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EFFECT OF STRAIN ON THE CORROSION RESISTANCE OF NITINOL AND STAINLESS STEEL IN SIMULATED PHYSIOLOGICAL ENVIRONMENT

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ABSTRACT

Electropolished SE-508 NiTi and passivated 316L stainless steel wires were deformed from 0% to 10% strain and were then corrosion tested in Hank's physiological solution. Results show that the breakdown potential and repassivation potential of NiTi were not affected by the strain. The breakdown and repassivation potentials were approximately 1080 mV vs. SCE and 980 mV vs. SCE, respectively for the Nitinol samples, independent of strain levels. However, the breakdown potential for the stainless steel wires decreased significantly as a function of strain. The breakdown potentials ranged from 770 mV vs. SCE for unstrained samples to 510 mV vs. SCE for the 10% strain specimens. Stainless steel specimens strained up to 8% exhibited a repassivation potential of approximately 70 mV vs. SCE. Stainless steel samples that were deformed to 10% strain did not show any repassivation potential during the reverse scan of the polarization test. Localized corrosion (pitting) initiated at the maximum strain area (in tension) on the stainless steel specimens.

KEYWORDS

Corrosion, Nitinol, Stainless steel, Strain, Polarization

INTRODUCTION

Like many biomaterials, Nitinol and stainless steel rely on a passive oxide layer to protect them against corrosion degradation *in vivo*. This oxide layer acts as a barrier against the immediate physiological environment and can prevent excessive uniform and localized corrosion from occurring. Both Nitinol and stainless steel corrosion behavior can be significantly improved by specific surface treatments such as electropolishing or passivation in an acid solution [1–3]. These passivation treatments homogenize the thickness topography and composition of the surface layer by forming passive oxide layers, predominantly titanium oxide on Nitinol and chromium oxide on stainless steel. Previous *in vitro* corrosion studies have shown that uniformity and composition of the passive oxide layer play major roles in the corrosion resistance of these materials [1, 2].

Still, although most implants are used under stress-strain conditions, which can affect the surface properties of the oxide layer of these materials, very few corrosion studies have investigated the specific effects of stress-strain on the corrosion resistance of metallic biomaterials. Furthermore, in the case of austenitic Nitinol, a stress-induced martensite phase can be formed starting at approximately 1–2% strain. Very few studies have explored how this phase change will affect the corrosion behavior of the material.

Therefore, the goal of this study is to assess the influence of strain on the corrosion resistance of passivated Nitinol and stainless steel implant materials.

EXPERIMENTAL

Materials

Nitinol (50.8 at.%Ni) wire (NDC, Fremont, CA) and 316L stainless steel wire (Fort Wayne Metals, Fort Wayne, IN) were used in this study. Before corrosion testing, both materials were passivated to obtain surface properties similar to implant devices. The Nitinol wire was straightened and electropolished before the experiments. In accordance with ASTM F86 standard, prior to testing, the stainless steel wire was in the cold-worked condition and was passivated in a 30% nitric acid solution for 30 minutes [3]. The wires were deformed in bending so as to obtain approximately four, eight, and 10% strain, which roughly corresponds to the middle and end of the superelastic plateau, and deformation of the martensite respectively for Nitinol. Straight wire was used to determine the corrosion resistance of unstrained Nitinol.

Corrosion Testing

In accordance with ASTM F2129-01, an EG&G Princeton Applied Research potentiostat model 273A was used to conduct the potentiodynamic polarization corrosion test. The potentiostat was controlled by a computer with 352 SoftCorrIII-DC corrosion test software [4]. A saturated calomel electrode (SCE) was used as a reference electrode for the potential. Two platinum auxiliary electrodes were used as counter electrodes. Testing was conducted in an appropriate polarization cell as recommended in ASTM F2129. The solution was first de-aerated for 30 minutes prior to immersion of the test sample and also throughout the test. Then, the Open Circuit Potential (OCP) was monitored for 1 hour. The polarization of the test specimen was then started 100 mV vs. SCE below the OCP at a voltage scan rate of 0.167 mV/sec. The potential scan was reversed once the potential reached a current density value that was approximately two decades higher than the current density at the onset of the breakdown potential. The tests were conducted in Hank's simulated physiological solution at an initial pH of 7.4±0.1. The solution was maintained at 37±1°C using a water bath. Three samples were tested for each material and strain level. The corrosion resistance of the devices was characterized in terms of their corrosion potential (E_{corr}), corrosion current density (I_{corr}) breakdown potential (E_{bd}) and repassivation potential (E_p).

After testing, the samples were inspected by optical microscopy and scanning electron microscopy (SEM) (JEOL JSM-5600) to determine pit initiation sites on the wires.

RESULTS AND DISCUSSION

Typical polarization curves for each material at different strain levels are presented in Figure 1 and Figure 2 below.

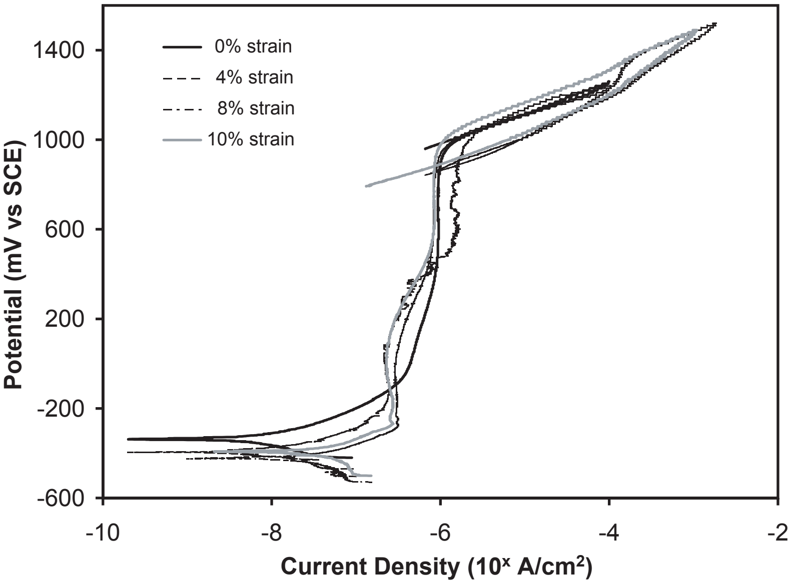

Figure 1 Polarization curves for Nitinol subjected to different strain levels.

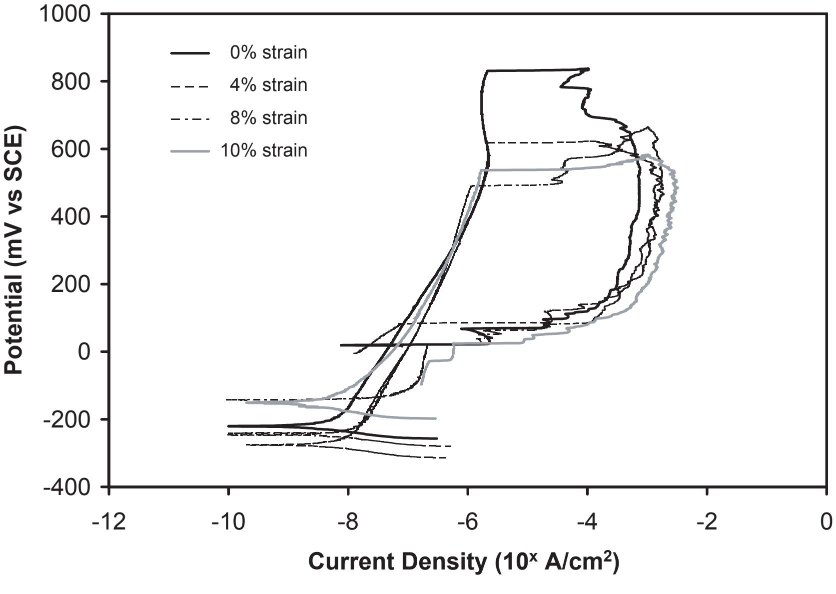

Figure 2 Polarization curves for stainless steel subjected to different strain levels.

As seen in Figure 1, Nitinol polarization curves were not significantly influenced by strain (see Figure 1). The passive region of the material remained practically unchanged for specimens deformed up to 10% bending strain. It is also important to note that Nitinol's excellent and uniform corrosion resistance is due to the electropolished oxide layer.

However, stainless steel's corrosion resistance was affected by strain (see Figure 2). Although its passive region was not significantly changed, the breakdown potential of the material was shifted to lower values.

The influence of applied strain on the corrosion test results for the Nitinol and stainless steel wires are summarized in Table 1 and Table 2, respectively.

Table 1 Corrosion Test Results for Nitinol Wire at Different Strain Levels (mean ±SD)

Bending strain %	**E_{corr} mV vs. SCE**	**I_{corr} nA/cm^2**	**E_{bd} mV vs. SCE**	**E_p mV vs. SCE**
0	–323±31	10±4	1143±73	1063±45
4	–408±29	25±11	1030±79	948±46
8	–462±35	46±11	1174±194	1059±237
10	–400±7	21±129	993±23	865±14

Table 2 Corrosion Test Results for Stainless Steel Wire at Different Strain Levels (mean ±SD)

Bending strain %	**E_{corr} mV vs. SCE**	**I_{corr} nA/cm^2**	**E_{bd} mV vs. SCE**	**E_p mV vs. SCE**
0	–215±76	3±1	769±65	68±46
4	–152±109	3±0	556±52	104±29
8	–188±78	4±3	515±32	36±149
10	–110±7	4±1	510±25	N/A[a]

[a] Specimens did not repassivate.

Based on the results reported in Table 1, none of the corrosion parameters (E_{corr}, I_{corr}, E_{bd}, and E_p) were significantly affected by an increase in the strain for Nitinol. Although the breakdown (E_{bd}) and repassivation potentials (E_p) seemed lower for the specimens strained up to 10%, none of the samples reached the breakdown of the oxide layer (pitting). These results were in accordance with a previous study conducted by Rondelli, who found that the breakdown potential of Nitinol specimens strained up to 4% in tension was not significantly affected [5].

Furthermore, these results indicate that the presence of stress-induced martensite in Nitinol does not significantly affect its corrosion resistance. Therefore, the uniformity and composition of the passive oxide layer, as opposed to the crystallographic phase, appeared to be the predominant factors in the corrosion behavior of Nitinol.

Stainless steel's corrosion potential (E_{corr}) and corrosion current density (I_{corr}) values were not significantly affected by an increased in strain (ref. Table 2). However, stainless steel's breakdown potential significantly decreased after applying 4% bending strain ($p<0.05$, Student T-test). Indeed, stainless steel breakdown potential decreased from 769 mV vs. SCE to 556 mV vs. SCE after 4% strain. Strain increase from 4% to 10% did not further affect the breakdown potential ($p>0.05$, Student t-test). For bending strains up to 8%, no significant effects were observed for stainless steel repassivation potential, in part because of the large variability in this parameter. However, the specimens that were bent up to 10% did not repassivate upon reversal of the potential scan. These results are in accordance with a study from Bundy et al., who found that 316L stainless steel's breakdown potential was significantly decreased after application of stress [6].

Visual inspection of the stainless steel test specimens after the corrosion test revealed that localized corrosion (pitting) had initiated at the maximum strain area (in tension) on the wires. Furthermore, superficial cracking of the oxide layer was observed in the same area (see Figure 3). No indication of localized corrosion was observed on the Nitinol wires. The surface of the Nitinol wires remained smooth and uniform even after 10% strain (see Figure 3). This result highlighted the benefits of a thin electropolished layer, which was able to sustain large deformation without cracking or peeling and therefore offers superior protection against corrosion. In another study, we showed that bending of heat treated Nitinol wires, which exhibited a thicker oxide layer, disrupted the protective oxide layer and led to a significant decrease in the corrosion resistance of the material [7].

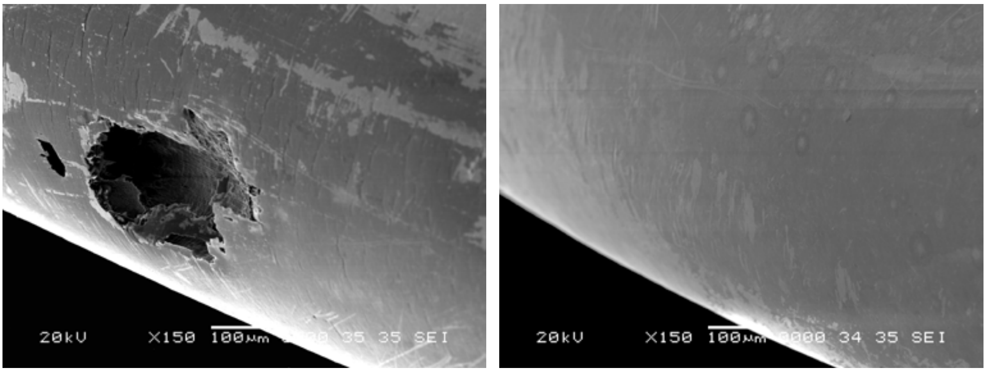

Figure 3 (left) Pit initiation site on stainless steel wire (10% strain) (right) Nitinol wire postcorrosion testing (10% strain).

These results emphasize the importance of the uniformity of the oxide layer to protect stainless steel and Nitinol against corrosion. Furthermore, disruption of the passive film during deformation and slow repassivation kinetics appear to be the underlying mechanisms of the decrease in the corrosion resistance of stainless steel.

Generally, the applied strains in this study were higher than the normal expected range for implant devices. For example, stainless steel balloon-expandable stents are usually designed to reach more than 25% strain during deployment [8]. However, the physiological strain range for implanted Nitinol stents is about 1–2% strain [9]. It is also not unusual for self-expandable Nitinol stents to be deformed up to 8% strain when constrained in the delivery system before deployment. Higher strain levels were investigated in this study to investigate Nitinol’s full superelastic plateau and determine if strain-induced corrosion effects would be observable.

CONCLUSIONS

This study investigated the influence of strain on the corrosion resistance of passivated Nitinol and stainless steel implant materials. Our results show that

- Nitinol’s corrosion resistance was not affected by strains up to 10%. Indeed, the uniformity of the protective titanium oxide layer on the electropolished Nitinol was not compromised by the deformation.
- The presence of stress-induced martensite did not affect Nitinol’s corrosion resistance. The composition and uniformity of the passive titanium oxide layer appear to be the predominant factor in the corrosion resistance of the material, independent of the underlying crystallographic phase.
- Stainless steel’s resistance to localized corrosion was affected by strain. Disruption of the passive film during deformation and slow repassivation kinetics appear to be the underlying mechanisms of the decrease in the corrosion resistance of stainless steel.

REFERENCES

1. C. Trépanier, M. Tabrizian, L’H. Yahia, L. Bilodeau, and D.L. Piron, *J Biomed Mat Res* **43** (Appl Biomater, 1998), p. 433.

2. R. Venugopalan and C. Trépanier, *Min. Invas. Ther. & Allied Technol.* **9** (2) (2000), p. 67.

3. F86–91, in *Annual Books of ASTM Standards, Medical Devices and Services* **13.01** (1991).

4. F2129-01, in *Annual Books of ASTM Standards, Medical Devices and Services* **13.01** (2001).

5. G. Rondelli and B. Vicentini, *J Biomed Mater Res* **51** (2000), p. 47.

6. K.J. Bundy, C.J. Williams, and R.E. Luedemann, *Biomaterials* **12** (1991), p. 627.

7. C. Trépanier, L. Zhu, J. Fino, and A.R. Pelton, in *SMST-2003: Proceedings of the International Conference on Shape Memory and Superelastic Technologies* (Pacific Grove, Calif.: International Organization on SMST, 2003, in press).

8. Seik Oh, in *ABAQUS Users’ Conference* (Newport, Rhode Island, 2000), p. 535.

9. T. Lopes, X. Gong, and C. Trépanier, in *SMST-2003: Proceedings of the International Conference on Shape Memory and Superelastic Technologies* (Pacific Grove, Calif.: International Organization on SMST, 2003, these proceedings).