Effect of Temperature and pH on the Corrosion Resistance of Nitinol

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EFFECT OF TEMPERATURE AND pH ON THE CORROSION RESISTANCE OF PASSIVATED NITINOL AND STAINLESS STEEL

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ABSTRACT

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. Results show that the ability of Nitinol to repassivate is reduced by an increase in temperature. No other major effects were observed by a change in temperature. Stainless steel corrosion rate, on the other hand, was the only parameter affected by an increase in temperature. Study of the effect of pH revealed that except for a change in the potential for oxygen evolution, other aspects of the corrosion resistance of NiTi were not affected. In contrast, the results for stainless steel indicate that both uniform corrosion rate and localized corrosion are affected by a decrease in pH.

INTRODUCTION

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 an Arrhenius relationship. This is the underlying principle for exposing implant devices to physiological solutions at temperatures much 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 a relatively short period of time. 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.

The pH of a solution is an important factor in the corrosion resistance of materials because hydrogen ions can interact and modify the surface and therefore alter the corrosion resistance of a material. 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. However, the literature reports that physiological pH can range from 1, such as in gastric secretions with high concentration of chloride ions, up to 9, such as in Brunner's gland secretions [2]. Therefore, the goals of this study are to assess the influence of temperature and pH on the corrosion resistance of Nitinol and stainless steel.

EXPERIMENTAL METHODS

Electropolished Nitinol (50.8%at. Ni) wire (NDC, Fremont, CA) and passivated (ASTMF86) 316L stainless steel wire (Fort Wayne Metals, Fort Wayne, IN) were used in this study [3]. The corrosion test method follows ASTM F2129 [4]. To assess the effect of temperature on the corrosion resistance of Nitinol and stainless steel, Hank's solution (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. 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. 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.

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 (10-60X).

EXPERIMENTAL RESULTS

A summary of the corrosion resistance of Nitinol tested between 10°C and 80°C is presented in Table 1 and in Fig. 1. Based on the shape of the polarization curves and inspection of the specimens after the tests, 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. It is 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 suggesting that the material is less able to repassivate and more susceptible to crevice corrosion at that temperature.

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

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

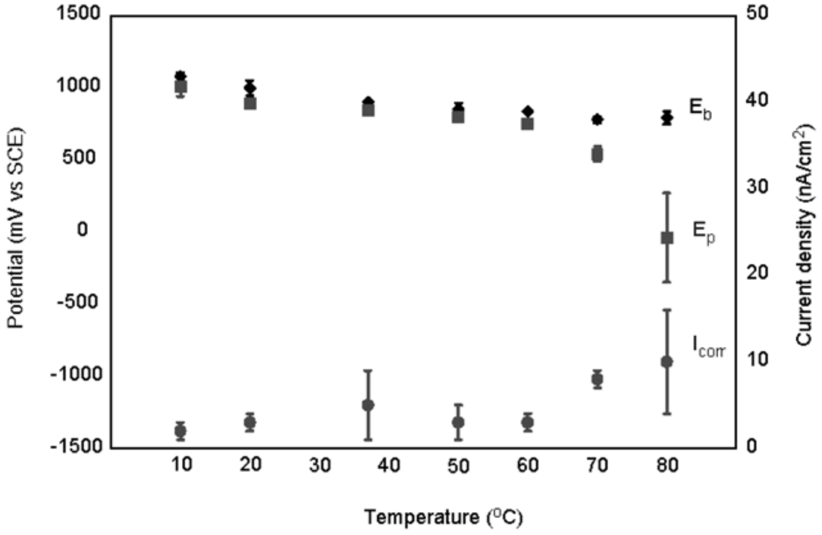

Fig. 1: Variation of E_b, E_p and I_{corr} as a function of temperature (Nitinol).

The corrosion current density, which is directly related to the corrosion rate, appears to slowly increase as a function of test temperature (refer to Fig. 1). However, because I_{corr} are all within the same decade, it cannot be concluded that this increase in I_{corr} is significant within the temperature range studied. These results suggest that temperature affects the ability of Nitinol to repassivate. However, no other effects, such as on the corrosion rate of the material, were observed with a change in temperature.

The corrosion test results of stainless steel tested between 10°C and 80°C are presented in Table 2 and in Fig. 2. As the temperature is increased, a shift in the polarization curve towards lower potentials, similar to the one observed for NiTi, is seen for stainless steel. However, in contrast 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. 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. Statistical analysis comparing the breakdown potential as a function of temperature using one-way ANOVA and Tukey's pairwise comparison show only a significant difference in the breakdown potentials between the 20°C and 37°C group. Therefore, we cannot conclude that temperature has an effect on the breakdown potential of stainless steel. Analysis of the variation of I_{corr} as a function of temperature reveals a strong correlation between the two variables. In contrast to NiTi, the corrosion current density of stainless steel (and consequently the 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 an Arrhenius law. No other effects were observed by a change in temperature.

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

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

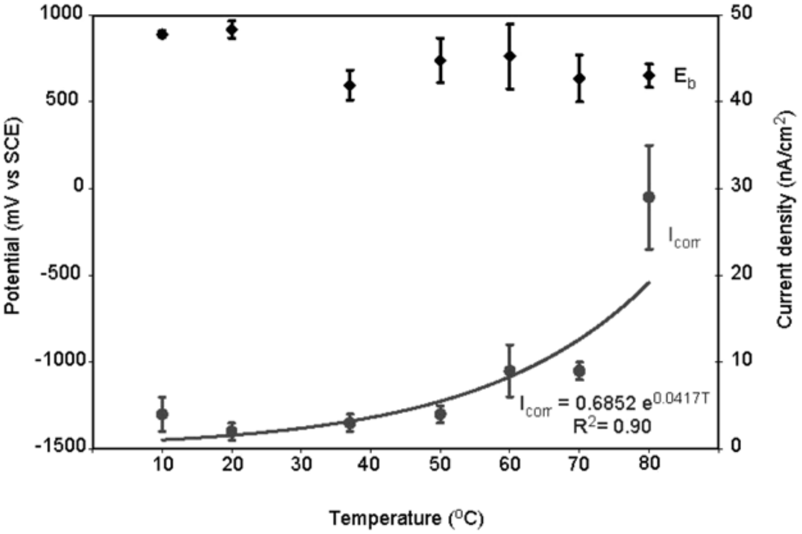

Fig. 2: Variation of E_b and I_{corr} as a function of temperature (stainless steel).

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 temperature.

A summary of the corrosion resistance of Nitinol tested at pH of 1.0, 7.4 and 9.0 is presented in Table 3. 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 potentials [5]. The variation in E_p is similar to E_b so the ability to repassivate of the material is not affected. No major differences could be found between the samples tested at 7.4 and 9.0. Furthermore, no differences were found in the corrosion current densities between all groups.

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

Tab. 3: Corrosion test results for Nitinol tested at different pH (mean±SD)

Therefore, except for a change in the potential for oxygen evolution, the corrosion resistance of NiTi was not 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 [6]. 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 [7].

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. 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 decrease in the breakdown potential and increase in the corrosion current density (which translates to corrosion rate) 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 from 7.4 to 9.0 did not affect the corrosion resistance of the material.

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 a variation in pH than the chromium oxide covering stainless steel.

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

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

CONCLUSIONS

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

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

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