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Effect of Chemical Passivation on Nitinol Based Implant

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Abstract: The present research looked at a passivation method for polished nitinol based implant and stent component after a standard heat setting treatment. Passivation of heat-treated samples in a nitric acid solution was followed by a series of corrosion tests, surface examination, and chemical analysis. The enhancement in corrosion resistance is suggested by a chemical study of passivation solutions. After prolonged immersion in saline solution, the enhanced corrosion resistance is maintained. The chemical treatment leads to a protective oxide layer that is less likely to chemically react with air and cause corrosion. On an implant surface that has undergone chemical cleaning, the chemical treatment that will hasten the creation of the passive coating must be performed. The surfaces of the passivated components must be chemically clean, and a visual inspection must reveal no etching, pitting, or freezing. The chemical passivation process stops the surface's corrosion from its path. A passivation treatment using 10 - 60% nitric acid at 80 - 90°C for 20 min has been successfully applied to mechanically polished nitinol, after a typical shape setting heat treatment. The process undergoes till the color of the nitinol implant changes from violet blue to polished white.

Keywords: Chemical Passivation, Nitinol Stent, Nitric Acid Solution

1. Introduction

A Passivation is a chemical treatment applied to provide resistance to oxidation, rusting and mild chemical attack. Passivation is the process of treating or coating a metal in order to reduce the chemical reactivity of its surface [14, 16] The Passivation process removes free iron (ferric material) from the surface of the parts that can be created during finishing operations such as milling, buffing, lapping, cutting etc [5, 8]. These contaminants create potential sites for corrosion that result in premature deterioration of the component [6, 22]. The acids used for passivation dissolve much of the alloyed iron on an atomic level at the surface leaving a chromium and nickel-rich surface [4, 7]. It then creates the formation of a thin oxide film that protects from corrosion [10]. The heat-setting and quenching processes involved in the manufacturing of metal causes oxidation of the nitinol implant to form a small “non-protective” surface oxide layer. [11, 24] The said layer when not removed leads to corrosion of the metal surface implant when it comes in contact with body fluids after implantation in the body lumen [13, 15]. In order to overcome the same, chemical passivation of a nitinol implant post heat setting and quenching process is introduced [9].

However, the conventional processes of chemical passivation have certain drawbacks [12, 20]. The conventional processes of chemical passivation are time consuming and involve long exposures of the nitinol implant to chemical solutions leading to leaching of important elements, thus resulting in brittleness of ultrathin nitinol [19]. A passivation treatment using 10 - 60% nitric acid at 80 - 90°C for 20 min has been successfully applied to mechanically polished nitinol, after a typical shape setting heat treatment [16]. Shape memory and super elastic nickel–titanium alloys have been more popular in minimally invasive medical devices in recent years. These devices are used in a variety of therapeutic settings, but are most commonly used in vascular and non-vascular stenting [18, 21]. Several factors, including long-term integrity and corrosion resistance, must be considered during the design stage of such devices [17]. The

corrosion behavior of nitinol is largely reliant on the surface condition and geometry of the component, as it is with other metallic materials. While there has been a lot of study and a lot of useful articles on the corrosion behavior of nitinol, some of the data has come from test specimens with surface conditions or geometries that aren't very useful.

Furthermore, it is encouraging that more attention is being paid to the impact of surface quality, and in particular, how to regulate and enhance it [1]. Surface treatment with a laser, [2] strain hardening, and [3, 23] chemical passivation has all been examined. Chemical passivation is appealing from a manufacturing stand point since it is simple and very affordable [27]. The passivation was done on electro polished stents at room temperature with a 10-60% nitric acid solution [25]. The passivated samples outperformed the electro polished and heat treated samples in terms of corrosion resistance. These passivated samples, however, did not appear to have been heat treated between electro polishing and passivation. Polishing, shaping, and subsequently a shape-setting heat treatment are basic processes in the production of numerous devices [26]. In this case, passivation of polished and then heat-treated samples would be more useful.

2. Materials and Methods

After the heat set/annealed, a chemical passivation process can be carried out by diluting one or more passivation solvents in water. Passivation solvents react with metal oxides on the non - protective oxide layer during the chemical passivation process. The interaction of passivation solvents with metal oxides leads free ions on nitinol implant surface and beneath to dissolve. The passivation solvents enter the radial gap generated between both the non protective oxide layer and metal oxide to separate from the nitinol implant surface, causing a pressure to build up. This leads dissolved ion and metal oxides to separate from the surface (outer and inner surface). Following the separation of the metal oxides, the passivation solvents generate a protective oxide layer on the nitinol implant surface. Nitric acid, citric acid and other passivation solvents are example of passivation solvents. The passivation solvents indicated above are powerful oxidizers.

To carry out the chemical passivation procedure, nitric acid is employed as the passivation solvent. Nitric acid is mixed with water to make the passivation solution. The passivation solution concentration might range from 10% to 50% (v/v). The passivation solution is applied on the nitinol implant. The Implant is submerged in a beaker containing a nitric acid and water passivation solution. A magnetic stirrer may stir the beaker (as shown in Figure 1). At a speed of 200 - 500 rpm, the magnetic stirrer may stir the passivation solution containing the nitinol implant. The passivation solutions temperature might vary from 20°C to 60°C. The passivation procedure might take anywhere between 10 to 60 minutes to complete. The chemical passivation procedure is used to remove the non protective oxide layer that forms on the nitinol implant surface during the heat setting/annealing or quenching processes. Upon this surface of the nitinol implant, oxides of iron, nickel, and titanium create a non protective oxide layer.

When the nitinol implant comes into touch with bodily fluids after implantation, the non protective oxide layer corrodes it, resulting in the production of dangers inside the human body. The implant is washed with an alkalizing solution after being exposed in the passivation solution. The alkalizing solution, for example, is a saturated sodium bicarbonate solution of 0.1 N. In deionized water, the sonication process is carried out. The sonication process might take anywhere from 20 to 30 minutes to complete. The aforesaid mention process relate to one chemical passivation cycle. Each chemical passivation cycle is repeated till the time the non - protective oxide layer is completely removed from the surface of the nitinol implant. The process is performed for about 5-10 cycles. During each process, the nitinol implant is observed for the visualization and verification. The process undergoes till the color of the nitinol implant changes from violet blue to polished white. The implant is soaked in a soaking solution of nitric acid 30-35% (v/v). The soaking process is performed for a short duration of time 30-35 minutes. Soaking the implant in nitric acid solution assures that the protective oxide layer fully covers the nitinol implant.

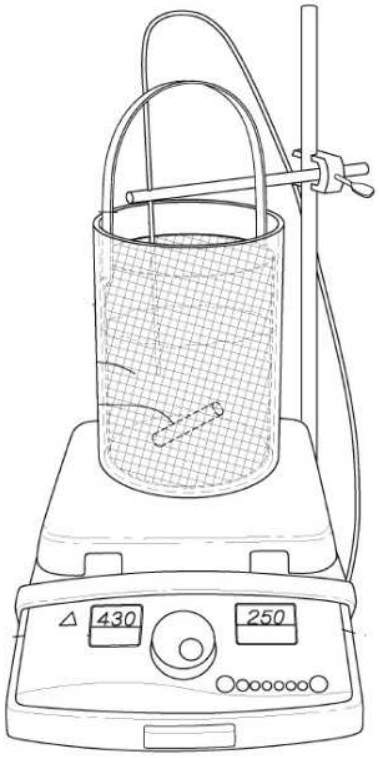

Figure 1. *Instrument of Chemical Passivation.*

3. Result

According to ASTM F 2129-17, the cyclic potentiodynamic polarization tests of nitinol stents were done using a PBS solution containing 0.720 gm of anhydrous di sodium hydrogen phosphate (Na_2HPO_4), 0.120 gm of potassium dihydrogen phosphate (KH/PO_4), 4.0 gm of sodium chloride

(NaCl), and D. M. lnert Nitrogen gas purging at 150cm^3/min with 500ml of water. Potentio stat Corrtest SC150 was used to get the Cyclic Polarization curve. The following are the test parameters that were used: The scan rate was 0.167 mV/s, with a 60-minute conditioning period at -1.0 V.

Potentiodynamic polarization is an electrochemical research method that alters the electrochemical potential (V) of a test sample by passing current between a metal sample of interest and an inert electrode in a specified solution. The open circuit potential refers that the potential established between the working electrode (the metallic surface to be analyzed) and the environment in regard to a reference electrode, which will be put in the electrolyte near the working electrode.

The cyclic Potentiodynamic polarization curve demonstrates that the sample indicate protective behavior, as evidenced by the creation of a hysteresis loop with a protection potential of 402 mV, as shown in a Figure 1. Its corrosion resistance is demonstrated by the lack of a break down potential until 524 mV. All of the potentials given are for a Saturated Calomel Electrode with a double salt bridge (SCE).

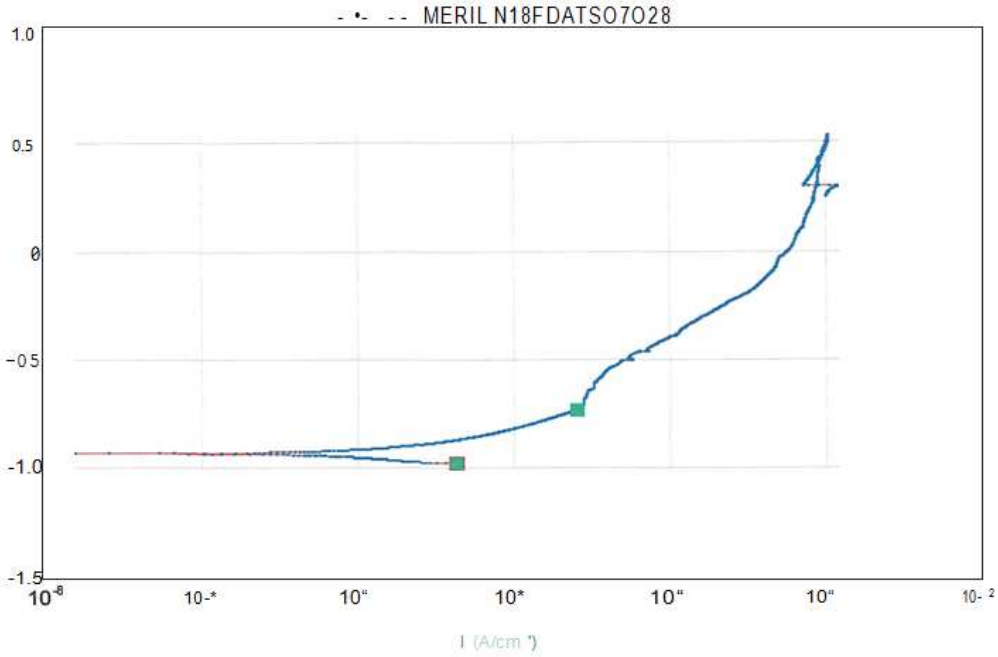

Figure 2. *Cyclic Potentiodynamic Polarization.*

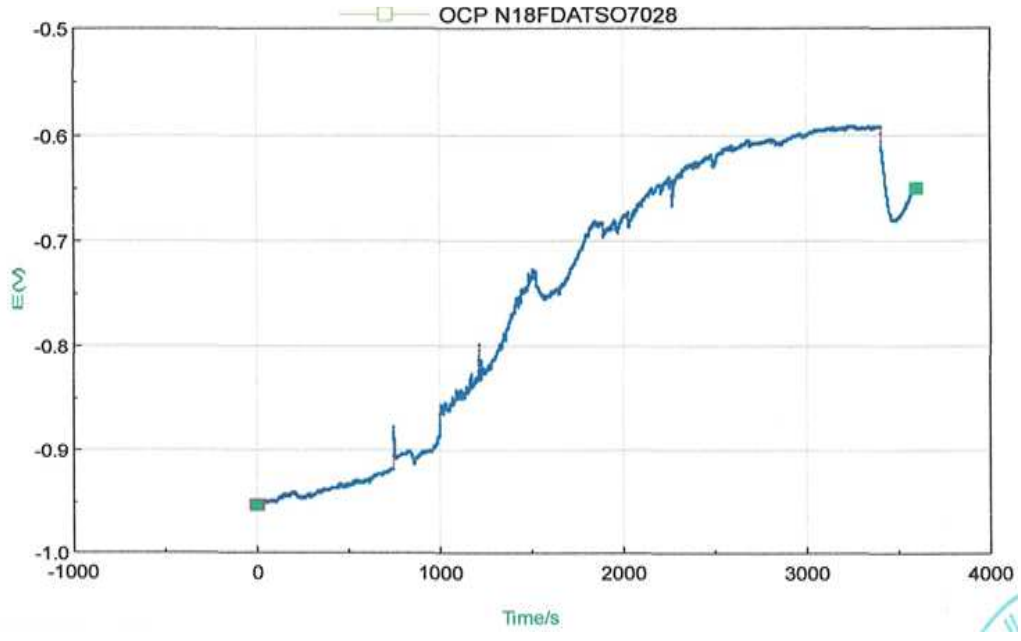

Figure 3. *Open Circuit Potential.*

The cyclic Potentiodynamic Polarization was tested a second time, and Figure 4 curve shows that the sample did not break

down until 1.5 V Potential, indicating excellent corrosion resistance. The figure depicts near-perfect corrosion resistance with no signs of breakdown. All potentials are in relation to a saturated calomel electrode with a double salt bridge (SCE).

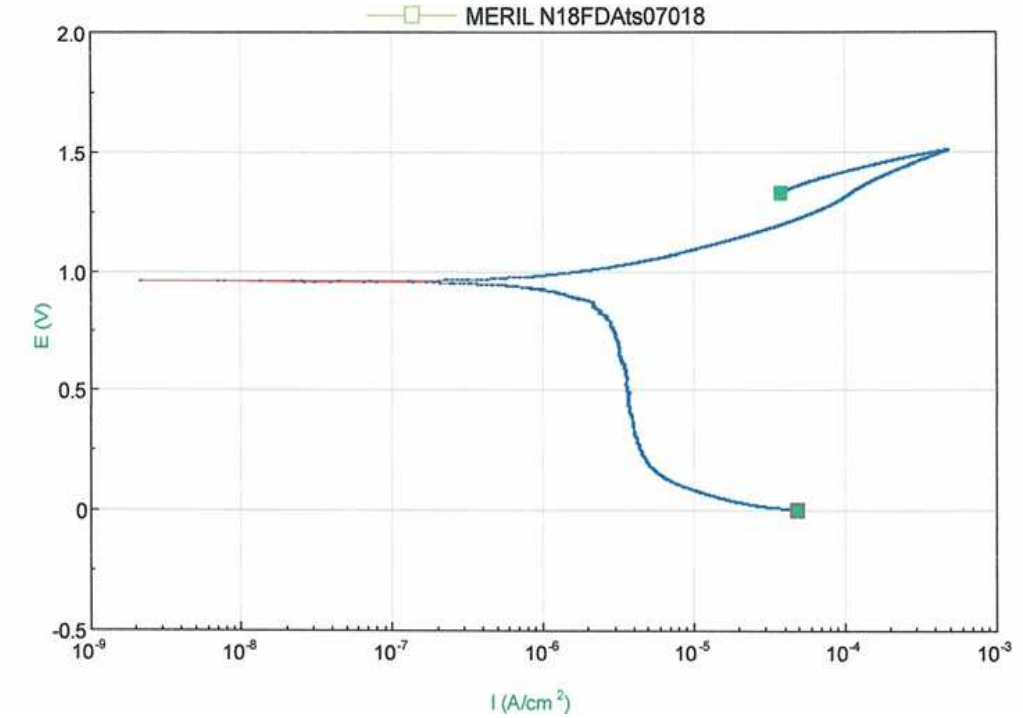

Figure 4. *Cyclic Potentiodynamic Polarization.*

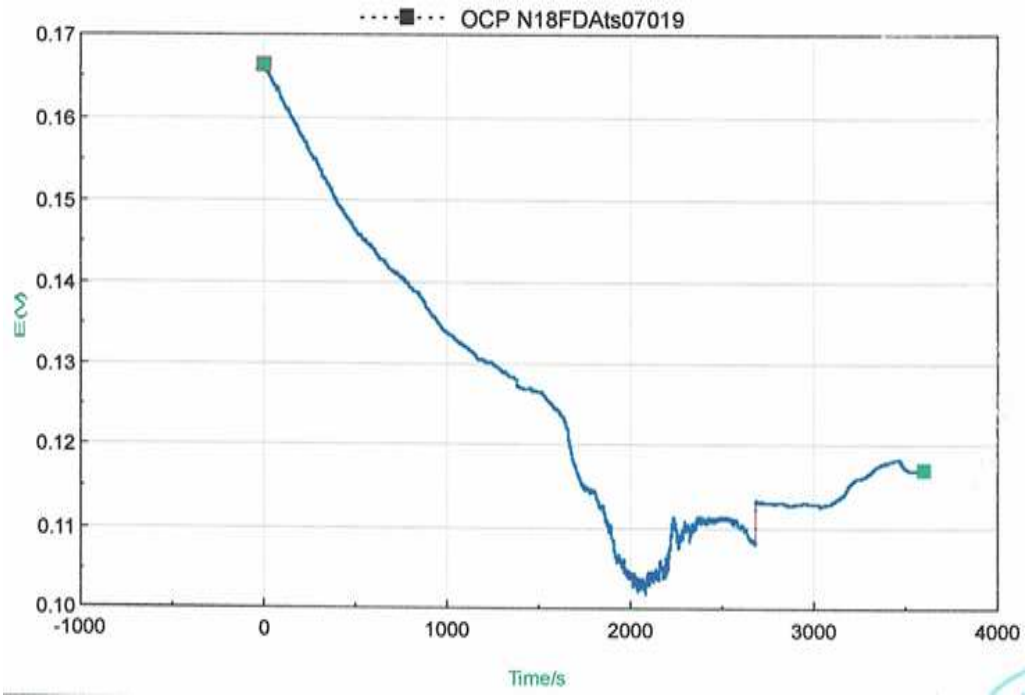

Figure 5. *Open Circuit Potential.*

4. Discussion

The sodium bicarbonate solution neutralizes excess of nitric acid present on the surface of the nitinol implant. The sodium bicarbonate solution prevents the unnecessary hazards that may be caused by the nitric acid solution. The sonication process used for remove a weak layer of metal oxide formed during the passivation on the surface of the nitinol based stent. The weak layer of metal oxide acts as a barrier for further reaction of passivation solvent with free metals and it leads to saturation of electrochemical reaction during the passivation

process. The protective oxide layer generated by the passivation solvent on nitinol stent surface. This prevents corrosion of the nitinol substance when it comes into touch with bodily fluids. During the sonication process, ultrasonic vibrations are produced which causes the separation and removal of impurities and contaminants which are adhered on the stent. The shorter passivation time and regular intervals of sonication between the passivation cycles may lead to reduction in the saturation of chemical reaction by the passivation solvent and it results in uniform passivation of metal stent with reduction in time for passivation process. The change in colour of the nitinol implant stent is observed after each passivation cycle. The change in the colour indicates the removal of the non-protective oxide layer. The use of nitric acid solution also helps in reducing surface damage after the non-protective oxide layer is removed from the surface (outer surface 1 & inner surface). The Figures 6 and 7 show the nitinol stent before and after the chemical passivation process.

Figure 6. *Before Chemical Passivation.*

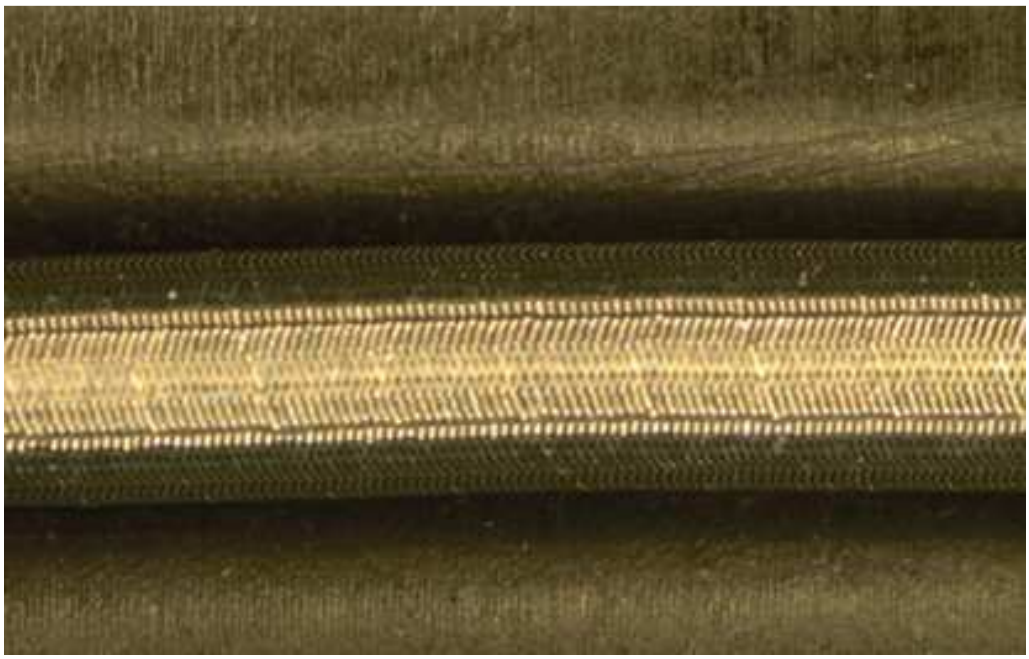

Figure 7. *After Chemical Passivation.*

5. Conclusion

After a heat setting treatment, mechanically polished nitinol implant was effectively passivated using nitric acid which provides resistance to oxidation, rusting and mild chemical attack. Heat treatment increases oxide thickness, but further passivation has no effect. As a result, improvements in corrosion behavior following passivation are mostly due to a reduction. Corrosion resistance measurements show that the advantage of the passivation is still visible after extended durations of immersion.

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