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*Short Communication*

# Enhancement of Corrosion Resistance of a Biomedical Grade NiTi Shape Memory Alloy by Cyclic Potentiodynamic Polarization in PBS Solution

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In this work, corrosion resistance of the passive films formed on a biomedical grade NiTi shape memory alloy (SMA) surface in phosphate buffered saline (PBS) was improved using a simple linear cyclic potentiodynamic polarization technique. The results shown that the modification of NiTi SMA surface by cyclic potentiodynamic polarization between -0.9 V and a given anodic potential for a specified cyclic scan number resulted in a formed passive film which obviously enhanced corrosion resistance (both pitting and general) when compared to the naturally formation of a passive film. The influence of anodic potential limit and scan numbers on the pitting corrosion resistance was discussed. The capacitance analysis demonstrated that cyclic potentiodynamic polarization for the NiTi SMA surface under the given conditions caused an evident improvement of the surface's general corrosion resistance.

**Keywords:** NiTi SMA; Biomedical; Corrosion; Passive films; PBS solution

## 1. INTRODUCTION

Equiatomic NiTi shape memory alloy (SMA) is a suitable material used in medical application for unique properties of its biocompatibility and shape memory effect. NiTi SMA has lower elastic modulus than titanium alloys and CoCrMo alloys. In addition, the superelastic property is one of unique properties of NiTi SMA. Therefore, NiTi SMA has been widely used for implants that can be self-expanding, self-compressing and self-locking, providing great opportunities for many medical applications, from surgical and orthodontic implants to vascular stent [1]. It has been shown that NiTi SMA with a thin film is a promising material from which to fabricate micro medical devices for Bio-

Micro-Electro-Mechanical System (Bio-MEMS) such as microstents, micropumps and microwrappers for neurovascular blood vessels [2].

To be used in humans, the most important characteristics of NiTi SMA are surface property and corrosion resistance that would be compatible with the environment of human vivo. It is well known that resistance of corrosion of NiTi SMA can influence the biocompatibility which is essential for the implant biomaterial. Few papers have shown that NiTi SMA presents poor corrosion resistance to localized corrosion in simulated human body fluids. In particular, they are serious problems that the Ni ions are released into the human body from NiTi SMA for its toxicity and carcinogenesis [1]. A great many toxic and allergenic Ni ions is released from the surface when a NiTi SMA film with high Ni content is exposed to human body fluids. Therefore, it is essential to modify the surface of NiTi SMA to enhance their pitting corrosion resistance and prevent Ni ion release into human body fluids [3-5].

Many surface treatment methods have been reported, such as chemical surface passivation, anodization, plasma polymerization, reduction annealing, and electropolishing [6-14], to enhance the pitting corrosion resistance of the biochemical alloys. Among them, the electrochemical method is advantageous for its simplicity and feasibility. The anodization method has been reported to enhance the resistance to corrosion of NiTi SMA [2, 6]. N. Bayat et al. [6] proposed that the exposure of NiTi SMA surface to Hank's solution under different voltages leads to a passive film that is related to a higher grain boundary density. However, the surface treatment of NiTi SMA by cyclic potentiodynamic polarization has not been reported.

In this study, a simple cyclic linear potentiodynamic polarization technique is used to form passive films on the NiTi SMA in phosphate buffered saline (PBS) to improve its corrosion resistance. The effect of cyclic scan numbers and anodic potential limit on the corrosion resistance is discussed.

## 2. EXPERIMENTAL DETAILS

The specimens were cut from a tubular product of NiTi shape memory alloy with the diameter of 1.8 mm. The chemical composition of NiTi alloy is listed in Table 1. The specimens were cut into Φ1.8 mm × 30 mm, grinded sequentially to 1000 grit SiC paper, cleaned in deionized water, and then degreased in alcohol.

**Table 1.** Chemical composition of NiTi alloy (wt. %)

| Ni | Ti | C | Cr | Cu | Nb | Co | Fe | H | N | O |
|---|---|---|---|---|---|---|---|---|---|---|
| 55.85 | 43.85 | 0.034 | ＜0.005 | ＜0.005 | ＜0.005 | ＜0.005 | 0.019 | 0.00017 | 0.002 | 0.028 |

The cyclic potentiodynamic polarization experiment and the electrochemical impedance spectroscopy (EIS) measurement were carried out in 0.1 M phosphate buffer solution pH 7.4 (PBS). The solutions were made up by dissolving the solid substance in the deionized water. Solutions with pH ranging from 7.2 up to 7.4 were prepared with the 0.1 M NaOH. All tests were carried out at 37 ℃

in deoxidized solutions that were obtained by continuously filling in with $N_2$ to the electrochemical cell. The AUTOLAB PGSTAT128N was utilized to perform the electrochemical tests, using a standard three-electrode electrochemical cell. The counter electrode was two graphite electrodes, and all potentials were referred to a saturated calomel electrode (SCE).

The modification of the surface were carried out through the cyclic potentiodynamic polarization of the electrode in a PBS solution between -0.9 V and a given anodic potential (0.3 V, 0.6 V, 0.8 V, 1.0 V, 1.1 V respectively) at a scan rate of 0.1 V/s for 100 sweeps and between -0.9 V and 0.8 V for a specified number of cycles (50 sweeps, 80 sweeps, 100 sweeps, 150 sweeps, 200 sweeps respectively). Once the cyclic polarization was completed, the open circuit potential (OCP) was monitored for 1 hour to guarantee its stability. Then, the potentiodynamic polarization curves were measured at a scan rate of 1 mV/s from OCP to +1.4 V (SCE). The electrochemical impedance spectroscopy (EIS) measurements were carried out over a frequency ranging from 100 kHz to 10 mHz using a 10 mV amplitude sinusoidal voltage. The impedance data was analyzed by the commercial software ZsimpWin.

## 3. RESULTS AND DISCUSSION

### *3.1 Corrosion behavior*

Fig. 1 shows the potentiodynamic polarization curves of both the unmodified and modified NiTi surface in a PBS solution. The unmodified surface is the NiTi SMA surface on which a passive film was grown by immersing in the PBS solution for 1 h under OCP. The modified specimen is corresponds to the specimen experienced cyclic potentiodynamic polarization sweep between -0.9 V and 0.3 V for 100ycles. It is shown that corrosion potential is shifted positively because of the surface modification. Pitting potential ($E_b$) of the as-received and modified NiTi specimens is 0.319 V and 0.668 V, respectively. In addition, the current oscillations in the passive region, which is related to the metastable pitting events [15-16], are significantly reduced after the modification of the specimen surface. All the observations demonstrate that the cyclic potentiodynamic polarization under the applied conditions enhances the pitting corrosion resistance of NiTi SMA.

During the cyclic potentiodynamic polarization treatment of the NiTi specimen, the anodic potential limit and cyclic scan numbers will significantly influences the corrosion resistance of the NiTi surface passive film. Therefore, effects of these two factors on the pitting potential were investigated to obtain the optimizing parameters. Fig. 2 shows that the pitting potentials are related with the anodic potential limits (a) and cyclic sweep numbers (b). It is shown in Fig. 2a that all modified NiTi SMA surfaces demonstrate higher corrosion resistance performance than the unmodified NiTi SMA surfaces. The pitting resistance increases with an increase of the anodic potential limit. The pitting corrosion resistance reaches a maximum at 0.8 V. With further increase of the anodic potential limit, the pitting resistance is essentially constant. As a result, the optimizing value for the modified NiTi SMA surface was an anodic potential limit of 0.8 V.

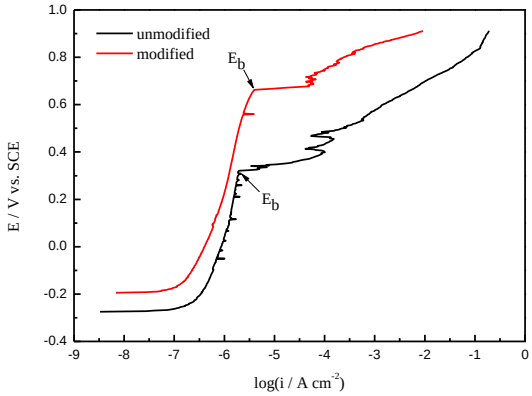


**Figure 1.** Potentiodynamic polarization curves of the unmodified and modified NiTi alloy surfaces. The modified surface is a passive film which was formed by cyclic potentiodynamic polarization of the electrode in 0.1 M PBS between -0.9 V and 0.3 V at a scan rate of 0.1 V/s for 100 sweeps.

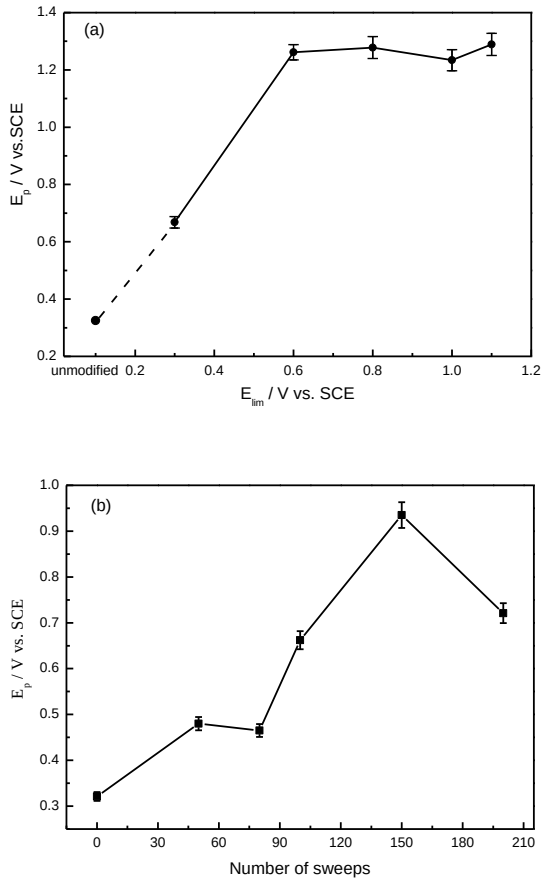


**Figure 2.** The pitting potential influenced by (a) the anodic potential limit and (b) cyclic scan numbers used for the modified NiTi SMA surface. The modified passive surface for the data shown in (a) was done by cyclic potentiodynamic polarization of the electrode in 0.1 M PBS between -0.9 V and $E_{\text{lim}}$ at a rate of 0.1 V/s for 100 sweeps, and for the data presented in (b) between -0.9 V and 0.8 V for the specified cyclic scan numbers.

The influence of the sweep number on the pitting potential during the electrode modification was shown in Fig. 2b. In the tests, the anodic potential limit is kept at the optimizing value of 0.8 V. It is seen that the pitting potential increases with the sweep numbers, reaching a maximum at 150 sweeps.

Further increase in the number of the modification sweeps results in a negative shift of the pitting potential. The film of NiTi SMA is formed and dissolved simultaneously during the process of cyclic potentiodynamic polarization. Further, the passive film thickness is probably responsible for the pitting corrosion resistance. With an increase in the cyclic scan numbers, the formation rate of passive film is faster than the dissolution rate that results in the growth of passive film in thickness. The formation rate of passive film is gradually equal to the dissolution rate under a maximum number of 150 sweeps. However, with further increasing in the cyclic scan numbers, the passive film dissolution is gradually faster than the passive film formation, leading to the decreasing thickness of passive films.

### *3.2 EIS studies*

The influence of surface modification on the pitting corrosion resistance of the surface was investigated through EIS measurements. Fig. 3 shows the EIS spectra recorded on the modified and unmodified surface of NiTi SMA in PBS solution. The radius of the semi-circular arc is significantly increased after the modification of the specimen surface, indicating an enhancement of the polarization resistance.

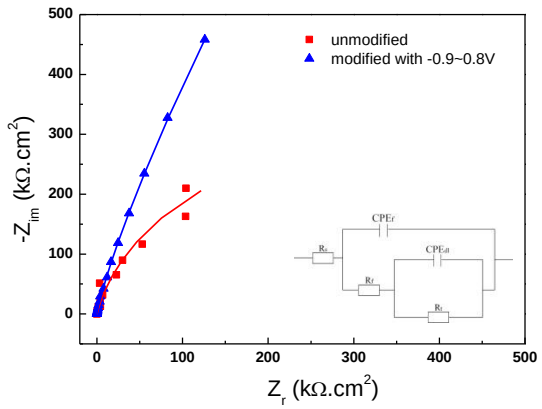


**Figure 3.** Nyquist diagrams of the unmodification (■) and modification (▲) of NiTi SMA surface in 0.1 M PBS solution with pH 7.4 and 37 ℃. The modification of NiTi SMA surface was done by cyclic potentiodynamic polarization of the electrode in 0.1 M solution PBS between -0.9 V and +0.8 V at a rate of 0.1 V/s for 150 sweeps.

**Table 2.** Best fitting parameters for the impedance spectra data presented in Fig. 3

| | $R_f$/Ω cm$^2$ | $R_t$/Ω cm$^2$ |
|---|---|---|
| Unmodified | 164.3 | $5.8\times10^5$ |
| Modified | $2.9\times10^5$ | $2.43\times10^6$ |

Different electrical equivalent circuits had been presented for explaining impedance spectra on a passive surface of the metal. According to some references [17-21], the EIS data can be fitted employing the equivalent circuit model inserted in Fig. 3, in which the $R_s$ is solution resistance, the $CPE_f$ is the constant phase element of the passive film layer, the $CPE_{dl}$ is the double layer capacitance, $R_f$ is passive film resistance, and $R_t$ is the charge transfer resistance. It can be seen that the equivalent circuit fits the test data well in most of the frequency range, which makes clear that the equivalent circuit is suitable.

Table 2 illustrates the EIS fitting results of the as-received and the surface-modified specimens. It is seen that both the film resistance ($R_f$) and the charge transfer resistance ($R_t$), especially the former, is increased after the surface treatment using cyclic polarization technique. The film resistance of the modified specimen is almost three orders of magnitude larger than the as-received specimen, indicating a better resistance of the surface film against corrosion process. In conclusion, the cyclic polarization technique is a promising method to improve the pitting corrosion resistance of NiTi SMA in PBS solution.

## 4 CONCLUSIONS

In this work, a cyclic polarization method is proposed to improve the corrosion resistance of NiTi SMA in PBS solution. Corrosion resistance is significantly improved after the modification using this technique, which is demonstrated by the polarization curve and EIS measurements. Results show that the optimizing anodic potential limit and sweep number are 0.8 V and 150 cycles, respectively, under which the specimen exhibits a higher pitting potential. EIS results show that cyclic polarization technique mainly modifies the surface passive film resistance, which present a three orders of magnitude larger than the as-received specimen.

## References

1. J.H. Sui and W. Cai, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 251 (2006) 402-406.
2. T. Shahrabi, S. Sanjabi, E. Saebnoori and Z.H. Barber, *Mater. Lett.*, 62 (2008) 2791-2794.
3. Z.D. Cui, H.C. Man and X.J. Yang, *Appl. Surf. Sci.*, 208-209 (2003) 388-393.
4. F.T. Cheng, P. Shi, G.K.H. Pang, M.H. Wong and H.C. Man, *J. Alloys Compd.*, 438 (2007) 238-242.
5. P. Shi, F.T. Cheng and H.C. Man, *Mater. Lett.*, 61 (2007) 2385-2388.
6. N. Bayat, S. Sanjabi and Z.H. Barber, *Appl. Surf. Sci.*, 257 (2011) 8493-8499.
7. Penghui Li, Limin Li, Wenhao Wang, Weihong Jin, Xiangmei Liu, Kelvin W.K. Yeung and Paul K. Chu, *Appl. Surf. Sci.*, 297 (2014) 109-115.
8. Lakshman Neelakantan, Srinivasan Swaminathan, Michael Spiegel, Gunther Eggeler and Achim Walter Hassel, *Corros. Sci.*, 51 (2009) 635-641.
9. L. Zhu, C. Trepanier, J. Fino and A.R. Pelton, in: S.M. *Materials & Processes for Medical Device Conference*, 2003.
10. B. O'Brien, W.M. Carroll and M.J. Kelly, *Biomaterials*, 23 (2002) 1739-1748.
11. Zhendi Yang, Xiaojin Wei, Wei Gao and Peng Cao, *Sur. Coat. Technol.*, 252 (2014) 142-147.
12. Tingting Zhao, Yan Li, Yan Xiang, Xinqing Zhao and Tao Zhang, *Sur. Coat. Technol.*, 205 (2011) 4404-4410.

13. D. Vojtěch, M. Voderová, J. Fojt, P. Novák and T. Kubásek, *Appl. Surf. Sci.*, 257 (2010) 1573-1582.
14. Karrina McNamara, Syed A.M. Tofail, Derek Conroy, James Butler, Abbasi A. Gandhi and Wynette Redington, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 284 (2012) 49-52.
15. Yuming Tang, Yu Zuo, Jiani Wang, Xuhui Zhao, Ben Niu and Bing Lin, *Corros. Sci.*, 80 (2014) 111-119.
16. H. Luo, C.F. Dong, X.G. Li and K. Xiao, *Electrochim. Acta*, 64 (2012) 211-220.
17. G.A. Ragoisha, T.A. Auchynnikava, E.A. Streltsov and S.M. Rabchynski, *Electrochim. Acta*, 122 (2014) 218-233.
18. B. Guitián, X.R. Nóvoa and B. Puga, *Electrochim. Acta*, 56 (2011) 7772.
19. H. Luo, C.F. Dong, K. Xiao and X.G. Li, *Appl. Surf. Sci.*, 258 (2011) 631.
20. A. Kocijan, D.K. Merl and M. Jenko, *Corros. Sci.*, 53 (2011) 776.
21. C. Andrade, M. Keddam, X.R. Nóvoa, M.C. Pérez, C.M. Rangle and H. Takenouti, *Electrochim. Acta*, 46 (2001) 3905.