-6Al-4V alloys were used as working electrodes, the auxiliary electrode was Pt electrode, and the reference electrode was a saturated calomel electrode (SCE). The tests were carried out in artificial saliva containing different concentrations of fluorine ion at 37 °C. The OCP measurements were performed before polarization and EIS, polarization curves were performed from a potential of −250 mV up to a potential of +2000 mV with respect to the corrosion potential (E_{corr} *vs*. SCE) at a scan rate of 1 mV/s, EIS measurements were conducted at the end of open circuit potential (OCP) measurements to ensure it was in steady state and carried out in a frequency range of 0.1-10^5 Hz using a 10 mV peak-to-peak potential perturbation. The EIS tests were carried out in triplicate to ensure reproducibility.

2.4 Surface analysis by SEM (scanning electron microscopy)

After immersion in artificial saliva with and without 1000 ppm fluorine ion for 5 d, the samples were taken out and carefully washed with distilled water and fixed by 2.5% glutaraldehyde for 15 min. And then the corrosion surfaces were characterized by FEI Quanta 200 scanning electron microscopy.

3. RESULTS AND DISCUSSION

3.1Electrochemical experiments results

3.1.1 The results of OCP

Figure 1 presented the OCP results of Ti-6Al-4V alloys in artificial saliva with or without NaF after 5 d immersion. It is clear that the OCP in all cases decreased significantly in the initial and then tended to reach a relatively steady state after 200 s. Furthermore, figure 1 also clearly shows that the value of OCP in the presence of NaF was higher than that in the absence of NaF, indicating that the OCP of Ti-6Al-4V alloys in artificial saliva with NaF moves to positive region compared with that without NaF. In addition, the value of OCP firstly increased with increasing fluoride content up to 1000 ppm, and then reduced in solution with fluoride level higher than 1000 ppm.

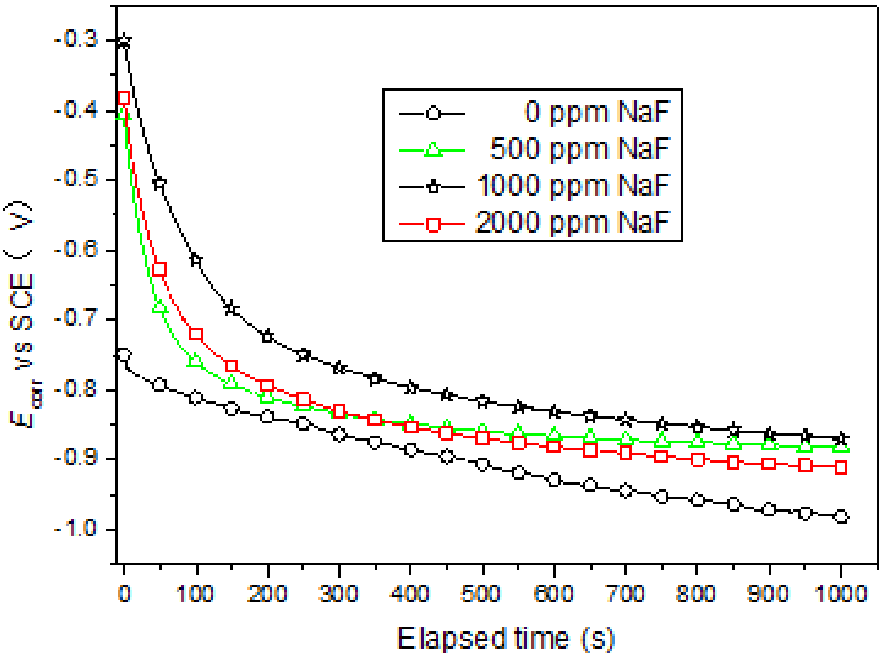

Figure 1. Open-circuit potential of Ti-6Al-4V alloys after 5 d immersion in artificial saliva without and with fluorine ion.

3.1.2 Potentiodynamic Polarization Curves

To elucidate the effect of F^- in the corrosion of Ti-6Al-4V alloy more clearly, potentiodynamic polarization was measured after 5 d immersion in artificial saliva with and without NaF, and the polarization curves were showed in Figure 2.

As can be seen from this figure, the anodic and cathodic branches were obviously shifted to higher current density region while the corrosion potential obviously shifted to more positive direction in the presence of NaF, showing that the presence of NaF clearly accelerated the corrosion of Ti-6Al-4V alloy. And with increase of the concentration of NaF from 500 to 2000 ppm, the anodic branch moved to higher current density region though it shifted to opposite direction in the weak polarization regions, the interaction of changes in the anodic and cathodic branches resulted in a slight increase of corrosion current density. Furthermore, Figure 2 also indicates that weak passivity occurred in the absence of NaF while active corrosion behavior was exhibited in the presence of NaF, which confirmed the passive film formed on Ti-6Al-4V alloy could be broken down by fluorine ions.

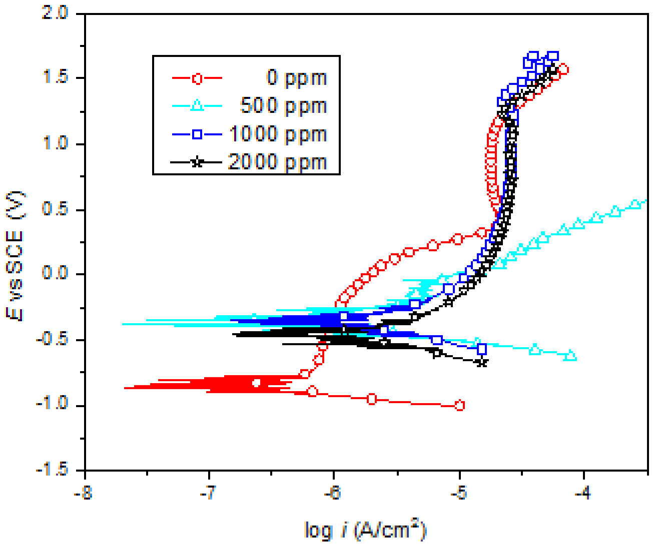

Figure 2 Polarization curves of Ti-6Al-4V alloy immersed in artificial saliva with and without fluorine ion for 5 d.

Polarization parameters including E_{corr}, i_{corr}, β_a, β_c were fitted and listed in Table 1. Here, E_{corr} is the corrosion potential, β_c is cathodic Tafel slopes, β_a is anodic Tafel slopes, i_{corr} is corrosion current density.

Table 1. Parameters of polarization curves of Ti-6Al-4V alloys immersed in solutions without and with NaF for 5 d.

C_{NaF} (ppm)	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	β_a (mV/deg)	β_c (mV/deg)
0	-861.03	0.63	1059.18	102.04
500	-345.33	5.01	420.35	238.29
1000	-913.86	6.31	666.11	151.39
2000	-236.80	6.62	671.20	230.04

Apparently, the i_{corr} in the presence of NaF was significantly higher than that in the absence of NaF, but with increase of the concentration of NaF from 500 to 2000 ppm, the i_{corr} increased slightly from 5.01 to 6.62 $\mu A/cm^2$, which indicates that the corrosion rate was accelerated in the presence of NaF though it increased slowly with increasing the concentration of NaF from 500 to 2000 ppm.

3.1.3 Electrochemical Impedance Spectroscopy (EIS) Studies

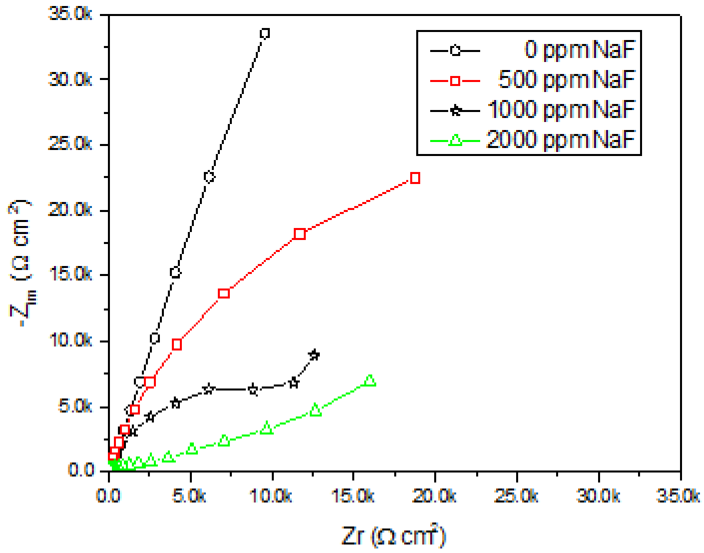

Figure 3. Nyquist plots of Ti-6Al-4V alloy immersed in artificial saliva without and with fluorine ion for 5 d.

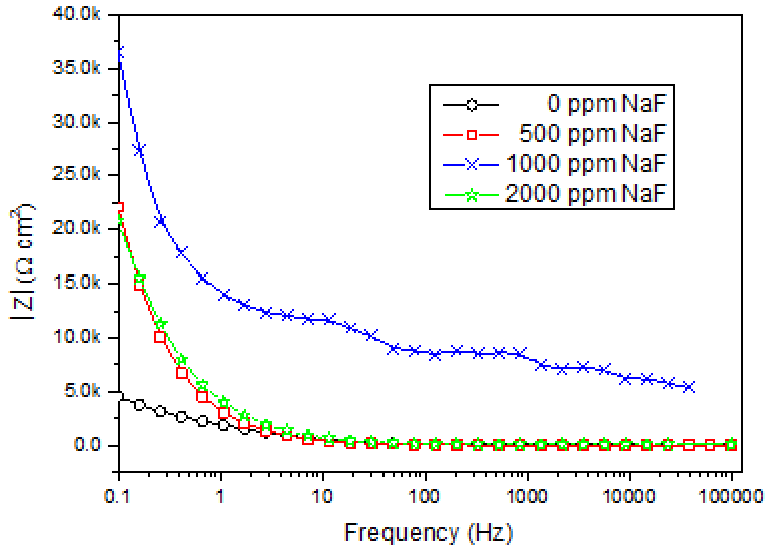

Figure 4. Bode modulus diagrams of Ti-6Al-4V alloy immersed in artificial saliva without and with fluorine ion for 5 d.

EIS of Ti-6Al-4V alloy immersed in artificial saliva containing different concentrations of NaF for 5 d was carried out, the Nyquist plots, Bode modulus diagrams and Bode phase angle diagrams were respectively recorded in figure 3-5. Figure 3 clearly showed that, the appearances in the presence of different concentrations of NaF are similar to that in the absence of NaF in general, that is, all of Nyquist plots are a part of the imperfect semicircles, and this is attributed to the frequency dispersion [4,17]. The fact that impedance diagrams have an appearance of a part of the imperfect semicircles shows that the corrosion of Ti-6Al-4V is mainly controlled by a charge transfer process, and the presence of NaF does not change the mechanism of dissolution [4,18].

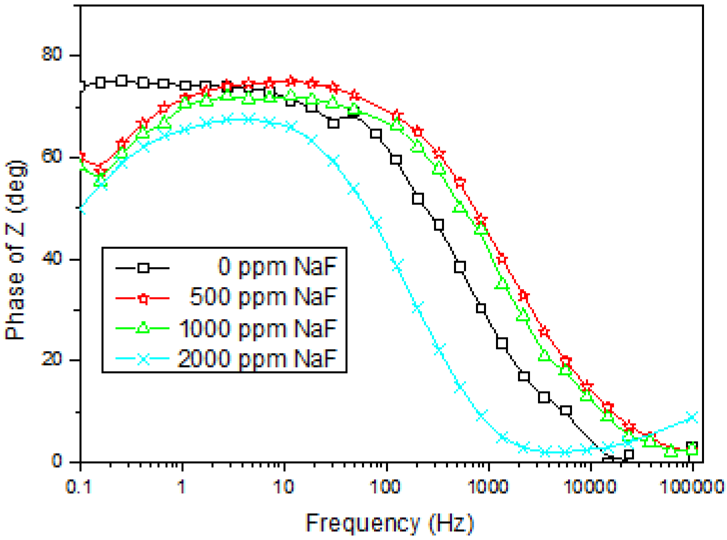

Figure 5. Bode phase angle diagrams of Ti-6Al-4V alloy immersed in artificial saliva without and with fluorine ion for 5 d.

In the artificial saliva medium with and without NaF, the impedance in the diagrams is more than 10 kΩ cm^2, which suggests the existence of a passive film, while the values of impedance become smaller with increasing the concentration of NaF, which suggests the film becomes more non-protective in the presence of NaF [4,19]. The similar phenomenon could be observed in Figures 4, Bode modulus diagrams were split with two slopes in the linear range, suggesting the interaction of at least two time constants. From Bode phase angle diagrams obtained for Ti-6Al-4V alloy electrodes (Figures 5), obviously, a highly capacitive behavior is indicated from medium to low frequencies by phase angle approaching 80° in the absence of NaF, implying that a high stable film is formed on the surface of Ti-6Al-4V alloy in artificial saliva without NaF [1,4], but with the presence of NaF, the phase angles at low frequencies clearly decreased with increasing the concentration of NaF, and presented a large phase angle peaks, indicating that the passivation of Ti-6Al-4V alloy has been destroyed by NaF. This is in accordance with the results obtained from polarization results. In fact, the large phase angles peak could be indicative of the interaction of at least two-time constants. Mansfeld et al. [19] and Tian et al. [19] suggested two-time constants relate to a two-layer structure developed during the corrosion. According to literatures [1,4] the film on titanium alloys was consisted of a bi-layered oxide consisting of a porous outer layer and a barrier inner layer.

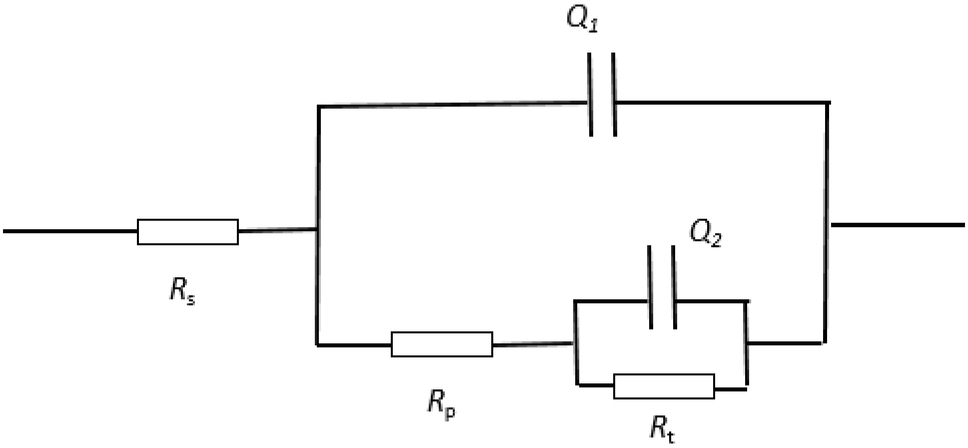

Figure 6. Equivalent circuits used for fitting the impedance spectra based on a double-layer model of surface film.

Therefore, a two-time constant equivalent circuit (Figure 6) was used to fit the experimental data. In the equivalent circuit, R_s is the solution resistance, R_t is the resistance of the barrier layer, and R_p is the resistance of porous layer. The double-layer capacitance at the film-solution interface (porous layer) and the capacitance of the film (barrier layer) were replaced by Q_1 and Q_2, respectively. The constant phase element (CPE) is usually used instead of a capacitance to account for the non-ideal capacitance response, due to the almost complete absence of pure capacitance in the real electrochemical process. A mathematical expression: n ($0 \leq n \leq 1$) is used to describe the roughness of materials. If $n = 0$, the impedance is entirely resistance, while it is capacitance if $n = 1$. Besides, $0 < n < 1$ represents one of the various causes for deviation from the ideal capacitance, which is related to the surface roughness, adsorption film, porous layer formation, and so on [4,20,21,22]. As is well known to us, the surface roughness is of considerable significance in creating pits, which further facilitate pitting corrosion [4,23]. The EIS parameters were fitted and listed in Table 2. It is clear that, the R_t was very large, which suggests the existence of a passive film, but with the presence of NaF, R_t decreased quickly, suggesting that the protectiveness of TiO_2 formed on the surface of Ti-6Al-4V alloy was damaged by fluoride ions. In addition, the R_p showed similar variation trends, which suggests that the dissolution of Ti-6Al-4V alloy was accelerated by NaF. The values of n_1 decreased from 0.92 to 0.80 and the n_2 decreased from 0.77 to 0.64 with increasing the concentration of NaF, which further shows that the viewpoint that the inhomogeneity of surface was increased due to the pitting of Ti-6Al-4V alloy.

3.2 Surface topography analysis with SEM

SEM was used to characterize the corrosion surface of Ti-6Al-4V alloy after immersion in solution. Figure 7 gave the surface morphologies of Ti-6Al-4V alloy immersed in artificial saliva without (A) and with 1000 ppm fluorine ion (B) respectively.

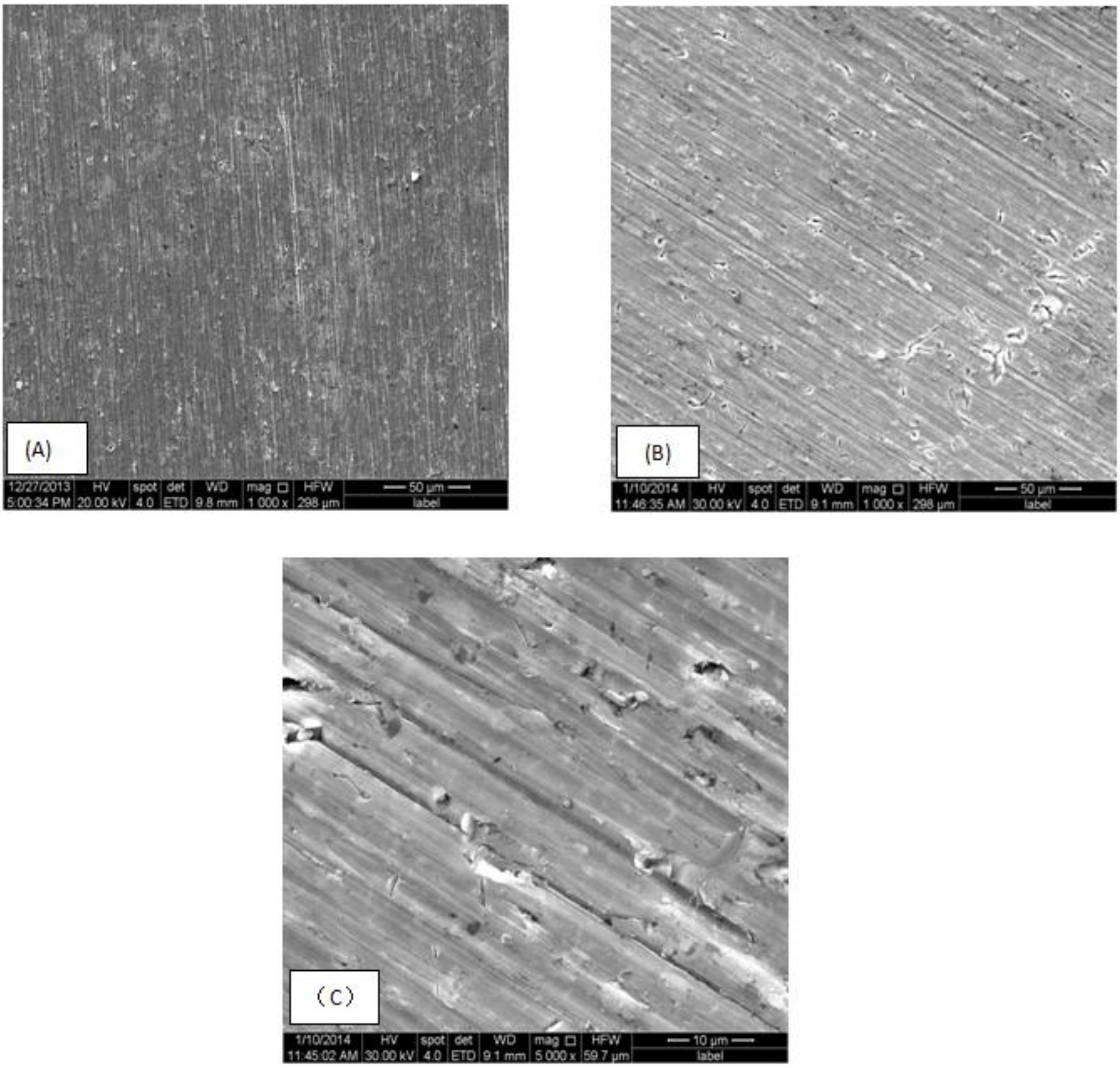

Figure 7. Surface morphologies of Ti-6Al-4V alloys immersed in solutions without (A) and with 1000 ppm NaF and (C) magnified view of (B).

As can be seen from this figure, abrading scratches still were observed. In addition, more uneven phenomenon and pitting were clearly observed in the presence of 1000 ppm NaF compared to in the absence of NaF. Magnified view of the surface in the presence of 1000 ppm NaF, obvious pitting was distinctly observed. That is, the formation of pitting was affected by fluorine ion significantly. As a consequence, at the microscopic level, the effect of fluorine ion on generating pitting could not be ignored. This result was also confirmed by Schiff et al. [6]. Schiff et al. reported the effects of F^- on titanium and its alloys, they believed that the F^- could damage the passive film of it and lead to the pitting corrosion.

3.3 Discussion

Ti-6Al-4V alloy is widely used in dental implantology fields due to its good corrosion resistance, suitable mechanical properties and good biocompatibility. The biocompatibility and corrosion resistance may be due to the thin oxide layer, mainly TiO_2 formed on the surface of Ti-6Al-4V alloy [24]. The presence of fluoride ions could cause the breakdown of the protective passivation layer that normally exists on the titanium and its alloys, leading to pitting corrosion. In our study, obviously pitting was observed by SEM. That is, fluoride ions can lead to the pitting corrosion of Ti-6Al-4V alloy after 5 d immersion. The corrosion mechanism of Ti-6Al-4V alloy in the presence of NaF based on our experimental results could be attributed to the following reasons:

The good corrosion resistance of Ti-6Al-4V alloy is the result of the presence of a protective and self-adherent oxide film of a thickness of 2–6 nm formed on the titanium and its alloys' surface, which is mainly composed of titanium dioxide (TiO_2) [4,25,26], however a weaker dissolving capacity of TiO_2 in aqueous solution still exists, which can be attributed to the following dissolution equilibrium [4, 27]:

$TiO_2 \leftrightarrow TiO^{2+} + O^{2-}$

TiO^{2+} is unstable and easy to hydrolyze in artificial saliva solution, and react with Cl^-:

$TiO^{2+} + Cl^- + 2H_2O \leftrightarrow Ti(OH)_3Cl + H^+$

The produce of H^+ will decrease the pH, which has been confirmed by Qu et al. [4], As a result, the corrosion of titanium will lead to the decreasing of pH.

Table 2. EIS parameters of Ti-6Al-4V Alloy immersed in Artificial Saliva without and with NaF for 5 d.

NaF (ppm)	R_s ($\Omega\cdot cm^2$)	Q_1 ($10^{-5}\Omega^{-1}\cdot cm^{-2} S^{n1}$)	n_1	R_p ($\Omega\cdot cm^2$)	Q_2 ($10^{-5}\Omega^{-1}\cdot cm^{-2} S^{n2}$)	n_2	R_t (10^5 $\Omega\cdot cm^2$)
0	42.2	4.24	0.92	387.6	3.43	0.77	5.55
500	43.1	6.29	0.88	342.9	2.31	0.71	3.61
1000	47.4	1.68	0.82	256.8	2.87	0.68	2.43
2000	43.7	2.28	0.80	163.6	2.58	0.64	1.47

When NaF is added to the solution, fluoride ion becomes hydrofluoric acid partially depending on pH of the solution. The hydrofluoric acid further attacks the passive films on titanium surface.

$TiO_2 + 2HF = TiOF_2 + H_2O$;

$TiO_2 + 4HF = TiF_4 + 2H_2O$;

$Ti_2O_3 + 6HF = 2TiF_3 + 3H_2O$;

$TiO_2 + 4HF + 2NaF = Na_2TiF_6 + 2H_2O$;

Huang et al. [28] has identified the formation of Na_2TiF_6 on the surface of Ti-6Al-4V alloy immersed in acidic artificial saliva (pH: 5) containing 0.1 wt.% of NaF by XPS. Frateur et al [29] and

Rosalbino [30] suggested that the presence of fluorides and low pH caused formation of HF and $[HF_2]^-$ species that were able to dissolve the passive films on Ti alloys forming titanium fluoride or oxifluoride complexes:

$HF + F^- \leftrightarrow [HF_2]^-$
$TiO_2 + 6HF = TiHF_6^- + 2H_2O + H^+$
$TiO_2 + 3[HF_2]^- + 2H^+ = TiHF_6^- + 2H_2O$

Thus, in artificial saliva in the presence of NaF, complexes compounds such as TiF_3, TiF_4, $TiOF_2$ and Na_2TiF_6 etc. were formed on the surface of Ti-6Al-4V, which destabilize the passivation film. Therefore, F^- can damage the passive film of Ti-6Al-4V and lead to the pitting corrosion.

4. CONCLUSIONS

Obvious increase in OCP was observed with fluorine ion compared with that without fluorine ion. The value of OCP firstly increased with increasing fluorine content up to 1000 ppm, and then decreased in solution with fluorine level higher than 1000 ppm. The presence of fluorine ion was also associated with decreases in R_{ct} and increase i_{corr} values, indicating the corrosion rate was clearly accelerated in the presence of fluorine ion. And it is clear that the corrosion increased with increasing the concentration of fluorine ion. Scanning electron microscopy indicated that pitting occurred on the surface of Ti-6Al-4V alloy after immersion in artificial saliva containing fluorine ion. The presence of F^- caused the formation of Ti-F complexes and resulted in further dissolution of the passive film on.

ACKNOWLEDGEMENTS
This work was financially supported by the Chinese Natural Science Foundation under Grant Nos. 51361028, 51161025, 21162036 and 20762014.

References

1. S. L. de Assis, W. Stephan, C. Isolda. *Materials Electrochim. Acta* 51 (2006) 1815.
2. A. Robin, J. P. Meirelis. *Corros. Eng. Sci. and Tech*. 44 (2009) 352.
3. R.M. Urban, J.J. Jacobs, M.J. Tomlinson, J. Gavrilovic, J. Black, M. Peoch. *J. Bone Joint Surg. Am*. 82 (2000) 457.
4. Q. Qu, L. Wang, Y.J. Chen, L. Li, Y. He, Z.T. Ding. *Materials 7(*2014)5528.
5. D.A. Basketter, E. Whittle, B. Monk. *J. Contact Dermatitis* 42 (2000) 310.
6. R. Yamauchi, A. Morita, T. Tsuji. *J. Contact Dermatitis* 42 (2000) 52.
7. N. Schiff, B. Grosgogeat, L. Michele, F. Dalard. *Biomaterials* 23 (2002) 1995.
8. K. Yokoyama, T. Ogawa , K. Asaoka, J. Sakai. *Mater. Sci. and Eng*. A. 384 (2004) 19.
9. N. Schiff, B. Grosgogeat, M. Lissac, F. Dalard. *Biomaterials*. 25 (2004) 4535.
10. B.G. Liang, X.T. Shen, L. Liu et al. *J. ZheJiang Univ*. 4 (2010), 399.
11. X.J Li, J.Q Wang, E.H Han, W. Ke. *Acta Biomater*. 3 (2007) 807.
12. G. Mabilleau, S. Bourdon, M.L. Joly-Guillou, R. Filmon, M.F.Basle, D.Chappard. *Acta Biomater*. 2 (2006) 121.
13. S.Takemoto , M. Hattori , M. Yoshinari, E.Kawada, K.Asami, Y.oda. *J. Dent. Mater*. 23 (2004) 379.

14. S. Kumar, T.S.N. Sankara Narayanan, S.G.S. Raman, S. K. Seshadri. *Corros. Sci.* 52 (2010) 711.
15. M. A. Khan, R. L. Williams and D. F. Williams. *Biomaterials*. 17 (1996) 2117.
16. M. Geetha, A. K. Singh, K. Muraleedharan, A. K. Gogia and R. Asokamani. *J. Alloy Compd*. 329 (2001) 264.
17. M.Lebrini, M.Lagrenee, H.Vezin, M.Traisnel, F.Bentiss. *Corros. Sci*. 49 (2007) 2254.
18. L. Li, Q. Qu, W. Bai, F. Yang, Y. Chen, S. Zhang, Z. Ding. *Corros. Sci*. 59 (2012) 249.
19. F. Mansfeld. *Electrochim. Acta* 52 (2007) 7670.
20. B. Tian, D.B. Xie, F.H. Wang. *J. Appl. Electrochem*. 39 (2009) 447.
21. N.O. San, H. Nazır, G. Donmez. *Corros. Sci*. 64 (2012) 198.
22. Q. Qu, Y. He , L. Wang, H.T. Xu, L. Li , Y.J. Chen , Z.T. Ding. *Corros. Scice*. 91 (2015) 321.
23. S. Arash, K.Walid, O. Sasha. *Mater. Letts*. 23 (2008) 3906.
24. C. Ohkubo, S. Hanatani, T. Hosoi. *J. Oral. Rehabil*. 35 (2008) 706.
25. D.A. Baaketter, E. Whittle, B. Monk. Contact Dermatitis.42 (2000) 310.
26. T. Green, E. Machtei, J. Horwitz, M. Peled. Implant. Dent. 11 (2002) 137.
27. O.E.M. Pohler. Injury. 31 (2000) D7.
28. H.H. Huang. *Biomaterials*. 24 (2003) 275.
29. I. Frateur, S. Cattarin, M. Musiani and B. Tribollet: *J. Electroanal. Chem*. 48 (2000) 202.
30. F. Rosalbino, S. Delsante, G. Borzone, G. Scavino. *J. Mater. Sci.: Mater. M*. 5 (2012) 1129.