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Electrochemical behavior of nitinol alloy in Ringer's solution

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Corrosion behavior of Nitinol (nickel titanium) alloy has been examined in physiological Ringer's solution by means of electrochemical techniques (open-circuit potential measurement, potentiodynamic and potentiostatic polarizations) and capacitance measurements. The results show that the passive film is stable at open-circuit condition, but many of anodic current transients are observed at potentiodynamic and potentiostatic polarizations. The thickness of passive film decreased because of the occurrence of dissolution.

Introduction

Nitinol alloys have been used increasingly in medical implant devices [1–6] because of their shape memory effect, superelasticity, and radiopacity properties. However, the high content of Ni (~ 50%) has induced concern about its corrosion behavior [7, 8] and biocompatibility [9, 10]. The corrosion of Nitinol caused the nickel to dissolve into the corrosive medium and the titanium to oxidize [11]. Up to now, the corrosion behavior and biocompatibility of Nitinol alloy have not been adequately investigated, and the current results are controversial. Many studies [10, 12] suggested that NiTi has a certain cytotoxic effect on cells. Others [13–16] showed that Nitinol has good corrosion resistance and biocompatibility. Sarhar *et al.* [17, 18] reported that Nitinol wire exhibits greater corrosive tendency than stainless steel and titanium in 1% NaCl solution. Vicentini *et al.* [19] revealed that Nitinol alloy has poor pitting resistance compared to 316L stainless steel. Other authors [7, 8, 20–22] found that Nitinol wire gives more corrosion resistance than stainless steel. The amount of Ni released from Ni–Ti alloys in 0.9% NaCl solution was also found to be less than that from the SUS 316L stainless steel or dental Ni–Cr alloys [23, 24]. Rondelli *et al.* [25, 26] showed that a fairly good resistance to localized corrosion, similar to that of Ti–6A1–4V alloy, was observed in the potential range of practical interest, whereas a poor resistance to localized corrosion even worse than 316L stainless steel, was found in their potentiostatic scratch tests. Other results reported by Melton and Harrison [27] indicated that excellent general corrosion resistance is provided by the presence of the passive film, but under conditions where the film can be disrupted pitting or crevice corrosion can occur.

In our recent evaluations of the corrosion behavior and mechanism of implant materials, some work was done on Nitinol. The present paper presents our experimental results on the corrosion behavior of Nitinol and the stability of the passive film with potentiodynamic and potentiostatic polarization techniques in Ringer's solution. Capacitance measurements have also been taken to monitor the thickness change of the passive film. Because of the strong effects of surface finish on corrosion behavior [28–30], all the samples used in this study were given a passivation treatment after mechanical and electrochemical polishing.

Experimental

Ni–Ti alloy disks, 1.13 cm in diameter, were cut from a rod with diameter of 1.3 cm kindly supplied by Nitinol Devices & Components, Inc., Fremont, CA (NDC). The alloy composition is 55.2 Ni, 0.027 O, 0.01 C, 0.01 Cu, 0.01 Fe, 0.05 Al, 0.01 Si, < 0.05 Sn, < 0.02 W, 0.01 Nb and 0.05 Cr in wt %, the balance is Ti. The martensitic transformation temperature, Ms, is − 22 °C. After mechanically polishing down to 0.5 μm alumina, the specimens were degreased with acetone in an ultrasonic cleaner for 10 min. Then the samples were returned to NDC for electropolishing and passivation. For corrosion testing, the back of each disk was connected to a copper wire by silver conducting epoxy and the assembly was sealed by epoxy resin leaving a 1 cm^2 working area. The electrolyte of Ringer's solution was prepared from analytical reagents 8.6 g NaCl, 0.33 g KCl, and 0.3 g $\mathrm{CaCl_2 \cdot 2H_2O}$ in 1 L triply distilled water. A Princeton Applied Research Model 9700 corrosion cell was used, with a carbon rod as counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Potentiodynamic and potentiostatic anodic polarizations were taken at room temperature with a VoltaLab Model 21 Potentiostat/Galvanostat using VoltaMaster software (Radiometer America, Inc., Ohio 44145). The scan rate used for the potentiodynamic polarizations was 10 mV/min. Some potentiodynamic polarizations were interrupted every 200 mV for about 10–20 s to measure the capacitance. Before the anodic polarization, the working electrode was immersed in the electrolyte for 1 h. Then, the electrode was anodically polarized to the desired potential at a scan rate of 10 mV/min. The total charges passed were calculated by integrating the polarization curves and the current decay curves with the VoltaMaster software.

Results and discussion

The dynamic behavior of the passive oxide film can be monitored by measuring the variation of open circuit potential E_{corr} with time, which reflects the thinning or thickening of oxide film for passive metals. The increase of E_{corr} towards more noble values indicates a thickening of passive film, whereas its decrease towards the active direction means a thinning (film dissolution) [31]. Fig. 1 shows the typical open circuit potentials for Nitinol samples measured with time at different temperatures in physiological Ringer's solution. The open circuit potential E_{corr} varied with temperature, but no functional relationship was found between them. The fluctuations of E_{corr} at room temperature, 318 K and 328 K are instabilities of the passive film. However, E_{corr} tends to increase generally, which indicates growth of the film. At 338 K, the decrease of the E_{corr} at the first stage represents dissolution of the passive film, and the following increase of E_{corr} presents thickening of the film. The initial open circuit potential E_{corr} at body temperature (310 K) is -202 mV SCE. Within the 2 h, the E_{corr} does not change much. The nearly constant E_{corr} indicates that the thickness of the film does not change and the passive film of the Nitinol is stable at 310 K in Ringer's solution under open circuit condition. The simultaneous capacitance measurement gives a constant value of 0.039 μF through the 2 h measurement. The passive film is assumed to be a uniform dielectric, as done by many other authors [32, 33], behaving like a parallel plate capacitor. Its capacitance can be described by Equation 1.

$$c = \frac{\varepsilon\varepsilon_0 A}{\xi} \tag{1}$$

where ξ is the thickness of the film, A is the electrochemical area (1 cm^2), ε is the permittivity of the film, ε_0 is the permittivity of free space. Therefore, the constant capacitance indicates that the thickness of the film does not change and that the film is stable.

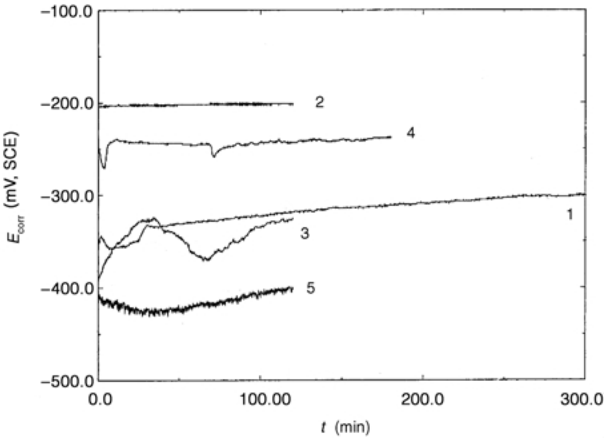

Figure 1 Variation of open circuit potential with time for Nitinol alloy in Ringer's solution at different temperatures. 1–298 K, 2–310 K, 3–318 K, 4–328 K, and 5–338 K.

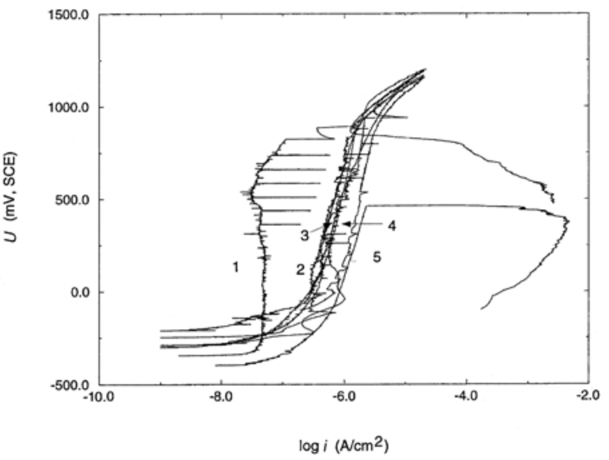

Figure 2 Potentiodynamic polarization curves taken at different temperatures in Ringer's solution for Nitinol alloy. 1–298 K, 2–310 K, 3–318 K, 4–328 K, and 5–338 K.

Fig. 2 presents the potentiodynamic polarization curves taken from different samples at different temperatures in Ringer's solution. As observed for Ti–6A1–4V alloy [34], there is no active–passive transition peak because of the thick oxide film on the surface. All the curves of Fig. 2 exhibit wide passive ranges, but the width is smaller compared to those of Ti–6A1–4V alloy [34]. At room temperature, the passive current is only 40 nA/cm^2, much smaller than those at higher temperatures and than the 600 nA observed for Ti–6A1–4V alloy [34]. Although with smaller passive current, the passive state is not stable. There are many current transients observed as abrupt changes and spikes, and at about 900 mV SCE, pitting corrosion develops. With rising temperature, the passive current increases greatly from 40 nA/cm^2 at room temperature to more than 1 μA/cm^2 at 338 K. The passive current at the body temperature (310 K) is about 400 nA/cm^2, much lower than those obtained by other authors in 1% NaCl solution [35], in 0.9% NaCl solutions with or without serum [36, 37], and in Ringer's solution [38]. A similar passive current was also obtained for a thin film Ni–Ti alloy in 0.9% NaCl solution [37]. Although smaller passive currents are observed, many anodic current transients exist in the passive potential range, which did not occur in other work [25, 35–38]. Some current transients involve a sharp rise and a sharp following fall of the anodic current, and others involve a sharp rise of the anodic current, a hold of the higher anodic current, and then a fall of the anodic current. These current transients indicate that depassivation and repassivation events occur [39]. Depassivation could arise chemically through localized dissolution of the passive film (pitting), or it could arise physically by mechanical rupture of the passive film, and result in the abrupt increase of the passive current. The localized dissolution often occurs in a defect area (pore, pit, ghost grain boundary, projected dislocation, and crack) of the passive film; therefore, its rate increases

TABLE I The pitting potentials determined for Nitinol alloy in Ringer's solution and for Ti–6Al–4V alloy in 0.2 N NaCl solution at different temperatures

Temperature (K)	Pitting potential (mV)	
	Nitinol	Ti–6Al–4V
298	850	1950
310	900	1500
318	870	1130
328	830	1020
338	480	910

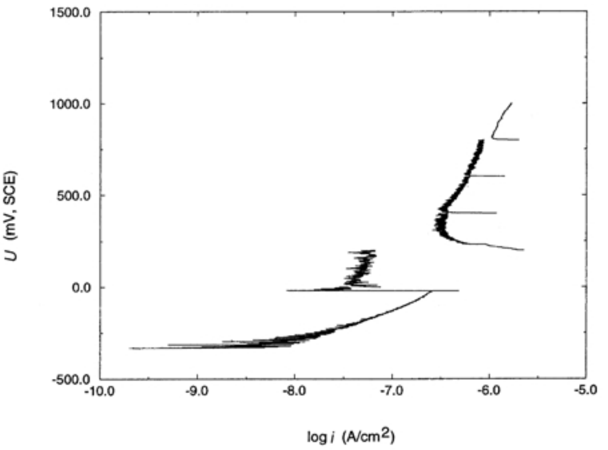

Figure 3 Potentiodynamic polarization curve of Nitinol alloy at 310 K in Ringer's solution, during which the capacitance measurement was made at different potentials.

with increasing defect concentration within the passive film. Porous Nitinol specimens were already found to actively corrode in a saline solution [37]. In addition, the superelasticity of Nitinol alloy can easily result in rupture and dissolution of the passive film. The falls of the anodic current in the current transients indicate the repassivation of the Nitinol. Even in the repassivation stage, significant dissolution may take place for the entire duration of the current decay [39, 40]. The kinetics of repassivation are very complicated and are affected by depassivation speed, solution resistance, and other factors [40–43]. The current decay of repassivation on Ti and Ti alloys follows logarithic law with log t [40, 43, 44] or roughly exponentially [39].

From Fig. 2, it is also seen that the temperature has an effect on the pitting potential. Generally, the pitting potential decreases with rising temperature and the hysteresis increases. At 338 K, the pitting potential is only 480 mV SCE compared to 850 mV at 298 K. At 310 K, the pitting potential is 900 mV SCE, higher than: 220 mV observed in 1% NaCl solution [35], 600 mV SCE in 0.9% NaCl + 18% serum solution [36], 600 mV SCE for annealed specimen and 250 mV SCE in Ringer's solution [38]; but lower than: 1350 mV SCE in 0.9% NaCl solution [36] and ~ 1600 mV SCE for thin film specimen in 0.9% NaCl solution [37]. Kim *et al.* [45] examined the corrosion behavior of stainless steel, nickel titanium, nitride-coated nickel titanium, epoxy-coated nickel titanium, and titanium orthodontic wires at room temperature in 0.9% NaCl solution potentiostatically, and found that the pitting potentials of stainless steel, two nickel titanium wires, nitride-coated nickel titanium, epoxy-coated nickel titanium, and titanium were 400, 300, 750, 300, 1800, and > 2000 mV, respectively. Therefore, the pitting potential of 850 mV at room temperature in this study is higher than those of stainless steel, nickel titanium wires, nitride-coated nickel titanium and lower than those of epoxy-coated nickel titanium, and titanium. The pitting potentials of Nitinol alloy obtained here are also much lower than those of Ti–6A1–4V alloy in the same solution [46], as shown in Table I.

For the sample polarized at 310 K, a capacitance measurement was taken before and after the polarization. The capacitance before polarization was 0.028 μF, but after polarization the capacitance increased to 5.03 μF, indicating that the passive film may be reduced in thickness because of dissolution. Following this polarization, the capacitance was monitored for 24 h under open circuit to investigate the film stability. It was found that the capacitance was nearly the same 5.03 μF with a fluctuation of ± 0.02 μF, indicating that the passive film is stable under open circuit condition.

In order to monitor the thickness change of the passive film during the potentiodynamic polarization, the capacitance was measured. Fig. 3 shows the potentiodynamic polarization curve at 310 K interrupted at different potentials for the capacitance measurement. After each measurement, the polarization was resumed by continuing the potential scan from the interrupted potential at the same scan rate of 10 mV/min. When the polarization was interrupted, the film capacitor will discharge and the open circuit potential decreases. Therefore, when the polarization was resumed, there is a current transient, as shown in Fig. 3. The measured capacitances, as shown in Table II, were found to increase with the polarization up to 800 mV SCE and then to decrease. The increase of the capacitance with potential indicates that the thickness of the passive film was reduced or the dielectric constant of the passive oxide film changes to a larger value. The possibility of the latter is very small because the dielectric constant must increase more than 100 times to contribute the large increase of the capacitance between 0 mV and 200 mV. Hence, the capacitance measurement indicates a thickness reduction of the passive film during the potentiodynamic polarization. All these results indicate that the passive film of a Nitinol alloy with this kind of passivation treatment is not stable and its dissolution occurs when electrical signals (potential or current) are applied. Therefore, NiTi materials with such passivation treatment may not be suitable for use as implantable devices in all cases, and more study is needed. The instability of the passive film is related to its characteristics. Many studies [22, 47–51] indicated that the

TABLE II The capacitance measured at different potentials during a potentiodynamic polarization at 310 K in Ringer's solution for passivated Nitinol alloy

Potential (mV)	0	200	400	600	800	1000
Capacitance (μF)	0.019	2.89	6.54	8.01	10.90	6.08

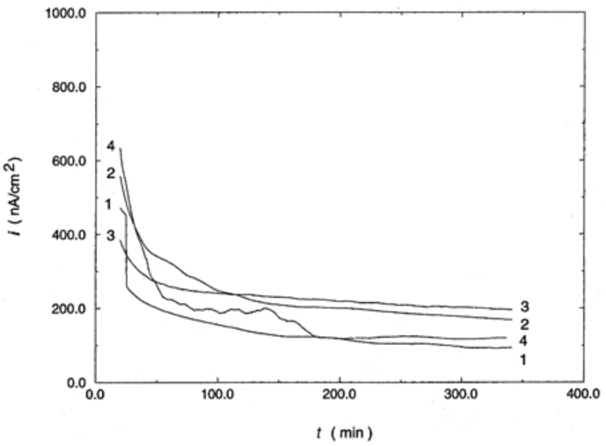

Figure 4 Potentiostatic anodic-current transients (fluctuations averaged) for Nitinol alloy at different overpotentials. 1–0.74 V, 2–0.90 V, 3–1.08 V and 4–1.36 V.

passive film of Nitinol alloy consists mainly of titanium oxide (TiO_2) and smaller amounts of nickel oxides (NiO and Ni_2O_3) and metallic Ni. The corrosion resistance of Nitinol alloy is due to the stable TiO_2 layer. Because the nickel oxide is not so stable and metallic Ni exists in the passive film, nickel may dissolve more easily than titanium and result in film damage. Sarhar *et al.* [18] thought that pitting could be due to selective dissolution of nickel from the film. In addition, irregular structures and defects may exist on the surface, where selective dissolution of nickel may occur [47].

Fig. 4 shows the anodic current transient curves of Nitinol alloy from potentiostatic polarizations at different overpotentials, 0.74, 0.90, 1.08, and 1.36 V at 310 K in Ringer's solution for 6 h. Under all potentials, no superpolarization [52, 53] appeared and the anodic current decays rapidly in the initial stage and reaches steady state at about 0.5 h. The steady-state anodic currents increase with the applied overpotential except the one at 1.36 V overpotential polarization, where the steady-state anodic current is lower than those at 0.90 and 1.08 V. In fact, many current transients occur during the anodic-current decay, indicating breakdown of the passive film. The anodic-current decay curves in Fig. 4 are averaged to remove noise. Fig. 5 shows the relationship between the logarithm of the current density and time at the first half-hour of the polarization. The nearly straight lines indicate that the anodic-current decays exponentially during this stage with a time constant of 52 min, independent of the applied overpotential. The fluctuations of the anodic current represent the dissolution and repassivation of the film.

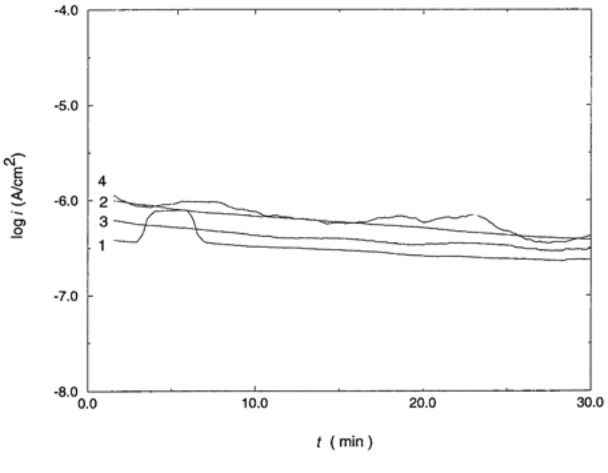

Figure 5 Variation of log i with time at the initial 30 min of potentiostatic polarizations at different overpotentials. 1–0.74 V, 2–0.90 V, 3–1.08 V and 4–1.36 V.

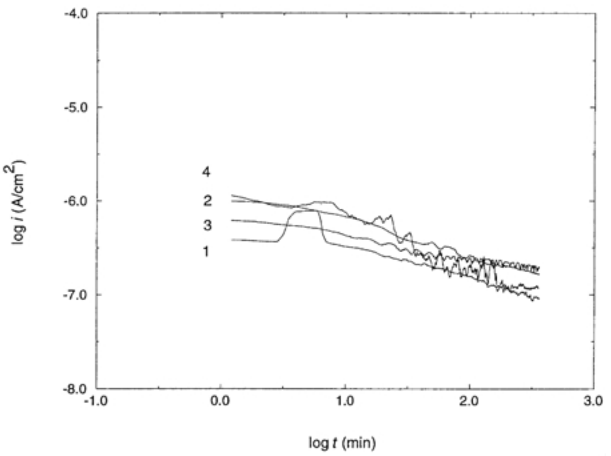

Figure 6 Variation of log i with log t for Nitinol alloy potentiostatic polarizations at different overpotentials. 1–0.74 V, 2–0.90 V, 3–1.08 V and 4–1.36 V.

Fig. 6 shows the relationship between logarithm of the current density and logarithm of time. It is seen from Fig. 6 that after about 10 min polarization, the log i vs log t is an approximately linear relationship, that is, the anodic current and time follows the ''experimental law'':

$$i = at^{\lambda} \tag{2}$$

where i and t are the anodic current and time, respectively, a and λ are constants. Lohrengel *et al.* [54, 55] indicated that λ is -1 for high field growth, -0.5 for diffusion controlled processes, 0 for corrosion and the 1-dimensional growth of surface nuclei. In Fig. 6, λ is between -0.2 and -0.4 in the applied overpotential range, which is between -0.5 and 0. Therefore, the determined λ also indicates the occurrence of corrosion and dissolution when Nitinol is polarized in Ringer's solution.

Before 10 min, plateaus in Fig. 6 are observed at the early stages of the anodic current decays. The duration of these plateaus is much longer than those of about 20 μs observed in the current decay of the repassivity of titanium alloys in aqueous chloride solutions [40, 43], of about 20–50 ms for Ti–6A1–4V alloy in 1 N NaCl solution [44], and of about 10 s for Ti–6A1–4V alloy in step-potentiostatic polarization in 0.2 N NaCl solution [46], but much smaller than about 50 min for Ti–6A1–4V alloy potentiostatic polarization in 0.2 N NaCl solution [46]. Previous studies [44, 56, 57] attributed the length of the plateau to the time required for the formation of the initial monolayer of oxide on-bare metal and concurrent dissolution. But this explanation is obviously not appropriate for the longer and various lengths observed in film covered Ti–6A1–4V alloy [46] and NiTi in this study. For Nitinol alloy, the dissolution of passive film may occur mainly during the plateaus because of a large number of anodic-current transients. The thickening of the passive film is the main process in the plateaus (early

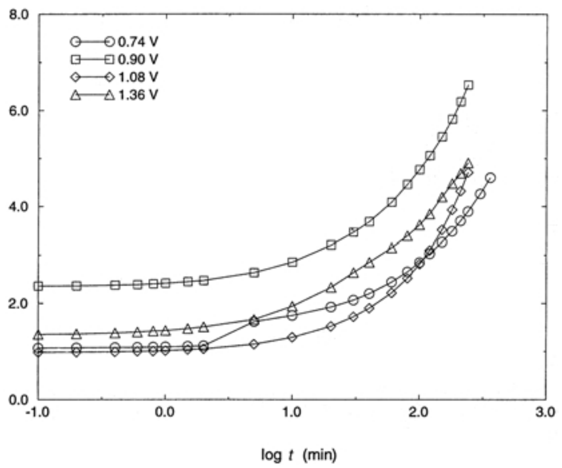

Figure 7 Variation of charge Q with log t during potentiostatic polarizations at different overpotentials.

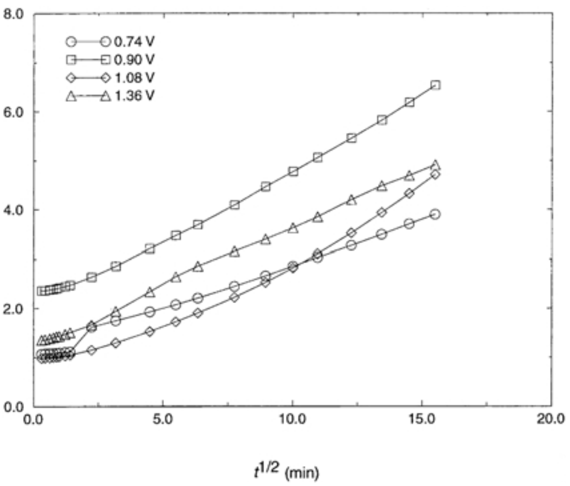

Figure 8 Variation of charge Q with square root time during potentiostatic polarizations at different overpotentials.

stage of potentiostatic polarization) for Ti–6A1–4V alloy [34, 46].

The variations of charges determined from the potentiostatic polarization decays are shown in Fig. 7 with the logarithm of time. The non-linear relationships between the charges and log t at all the potentials indicate that the potentiostatic polarization of Nitinol alloy in Ringer's solution does not follow the logarithmic growth law of passive film. But the nearly linear relationships between the charge and $t^{1/2}$ shown in Fig. 8 indicate that the potentiostatic polarization of Nitinol alloy follows a growth by diffusion. It is also found that the logarithm of the anodic current and the charge are not linear as that for Ti–6A1–4V alloy [34]. All the above results indicate that Nitinol alloy has different electrochemical behaviors compared with Ti–6A1–4V alloy in 0.2 N NaCl solution.

Conclusion

The passive film of the Nitinol alloy examined in this study is stable at open-circuit condition. It is also stable for the relatively small variations in temperature seen *in vivo*. But it is not stable when electrical signals (potential or current) exist. NiTi alloy has different electrochemical behaviors from those for Ti–6A1–4V alloy in 0.2 N NaCl solution. Although small passive currents and large passive potential ranges are observed, strong anodic dissolution of the passive film occurs during potentiodynamic and potentiostatic polarizations in Ringer's solution and results in thinning of the passive film. Therefore, particular care must be taken when using Nitinol in medical implant devices.

We note that our work only applies to general and to pitting corrosion. It does not cover crevice or galvanic corrosion, which may occur due to the design, construction, or use of certain devices such as stents.

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