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Studies of passivation, repassivation and metastable pitting of 316L stainless implant in bone solution

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ABSTRACT

Passivity, its stability and breakdown, leading to localized corrosion such as pitting is the most important phenomenon for austenitic stainless steel in vivo solution. Because growth of it helps to aggravate other forms of corrosion, leading to failure of implant material. All pits, once initiated may not grow. Many of initiated pits are metastable and may be healed by repassivation. Only those of metastable pits which find favorable conditions grow into stable pits. Studies of repassivation and formation and life of metastable pits have been investigated by cyclic polarization and current transients at different fixed potential within passive. Pits were generated by passing anodic currents within passive region and the characteristic studies repassivation leading to death of pits or formation of stable pits have been investigated. It was found a number pits initiate well below pitting potential. Out of them only a few may grow to stable, depending on diffusion of ions and formation of porous plug over the pit mouth and other may live for few seconds, called metastable pits and cease to grow further due to favorable condition of repassivation.

KEYWORDS

Stainless steel;
Polarization;
Passivity;
Pitting corrosion;
Repassivation.

INTRODUCTION

Human tissue may appear to be chemically inert; however, at the molecular level, human tissue is a dynamic environment for immersed metals. Metals implanted into this saline milieu inevitably undergo corrosion, producing detrimental effects both locally and systemically within the human body. The degradation of implanted materials can be brought down to minimum by Passivation. Metals and alloys, such as titanium, cobalt-chromium, and stainless steels, exhibiting passivation have been used as implant materials. Among the metallic materials, AISI 316L stainless steel is most commonly employed for temporary devices such as fracture plates, bone screws and hip nails due to its low cost and acceptable biocompatibility[1–5]. However, there are many problems related to plate breakage and irritation regarding the fixation devices for osteosynthesis treatment[6–8]. It has been often reported to suffer from severe crevice and galvanic corrosion, primarily due to the presence of occluded sites and high chloride concentration in physiological fluid[9]. The corrosion of the stainless steel implant releases metal ions such as Fe, Ni and Cr, which produce local systematic effects and thereby plays a role in prosthetic loosening. A study showed that AISI 316L stainless steel produces corrosion products above certain non-lethal concentrations and thereby disturb the proliferation/ differentiation relationship of osteoblastic human alveolar bone cell cultures in a dose dependent manner[10].

Extensive research works have been made and still are being carried out to enhance its corrosion resistance and make it more biocompatible. Tomonori Nakanishi and et.al.[11] made solution nitriding of 316L steel and reported to have increased pitting corrosion resistance. Various surface modification techniques, such as plasma ion implantation[11-13], laser melting[14-17] and laser surface alloying[18,19] physical and chemical vapor deposition (PVD and CVD)[20,21] thermal oxidation[22] electrochemical surface modification/anodizing[23] have been tried out to improve wear, corrosion, and fretting resistance of orthopaedic implants. However, each of these methods has limitations concerning the performance of tailored surfaces and their complex operating procedures.

Pitting is the most important form of corrosion for austenitic stainless steel in vivo solution. Because growth of it helps to aggravate other forms of corrosion, leading to failure of implant material. Pitting can be mitigated by passivation. Breakdown of passive film leads to initiation of pitting. But all pits, once initiated may not grow. Many of initiated pits are metastable and may be healed by repassivation. Only those of metastable pits which find favorable conditions grow into stable pits[24]. In the present investigation passivation, repassivation and metastable pitting characteristics of 316L stainless steel have been made in Hank and Bone solution by different types of polarization.

EXPERIMENTAL

316L stainless steel samples of 1X2 cm^2 were and polished up to 3/0 emery paper, washed with acetone and air-dried by hot air. The samples were observed with low magnification microscope to find any surface defect of any pit or deep scratch. If any deep scratch or pits were observed, the samples were further polished. This procedure continues until and unless the samples become pit free. ., Artificial Bone fluid solution. was prepared by mixing the analytical grade reagents and double distilled water, with pH value of 7.4 ± 0.2. Composition of the solutions is listed in TABLE 1. The electrolyte of about 100 ml without aeration was used and temperature was maintained at 37 ± 1ºC .

Potentiostatic polarization, Cyclic polarization and Repassivation experiments were conducted in Gamry instrument. The arrangement electrochemical cell is shown in figure 1

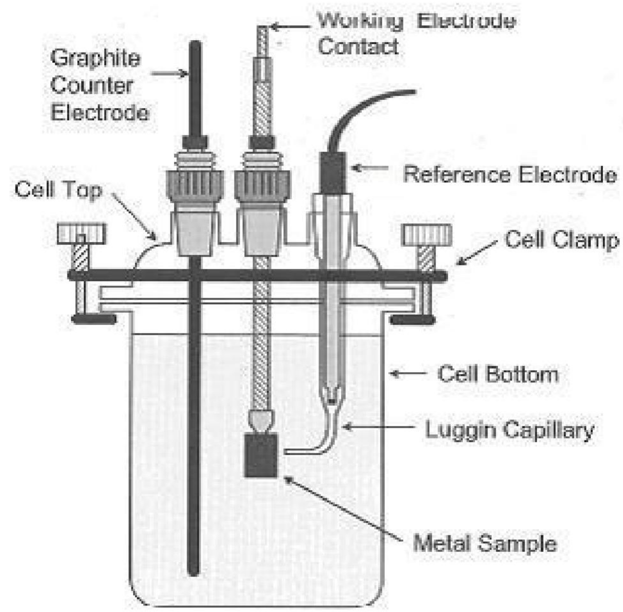

Figure 1 : Showing experimental electrochemical cell for corrosion study

RESULTS AND DISCUSSIONS

Figure 2 shows the cyclic polarization scan in bone fluid solution. The material is found to prone to passivity breakdown and localized corrosion. The reverse scan cuts the forward scan at 144.8mV volt vs. SCE This point is Repassivation Potential E_{RP}, below which the material is said to be protected against the localized corrosive environment. Since the pitting potential E_{pit} is greater than E_{RP}, localized corrosion initiates and the time of initiation depends on the difference between (E_{pit} - E_{RP}). If E_{pit} is closer to E_{RP}, time of initiation is longer. If E_{pit} is below E_{RP}, localized attack will not continue.

Pits start initiating at certain potentials within passive region. These pits may get repassivated when they are called metastable pits but under certain conditions when the passive force is not enough to cover the exposed local surface area by newly formed oxide layer, the metastable pits grow into stable pits. In the following sets of figures under the study of CPP scan; the aspects of these repassivations have been studied.

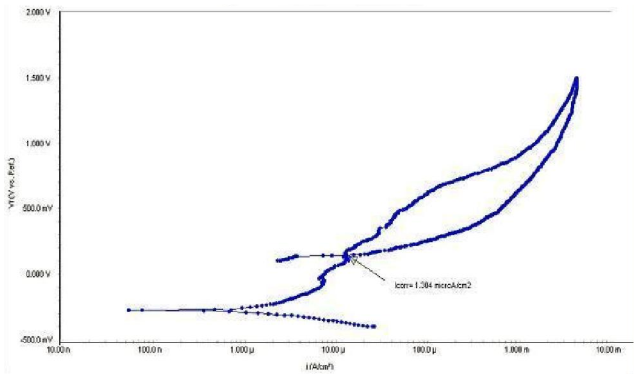

Figure 2 : Cyclic polarization scan of the specimen in bone fluid solution

In the series of experiments from Figure 3-6, the specimen is first induced to pit (stimulating phase) by applying a large anodic potential. After pitting has been initiated, the potential is dropped to an already selected test potential to find if the sample is going to repassivate or not. If the specimen repassivates, the process of stimulation and repassivation is repeated at more anodic potential. This technique determines the Critical Repassivation Potential. The experimentation ends during repassivation when the current exceeds the limit indicating of pitting or when the specimen does not pit during stimulation phase. The potential has been stepwise increased within passivity region in Figure 3 to 6, from the lowest value of –0.113 volt vs. SCE to a highest value of +0.184 volt vs. SCE. It is seen in figure 3 that repassivation line is absent. This is due to the fact that at such low potential, within the passive region, pits have not initiated. In figure 4 two trends of lines are shown (blue line indicates stimulation phase while red one indicates repassivation phase).

It is seen that at –0.0535 volt of applied potential of stimulating phase, pits have been forced to initiate by applying current density of the order 579nA/cm^2 that then drops down to 208nA/ cm^2. The repassivation has simultaneously started with a cathodic current density and the pits have been repassivated. Increase of potential to 0.045volt in figure 5 exhibit new stimulating phase and one repassivation state. Similarly in figure 6, at a much higher potential of 0.184 volt, series of lines are found for stimulating as well as for repassivation phase. For phase 3 of very high anodic potential, repassivation phase is absent. It indicates that at this potential, the pits generated are transformed into stable pits.

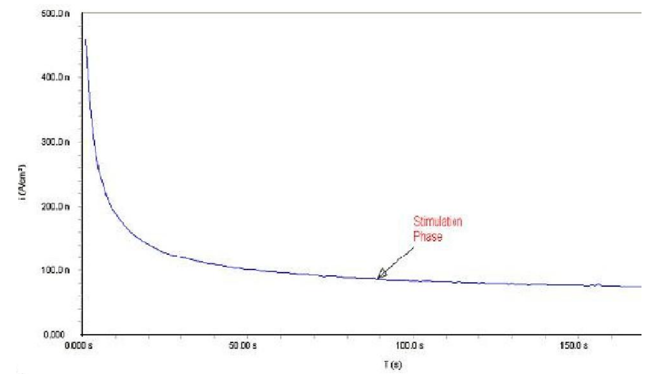

Figure 3 : Critical pitting potential scan of the specimen – 0.113 volt in bone fluid solution

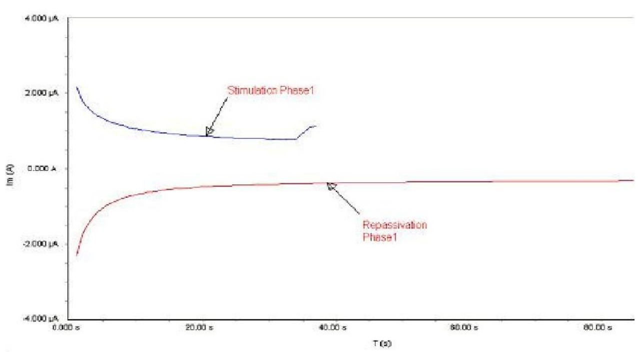

Figure 4 : Critical pitting potential scan of the specimen at – 0.053 volt in bone fluid solution

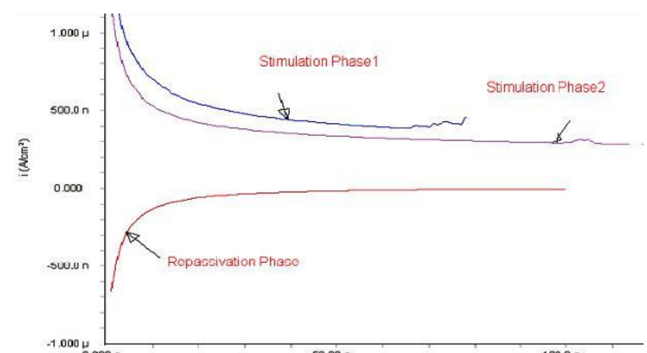

Figure 5 : Critical pitting potential scan of the specimen at 0.054 volt in bone fluid solution

For the series of experiments of potentiostatic scan, from Figure 7-12, sample is held at open circuit potential for few seconds and there after it is potentiostated at initial fixed $E_{initial}$ value and is held at this potential for 100 seconds, after which current transit (current vs.

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time) is studied. Potential is then jumped to E_{final} and is held at that potential and again current transit is studied. Figure 7 shows such a potentiostatic scan where the initial potential and final potential have been selected from within the passive region (See Figure 2 of cyclic polarization), starting from lower region of the passive curve. It is seen from current transit study that after the potential jump in final stage, current steadily decreases with time indicating no formation of any metastable pits. At stepwise higher potentials in figure 8 & 9, similar trend has been encountered. However, from figures 10, 11 and 12, it is interesting to find from current transit trend of the second part of the trend i.e., when the specimen is fixed at E_{final}, there are jumps of current at different time indicating initiation of pits. But with passage of time, the current density drops down to repassivation and healing of pits. Therefore, these are called metastable pits. From figs.11 to 12, it is found that the metastable pits grow into stable pits and repassivation force is not enough to passivate the deteriorating local passivity layer.

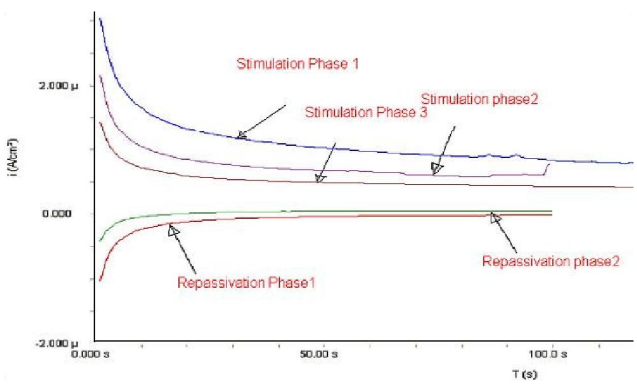

Figure 6 : Critical pitting potential scan of the specimen at 0.184 volt in bone fluid solution

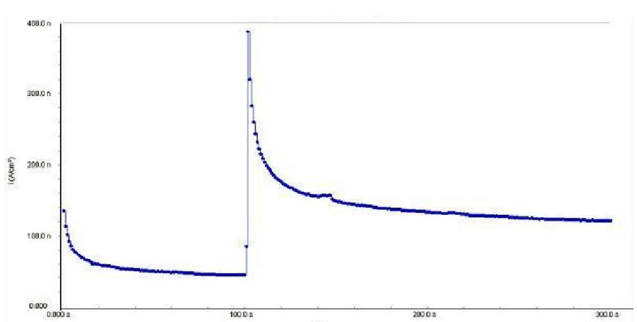

Figure 7 : Potentiostatic scan of the specimen between -0.113 to –0.053 volt in bone fluid solution

It is interesting to note from the above discussion that 316L stainless steel in Bone Fluid Solution, does not exhibit any pitting up to 0.053 volt and above it metastable pits start growing and from 0.154 volt vs. SCE, formation of stable pits start occurring.

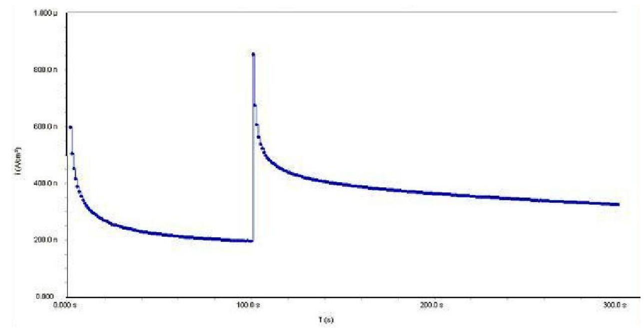

Figure 8 : Potentiostatic scan of the specimen between -0.053 to 0 volt in bone fluid solution

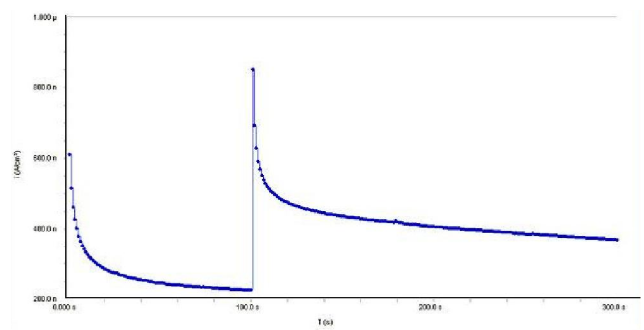

Figure 9 : Potentiostatic scan of the specimen between 0to 0.053 volt in bone fluid solution

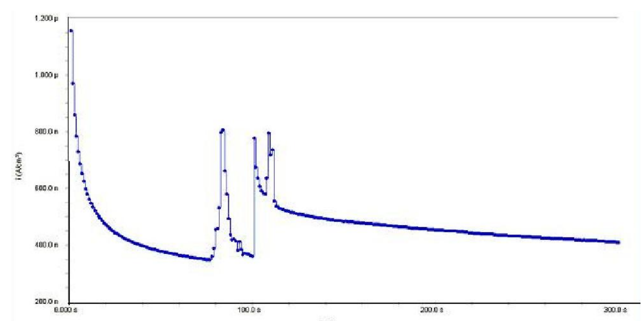

Figure 10 : Potentiostatic scan of the specimen between 0.053to 0.089 volt in bone fluid solution

Metastable pits occur over a wide potential range, well below the normal pitting potential, and can be observed electrochemically by the random occurrence of a small rise in current transients, which vary in magnitude and shape with typical lifetimes in the order of few seconds. However, only a small fraction of the events produce a propagating pit and only small fractions of these survive long enough to be considered stable. During the early stage of pitting of some passivated metals and alloys, small current fluctuations are observed, which are the results of very small local corrosion and repassivation due to formation of metastable pitting. The rate of growth of individual corrosion pit is controlled by diffusion of the dissolving metal cations from the pit interior, the surface of which is saturated with the metal chloride. There is a critical value of the product of the pit radius and its dissolution current density,termed the 'pit stability product[24] below which the pit is metastable and may repassivate, and above which the pit is stable. All pits, whether metastable, or destined to become stable, grow initially in the metastable condition, with a pit stability product which increases linearly with time, but below the critical value. Metastable growth requires a perforated cover over the pit mouth to provide an additional barrier to diffusion, enabling the aggressive pit anolyte to be maintained. In this state, pits grow at a constant mean current density which is maintained by periodic partial rupture of the cover. Stable pit growth is then achieved when the cover is no longer required for continued propagation, and the pit depth is itself a sufficient diffusion barrier; a constant mean pit stability product above the critical value characterizes stability. If the cover is lost prematurely, before the critical pit stability product is achieved, the pit anolyte is diluted and repassivation is inevitable.

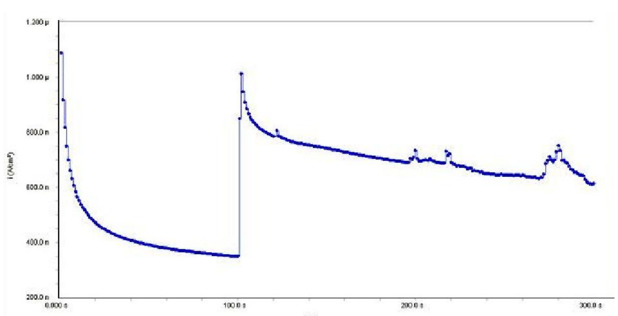

Figure 11 : Potentiostatic scan of the specimen between 0.089to 0.154 volts in bone fluid solution

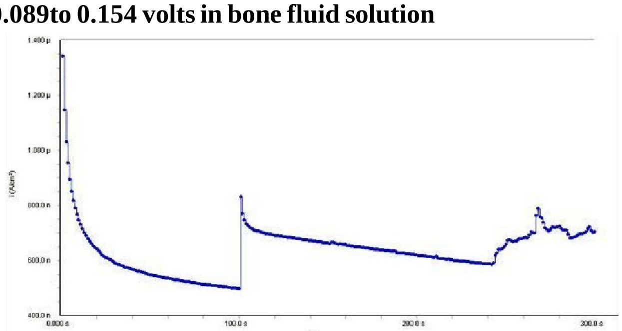

Figure 12 : Potentiostatic scan of the specimen between 0.154to 0.184 volts in bone fluid solution

CONCLUSION

The repassivation potential of 316L stainless steel implant in bone solution is 144.8mV volt vs. SCE which is below pitting potential. So it is prone to localized attack. Metastable pits are generated at potentials within passive region and well below pitting potential. At lower potential less 0.045 vs. SCE, pits initiate and get passivated, while at higher potential metastable pits grow into stable pits. 316L stainless steel in Bone Fluid Solution, does not exhibit any pitting up to 0.053 volt and above it metastable pits start growing and from 0.154 volt vs. SCE, formation of stable pits start occurring.

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