

An electrochemical study of the crevice corrosion resistance of NiTi in Hanks' solution

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Abstract

The crevice corrosion resistance of NiTi in Hanks' solution at 37 °C was assessed by employing electrochemical methods. NiTiCu, commercially pure Ti (cp Ti), Ti6Al4V, and 316L stainless steel were included in the study for comparison. The susceptibility to crevice corrosion was investigated by using a potentiostatically controlled stimulation–repassivation scheme in the presence of a crevice former. Susceptibility to crevice corrosion is characterized by the critical potential for crevice corrosion (E_{cc}), which is defined as the highest potential at which crevice-corroded surfaces repassivate after stimulation. The crevice corrosion rates in the propagation stage, which was characterized by crevice solution with low pH value and high chloride concentration, were assessed by determining the galvanic current between a small sample in contact with simulated crevice solution and a large sample of the same material in contact with bulk solution. Based on the results of the stimulation–repassivation tests, the susceptibility of various samples to crevice corrosion in Hanks' solution at 37 °C and pH 7.4 may be ranked in ascending order as: cp Ti \approx Ti6Al4V \ll 316L < NiTiCu < NiTi. The beneficial effect of Cu could be attributed to the redeposition of Cu inside the crevice, as evidenced by EDS analysis. Once crevice corrosion had started, the crevice corrosion current densities for different samples did not differ much, all being of the order of a few mA/cm² in a model crevice solution of high acidity (pH 1) and high chloride concentration (146 g/L of NaCl).

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1. Introduction

Crevice corrosion refers to the localized corrosion occurring on a metallic material in contact with electrolyte in a small and occluded space (that is, a crevice). Crevices are present almost everywhere in practical cases; they may be formed between metallic parts or between a non-metallic part and a metallic part, or under debris on a metallic part. Passive metallic materials are particularly susceptible to crevice corrosion in chloride-containing environments. It is generally believed that crevice corrosion is initiated by the depletion of oxygen in the crevice solution when the corrosion reaction there has consumed the dissolved oxygen and supply from outside the crevice is limited to diffusion only. A macroscopic differential aeration cell is thus set up with the metallic surface inside the crevice act-

ing as anode and the bulk metallic surface outside acting as cathode. As the corrosion reactions in this cell proceeds, the concentration of metallic ions in the crevice solution increases due to anodic dissolution. The metallic ions attract chloride ions from the bulk solution to maintain electrical neutrality and form unstable metallic chlorides, which then hydrolyze to produce H⁺ ions, thus lowering the pH of the crevice solution. The increase in acidity of the crevice solution further increases the dissolution rate of metal, thus attracting more chloride ions and further lowering the pH. That is, the whole process is autocatalytic and the crevice solution is becoming more and more aggressive because of increased concentrations of chloride and H⁺ [1].

Shape memory alloys (SMAs) have recently emerged as popular materials in the field of medicine and dentistry by virtue of their unique thermomechanical properties such as shape memory effect and superelasticity [2]. Among several tens of SMAs available, nickel titanium (NiTi) is the most popular because of its excellence in thermomechanical properties and biofunctionality [3–5]. Though NiTi is regarded as corrosion resistant

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Table 1
Nominal composition in wt.% of the samples studied (minor elements are omitted)

Material	Ti	Ni	Cu	Al	V	Fe	Cr	Mo
NiTi	45	55						
NiTiCu	45	47	8					
cp Ti	100							
Ti6Al4V	90			6	4			
316L		12				Balance	18	2.5

for general applications, its corrosion behavior requires careful examination when it is to be used as an implant material. There has been some concern on the safety of NiTi for long-term *in vivo* applications because Ni is allergenic and toxic when present at an elevated level in the human body. Electrochemical studies of the pitting corrosion behavior NiTi in simulated body fluids has been widely reported [6 and references therein, 7–10]. The results among these studies varied because of the difference in the quality and surface finish of the NiTi samples tested and of the test methodology [11].

The presence of crevices is common and almost unavoidable with implants, and crevice corrosion is one possible mode of implant degradation. In fact, crevice corrosion in implants has been reported [12,13]. While the pitting corrosion behavior of implant materials has been widely studied, reports on the crevice corrosion behavior of implant materials in simulated body fluids are much less common [6,14,15]. The present study aims at investigating the susceptibility to crevice corrosion and the crevice corrosion rate of NiTi in Hanks' solution by electrochemical methods. The crevice corrosion behavior of NiTi will be compared with three common implant materials (cp Ti, Ti6Al4V, and 316L stainless steel) and a potential implant material (NiTiCu), which is attractive because of its narrow stress/thermal hysteresis loop.

2. Experimental details

2.1. Materials

Five types of materials including NiTi, NiTiCu, commercially pure Ti, Ti6Al4V, and 316L stainless steel (with nominal composition in wt.% shown in Table 1) were investigated in the present study. The samples were polished successively with different grades of SiC paper down to 1500 grit, and then ultrasonically cleaned successively in acetone, ethanol, and deionized water.

2.2. Potentiostatic polarization and repassivation test

To assess the susceptibility to crevice corrosion, potentiostatic stimulation and repassivation tests conforming to ASTM Standard F 746-04 [16] were performed using an EG & G PAR 2273 corrosion system. The method was adapted from ASTM Standard F 746-04 for flat samples instead of rod samples. Adaptation of the crevice former for samples with shapes different from rods has been reported in the literature [6]. The sample under test was put in a sample holder and pressed against a washer, which acted as a crevice former. The washer had inner and outer diameters of 12 and 16 mm, respectively, exposing a sample area of about 1.1 cm² to the electrolyte. To ensure similar crevice geometry, a torque of 110 cN m (using a torque wrench) was used every time in screwing the sample against the washer. Hanks' solution (a simulated body fluid with composition shown in Table 2) at pH 7.4, kept at 37 °C and open to air, was used as the electrolyte. To avoid conditions of inconsistent 'wetting' of the sample

Table 2
Chemical composition of Hanks' solution

Component	Concentration (g/L)
NaCl	8.0
CaCl ₂	0.14
KCl	0.4
NaHCO ₃	0.35
Glucose	1.0
MgCl ₂ ·6H ₂ O	0.1
Na ₂ HPO ₄ ·2H ₂ O	0.06
KH ₂ PO ₄	0.06
MgSO ₄ ·7H ₂ O	0.06

surface by the electrolyte beneath the washer, samples were immersed in Hanks' solution prior to tightening the screw [17]. A saturated calomel electrode (SCE) was used as the reference electrode and a pair of graphite rods, as the counter electrode. The open-circuit potential of the sample was continuously monitored for 1 h, starting immediately after immersion in the electrolyte. The potential E_1 at the end of 1 h was recorded. The potential was then potentiostatically shifted to +800 mV (SCE) to stimulate crevice corrosion. According to ASTM F 746-04, stimulation of localized corrosion is marked by one of the following conditions: (i) the polarization current density exceeds 500 $\mu\text{A}/\text{cm}^2$ instantly; (ii) the current density does not exceed 500 $\mu\text{A}/\text{cm}^2$ within 20 s, but is increasing in general; (iii) these two conditions are not met in the first 20 s, but are met in a subsequent period of 15 min. If crevice corrosion was stimulated, the potential was immediately returned to E_1 or another preselected potential E_i (E_1 was the first preselected potential) to determine if the sample would repassivate or if crevice corrosion would propagate at the preselected potential. According to ASTM F 746-04, repassivation is manifested by a current density that quickly drops to zero or to low values (of the order of 1 $\mu\text{A}/\text{cm}^2$) at the preselected potential for a period of 15 min. If the sample repassivated, the potentiostatic stimulation–repassivation steps were repeated between +800 mV (SCE) and E_2 , where E_2 was the smallest multiple of 50 mV on the noble side of E_1 . The test was repeated until crevice corrosion continued at a certain preselected level E_n . Then, the critical potential for crevice corrosion E_{cc} was reported as E_{n-1} , that is, $E_n - 50$ mV. The stimulation–repassivation scheme is shown in Fig. 1. After the test, the sample surface was examined for evidence of crevice corrosion.

If crevice corrosion was not stimulated at +800 mV (SCE), the test was terminated and the sample material was regarded as very resistant to crevice corrosion and the critical potential for crevice corrosion was reported as >+800 mV (SCE) under the test condition.

Triplicate samples were used in the stimulation–repassivation tests.

2.3. Test using compartmentalized cell

The compartmentalized cell provides a convenient way of assessing the crevice corrosion rate at the propagation stage of crevice corrosion. At the propagation stage, the crevice solution is different in pH value, chloride concentration and degree of aeration from the bulk solution outside the crevice [18–20]. The cell in the present study consisted of two compartments B and C (Fig. 2). Com-

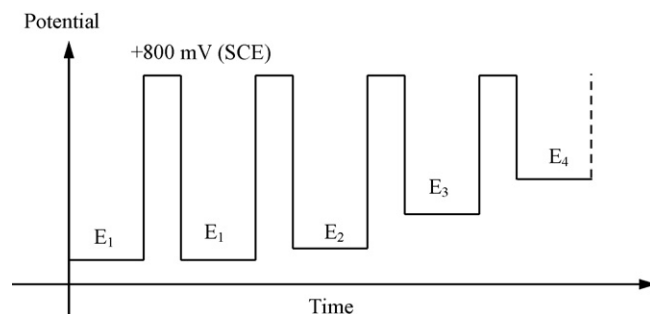


Fig. 1. The potentiostatically controlled stimulation–repassivation scheme.

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