Effect of Temperature and pH on the Corrosion Resistance of Nitinol

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Abstract

Few studies have investigated the effects of temperature on the corrosion resistance of Nitinol even though it is well known that temperature may affect the corrosion behavior of metals by increasing their corrosion rate and/or affecting their resistance to localized corrosion (pitting). Similarly, most corrosion studies of implant devices have investigated the corrosion resistance of Nitinol at a physiological pH of 7.4 without further study of the effect of other pH values. However, the literature reports that physiological pH can range from 1 to 9 depending on the type of body fluids. Therefore, the goals of this study were to assess the influence of temperature and pH on the corrosion resistance of Nitinol. Electropolished NiTi and passivated 316L stainless steel wires were tested in Hank's physiological solution at temperatures ranging from 10°C to 80°C and pH varying from 1 to 9. The cyclic potentiodynamic tests performed in this study follow ASTM standard F2129. Results show that Nitinol's ability to repassivate is significantly reduced by an increase in temperature. No other significant effects were observed by a change in temperature. Stainless steel corrosion rate, on the other hand, was significantly affected by an increase in temperature while the other parameters remained very stable. Study of the effect of pH revealed that except for a change in the potential for oxygen evolution, the corrosion resistance of NiTi was not significantly affected by a variation in pH. In contrast, the results for stainless steel indicate that both uniform corrosion rate and localized corrosion are affected by a decrease in pH.

Introduction

In vivo corrosion of implant devices involves the interaction between a metallic implant and it's environment. Corrosion resistance will be affected both by the surface properties of the implants and by the nature of it's environment. This paper will address two of the most important environmental variables, which are temperature and pH.

Temperature can affect the corrosion behavior of materials in different ways [1]. If the corrosion rate is only controlled by the metal oxidation process, the corrosion rate will increase exponentially with an increase in temperature following Arrhenius equation. This is the underlying principle for exposing implant devices to physiological solutions at temperatures significantly higher than normal body temperature. By increasing the temperature (and corrosion rate) the test is accelerated and can therefore be used in a laboratory setting to obtain information on materials corrosion resistance in reasonable time. However, it's important to highlight that this direct correlation between temperature and corrosion rate is not always present. Temperature can also affect the nature of the environment by changing the solubility of a constituent and/or changing the pH of a solution that can both affect the corrosion behavior of a material. Furthermore, a change in temperature can also affect the resistance of a material to localized corrosion (pitting). To date, few studies have investigated the effect of temperature on Nitinol in a physiological environment.

PH is an important factor in the corrosion resistance of material because hydrogen ions can interact with a material and modify it's surface which can affect it's corrosion resistance. Moreover, interactions between pH and dissolved species such as chloride ions can enhance the effect of hydrogen ions. Still, most corrosion studies of implant devices have investigated the corrosion resistance of Nitinol at a physiological pH of 7.4 without further study of the effect of other pH values. However, the literature reports that physiological pH can range from 1, such as in gastric secretion with high concentration of chloride ions, up to 9, such as in Brunner's gland secretions, depending on the type of body fluids [2]. Therefore, the goals of this study are to assess the influence of temperature and pH on the corrosion resistance of Nitinol.

Materials and Methods

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. The stainless steel wire was in the

cold-worked condition and was passivated in a 30% nitric acid solution for 30 minutes in accordance with ASTM F86 standard prior to testing [3]. To assess the effect of temperature on the corrosion resistance of Nitinol and stainless steel, the Hank's solution (H6136, Sigma Aldrich, pH of 7.4) was cooled down or heated up using a temperature controlled water bath to 10°C, 20°C (room temperature), 37°C, 50°C, 60°C, 70°C and 80°C. The accuracy of thetemperatures is ±1°C, except for room temperature, which is controlled around ±2°C.

To assess the effect of pH, sufficient quantity of 1N HCl or NaOH were added to 37°C Hank's solution to obtain pH values of 1.0, 7.4 and 9.0. The accuracy of the pH values is 0.1. In order to stabilize the pH, the Hank's solution was modified according to ASTM F2129 by adding 1.45g/L $NaHCO_3$ and by de-aerating the solution with a mixture of 5% CO_2 in nitrogen.

In accordance with ASTM F2129, an EG&G Princeton Applied Research potentiostat model 273A was used to conduct the potentiodynamic polarization corrosion test. The potentiostat is controlled by a computer with PowerCORR software from AMETEK/PAR [4]. A saturated calomel electrode (SCE) is used as a reference electrode for the potential. Two platinum auxiliary electrodes are used as counter electrodes. Testing was conducted in an appropriate polarization cell. The solution was first de-aerated with nitrogen gas in the case of the temperature study, or with a mixture of 5% CO_2 and nitrogen for the pH study, for 30 minutes prior to immersion of the test sample and throughout the test. Then, the Rest Potential (E_r) was monitored for 1hour. The polarization of the test specimen was then started 100 mV vs SCE below E_r 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 (E_b). Unless otherwise specified, three samples were tested for each material and condition. The corrosion resistance of the samples was characterized in terms of their breakdown potential (E_b) and repassivation potential (E_p). In addition, the corrosion current density (I_{corr}) was also determined. After testing the samples were inspected with an optical microscope.

Results and Discussion

Effect of temperature

A summary of the corrosion resistance of Nitinol tested between 10°C and 80°C, based on E_b, E_p, and I_{corr}, is presented in Table 1 and in Figures 1-3.

As the temperature is increased, the entire polarization curve for Nitinol is slowly shifted to lower potentials. Based on the shape of the polarization curves and inspection of the specimens after the tests, the breakdown of the oxide layer

(E_b) coincides with the potential for oxygen evolution for samples tested between 10°C and 70°C. Therefore, the small shift in E_b for samples tested between 10°C and 70°C appears to be related to a change in the potential at which oxygen is being produced on the sample rather than to a difference in the corrosion resistance of the material. A typical curve for Nitinol tested between 10°C and 70°C is represented by the 10°C curve in Figure 3. It's important to note the small hysterisis between E_b and E_p indicating superior ability of the material to repassivate and low susceptibility to crevice corrosion. Starting at 60°C, the samples start to exhibit a different corrosion behavior. Although E_b appears to still overlap with oxygen evolution, the ability of the material to repassivate after breakdown of the oxide layer is progressively reduced. The samples tested at 80°C are characterized by a large hysterisis between E_b and E_p (refer to 80°C curve in Figure 3) suggesting that the material is less able to repassivate and more susceptible to crevice corrosion at that temperature.

The corrosion current density, which is directly related to the corrosion rate, appear to slowly increase as a function of test temperature (refer to Fig. 2). However, because the corrosion current densities are all within the same decade, it cannot be concluded that this increase in corrosion current density is significant within the temperature range studied.

Table 1: Corrosion test results for Nitinol at different temperatures (mean±SD)

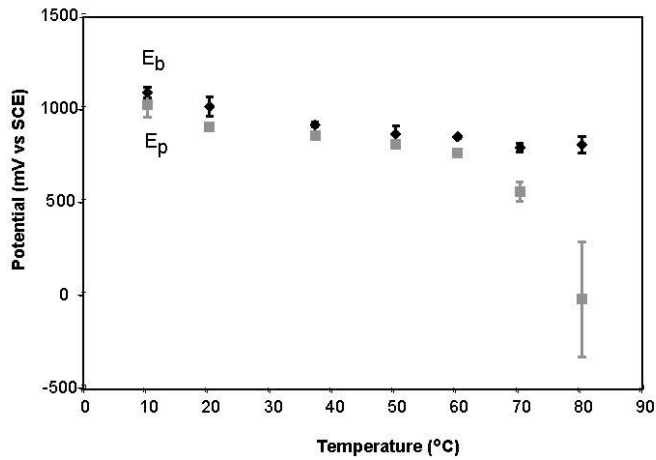| Temp. °C	E_b mV vs SCE	E_p mV vs SCE	I_{corr} nA/cm^2
10	1076±30	1010±70	2±1
20	998±52	889±20	3±1
37	902±13	845±6	5±4
50	852±42	795±8	3±2
60	836±6	748±14	3±1
70	778±23	542±51	8±1
80	792±44	-39±309	10±6

Figure 1: Variation of E_b and E_p as a function of temperature (Nitinol).
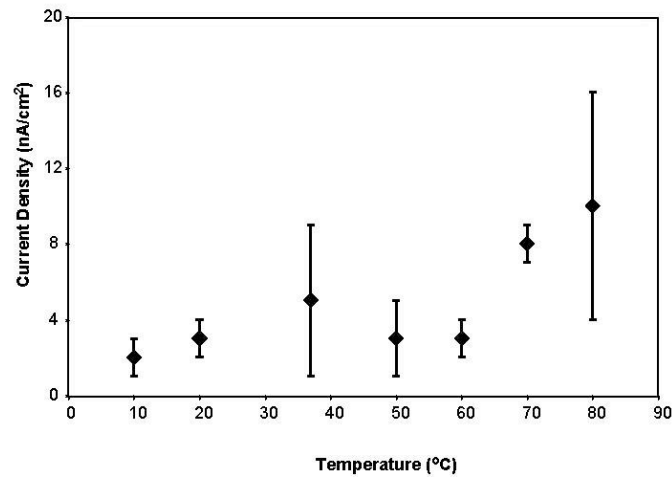

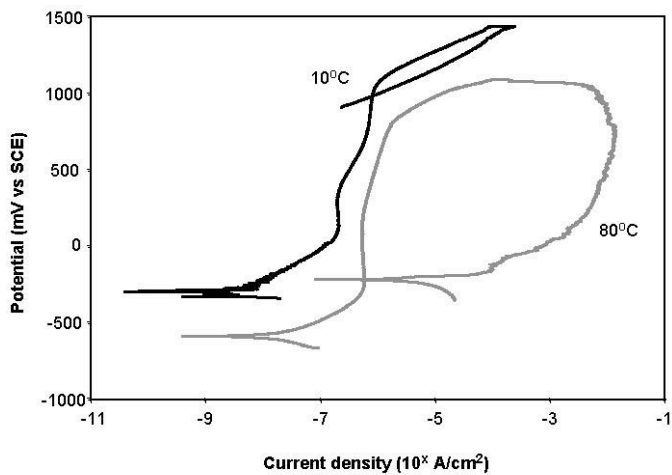Figure 2: Variation of I_{corr} as a function of temperature (Nitinol).

Figure 3: Polarization curves for Nitinol tested at 10°C and 80°C.

These results suggest that temperature affects Nitinol's ability to repassivate. However, no other significant effects, such as on the corrosion rate of the material, were observed with a change in temperature.

In another study, Sun, et. al. studied the effect of temperature (25°C-65°C) on the passive current density and pitting potential of electropolished NiTi in Ringer's solution [5]. Their results show an increase in the passive current density and a decrease in the breakdown potential as a function of temperature. Unfortunately, they did not publish the raw data and did not mention the sample size studied so we cannot conclude on the significance of these results. Furthermore, significant noise in their data suggests that the surface treatment or the test set-up were not optimized.

The corrosion test results of stainless steel tested between 10°C and 80°C are presented in Table 2 and in Figures 4 and 5. Typical polarization curves for stainless steel tested at 10°C and 80°C are presented in Figure 6 to illustrate the shift in the different parameters.

As the temperature is increased, a shift in the polarization curve toward lower potentials, similar to the one observed for NiTi, is seen for stainless steel. However, as opposed to NiTi, the breakdown potential of the oxide layer (E_b) does not correspond to the potential for oxygen evolution. Consequently, variation of E_b indicates a change of the corrosion resistance of the material to localize corrosion.

Table 2: Corrosion test results for stainless steel at different temperatures (mean±SD)

Temp. °C	E_b mV vs SCE	E_p mV vs SCE	I_{corr} nA/cm^2
10	890±18	n/a	4±2
20	917±50	156±16*	2±1
37	596±86	n/a	3±1
50	740±128	n/a	4±1
60	761±188	n/a	9±3
70	635±135	n/a	9±1
80	650±67	-447**	29±6

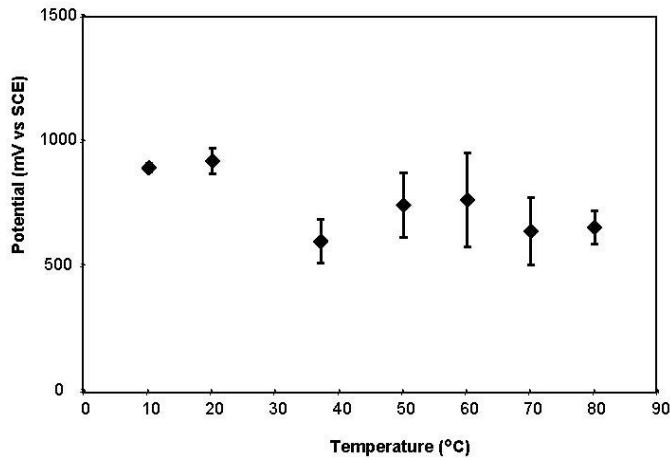*2 of 3 samples repassivated
**1 of 3 samples repassivated

Figure 4: Variation of E_b as a function of temperature(stainless steel).
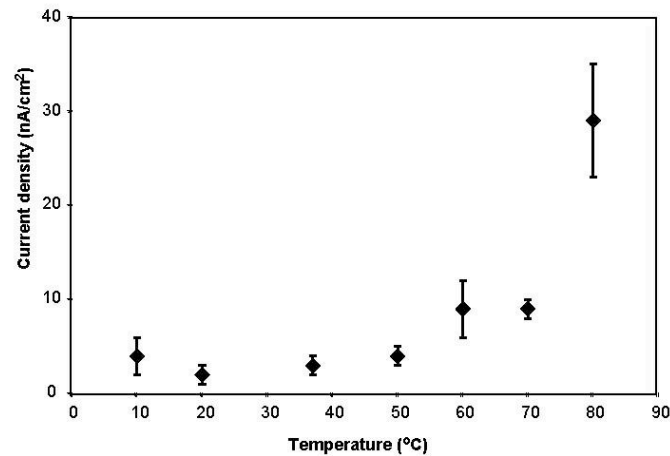

Figure 5: Variation of I_{corr} as a function of temperature (stainless steel).

The distribution E_b as a function of temperature suggests that E_b is greater for the 10°C and 20°C groups than for the 37°C - 80°C groups (refer to Figure 4). It is important to note that as opposed to NiTi, only a few stainless steel's samples were able to repassivate after the breakdown potential. This result sugests that stainless steel is less able to repassiavte it's surface and is more susceptible to crevice corrosion then NiTi. Analysis of the variation of I_{corr} as a function of temperature reveals a strong correlation between the two variables. In contrast to NiTi, stainless steel's corrosion current density (and therefore corrosion rate) increases exponentially as a function of temperature. This result suggests that stainless steel corrosion rate may be controlled by the metal oxidation process and that it may follow Arrhenius law.

These results indicate that stainless steel's corrosion rate is significantly affected by temperature. However, no other significant effects were observed by a change in temperature.
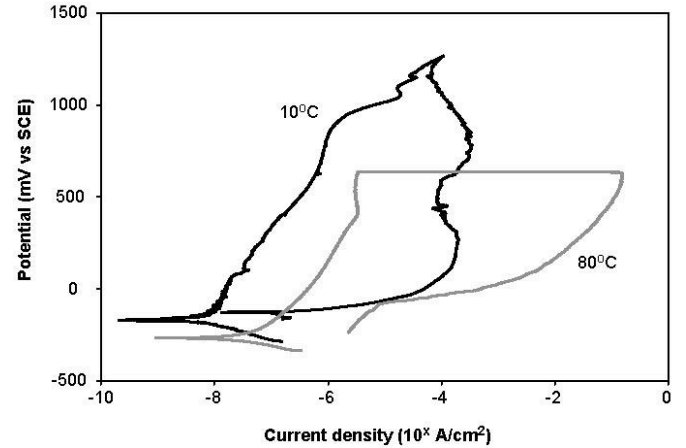

Figure 6: Polarization curves for stainless steel tested at 10°C and 80°C.

These results suggest that Nitinol and stainless steel have different corrosion mechanisms (localized corrosion vs uniform corrosion processes respectively) that are affected by an increased in temperature.

Effect of pH

A summary of the corrosion resistance of Nitinol tested at pH of 1.0, 7.4 and 9.0 is presented in Table 3 and in Figure 7.

Polarization of NiTi in Hank's solution at a pH of 1 resulted in a shift of the curve toward greater values of potential. Similar to the previous study, E_b coincides with oxygen evolution. Therefore, the small shift in E_b can be related to a change in the potential at which oxygen is being produced in the solution. This result is in agreement with the Pourbaix diagram for water: more acidic pH shifts the oxygen evolution reaction to higher potrntisl [6]. The variation in E_p is similar to E_b so the ability to repassivate of the material is not affected. No significant difference could be found between the samples tested at 7.4 and 9.0. Furthermore, no significant differences were found in the corrosion current densities between all groups.

Table 3: Corrosion test results for Nitinol at different pH (mean±SD)

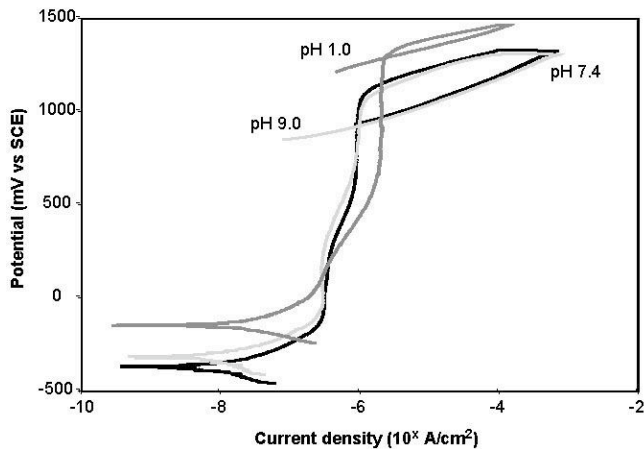| pH	E_b mV vs SCE	E_p mV vs SCE	I_{corr} nA/cm^2
1.0	1334±7	1287±6	11±3
7.4	1079±10	925±6	6±1
9.0	1063±4	943±35	6±1

Figure 7: Polarization curves for Nitinol tested at 10°C and 80°C.

Therefore, except for a change in the potential for oxygen evolution, the corrosion resistance of NiTi was not significantly affected by a variation in pH. This result is in agreement with the findings from another study showing that titanium is passive down to a pH of 0 in HCl solution [7]. Electropolished NiTi is protected by a titanium oxide layer similar to the one found on titanium which may explain the similar resistance to corrosion in low pH solutions containing chloride ions.

The corrosion test results for stainless steel tested at pH of 1.0, 7.4 and 9.0 are presented in Table 4 and in Figure 8.

Table 4: Corrosion test results for stainless steel at different pH (mean±SD)

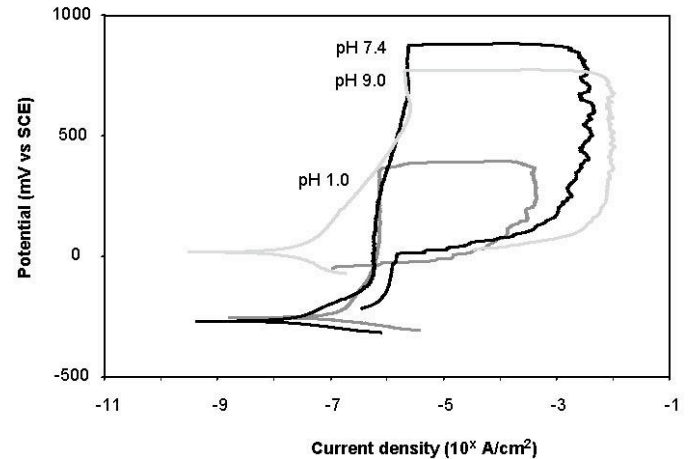| pH	E_b mV vs SCE	E_p mV vs SCE	I_{corr} nA/cm^2
1.0	392±19	-42±75*	115±99
7.4	871±89	n/a	12±9
9.0	786±94	n/a	13±2

*3 of 4 samples repassivate

Figure 8: Polarization curves for stainless steel tested at pH of 1.0, 7.4 and 9.0.

The polarization curves obtained for stainless steel tested at a pH of 1.0 indicate that the material was strongly affected by the difference in pH. A significant decrease in the breakdown potential and increase in the corrosion current density (which translates to corrosion rates) of the specimens were observed. It is interesting to note that although the general corrosion resistance of the material was severely deteriorated by exposure to the acidic solution, the material was able to repassivate (presence of E_p). Repassivation may have been possible because the samples in this group were polarized to low potentials. Repassivation of the material at a pH of 7.4 and 9.0 was not observed. Increase in the pH up to 9.0 did not affect the corrosion resistance of the material.

Thus, these results indicate that both uniform corrosion rate and localized corrosion are affected by a decrease in pH. These results for 316L stainless steel are in agreement with the results obtained in a previous study performed on iron in HCl solution. The results from that study showed that iron's corrosion rate was fast at pH lower than 3 [8].

A recent study performed by Huang, investigating the effect of stress and pH in acid artificial saliva (pH of 2 and 5) on the corrosion resistance of NiTi and stainless steel orthodontic archwires, found different results [9]. The investigator found that pH had a significant detrimental effect on the pitting potential, protection potential and passive current density for both NiTi and stainless steel specimens. The differences in our results can be explained by the different surface finish of our specimens which were electropolished. The Nitinol used in Huang's study exhibited a very rough surface characteristic of as-drawn non-passivated Nitinol. As several previous studies have shown, electropolished Nitinol possess superior corrosion resistance compared to other surface treatment which protects the material against aggressive environments [10,11,12].

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These results suggest that Nitinol and stainless steel are affected differently by a decrease in pH. The titanium oxide layer on Nitinol appears more resistant to pH than the chromium oxide covering stainless steel.

Conclusions

This study investigated the effect of temperature and pH on the corrosion resistance of passivated Nitinol and stainless steel implant materials. Our results show that:

- An increase in temperature affects Nitinol's resistance to localized corrosion by lowering it's ability to repassivate. The uniform corrosion rate of the material was not affected by temperature.
- stainless steel's uniform corrosion resistance (corrosion rate), however, is significantly affected by temperature. No significant effects were observed the resistance of the material to localized corrosion (pittung).
- Except for a change in the potential for oxygen evolution, the corrosion resistance of NiTi was not significantly affected by a variation in pH.
- Both uniform corrosion resistance and localized corrosion (pitting) are affected by a decrease in pH.

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