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Effect of pH, temperature and Cl^- concentration on electrochemical behavior of NiTi shape memory alloy in artificial saliva

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Abstract The cooperation of pH, temperature and Cl^- concentration on electrochemical behavior of NiTi shape memory alloy in artificial saliva was studied using orthogonal test method. The results showed that the pitting potential for NiTi in artificial saliva decreased at low and high pH; at 25°C, the pitting potential was the lowest compared to those at 10°C, 37°C and 50°C; when the Cl^- concentration was not less than 0.05 mol/L the pitting potential decreased with the increase of Cl^- concentration. The free corrosion potential of austenitic NiTi was lower than that of mixture of austenite and martensite.

1. Introduction

Equiatomic Nickel-Titanium (NiTi) possesses a good shape memory effect, super-elasticity and biocompatibility, which make it very suitable for medical applications [1–7]. Solid NiTi has been widely used to correct skeletal-muscular anomalies in orthodontic devices for simultaneous teeth dislodgment and stabilization, in orthodontic correcting systems [8–10]. The quality of correcting system is highly enhanced due to the constant force action of super-elasticity. A great deal of literature related to nickel toxicity exists [11] and NiTi in body solution has been considered to have good corrosion resistance due to the formation of a thin oxide film formed on NiTi alloy [12]. It has been found that Cl^- can cause pitting corrosion and break down the surface film [13]. The effect of sole parameter of pH, Cl^- concentration on corrosion of NiTi in saliva has been studied [14–16]. The corrosion rate increased with the increasing Cl^- concentration and pH. Because the pH, Cl^- concentration and temperature of saliva can change simultaneously at a relatively large range when people taking food with respect to individual dietetic habit, saliva can be the most severe aqueous environment inside human body. Up to now, the cooperative effect of pH, Cl^- concentration and temperature on corrosion behavior of NiTi is less studied. This work aimed to study the effect of pH, temperature and Cl^- concentration on electrochemical behavior of NiTi shape memory alloy in artificial saliva.

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2. Experimental

Material used was NiTi with 50.9 (at.%) Ni and 49.1 (at.%) Ti. The material was heated at 800°C for 10 h, water cooling to room temperature, then heated at 500°C for 90 min, and then water cooling to room temperature. The phase transformation temperature was measured using differential scanning calorimeter (DSC) method with scan rate of 10°C/min and temperature range between $-20°C - 100°C$.

The 10×10 mm^2 sample was wire-cut. The sample surface except the exposed area was covered using epoxy. The sample surfaces were polished to 800 grit aluminum oxide waterproof abrasive paper, degreased in acetone, and dried using a hairdryer.

The solution was synthetic saliva [17], and its composition was listed in (Table 1). The Cl^- concentration was adjusted by adding NaCl, and pH was adjusted by adding lactic acid or NaOH. Temperature was monitored by temperature control device with accuracy of $\pm 1°C$.

The samples, Pt wire and a saturated calomel electrode (SCE) were used as working electrode, counter electrode, and reference electrode respectively. Electrochemical

Table 1 Synthetic saliva used in the tests

Composition	mg/L
Na_2HPO_4	260
NaCl	700
KSCN	330
KH_2PO_4	200
$NaHCO_3$	1500
KCl	1200

Table 2 Orthogonal design form for variables for potentiodynamic polarization test

	Variables		
Level	T (°C)	Cl^- (mol/L)	pH
1	10	0.028	3.0
2	25	0.05	7.6
3	37	0.10	6.0
4	50	0.50	9.0

polarization curves were measured using Solartron 1287 potentiostat with scan rate of 0.5 mV/s. Scan was stopped when current density reached to 10^{-3} A/cm^{-2}. In order to reduce the expenditure of tests and time, the orthogonal test design was applied [18, 19]. The variables investigated were pH, Cl^- concentration and temperature, which were adjusted within the selected range. For a complete factorial experiment with all possible combinations of level n of different factos k, a number of k^n tests are necessary. A three-factor, four-level, fractional factorial experiment design (Table 2), developed from orthogonal design [18, 19], was applied with reduced experiments. The average free corrosion potential and pitting potential at level i over all the possible variations of other variables was obtained. The objective of this design is that the number of the experiments should be as small as possible (reduced from 81 to 16), and the interactions between factors can be evaluated.

3. Results

Effect of temperature on polarization behavior of NiTi in artificial saliva at various pH and Cl^- concentrations was shown in Fig. 1. The average free corrosion potential was −0.324 V/NHE, −0.318 V/NHE, −0.38 V/NHE and −0.376 V/NHE, and average pitting potential was 0.958 V/NHE, 0.277 V/NHE, 0.819 V/NHE and 0.944 V/NHE at 10°C, 25°C, 37°C and 50°C respectively. The average free potentials at 10°C and 25°C were similar, at 37°C and

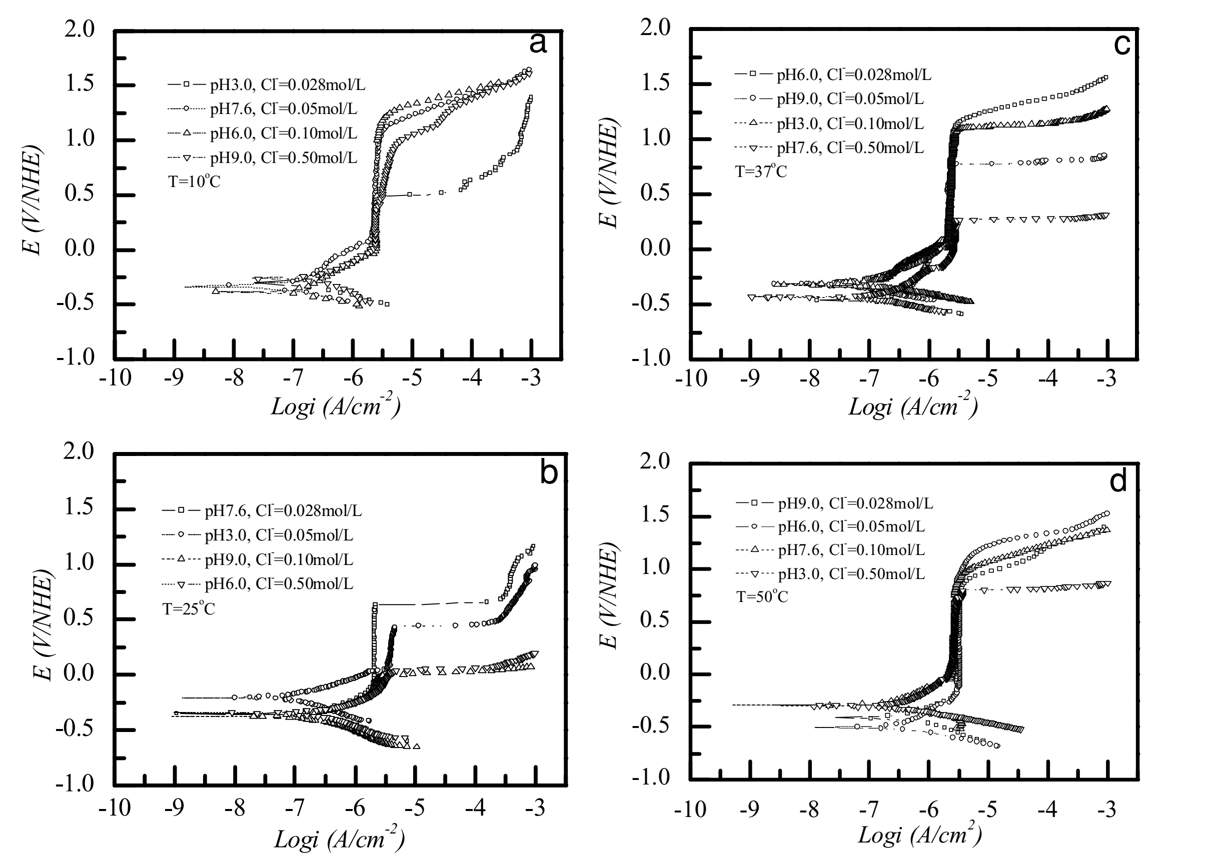

Fig. 1 Potentiodynamic polarization curves for NiTi in synthetic saliva of (a)10°C, (b) 25°C, (c) 37°C, and (d) 50°C at various pH and Cl^- concentrations.

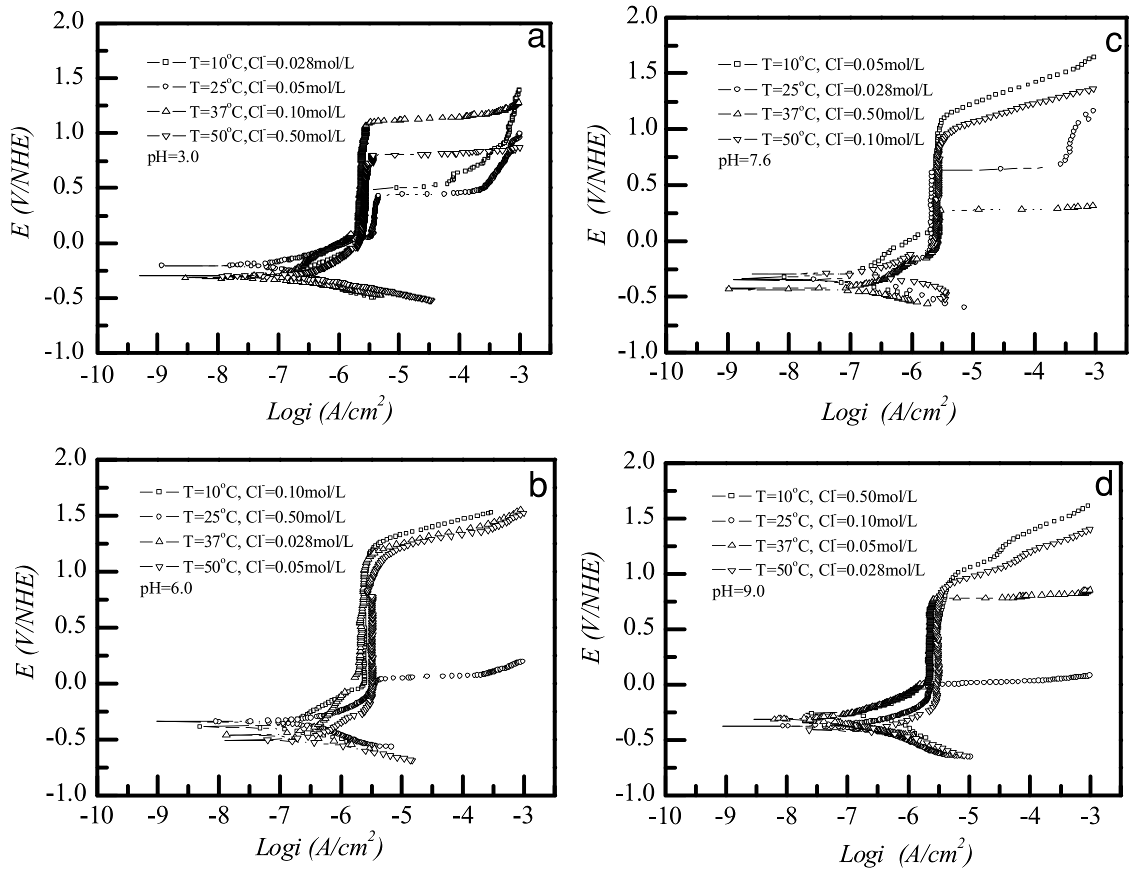

Fig. 2 Potentiodynamic polarization curves for NiTi in synthetic saliva of pH (a) 3, (b) 6, (c) 7.6, and (d) 9.0 at various temperature and Cl^- concentrations.

50°C were similar. The average pitting potential was lowest at 25°C.

Effect of pH on polarization behavior of NiTi in artificial saliva at various temperature and Cl^- concentrations was shown in Fig. 2. The average free corrosion potential was −0.283 V/NHE, −0.423 V/NHE, −0.354 V/NHE and −0.339 V/NHE, and average pitting potential was 0.704 V/NHE, 0.892 V/NHE, 0.751 V/NHE and 0.651 V/NHE when pH changed from 3.0 to 9.0. At pH 6, the free corrosion potential was the lowest, and the pitting potential was the biggest.

Effect of Cl^- concentration on polarization behavior of NiTi in artificial saliva at various temperature and pH was shown in Fig. 3. The free corrosion potential was −0.384 V/NHE, −0.34 V/NHE, −0.342 V/NHE and −0.333 V/NHE, and pitting potential was 0.779 V/NHE, 0.863 V/NHE, 0.834 V/NHE and 0.523 V/NHE when Cl^- concentration at 0.028 mol/L, 0.05 mol/L, 0.10 mol/L, and (d) 0.50 mol/L respectively. At pH 6, the free corrosion potential was the lowest and the pitting potential was the biggest. The free corrosion potential increased with the increase of Cl^- concentration, and the pitting potential decreased with the increase of Cl^- concentration.

4. Discussion

As shown in Fig. 1–3, NiTi SMA presented self-passivity in artificial solution, and its passive currents did not change at most of the test conditions. The change of pH, temperature and Cl^- concentration significantly affected the pitting potential and the passive region but the value of passive current density.

The effect of temperature on the free corrosion potentials of NiTi in artificial saliva at various pH and Cl^- concentrations was shown in Fig. 4. The free corrosion potentials were similar at 10°C and 25°C, and similar at 37°C and 50°C, moreover, the free corrosion potential at 10°C and 25°C were more positive than those at 37°C and 50°C. It means the surface states of samples were similar at 10°C and 25°C, and as well as at 37°C and 50°C.

The DSC result as shown in Fig. 5 indicated that $A_s = 22.5°C$, $A_f = 26.5°C$, $M_s = -8.5°C$, and $M_f = -10°C$, so NiTi SMA was pure austenitic phase at 37°C and 50°C, and mixture of martensite and austenite at 10°C and 25°C. The free corrosion potential of austenitic NiTi SMA was lower than that of the mixture of austenite and martensite, which means the austenitic NiTi was more

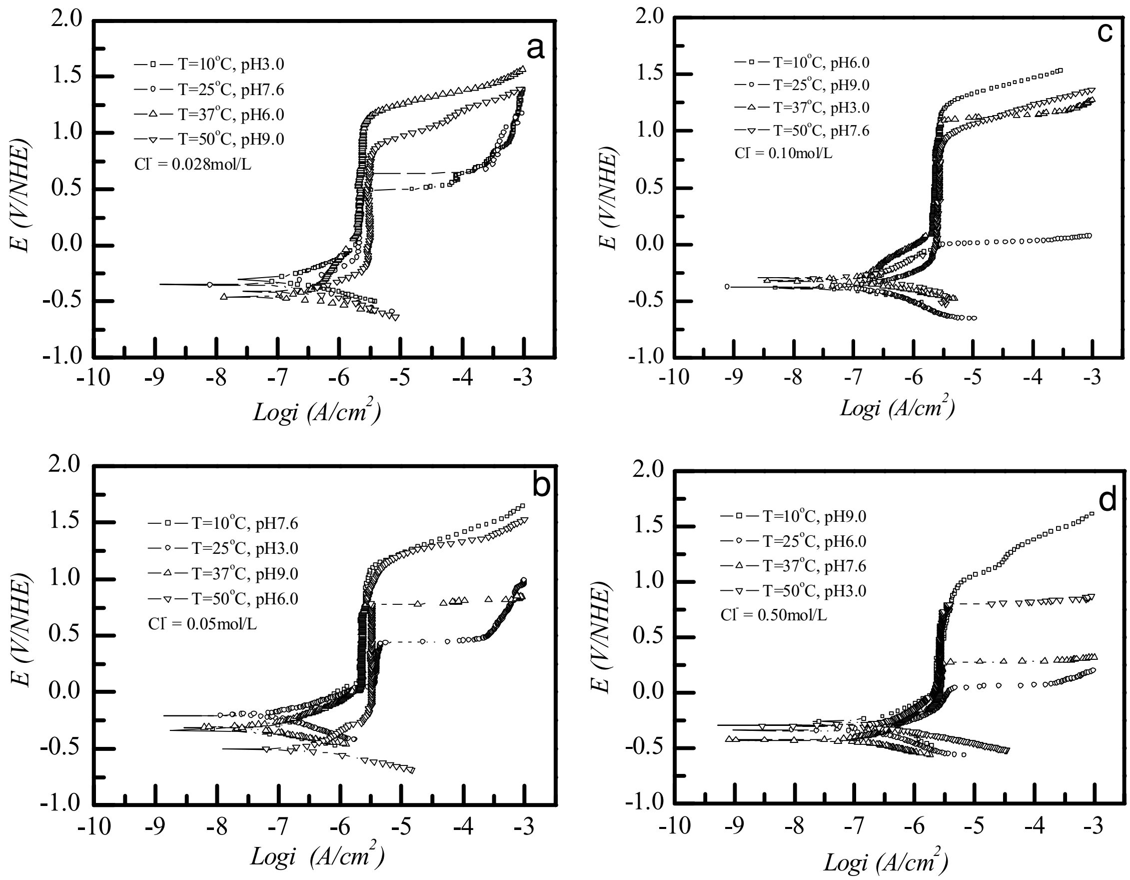

Fig. 3 Potentiodynamic polarization curves for NiTi in synthetic saliva with Cl^- concentration at (a) 0.028 mol/L, (b) 0.05 mol/L, (c) 0.10 mol/L, and (d) 0.50 mol/L at various pH and temperature.

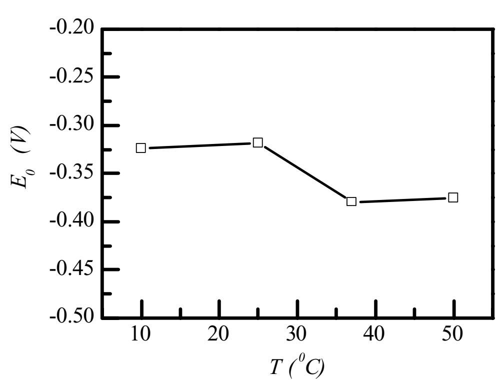

Fig. 4 Influence of temperature on the E_0 of NiTi in the synthetic saliva.

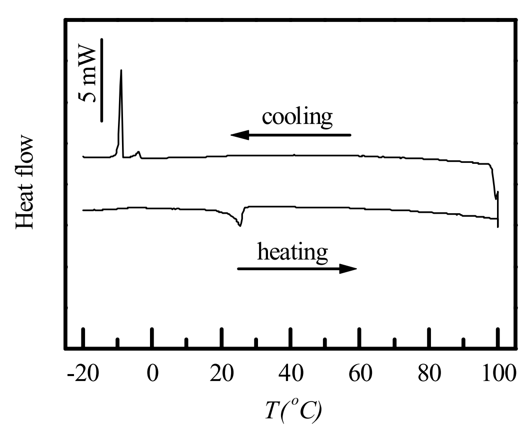

Fig. 5 DSC result of NiTi SMA after heat treatment.

electrochemically active than the mixture of austenite and martensite.

The influence of temperature on pitting potential of NiTi in artificial saliva at various pH and Cl^- concentrations was shown in Fig. 6. It can be seen that the pitting potential was lowest at 25°C, and similar at other three temperatures. 25°C is the temperature between A_s (22.5°C) and A_f (26.5°C) so the phase transformation would cause the instability of the surface film of NiTi SMA at 25°C and therefore pitting could occur more easily than at other three temperatures.

As shown in Fig. 7, the free corrosion potential of NiTi was lowest at pH 6, and the pitting potential was highest at pH 6. It means at pH 6, the passive region was largest and the passive film was most stable. At acidic or alkaline saliva, the film was less stable than at neutral saliva.

The effect of Cl^- concentration on free corrosion potential and pitting potential of NiTi SMA in artificial saliva at various temperature and pH was shown in Fig. 8. It can be seen that

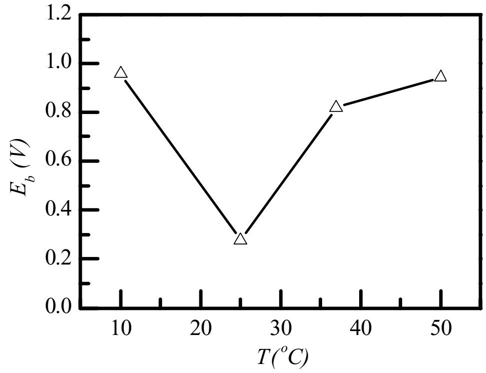

Fig. 6 Influence of temperature on the E_b of NiTi SMA in artificial saliva.

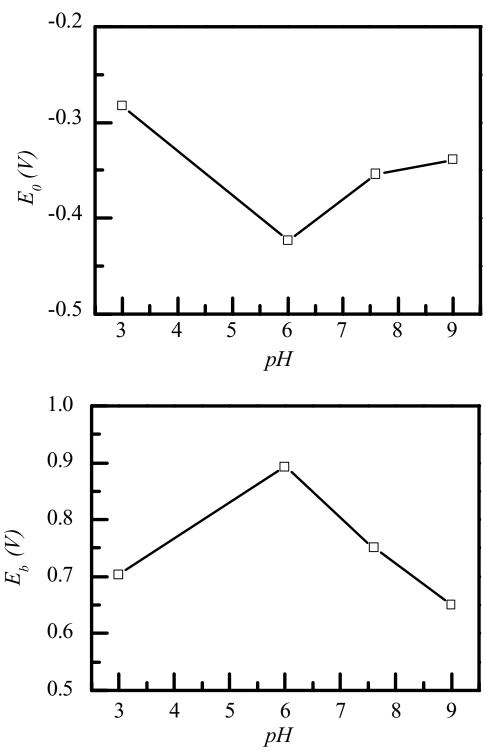

Fig. 7 Influence of pH on (a) free corrosion potential, (b) pitting potential of NiTi in artificial saliva.

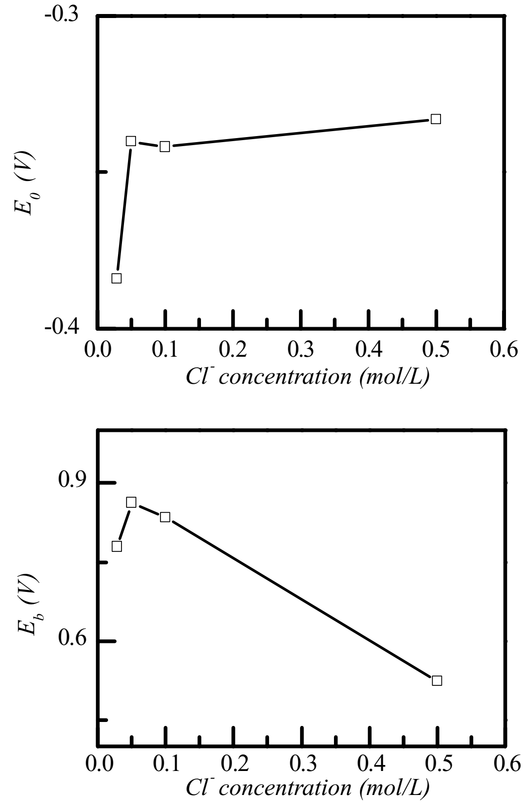

Fig. 8 Influence of Cl^- concentrations on (a) free corrosion potential, (b) pitting potential of NiTi in artificial saliva.

Table 3 Analysis of orthogonal design. $E_{0,i}$ $E_{b,i}$ are the average potential at level i over all the possible variations of other variables. $\boldsymbol{R}_0$, $\boldsymbol{R}_b$ are the maximum difference of $E_{0,i}$ $E_{b,i}$ respectively

	Variables		
	T (°C)	Cl^- (mol/L)	pH
$E_{0,1}$	−0.324	−0.384	−0.283
$E_{0,2}$	−0.318	−0.34	−0.423
$E_{0,3}$	−0.38	−0.342	−0.354
$E_{0,4}$	−0.376	−0.333	−0.339
$\boldsymbol{R}_0$	***−0.62***	***−0.051***	***−0.14***
$E_{b,1}$	0.958	0.779	0.704
$E_{b,2}$	0.277	0.863	0.892
$E_{b,3}$	0.819	0.834	0.751
$E_{b,4}$	0.944	0.523	0.651
$\boldsymbol{R}_b$	***0.681***	***0.34***	***0.241***

at lowest Cl^- concentration, 0.028 mol/L, the free corrosion potential of NiTi SMA was the lowest and the pitting potential was relatively high. The passive region was biggest at lowest Cl^- concentration. When Cl^- concentration was equal or more than 0.05 mol/L, the free corrosion potentials increased and kept stable, but the pitting potential decreased with the increase of Cl^- concentration. It means pitting for NiTi in artificial saliva occurred more easily with the increase of Cl^- concentration.

After the orthogonal test of three variables, including pH, temperature and Cl^- concentration, the interaction of these three variables could be analyzed. The average potential at level i over all the possible variations of other variables and the maximum difference R of the average potentials were listed in (Table 3). Both the free corrosion potential and pitting potential were most sensitive to temperature, which means temperature mainly decides the corrosion behavior of NiTi SMA because it controls the phase transformation which can change the surface state. Cl^- concentration has least effect on the free corrosion potential compared to pH and temperature. The pH has least effect on the pitting potential compared to Cl^- concentration and temperature.

5. Conclusions

For electrochemical behavior of NiTi49.1 SMA in artificial saliva, the following conclusions were obtained:

1) NiTi SMA in artificial saliva was self-passivated.
2) The significance of dominating factors in free corrosion potential is in the order of temperature, pH and Cl^-; in pitting potential is in the order of temperature, Cl^- and pH.
3) When temperature of saliva was between A_s and A_f, the surface film was unstable and pitting occurred most easily.
4) Austenitic NiTi was more electrochemically stable than mixture of austenite and martensite.
5) At pH6, NiTi was more stable than in acidic or alkaline saliva.
6) When Cl^- concentration was less than 0.05 mol/L, the passivity of NiTi in saliva was very well. After Cl^- concentration was not less than 0.05 mol/L, pitting occurred more easily with the increase of Cl^- concentration.

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References

1. F. X. GIL, J. M. MANERO and J. A. PLANELL, *J. Mater. Sci. Mater. Med.* **7** (1996) 403.
2. M. THEIR and D. TREPPAMANN, *J. Mater. Sci. Mater. Med.* **3** (1992) 229.
3. M. P. FILLEUL and S. CONSTANT, *Mater. Sci. Eng. A* **273–275** (1999) 775.
4. T. W. DUERIG, A. R. PELTON and D. STOCKEL, *Bio-Med. Mat. and Eng.* **6** (1996) 255.
5. T. G. FRANK, W. XU and A. CUSCHIERI, Shape Memory Applications in Minimal Access Surgery—The Dundee Experience. *Proc. Sec. Int. Conf. Shap. Mem. and Super. Techn.*, edited by A. Pelton, D. Hodgson, S. Russell and T. Duerig, (1997) p. 509.
6. S. A. SHABALOVSKAYA, *Bio-Med. Mat. and Eng.* **6** (1996) 267.
7. K. OTSUKA and X. B. REN, Intermetallics **7** (1999) 511.
8. G. F. ANDREASEN, T. B. HILLEMAN, *J. Ame. Dent. Asso.* **82** (1971) 1373.
9. V. DANILOV, M. CHITALIN and T. MAKLJUK, D. KOLCHIN, "On correction and stabilization of sacrolumbar scoliosis." *Conf. Proc.: Superelastic Shape Memory Implants in Medicine:* 47–48; Tomsk, November **24–26** (1995).
10. S. FEYODOROV, "Clinical methods of loose teeth splitting using NiTi alloys." *Conf. Proc.: Superelastic Shape Memory Implants in Medicine:* 189–190; Tomsk, November **24–26** (1995).
11. S. LACY, K. MERITT and S. BROWN, *J. Biomed. Mater. Res.* **32** (1996) 279.
12. S. A. SHABALOVSKAYA and J. W. ANDEREGG, *J. Vac. Sc. Tech.* A13(**5**) (1995) 2624.
13. M. POURBAIX, *Biomaterials* **5** (1984) 122.
14. Y. CHENG, W. CAI and L. C. ZHAO, *J. Mat. Sci. Lett.* **22** (2003) 239.
15. M. DARABARA, L. BOURITHIS and S. ZINELIS, *International Endodontic Journal* **37** (2004) 705.
16. H. H. HUANG, *J. Biomed. Mater. Res.* 66(**4**) (2003) 829.
17. L. E. MEDAWAR, P. ROCHER and J. C. HORNEZ, *Biomol. Eng.* **19** (2002) 153.
18. Scientific Institute of Shanghai, 1975, Method of orthogonal design, 1st edn (Shanghai: People's Publishers of Shanghai) (in Chinese).
19. A. V. GERAMITA, J. M. GERAMITA and J. SEBERRY WALLIS, Orthogonal designs. *Linear and Multilinear Algebra* **3** (1976) 281.