Corrosion behavior of NiTi alloys used in orthopedic implants and prosthetic devices

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Abstract

Equiatomic Nitinol shape memory alloys (NiTi) have many applications in the biomedical industry. However, in spite of their favorable properties, its anti-corrosion properties may not be adequate in some applications. Excessive corrosion of the materials may lead to out-diffusion of toxic nickel ions from the materials into surrounding body fluids and tissues. Hence, the corrosion properties of NiTi are very important from the practical point of view. In this chapter, the in vitro and in vivo corrosion behavior of the materials is described from the perspective of orthopedic implants and prosthetic devices.

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Abbreviations and symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCr</td>
<td>cobalt-chromium</td>
<td>$E_{\text{corr}}$</td>
<td>free corrosion potential</td>
</tr>
<tr>
<td>CuNiTi</td>
<td>copper-nickel-titanium</td>
<td>$I_{\text{corr}}$</td>
<td>corrosion current density</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>titanium-6% aluminum-4% vanadium (alloy)</td>
<td>$E_{\text{bd}}$</td>
<td>breakdown potential</td>
</tr>
<tr>
<td>TiO2</td>
<td>titanium (di)oxide</td>
<td>$E_{\text{p}}$</td>
<td>passivation potential</td>
</tr>
<tr>
<td>SMA</td>
<td>shape memory alloy</td>
<td>$I_{\text{p}}$</td>
<td>passivation current density</td>
</tr>
<tr>
<td>PTN</td>
<td>porous titanium nickel</td>
<td>$E_{\text{pit}}$</td>
<td>pitting potential</td>
</tr>
<tr>
<td>$A_s$</td>
<td>austenite start</td>
<td>$E_{\text{galv}}$</td>
<td>galvanic coupling potential</td>
</tr>
<tr>
<td>$A_f$</td>
<td>austenite finish</td>
<td>$E_{\text{cc}}$</td>
<td>crevice corrosion potential</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{SCE}$</td>
<td>saturated calomel electrode</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(reference electrode)</td>
</tr>
</tbody>
</table>

1. Background

Since nearly equiatomic Nitinol alloy or NiTi was first introduced in the 1970s, it has become a very attractive material in biomedical applications. Because of the combination of unique mechanical properties such as shape memory effect, superelasticity, and good biocompatibility comparable to or better than that of Ti, NiTi has undergone significant development in orthopedics and orthodontics. For instance, the shape memory effect of a predeformed device after heating is successfully utilized in orthopedic practice and the superelastic property allows for the design of shape memory devices with a constant stress over a wide range of strain and shape [1].

The primary requirement for any materials to be implanted into the body is that it should not cause any adverse host reactions or severe material reactions in the body environment. However, the physiological environment is a typically 37°C aqueous solution with a pH of 7.4 consisting of dissolved gases (such as oxygen), electrolytes, cells, and proteins. Metals in this environment can be corroded leading to deterioration and dissolution of the metals via chemical reactions. Because corrosion causes metallic implants to release ions, the fate of the implants and body tissues are jeopardized. For example, the type and concentration of released corrosion products can alter the functions of cells in the vicinity of the implants as well as cells at remote locations after transport of the corrosion by-products to distant sites inside the body. The corrosion resistance of metallic implants is included in the topic of biocompatibility [2]. It is true that every metallic device after implantation in the body will corrode and the questions are when and to what extent.

As far as NiTi (55 weight% Ni) is concerned, dissolution of Ni ions which may induce allergic, toxic, and carcinogenic effects poses the greatest problem for NiTi implanted into the human body. The corrosion performance of NiTi alloy can range from excellent to poor in the body. The reason is related to the presence of impurities, structure, and surface modification. In addition,
physiologically not only the type and concentration of chemical ingredients (pH, chloride content, etc.) can vary, but also the physical and mechanical parameters such as temperature, pressure (e.g. of oxygen), flow velocity, static, dynamic, tensile and compressive stress, friction, and wear constantly change [3].

This chapter discusses the in vitro and in vivo corrosion behavior of NiTi alloy. The objective is to make readers more aware of the fundamental and NiTi-specific aspects of corrosion.

2. Materials and applications

Since Buehler et al discovered the shape memory effect in NiTi alloys at Naval Ordinance Laboratory in the 1960s [4]. The materials are commonly known as NiTi alloys and many studies have been conducted on the potential applications of NiTi alloy to biomedical engineering and medicine. Some of the examples are listed in Table 1.

Table 1. Highlights of research activities on medical NiTi alloy.

<table>
<thead>
<tr>
<th>Country</th>
<th>Research course</th>
</tr>
</thead>
<tbody>
<tr>
<td>U.S.A.</td>
<td>- In 1960s, NiTi orthodontic wires were applied in practice and studies on porous NiTi SMA commenced.</td>
</tr>
<tr>
<td></td>
<td>- From 1983 to 1986, NiTi self-expanding stents were implanted into animals.</td>
</tr>
<tr>
<td></td>
<td>- In 1990, NiTi nails produced in Mitek company were accepted by FDA;</td>
</tr>
<tr>
<td></td>
<td>- Since 1990s, minimally invasive medical instruments made of NiTi have been developed.</td>
</tr>
<tr>
<td></td>
<td>- In 1970, the Committee for NiTi Multi-purpose Development was formed to concentrate on orthopedics.</td>
</tr>
<tr>
<td>Japan</td>
<td>- In 1981, NiTi devices were used in orthopedic surgery;</td>
</tr>
<tr>
<td></td>
<td>- In 1985, NiTi implants were allowed by the Japanese Committee for Care &amp; Welfare Concerns.</td>
</tr>
<tr>
<td></td>
<td>- Since 1990s, many kinds of artificial orthopedic instruments made of NiTi have been used extensively.</td>
</tr>
<tr>
<td>Russia</td>
<td>- In 1979, base research on NiTi alloy as medical implants began.</td>
</tr>
<tr>
<td></td>
<td>- In 1983, stents visible to X-ray were developed.</td>
</tr>
<tr>
<td></td>
<td>- In 1993, researchers began studying prosthetic vascular stents.</td>
</tr>
<tr>
<td></td>
<td>- In 1971 researchers began investigating the mechanism and applications of NiTi alloy.</td>
</tr>
<tr>
<td>Germany</td>
<td>- Since 1980, applications of NiTi alloy in orthopedics have been developed.</td>
</tr>
<tr>
<td></td>
<td>- In 1989, NiTi was applied to oral implants and orthopedics.</td>
</tr>
<tr>
<td></td>
<td>- Since 1990s, esophagus and urethra stents have been invented.</td>
</tr>
<tr>
<td>China</td>
<td>- In 1971, researchers began the study on NiTi shape memory alloy.</td>
</tr>
<tr>
<td></td>
<td>- In 1980, clinical applications in orthodontics began.</td>
</tr>
<tr>
<td></td>
<td>- In 1989, esophagus and urethra stents were clinically applied.</td>
</tr>
<tr>
<td></td>
<td>- Nowadays, NiTi vascular stents are widely studied.</td>
</tr>
</tbody>
</table>
As one kind of medical implant materials, NiTi alloy is particularly interesting because of not only its significant shape memory effect, but also its superelastic deformation, which is not present in other conventional medical alloys such as 316L stainless steel, pure titanium, etc. Besides, the good mechanical performance also offers great promise.

2.1 Shape memory effect

NiTi alloy that is shaped or bent to a limited extent at a given temperature and then reshaped at another higher temperature will return to the original shape when it is brought back to the shaping temperature. The shape memory effect is associated with a martensitic transformation. Fig. 1 shows the stress-temperature relation. There exits the hysteresis during the transformation of the SMA, which is characterized by four temperature ($M_s$, $M_f$, $A_s$, and $A_f$), indicating the initial and final transformation temperature. In the low-temperature phase, the alloy is in the martensitic condition that is soft and easy to deform. In the high-temperature phase, this alloy changes to the hard austenitic structure. The shape memory effect occurs through a rearrangement of the martensitic plates. During the cooling process, the austenite phase transforms into twinned martensite, and this alloy will be shaped under external stress. During heat treatment, the deformed martensite returns to the original austenite, which is the macroscopical shape effect phenomenon.

Figure 1. Schematic illustration of the martensite transformation and shape memory effect.
2.2 Superelasticity

The wide application of NiTi alloy in the biomedical fields is mostly attributed to its superelasticity. Polycrystal NiTi alloy deforms reversibly to very high strain up to 8%. In contrast, the maximum superelastic strain of single-crystal NiTi alloy is up to 10.7% [5], and it includes linear elasticity and non-linear elasticity [6]. The temperature has a large influence on non-linear elasticity and a little change in the temperature can cause large strain. Fig. 2 shows the micro-transformation of stainless steel and NiTi alloy. The former depends on the crystal slippage and the latter on twinned transformation. Under the same conditions, the residual deformation in NiTi alloy is just 1/10 of that for stainless steel. However, the elastic module can reach the bone module after suitable heat treatment.

![Schematic image of the superelastic effect](image)

**Figure 2.** Schematic image of the superelastic effect [6]. Data are reproduced with permission of the authors.

2.3 Mechanical properties

Besides the good shape memory effect and superelasticity, the binary NiTi alloy has good mechanical properties. The major physical properties and some of mechanical properties of NiTi alloy are listed in Table 2. Note that this is for the equiatomic alloy with an $A_f$ value of approximately 110 °C (230 °F). Selective hardening and proper heat treatment can greatly improve the ease in which the martensite is deformed, yields an austenite structure with much greater strength, and creates materials that spontaneously move themselves upon heating and cooling. One of the biggest challenges in using this family of alloys is the development of the proper processing procedures to produce the desired properties [7].
Table 2. Physical and mechanical properties of equiatomic NiTi alloys [7]. Data are reproduced with permission of the authors.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Property value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting temperatures, °C(°F)</td>
<td>1300 (2370)</td>
</tr>
<tr>
<td>Density, g/cm³(lb/in.³)</td>
<td>6.45 (0.233)</td>
</tr>
<tr>
<td>Resistivity, µΩ.cm</td>
<td></td>
</tr>
<tr>
<td>Austenite</td>
<td>~100</td>
</tr>
<tr>
<td>Martensite</td>
<td>~70</td>
</tr>
<tr>
<td>Thermal conductivity, W/m. °C</td>
<td></td>
</tr>
<tr>
<td>Austenite</td>
<td>18</td>
</tr>
<tr>
<td>Martensite</td>
<td>8.5</td>
</tr>
<tr>
<td>Corrosion resistance</td>
<td>Similar to 300-series stainless steel or titanium alloys</td>
</tr>
<tr>
<td>Young’s modulus, GPa (10^6 psi)</td>
<td></td>
</tr>
<tr>
<td>Austenite</td>
<td>~83 (~12)</td>
</tr>
<tr>
<td>Martensite</td>
<td>~28-41 (~4-6)</td>
</tr>
<tr>
<td>Yield strength, MPa (ksi)</td>
<td></td>
</tr>
<tr>
<td>Austenite</td>
<td>195-690 (28-100)</td>
</tr>
<tr>
<td>Martensite</td>
<td>70-140 (10-20)</td>
</tr>
<tr>
<td>Ultimate tensile strength, MPa</td>
<td>895 (130)</td>
</tr>
<tr>
<td>Transformation temperature, °C(°F)</td>
<td>-200 to 110 (-325 to 230)</td>
</tr>
<tr>
<td>Hysteresis [°C(°F)]</td>
<td>~30 (~55)</td>
</tr>
<tr>
<td>Latent heat of transformation, kJ/kg.atom</td>
<td>167</td>
</tr>
<tr>
<td>Shape memory strain</td>
<td>~8.5 -10%</td>
</tr>
</tbody>
</table>

2.4 Medical applications

Since the discovery of NiTi alloy and particularly in the early 1970s, the remarkable properties of SMA have prompted several investigations related to their applications in different fields. In this section, we discuss its biomedical applications.

1) Applications to orthodontic therapy - Based on the superelasticity, NiTi alloy wires are used in orthodontic therapy because of their high flexibility in bending without kicking. A superelastic NiTi wire not only increases the important force which is particularly favorable for large misaligned teeth, but also offers rapid orthodontic treatments [8, 9].

2) Applications to orthopedic and other bone-related surgery, e.g. spinal vertebra spacer [10] which assures the local reinforcement of the spinal vertebra. Another application is related to the healing process of broken and fractured bones, e. g. medical staples [11], and NiTi alloy is more effective than other materials in setting bones and promoting healing [9].

3) Cardiovascular applications, e. g. blood-clot filters [12], vascular stent [13] - The superelastic properties of NiTi alloy enable its use in invasive surgery to reach narrow places.

4) Applications to surgical instruments, e.g. SMA basket [14], intra-aortic balloon pump [10], etc. - Among the advantages of these tools, one can
emphasize their flexibility as well as their possibility to recover their former shape when heated. Potential applications of NiTi alloys include hip protheses, anterior cruciate ligament prostheses, and endoprotheses.

3. In vitor corrosion of NiTi alloys

3.1 Electrochemistry and basic corrosion process

3.1.1 Corrosion reactions and thermodynamics

Corrosion is one of the major processes that cause problems when metals and alloys are used as implants in the body [15]. It typically is a chemical process and takes place via electrochemical reactions through the conversion of metal atoms from the metallic to the non-metallic state of chemical compounds or dissolved ions. During the corrosion process, the total rates of the oxidation and reduction reactions that are termed electron production and electron consumption, respectively must be equal. The overall reaction rate is controlled by the slowest step of these two processes [3, 16, 17].

The protective film on the surface of metals and alloys in medical implants is favorable to its passivity in the body thereby inhibiting rapid corrosion and limiting the current flow and release of corrosion products to a very low level. For metallic surgical implants, the types of corrosion consist mainly of pitting, crevice, galvanic, intergranular, stress-corrosion cracking, corrosion fatigue, and fretting corrosion. Although corrosion can be classified into many different types, all corrosion effects in aqueous solutions are based on two fundamental reactions [3]:

(1) Under anaerobic conditions, water is the oxidizing agent. Metal oxides, hydroxides or hydrated oxides and gaseous hydrogen are formed according to the following general equation:

\[ M_e + n \cdot H_2O \leftrightarrow M_e(OH)_n + n/2 \cdot H_2 \]  

(2) Under aerobic conditions, oxygen is the oxidizing agent. Metal oxides and hydroxides or hydrated oxides are also formed, but the reaction takes place without the formation of hydrogen. The general reaction is:

\[ M_e + n \cdot H_2O + n/2 \cdot O_2 \leftrightarrow M_e(OH)_n \]  

The pH value plays an important role in corrosion. However, as a consequence of the autoprotolysis equilibrium of water

\[ H_2O \leftrightarrow H^+ + OH^- \]  

The basic reactions (1, 2) remain valid in acidic and alkaline media.
Although from an energetic point of view, these two basic reactions can proceed simultaneously, the reaction with oxidation is preferred kinetically. In physiological environments, corrosion of surgical metals and alloys always proceeds according to eq. 2, i.e. aerobically. The electrochemical reaction cell consists of two conducting and electrically connected electrodes in the body fluid. The two electrodes can be dissimilar metals, or they can have different surface areas of the same metal, defects, impurities, precipitate phases, concentration differences of gas, solution or metal ions, or other variables.

At the anodic reactions (loss of electrons), the representative oxidation of metals or alloys reaction is:

\[
\text{Metal (Me)} \rightarrow \text{Me}^{n+} + ne^- \tag{4}
\]

At the cathodic reactions (consumption of electrons), the typical reduction reaction of oxygen is:

\[
\begin{align*}
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- & \rightarrow 4\text{OH}^- \\
\text{O}_2 + 4\text{H}^+ + 4e^- & \rightarrow 2\text{H}_2\text{O} \\
2\text{H}^+ + 2e^- & \rightarrow \text{H}_2
\end{align*}
\tag{5}
\]

After implantation of the medical metals or alloys, due to the lower thermodynamic stability compared to that of metal oxide and corrosion products, they are easily corroded in the physiological environment. The driving force is the different electrode potential between the oxidation and reduction reactions. The change in free energy, \(\Delta G\), associated with the electrochemical reaction can be written as [7, 18]:

\[
\Delta G = -nFE ,
\tag{6}
\]

where \(n\) is the number of electrons, \(F\) is the Faraday constant (96,500 C), and \(E\) is the cell potential. A negative \(\Delta G\) results in an increased tendency for the electrochemical reaction to occur.

According to the Nernst equation, the half reactions of corrosion are equilibrium reactions of which there is a quantitative relationship between the metal ions concentration and electric potential. Combing the standard oxidation potentials of metals and the metal ion concentration in the test solution, the practical electric potential can be obtained for metal oxidation as [3]:

\[
\begin{align*}
\text{Metal (Me)} & \rightarrow \text{Me}^{n+} + ne^- \\
E_{Me/Me^{n+}} & = E_{0Me/Me^{n+}} + (RT/nF)\ln[M^{n+}]
\end{align*}
\tag{7}
\]
For the reduction of oxygen: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

$E_{o^{\circ}_\text{c}} = 1.219 - 0.059 \cdot pH$

$^\circ c(O_2) = \text{partial pressure of } O_2 \text{ in air } = 0.2 \text{ bar.}$

During the practical measurements, the observed electric potential may be different to that evaluated thermodynamically. The reason is that the metal surface is covered by the corrosion products forming passivation films which depress subsequent corrosion attack on surgical metals or alloys. The dissolution reactions are irreversible, and only when the corrosion potential is over the critical potential, the reactions proceed. Therefore, although corrosion is favorable due to decreased energy, it can be inhibited. In addition, because of the uncertain kinetic factors, corrosion may proceed slowly.

The kinetics of implant metals or alloys corrosion is related to the environmental composition, environmental effects (such as motion or load), and other environmental factors which determine the corrosion performance of implants [7, 16].

(1) Mechanical forces imposed on the implant

After implantation inside the human body, implants are subjected to both static and dynamic loads depending on the activity of the patient, i.e. an implant introduced into a patient to repair a fractured bone must have sufficient strength to sustain and transmit the load actions resulting from joint and muscular forces. The load varies with the position in the walking cycle and reaches a peak of about four times the body weight at the hip and three times the weight at the knee. The frequency of loading and load cycles encountered over a specific time period are also important. A fast rate of walking corresponds to one complete walking cycle (two steps) per second [16, 19].

(2) Physiological environment

The human body is a harsh environment for metals and alloys being in an oxygenated saline solution with a salt content of about 0.9% at pH~7.4 and temperature of 37±1°C (98.4°F). When an orthopedic implant is surgically inserted into the human body, it is constantly bathed in extracellular tissue fluids (Fig. 3). All surgically implantable metallic materials, including the most corrosion resistant materials, undergo chemical or electrochemical dissolution at some finite rates due to the complex and corrosive environment in the human body. The body fluid is composed of water, complex compounds, dissolved oxygen, large amounts of sodium (Na⁺) and chloride (Cl⁻) ions and other electrolytes like bicarbonate and small amounts of potassium, calcium, magnesium, phosphate, sulphate and amino acids, proteins, plasma, lymph etc.
The ionic species also perform numerous functions including maintenance of the body pH and participation in the electron transfer reactions. After surgical implantation, the internal body environment is greatly disturbed, for example, disturbance of blood supply to the bones and variation in the ionic equilibrium. Normal imbalance occurs in the fluid compartment and transport of ions and non-uniform changes normally lead to disease states. From an electrochemical viewpoint, the initiation of corrosion can be due to the various conditions existing on the implant surface. These conditions may be responsible for the formation of electrochemical cells accompanied by active metal dissolution at favored localized spots at the implant-body fluid interface. There are other factors which can alter the local environmental conditions and lead to various forms of corrosion and/or failure of the implant. An orthopedic implant is considered to have failed if it is prematurely removed from the body due to severe paining, inflammation, and other reactions with the body like corrosion and wear [16, 20].

![Figure 3. Ionic composition of blood plasma, interstitial fluid and intracellular fluid](image)

**Figure 3.** Ionic composition of blood plasma, interstitial fluid and intracellular fluid [20]. Data are reproduced with permission of the authors.

**3) Tissue-implant interactions**

In addition to the hostile environment and a significant load encountered by the implant, the interactions between the materials and tissues are of prime importance. Such interactions induce corrosion and ionization of the implanted device. Corrosion can have two effects. First of all, the implant may weaken and premature failure will result. The second effect is the tissue
reaction leading to the release of corrosion products from the implant. No metallic material is totally resistant to corrosion or ionization within the living tissues. *In vivo* studies have shown that implantation of devices made of most alloys significantly increases the concentrations of various ions adjacent to the tissues. Moreover, once a foreign material is implanted, there are several ways in which the body can react unfavorably. The presence of the implant may inhibit the defense mechanisms of the body leading to infection finally necessitating the removal of the implant. If infection does not occur or is controlled, the tissue response may range from mild edema to chronic inflammation and alteration in bone and tissue structures. This necessitates that the materials used in making implants must be inert or well tolerated by the body environment. The response of the body to an inert implant leads to the development of a fibrous collagen sheath of low cellularity which encapsulates the implant and separates it from the normal tissue. This obviously matures with time, varies in thickness in its organization, and establishes a favorable relationship with the adjacent tissue (Fig. 4). The capsule may contain an area of necrosis adjacent to the implant surrounded by a region of chronic cellular infiltration. In some cases, the capsule has a well-defined boundary but in other cases, it extends irregularly and diffuses into the surrounding muscle. The thickness of the fibrous sheath depends on the corrosion resistance of the materials. The materials producing the thinnest sheaths are regarded to be best tolerated by the body [16, 21].

![Figure 4](image-url)

**Figure 4.** Generalised fibrous capsule forming in response to intramuscularly implanted metal [16]. Data are reproduced with permission of the authors.
(4) Other variables
Besides the above common factors that influence the corrosion behavior of metallic implants, there are other variables causing implantation failure [16, 21, 22].

4.1) Fatigue loading: Fatigue failure is defined as failure due to dynamic as well as cyclic loading of stress imposed on the implant. The majority of failures for load-bearing surgical implant metals or for metals used in cyclic-motion applications are fatigue failures. Many corrosion fatigue failures would not occur without the combined, complementary action of these factors. In many cases, cracks are initiated from hidden chemical attack, surface damage, minute flaws, chemical attack, and other causes.

4.2) Fretting: Wear is mechanical removal of materials during the process of relative motion between two or more contacting surfaces. Fretting corrosion involves wear and corrosion, in which particles removed from the surface form oxides that are abrasive and increase the wear rate. For joint prostheses, four types of mechanism associated with the fretting of metal components in joint prostheses: (i) abrasive, (ii) adhesive, (iii) fatigue, and (iv) corrosive. Fretting corrosion can have significance for metallic surgical implants because it offers mechanisms of metal ion release in the body and of mechanical failure.

3.1.2 Corrosion tests for NiTi alloys in simulated body fluids
Since NiTi alloy, like other implant materials, achieves passivity depending on the presence of a passive film on its surface to inhibit corrosion and decrease current flow and the release of corrosion products, it is important to identify the methods to evaluate the passive film breakdown resistance and the proneness to damage. Some authors have found that this alloy exhibits in fluids simulating the aggressiveness of human body a completely satisfactory behavior similar to that of titanium and characterized by different corrosion types which are pertinent to the currently used alloys such as pitting, crevice, galvanic, intergranular, stress-corrosion cracking, corrosion fatigue and fretting corrosion. More information on all of these types of corrosion is available in the corrosion section in Fundamentals, Testing, and Protection, Volume 13A of ASM Handbooks. The interaction between the implant materials and biological environment happens at the materials surface, often resulting in the change of biofunctionality and failure of implantation surgery. Therefore, the experimental measurements should be carried out before the biomedical devices are implanted into the body. The biological environment is classified into four categories [23]:
a. Physiological environment, which is controlled by chemical (inorganic) and thermodynamic conditions;
b. Biological and physiological environment, the physiological conditions with suitable cell products such as serum albumen, enzyme, etc.;
c. Biological environment, biological and physiological environment with suitable living cells;
d. Environment next cells, a special environment close to zoetic active cells.

It is difficult to define the environment in which the implants are placed correctly. Hence, in vitro corrosion tests are commonly carried out in the physiological or biological & physiological environment. The common test solutions are simulated body fluids. The compositions of these solutions are listed in Table 3. Ideally, the normal body solution pH value is 7.4. In case of wound or infection, the body pH can vary from 5.4 to 7.8 [7].

### Table 3. Different simulated body fluids.

<table>
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<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>142</td>
<td>141.7</td>
<td>156</td>
<td>143</td>
<td>200</td>
<td>142</td>
<td>142</td>
<td>140</td>
</tr>
<tr>
<td>K⁺</td>
<td>5.0</td>
<td>5.8</td>
<td>5.8</td>
<td>5.0</td>
<td>10</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1.5</td>
<td>0.9</td>
<td>/</td>
<td>0.8</td>
<td>/</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2.5</td>
<td>1.3</td>
<td>4</td>
<td>1.8</td>
<td>/</td>
<td>2.5</td>
<td>2.5</td>
<td>/</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>103</td>
<td>147.7</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>103</td>
<td>98</td>
<td>/</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>27</td>
<td>4.2</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>27</td>
<td>27 (acetate)</td>
<td>23 (gluconate)</td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>1.0</td>
<td>0.78</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>1.0</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.5</td>
<td>0.4</td>
<td>/</td>
<td>0.8</td>
<td>/</td>
<td>0.5</td>
<td>0.5</td>
<td>/</td>
</tr>
<tr>
<td>Glucose</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>1.0 g/L</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>pH</td>
<td>7.2–7.4</td>
<td>7.4</td>
<td>7.4</td>
<td>7.4</td>
<td>7.2–7.4</td>
<td>7.4</td>
<td>7.4</td>
<td>7.4</td>
</tr>
</tbody>
</table>
3.1.3 Corrosion behavior under different testing conditions

3.1.3.1 Corrosion studies with surface control

As far as the corrosion behavior of metals is concerned, the surface oxide layer plays an important role in influencing the corrosion properties. With the improvement of surface treatment, the surface conditions of NiTi alloy can be basically controlled. The most common method to treat NiTi surface is by electrochemical techniques as well as oxidation in various media. Some of these techniques promote the growth of passive native films that are highly adhesive and do not crack or break due to dynamic properties of NiTi alloy [1]. The methods include surface oxidization in air/oxygen atmosphere, boiling water and steam, and by chemical/electrochemical ways. Different methods result in drastically different NiTi surface chemistry and may cause different corrosion behavior.

NiTi alloy exhibits different oxidation behavior in air at temperatures below and above 500 °C. In the lower temperature range, a layer of TiO and metallic fcc and hcp nickel is formed and covered by a TiO₂ layer with NiTiO₃. The oxide scale is smooth and protective. At temperatures of 600 °C or above, rutile is formed at the air/oxide interface with an underneath layer containing NiTiO₃ when oxidized at 800 °C. The oxidation treatment close to 500 °C produces a smooth protective nickel-free oxide layer. The surface becomes rough (600 °C) and the top rutile layer has a clearly visible porous structure (800 °C) [30]. Air aging leads to only one titanium surface species, Ti⁴⁺, characteristic of TiO₂. The electrochemical treatment results in the presence of various titanium species: Ti⁰, Ti³⁺, and Ti⁴⁺ indicating incomplete surface passivation [31]. Fig. 5 presents typical potentiodynamic curves for the as-received, heat-treated, air-aged, passivated and electropolished specimens. All the treated samples show increase in pitting potential values, denoting a higher resistance to localized corrosion of treated samples. Furthermore, this improvement is most prominent in the EP samples, which are up to 800 mV with no hysteresis on the reverse scan in potentiodynamic tests [31]. The corrosion rate of the EP specimens is about 8 ×10⁻⁵ mm/year that is at least one order of magnitude lower than that of mechanically polished NiTi alloy [32]. However, the non-uniform oxide composition and partial amorphization depending on the film forming potentials inhibit the effect of corrosion resistance in the EP procedure. The presence of crystalline together with amorphous layers leads to structural heterogeneity making the surface more vulnerable to corrosion [33, 34].

Boiling in water after preliminary chemical etching in a HF/HNO₃ solution yields a surface with very low Ni concentration (occasionally 0%). Etching removes surface materials exposed to prior processing procedures and leads to various surface defects and heterogeneity. It also selectively removes nickel and oxidizes titanium. Changes of the color of the etching solution to green
Figure 5. (a) Potentiodynamic polarization curves and (b) pitting potentials for NiTi alloy stent after different treatment in simulated body fluids. (NT, nontreated; AA, air-aging; HT, heat-treated; EP, electropolishing; PA, passivated in nitric acid.) [31]. Data are reproduced with permission of the authors.

indicate leaching of Ni\textsuperscript{2+} ions. During subsequent treatments in water, a homogeneous TiO\textsubscript{2} based oxide film forms. The Ni surface concentration and Ti/Ni ratio dramatically depend on the duration of treatment in water. Longer boiling, however, results in higher Ni surface concentrations. The depth profiles of NiTi boiled in water indicate that the innermost surface layers are also depleted of nickel (<5 at. %) up to a depth of 5~10 nm. The thickness of the formed films ranges from 10 to 26 nm depending on the duration of the treatment. The potentiodynamic curves from a raw wire and a wire chemically etched in a HF/HNO\textsubscript{3} solution and boiled in water are shown in Fig. 6. The raw wire does not show a passive zone and shows a breakdown potential of about 350 mV. In comparison, the wires after chemical etching and boiling in water do not suffer corrosion breakdown up to 1~1.2 V and exhibit instantaneous repassivation in the reverse scan [1, 35, 36]. With further polarization in the anodic direction, chemically etched and boiled in water, the sample surface remains stable up to 2 V resembling the corrosion behavior of oxidized pure Ti and the surface on NiTi samples subjected only to chemical etching and repassivation. The water treatment results in a thicker amorphous oxide film, less leaching of more Ni, and consequently better cell response [37].

Previous studies have shown that the formed surface oxide layers have some differences between removal of an existing oxide layer and oxidation. Cisse has investigated the corrosion behavior and Ni ion release of NiTi alloy after chemical passivation (CP), electrochemical polishing (EP), mechanical polishing (MP), straw-colored oxide deposition (SCO), and blue-colored oxide deposition (BO) [38].

The $E_{\text{corr}}$ is an indicator of the stability of surface conditions. The most active $E_{\text{corr}}$ is obtained on NiTi (MP) and increases in the order: MP<SCO<EP<CP<BO. The $I_{\text{corr}}$ decreases by electropolishing followed by
Figure 6. (a) Potentiodynamic polarization curves and (b) localized corrosion potentials for as-received; chemically etched in HF/HNO₃ solution; and chemically etched+boiled in water raw (originally black) wires in 0.9% NaCl solution [1,36]. Data are reproduced with permission of the authors.

Figure 7. Cyclic polarization curves in deaerated Hank’s balanced salt solution of NiTi samples [38]. Data are reproduced with permission of the authors.
chemical passivation (3.51 nA/cm²), electropolishing (14.36 nA/cm²), blue-colored oxide finishing (32.34 nA/cm²) and straw-colored oxide finishing (6.76 nA/cm²) in comparison with the mechanical polishing (70.62 nA/cm²). The lowest corrosion rate is obtained on the CP samples (0.11 × 10⁻³ mm/year) and the highest one on MP (2.26 × 10⁻³ mm/year). Therefore, the \( E_{\text{corr}} \) and corrosion rate increase in the order CP<SCO<EP<BO<MP. For the different modified samples, there is a no significant difference in the pitting corrosion potential (\( E_b-E_p \)) of the various electrodes (0.53 V/SCE for BO, −0.09 V/SCE for MP, −0.12 V/SCE for CP, and −1.91 V/SCE for SCO), and the susceptibility to pitting corrosion is low due to their tiny hysteresis loop. However, for the EP sample where no hysteresis loop is formed during cyclic polarization measurement, there is absolutely no chance for pitting corrosion. This indicates that the EP sample has the most stable and corrosion resistant surface layer. Thus, the EP sample exhibits no susceptibility to localized corrosion (crevice corrosion and pitting corrosion) when placed in a living body. Ni ions released during a 25-day immersion period are highest from the SCO sample (0.002 mg/day). This Ni level is negligible compared to the daily intake of Ni in the diet and should be insufficient to cause cytotoxicity [38].

3.1.3.2 In vitro potentiodynamic and potentiostatic polarization

The role of the surface oxide film has been discussed in the previous section. With the exception of noble metals, the corrosion resistance depends on the protective oxide films rather than the intrinsic non-reactivity, and so the formation of the surface oxide film is of great importance for NiTi. Previous studies disclose controversial corrosion characteristics of NiTi alloy from unpredictable or poor to excellent and comparable to that of pure titanium [1]. Potentiodynamic and potentiostatic tests are commonly used to evaluate the corrosion resistance. For potentiodynamic tests, the polarization is conducted by a slow scanning rate in an anodic direction (600 mV/h), and a potential corresponding to 100 µA/cm⁻² current density is considered \( E_{\text{pit}} \). A modified potentiostatic ASTM F746 test has been established as a screening test to rank surgical alloys with respect to their resistance to localized corrosion (pitting or crevice) in a 0.9% NaCl solution [39]. During this test an abrupt “electrochemical damage” is achieved by abruptly applying a potential of +800 mV vs SCE during a “stimulation step”. If after 15 min localized corrosion has not been initiated, the material is considered to be immune to localized corrosion; otherwise, a voltage step back to a preselected potential is made (repassivation step). The test consists of alternating steps between stimulation at +800 mV and repassivation to a preselected potential, up to a critical potential at which repassivation does not take place. The increase in the potential value between each repassivation step is 50 mV. The pitting potential determined from
potentiodynamic tests can be more noble with respect to a static pitting potential because pitting initiation is a very slow process [1].

Aimed at the corrosion resistance of NiTi alloys, Rondelli has conducted lots of research work [42~44]. Through the ASTM potentiodynamic and potentiostatic techniques the corrosion resistance of NiTi has been measured in various simulated body fluids and compared to that of stainless steel, Co-Cr alloys, and titanium. Meanwhile, various factors influencing the corrosion behavior of NiTi, such as surface roughness, dipping in acids, pH values, alloying, stress, etc., are also evaluated. Potentiodynamic tests, implying slow potential scans without mechanical damage to the surface film, show for the NiTi a pitting corrosion resistance similar to that with stainless steel and specimens passivated by dipping in a suitable HF/HNO₃ mixture, comparable even to Co-Cr alloy and titanium. Under passive conditions, the reason that NiTi alloy exhibits higher passivity current density than other materials commonly used as implants is the high nickel content of the alloy. NiTi alloy as a cast alloy outperforms Co-Cr and stainless steel showing a low anodic current up to 800~1200 mV and no corrosion attack above that potential. However, although mechanically polished NiTi is auto-passivating, the pitting potential value is not reproducible and varies from 240 to 1000 mV [45]. In potentiostatic tests, mechanically polished NiTi reveals a localized corrosion potential inferior to that of other implant as cast alloys, as shown in Fig. 8 [1, 44].

The above mentioned work was carried out on bulk NiTi alloy. The corrosion behavior of as-received wires has also been performed that represents a type of NiTi device. Carroll points out that fresh films on the wire cross-section offer much better corrosion protection than thick films on the

![Figure 8. Modified ASTM F746 tests on mechanically polished surface in 0.9% NaCl solution at 37 °C [44]. Data are reproduced with permission of the authors.](image)
side surface of the wires, and the breakdown potentials vary in a wide range (250~1100 mV [46], which corresponds to the surface composition of wires obtained from various sources varies significantly [36]. Heat treatment can lead to the formation of precipitates, most probably of the Ni$_3$Ti phase, which cause the tremendous drop in breakdown potentials of NiTi wires [47,48]. Another interesting observation made is based on a comparison of NiTi corrosion in various media simulating extra cellular body fluids and in actual body fluids. It turns out that the Ringer’s solution (pH = 7.4) is the least corrosive medium for NiTi, and the high acidic and high in Cl$^{-}$ ion content gastric juice is the most corrosive one. In artificial saliva, NiTi wires have sufficient resistance against pitting corrosion, similar behavior to the cobalt-based alloy. However, the stainless steel wire exhibits lower pitting potential [43, 46]. Unexpectedly, the two to three times increase of breakdown potentials observed by Carroll [46] in blood (>1000 mV) compared to physiological solutions is probably due to the inhibitory action of various blood components. Brown [49, 50] has observed inhibition of fretting corrosion of metals in the presence of blood proteins. However, the electrochemical corrosion is enhanced in similar solutions. Evidently, the corrosion behavior of NiTi in blood is rather unusual and possibly related to the adsorption of a specific protein to its surface. Vandenkerckhove [51] who has conducted potentiodynamic tests combined with impedance spectroscopy using wires points out that NiTi is readily passivated even in de-aerated solutions forming surface oxide layers with semiconducting nature. The 0.02 and 0.0006 mm/year corrosion rates in aerated and de-aerated solutions, respectively, obtained in their study can be defined as excellent (0.02~0.1 mm/year) and outstanding (<0.02 mm/year) according to Fontana classification [1,52]. For NiTi wires with the same commercial name the localized corrosion behavior seems not to highly depend on their shape or the geometry of the cross section; more generally it can be remarked that no evident differences among the various NiTi wires are seen [43].

### 3.1.3.3 Galvanic corrosion

Galvanic corrosion concerns the reaction of dissimilar metals. The electrochemical reaction that results when two dissimilar metals are in contact depends on the difference in the potentials of the two metals. The less noble metal becomes the anode and the other becomes the cathode [7]. In implant design especially for orthodontic implants, a combination of materials of different nature is required. An inappropriate combination may result in galvanic corrosion and complete failure of the implants. Venugolapan [53] investigates the corrosion performance of NiTi alloy coupled with different materials. It turns out that the Tafel regions of NiTi and pure Ti are very close to each other and so coupling NiTi-Ti can be considered as a safe couple. In
comparison, the NiTi-Pt pair causes extremely high corrosion current (836 nA/cm²) and corrosion rate, which should be avoided. Similarly, combinations of NiTi-PtIr and NiTi-AuPd alloys used for radio-opaque markers also result in high corrosion currents of 780 and 608 nA/cm², respectively. The smallest corrosion currents are observed in the couplings of NiTi with stainless steel, tantalum, and titanium (35, 12, and 22 nA/cm², respectively). When evaluating the corrosion behavior of these metals in physiological use, the area ratio of the anode to cathode must be taken into account. A larger anode coupled to a small cathode could produce a low current density, which would indicate a low corrosion rate. The opposite conclusion can be made if the sizes of the anode and cathode are reversed. Wire-bracket systems are commonly used in orthodontics to move teeth. The risk of corrosion caused by galvanic corrosion between wires and brackets is also measured. Masahiro Iijima [54] has conducted a quantitative assessment on the galvanic corrosion behavior of orthodontic archwire alloys coupled to orthodontic bracket alloys in 0.9% NaCl solution and studied the effects of surface area ratios. When the NiTi alloy is coupled with Ti (1:1, 1:2.35, and 1:3.64 of the surface area ratio) or β-Ti alloy is coupled with Ti (1:2.35 and 1:3.64 of the surface area ratio), Ti initially is the anode and corroded. However, the polarity reverses in 1 hour resulting in corrosion of the NiTi or β-Ti. The NiTi alloy coupled with SUS 304 or Ti exhibits a relatively large galvanic current density even after 72 hours. It is suggested that coupling SUS 304-NiTi and Ti-NiTi may remarkably accelerate the corrosion of NiTi alloy, which serves as the anode. The different anode-cathode area ratios used in this study has little effects on the galvanic corrosion behavior. The galvanic corrosion behavior between two titanium alloy wires, NiTi and CuNiTi and three brackets: Ti, FeCrNi and CoCr have also been measured in different test solutions. The metal ions released by wire-bracket combination in the different solutions are shown in Fig. 9 [1,55].

The electrochemical investigation yields \( E_{corr} \) and \( E_{galv} \) values. In Fusayama-Meyer artificial saliva, the wires act as the anode and the brackets as the cathode. In contrast, the Elmex mouthwash solution results in different effects. The NiTi-CoCr and CuNiTi-CoCr pairs show that the bracket is the anode, but in Meridol Mouthwash solution, the \( E_{corr} \) results show that the NiTi wire (-350 mV vs SCE) acts as an anode when coupled with the three different brackets. In the CuNiTi pairs, the electrochemical results indicate that the FeCrNi and Ti brackets act as anodes while the CuNiTi wire is the anode when coupled with the CoCr bracket. After 2-month immersion in Fusayama-Meyer artificial saliva, the Ni ion concentrations are highest when the NiTi wire is coupled with the CoCr bracket (109µg/l), followed by the FeCrNi bracket (54.2µg/l), and finally the Ti bracket (16.7µg/l). Elmex Mouthwash leads to higher Ni ion releasing rate. The Ni ion concentrations are highest (586.3 µ g/l)
when this wire is coupled with the CoCr bracket, followed by the FeCrNi bracket (288 µg/l) and finally the Ti bracket (199.1 µg/l). Compared to the two previous solutions, the highest Ni ion concentration measured in Meridol is from the NiTi-CoCr pair (10,822 µg/l) where the value is 18 times higher than in Elmex® and 100 times higher than in Fusayama–Meyer artificial saliva. For the NiTi-FeCrNi pair, the Ni ion concentration is 4841 µg/l, which is 16 times higher than in Elmex and 90 times higher than in Fusayama–Meyer artificial saliva. Finally, for the NiTi-Ti pair, the Ni ion concentration is 2971 µg/l, i.e. 15 times higher than in Elmex and 200 times higher than in Fusayama–Meyer artificial saliva.

Measurements from the wire-bracket pairs using CuNiTi wire in Fusayama-Meyer artificial saliva show that Ni ion release is lowest (19.8 µg/l) for the CuNiTi-Ti combination. The Ni ion concentrations measured from the CuNiTi-CoCr and CuNiTi-FeCrNi pairs are higher by a factor of almost 2 (34.1 and 32.6 µg/l, respectively). In Elmex Mouthwash, the highest concentrations of released Ni ions are found when it is coupled with the FeCrNi bracket (232.9 µg/l). For the CuNiTi-CoCr pair, the concentration of released Ni ions is 91.2 µg/l. These values are distinctly higher than those measured in Fusayama-Meyer artificial saliva, in particular for the CuNiTi-FeCrNi pair where the Ni ion concentration is 7 times higher.
For the CuNiTi-Ti pair, the concentration of Ni ions released into the Elmex solution is negligible (6 µ g/l). In comparison, the quantity of Ni ions released into Meridol Mouth is similar to that found in Fusayama-Meyer artificial saliva, with the same classification from highest to lowest values: 44.1 µ g/l for the CuNiTi-CoCr, 39 µ g/l for the CuNiTi-FeCrNi pair and 16.2 µ g/l for the CuNiTi-Ti pair. A study on the wire and bracket in fluoride mouthwashes indicates that NiTi wires release the most ions in the presence of Meridol mouthwash while CuNiTi wires release the most ions in the presence of Elmex mouthwash. Based on the above data, the only combination that can be in orthodontic implants are NiTi-Ti and NiTi-porcelain [1].

3.1.3.4 Crevice corrosion

Crevice corrosion refers to localized corrosion occurring on a metallic material in contact with an electrolyte in a small and occluded space. 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. Data on crevice corrosion NiTi have not been published until recently. Studies conducted by Cheng [56] shed light on the crevice corrosion resistance of NiTi in Hank’s solution. Typical plots of the polarizing current density as a function of time at preselected potentials both at critical potential for crevice corrosion (E_{cc}) and immediately above are shown in Fig. 10.

**Figure 10.** Current density as a function of time for stimulated sample at preselected potentials near the critical potential for crevice corrosion: (a) NiTi; (b) NiTiCu; (c) 316L [56]. Data are reproduced with permission of the authors.
The results of the stimulation-repassivation tests in ASTM Standard F 746-04 indicate the susceptibility of crevice corrosion of the materials studied. The $E_{cc}$ of NiTi alloy is about -200 mV, which is more positive for NiTiCu and 316L, -50 and +150 mV, respectively. In comparison, Ti6Al4V and cp Ti have greater $E_{cc}$ values of over +800 mV. Therefore, the susceptibility to crevice corrosion may be ranked in ascending order as: cp Ti≈Ti6Al4V<316L<NiTiCu<NiTi. cp Ti and Ti6Al4V are very resistant to the initiation of crevice corrosion in Hanks’ solution. The presence of a large fraction of Ni in NiTi and NiTiCu, in addition to microstructural differences, significantly lowers the resistance to electrochemical stimulation. Cu addition to NiTi has a beneficial effect on improving the repassivation capability, possibly due to the redeposition of Cu inside the crevice. Though the materials behave differently in resisting the initiation of crevice corrosion, they corrode with similar rates once crevice corrosion has been initiated.

3.1.3.5 Mechanical scratch corrosion

Scratch corrosion test is used to measure the repassivation property of metal surface oxide film. Pessal [40] has proposed a method of measurement of the pitting potential that does not depend on the pit initiation time. In this method, the passive surface is scratched mechanically at various potentials starting from a potential lower than the pitting potential measured by the potentiodynamic method. The scratch results in a sharp increase in the anodic current followed by either rapid lowering to the starting potential value (for potentials lower than pitting) or continuous increase (for potentials higher than pitting). Whether or not this type of scratch can be applied in the body is questionable [41], but this test gives an idea about the repassivation ability of the materials. A scratch produced automatically by a ceramic stylus on electropolished NiTi surface at potentials not higher than +300 mV repassivates easily and shows superior scratch healing ability compared to stainless steel [1,53,56]. However, Rondelli [43] pointed out pitting potentials of NiTi alloy, determined by potentiostatic scratch tests ranging between +190 and +280 mV in physiological solution is lower than that of AISI 316L stainless steel. Data on manual scratch tests indicate that raw processed wires with black oxide have very low pitting potentials after a scratch is applied (~30-0 mV). In comparison, the treated wires by chemically etching and chemically etched with boiled in water have greater pitting potentials, and scratch repassivates at potentials in the (+100~200) mV range when scratch is also applied by hand [42]. The data indicate the pitting potentials of scratched wires whose surfaces are treated in various manners are similar. According to Kruger [57], repassivation potential of the oxide film critically depends on the applied load. That is why a slight difference in pitting potentials between various authors can be easily assigned to the
different load applied during automatic and manual scratch. The more aggressive corrosive action of artificial saliva and saline solutions compared to the Hunk’s and Ringer’s solutions can also contribute to the observed difference in repassivation potentials, and any pH (1.5, 3.0, 7.8) decrease has limited influence on the pitting potentials of NiTi alloy [43]. NiTi wires have corrosion resistance that is the same or superior to stainless steel and inferior to that of pure Ti in scratch tests. However, one has to remember that rapid repassivation observed in the case of Ti indicates a very reactive bulk. Despite this argument, the fact that NiTi repassivates much slower than a Co-Cr base alloy and Ti remains true. The ways to improve the rehealing capacity of the bulk of NiTi should be explored to make material safer in the body [1].

3.1.3.6 Corrosion behavior under stress

Another important aspect of the behavior of implant alloys is their corrosion performance under static stress and dynamic loading-unloading conditions in the body [1]. Static stresses affect the corrosion behavior of 316L stainless steel, Ti-6Al-4V, and Co-Cr-Mo alloy. Loading even within the elastic limits results in enhanced metal ion release [58, 59]. Loading past the yield point can definitely cause stress-enhanced release (SER), which is contributed to the lowering of breakdown potentials and increase of corrosion current. Moreover, stressed implants have more fragile passive layers which are more vulnerable to disruption by mechanical means than would be the same surface without stress [58]. There is little information about corresponding systematic studies on NiTi. Few known efforts are to measure the corrosion behavior of NiTi after various deformation [36, 59, 60] and under loads [42], though these studies could simulate the actual conditions of a dynamic implant working in the body under stress sometimes being deformed beyond the elastic limit. By use of potentiodynamic and potentiostatic ASTM F746, the effect of strain on corrosion behavior of superelastic NiTi has been studied [42]. No effect of 4% strain on potentiodynamic pitting potentials and localized corrosion potentials is observed, moreover, the presence of stress-induced martensite does not appreciably modify the localized corrosion resistance of NiTi wire, which is shown in Fig. 11. This result is of great importance because it demonstrates the resistance of the NiTi surface film to the damaging tensile stress that triggers stress corrosion cracking. This fact also suggests that the martensitic mechanism of deformation does not generate chemical heterogeneity sufficient to affect NiTi corrosion resistance. The diffusionless nature of thermoelastic martensitic transformation resulting in similar chemical compositions of martensite and austenite phases and the very small volume change during the transformation (0.5% at B2 $\Rightarrow$ B19 phase transformation and 0.2% at B2 $\Rightarrow$ R, rhombohedral phase transformations
are additional factors that contribute to the stable corrosion behavior of NiTi in two phase states. The fact that sometimes the corrosion resistance observed in martensitic and austenitic states in NiTi alloys of different compositions differs is related to the presence of precipitates rather than the crystal structure of the matrix. Thus, based on microscopic studies, Dutta concludes that NiTi$_2$ precipitates act as preferential sites for pit initiation in an equiatomic NiTi alloy and in an alloy slightly enriched by Ni [62]. NiTi alloys contain more than 50.5 at. % Ni show Ni$_3$Ti precipitates [63]. These precipitates evolve during annealing of the Ni52Ti48 alloy at ~750°C and instead of the difference in corrosion between martensite and austenite NiTi phases, they are responsible for the slightly higher corrosion rate observed in the Ni52Ti48 alloy compared to the equiatomic NiTi alloy, as shown in Fig. 12. Under the combining effect of load and pH value, NiTi and stainless steel wires in acidic artificial saliva show similar active-to-passive transition behavior. The mean $E_{\text{pit}}$ value and passive range for NiTi wire are much lower than those of stainless steel wire ($p<0.001$), regardless of the pH and load value. Decreasing the pH value leads to a decrease in the $E_{\text{pit}}$ and passive range for stressed NiTi and stainless steel wires ($p<0.05$). Furthermore, a more significant decrease ($\sim 600$ mV) in mean $E_{\text{pit}}$ value is observed from the stressed stainless steel wires when the pH is decreased from 5 to 2 compared with the stressed NiTi wires ($<210$ mV), regardless of the load. The load has no statistically significant influence on the $E_{\text{pit}}$ value for NiTi and stainless steel wires ($p>0.05$), which is also supported by Rondelli [1, 64, 42].

![Figure 11](image_url)

**Figure 11.** Pitting potentials of orthodontic wires obtained by potentiodynamic (a) and modified potentiostatic ASTM F746 (b) tests in deaerated 0.9% NaCl solution at 40°C in unstrained and strained up to 4% in tension mode wires [36]. Data are reproduced with permission of the authors.
Figure 12. Effects of strain induced by cold drawing (percent of the reduction in sample thickness) on the corrosion rate of pure Ti, Ni$_{52}$Ti$_{48}$ (austenitic), NiTi (martensitic) and TH-10 (TiNiMo based alloy) in 1% mass HCl solution [1,63]. Data are reproduced with permission of the authors.

Prymak [65] has investigated the fatigue of orthodontic NiTi and CuNiTi wires in different fluids under constant mechanical stress through dynamic mechanical analysis (DMA). The failure times are given in Table 4. NiTi wires have a longer lifetime in air compared to CuNiTi wires. Upon immersion in liquids, NiTi and CuNiTi wires show lifetimes of approximately the same order of magnitude. In comparison, steel wires have a longer lifetime in air and in most solutions. Besides, the chemical nature of the immersion fluid does not have a strong influence on the lifetime of NiTi and CuNiTi wires.

Table 4. Results of dynamic mechanical analysis: average time (min) for the wires to fracture within different environment (37 °C) [65]. Data are reproduced with permission of the authors.

<table>
<thead>
<tr>
<th>Environment/solution</th>
<th>Wire type</th>
<th>Ti18 1.25</th>
<th>CuNiTi 18</th>
<th>CuNiTi 19.25</th>
<th>CuNiTi 17.25</th>
<th>Steel 17-25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td></td>
<td>24.6 (11)</td>
<td>22.5 (41)</td>
<td>66 (11)</td>
<td>48 (7)</td>
<td>298 (306)</td>
</tr>
<tr>
<td>Distilled water</td>
<td></td>
<td>32.5 (4)</td>
<td>39.3 (12)</td>
<td>60.5 (56)</td>
<td>23.3 (45)</td>
<td>295 (42)</td>
</tr>
<tr>
<td>0.85 mM citric acid</td>
<td></td>
<td>39.3 (38)</td>
<td>28.3 (22)</td>
<td>66.3 (33)</td>
<td>26.7 (42)</td>
<td>290 (80)</td>
</tr>
<tr>
<td>150 mM NaCl in water</td>
<td></td>
<td>55.4 (88)</td>
<td>21.0 (26)</td>
<td>78.5 (66)</td>
<td>23.8 (29)</td>
<td>63.6 (54)</td>
</tr>
<tr>
<td>Artificial saliva</td>
<td></td>
<td>70.8 (4)</td>
<td>23.2 (11)</td>
<td>66.7 (27)</td>
<td>22.5 (18)</td>
<td>110 (14)</td>
</tr>
<tr>
<td>Fluorinated saliva</td>
<td></td>
<td>107 (3)</td>
<td>27.8 (14)</td>
<td>31.7 (21)</td>
<td>22.5 (18)</td>
<td>189 (48)</td>
</tr>
</tbody>
</table>

The frequency of the experimental deformation was 5 Hz. Therefore, the numbers given in minutes have to be multiplied by 200 to obtain the number of cycles until breakage. Standard deviations are given in parentheses.
3.1.3.7 Corrosion behavior of plastically deformed NiTi

The studies of the effects of deformation induced by cold drawing on the corrosion behavior of pure Ti, binary NiTi and multi-component Ti-Ni-Mo show that in the non-deformed state, pure Ti has the lowest corrosion rate almost similar to that of Ti-Ni-Mo alloy and significantly lower than that of binary NiTi alloy, as shown in Fig. 12 [55,66]. However, deformation causes the corrosion rate of pure Ti to increase with strain gradually, and in comparison, the corrosion rate of NiTi and Ti-Ni-Mo alloys remains stable up to 15% strain, and the open circuit potential becomes nobler after deformation with a maximum increase at about 7% strain. Itin [59] points out that the corrosion rate of the Ni52Ti48 austenite alloy deformed up to 70% by cold drawing does not change significantly compared to the non-deformed one and the total loss of its mass after 370 days of immersion in 1%HCl solution does not exceed 0.5%. The stable corrosion resistance of NiTi based alloys deformed in superelastic (ε < 8%) and plastic regimes is a unique feature of shape memory alloys that may greatly benefit implant service [1].

The effect of various degrees of deformation on corrosion behavior of NiTi has been investigated at specific locations [60]. Deformation (in compression mode) of the Ni48Ti52 alloys in the plastic regime >10% results in a tremendous improvement in corrosion resistance. The corrosion current density exhibits a tendency to decrease with increasing deformation. In contrast, the corrosion potentials shift to higher potential values with increasing strain up to 7.4% cold drawn alloys (elastic limit). The observed improvement in the corrosion results from the changes in the microstructure of martensite. At strains of up to 8%, the originally randomly oriented distribution of martensite plates evolves by a process of variant selection into a distribution where only one crystallographic martensite variant survives. Hence, the development of a single martensite variant provides more homogeneous bulk materials with a smaller area of grain boundaries. Any further deformation in the plastic region would normally result in internal stresses, particularly near precipitates, and preferential anodic dissolution at internally stressed sites. However, in the case of NiTi, the corrosion current drops further, and open circuit potentials improve within the plastic region of deformation. Finally, at about 25% strain, the polarization curve becomes similar to that of pure titanium in the unstrained state [1,60].

In various ways the corrosion behavior of annealed NiTi as a function of applied strain is similar to that just described for the cold drawn condition. Nevertheless, it is found that the annealed material deformed into the fully plastic region (24.4%) is significantly more corrosion resistant than the cold worked alloy deformed to similar conditions (24.5%). Similarly, increasing plastic deformation causes a transition region where the OCPs shifts toward more noble values. In particular, the outstanding corrosion resistance of the
annealed sample deformed to 24.4% deserves special considerations. The effect of strain on the corrosion current density of annealed samples is illustrated in Fig. 13. Here again one can observe a dramatic and rapid decrease in the corrosion current density with increasing strains that is lowest for the specimen deformed to 24.4%. All specimens but the ones annealed and strained to 24.5% exhibit severe crevice corrosion. Pits are generated at intermetallic particles (Ti2Ni) around the shielding produced by the teflon holder [60].

Thus, NiTi exhibits quite unique corrosion behavior after deformation in superelastic and plastic regimes in various deformation modes. Upon deformation in the tensile mode, the most damaging to the corrosion resistance of metals, NiTi maintains stable corrosion parameters [42], and in compression mode, its corrosion resistance remarkably improves especially after 25% strain [60]. It is not yet clear how the NiTi corrosion behavior will be modified upon bending when both tension (on one side of the sample) and compression (on the other side) are involved [1].

![Figure 13. Effect of straining on the corrosion current density of the cold drawn and annealed NiTi alloys [60]. Data are reproduced with permission of the authors.](image)

4. **In vivo corrosion of NiTi alloys**

Compared to the *in vitro* simulated body environment, the real body environment is more complicated and harsh. The body fluid comprises water, complex compounds, dissolved oxygen, large amounts of sodium (Na⁺) and chloride (Cl⁻) ions, and other electrolytes like bicarbonate and small amounts of potassium, calcium, magnesium, phosphate, sulphate, amino acids, proteins,
plasma, lymph, etc. Moreover, under the effects of human metabolism, the environment may change momentarily causing different materials and body reactions. Studies have indicated that the \textit{in vitro} corrosion rate of magnesium is about 4\textasciitilde5 times greater than that \textit{in vivo} [67]. Therefore, in order to investigate the bio-safety of NiTi in body clearly, short- and long-term implantation must be conducted. Due to the different surface condition of NiTi implants, controversial results have been obtained. During implantation, the oxide layer formed on a Ti implant grows and takes up minerals and other constituents of biofluids and these reactions in turn cause remodeling of the surface. Hanawa have found that the surface oxide film on implants consist of two layers, calcium phosphate and titanium oxide. In other words, calcium phosphate forms on a passive oxide film. This film is thicker on pure titanium than on titanium alloys (including NiTi), and the Ca/P value of the film is close to that of hydroxyapatite. The calcium phosphate formed on NiTi or Ti6Al4V is less similar to hydroxyapatite [68]. The \textit{in vivo} corrosion database on NiTi in general is limited.

The majority of observations based on short-and long-term implantation agree that NiTi implants do not show any corrosion signs in the body. However, occasionally slight corrosion is noticed on the surface of the retrieved implants. Slight marks of corrosion after 60 weeks of implantation have been observed in intramedullary NiTi rods [69]. Cragg has also found minimal corrosion on intraluminal NiTi stents implanted in the iliac arteries of sheep for 6 month and pitting was the predominant type of corrosion. Based on the size of the pits, the mean pit penetration rate is estimated to be 0.046 mm/year that is in agreement with that obtained by Vandenkerckhove [32]. This corrosion rate falls into the range of “excellent” according to Fontana’s classification [70]. However, it may not be satisfactory for the delicate NiTi devices made from a tiny NiTi wire of <0.2 mm diameter [1].

The corrosion resistance of the alloy and toxicity of the individual metals that make up the alloy are the main determinants of biocompatibility. Hence, the biocompatibility of NiTi has its own characteristics that are different from those of nickel or titanium alone. Owing to corrosion, nickel and titanium ions may dissolve from NiTi implants. To understand the possible host effects of NiTi, it is very important to understand the effects of its components, especially Ni.

There have been discouraging results obtained from NiTi stents retrieved from patients after service in the body with duration from 5 to 43 months. There are surface alteration, pitting corrosion, dynamic stress crack corrosion, and fracture. Furthermore, the absence of visual changes on the surfaces of retrieved NiTi implants does not necessarily mean that no surface degradation occurs. The increased concentration of Ni ions detected in blood and organs away from the implanted site indicates that degradation of NiTi surface takes
place even in those cases when no visual corrosion signs are observed. Castleman has first observed Ni release from NiTi in the case of implants in beagles in’s study [71]. By means of neutron activation analysis, the Ni ions concentration in bone adjacent to the implants is found to be 28±40 ppm and 9±13 ppm in remote organs after implantation for several months. These concentrations are detrimental to the body. Based on atomic absorption spectroscopic analysis, Matsumoto has detected Ni after NiTi implantation into rabbits [72]. The Ni blood concentration reaches the level of 28±11 ppb that is twice as high as that of 13±5 ppb in the normal state. After four weeks, the Ni concentration increases four times to 140±43 ppb in the kidneys, two times in the liver to 40±18 ppb, and ten times in urine to 90±35 ppb. However, the surface conditions and sterilization procedures are described neither in Catleman’s nor in Matsumoto’s studies. Due to the lack of sensitivity in the experiments, the Ni release results cannot be used to directly judge the biocompatibility of NiTi alloy [73].

Recently, Ni has been detected again on rats by use of graphite furnace atomic absorption spectroscopy. Not statistical difference is found between the Ni concentrations induced by NiTi (MP, autoclaved for 30 min at 121°C) and stainless steel (EP, autoclaved) implants. The highest Ni concentration of 1.4 ±1.0 ppm (dry weight) after 26 weeks of implantation is observed in the kidneys but it decreases after 60 weeks. On the other hand, the Ni ion concentration in the spleen increases between the 26th and 60th weeks from 0.17±0.06 ppm to a level that is a few times higher (1.14±1.1 ppm). Ryhänen has also reported a significant increase in the Fe content in the spleen upon exposure to stainless steel [1, 69, 74].

It must be pointed out that the absolute Ni concentrations with or without implants differ from one animal to another. Various authors have also reported numbers that may differ by as much as factor of ten. There are also some variations in the concentrations among different animal species. Hence, precaution must be taken to compare results from different experiments but a comparison between the Ni concentration before and after implantation in the same set of experiments is more reliable. The cited data on implantation in various animals unanimously suggest that Ni is indeed released from NiTi implanted inside the body. However, it should be pointed out that Ryhänen and probably Castleman and also Matsumoto have used NiTi implants with mechanically polished surface [1]. One has to start from this surface condition and then add many other steps to make the NiTi surface completely biocompatible. In almost all the comparative biological studies, NiTi is used in a mechanically polished finish state and stainless steel in the electropolished state. Nonetheless, the observed results for NiTi and stainless steel are usually similar, implying that NiTi performs as well as stainless steel even without special surface treatment. Application of preventive surface treatment tends to
make the surface more biocompatible. Another piece of evidence on NiTi corrosion performance in the body has been obtained from an in vivo corrosion study on dogs [75]. The as-received and “converted” to amorphous surface state NiTi and stainless steel wires are tested in forty dogs using open circuit potential and cyclic anodic polarization (potentiodynamic) measurements, which may introduce high corrosion resistance in vivo. However, the dramatic effect observed in the pictures of corroded “polycrystalline” wires must be interpreted carefully taking into account the analysis and experimental conditions. The breakdown potentials observed in vivo on NiTi wires with polycrystalline surfaces in the range 200~600 mV are in agreement with those obtained in vitro on as-received raw wires [1,37,42]. In fact, NiTi with polycrystalline and amorphous oxide films leads to very low current densities ($10^{-6}$~$10^{-8}$) A/cm$^2$. However, exposure of the 0.05 mm as-received NiTi wires for at least two hours during the potentiodynamic scans to potentials 2~5 times higher than their breakdown potentials inevitably results in severe corrosion and even complete wire dissolution. Another circumstance to consider is related to that this in vivo experiment has been conducted under rather unrealistic conditions at which the potential is set at +1.0 V and graft itself may also be a cause of the accelerated corrosion [1].

5. Porous NiTi alloy

Solid NiTi based SMAs have been used widely in biomedical orthopedic and orthodontic implants for many years. However, the applications are restricted due to their biomechanical incompatibility, for instance, higher Young’s moduli and mechanical properties compared with that of natural bone. More recently, porous titanium-nickel (PTN) (Fig. 14) has been introduced for tissue repair and reconstruction applications. PTN is commonly produced by self-propagating high-temperature synthesis with the use of an equivalent mix of titanium and nickel powders. Porous NiTi is a promising biomedical implant material due to some unique features. Its unique porous structure can permit bone tissue in growth, body fluid transportation, and firm fixation of prosthesis. The Young’s modulus and mechanical properties are a closer match to those of human body tissues thus solving the problem of “stress shield” when traditional solid metals are implanted. Its special superelasticity also matches the stress-strain behavior of bone tissues [76, 77].

There have not been a lot of published data on the corrosion behavior of PTN. The effect of the pores on corrosion characteristics of PTN in simulated body fluid has been investigated [76]. The potentiodynamic polarization tests show the breakdown potentials for PTN, 245±17 and 578±16 mV for pore sizes of 200 and 650 µm respectively in Hank’s solution. They are much smaller than that of the dense counterpart in a physiological solution. Similar results have been obtained by Schrooten [77]. The PTN with a pore diameter of
Figure 14. Photograph of a PTN interbody fusion device with inter-connected porosity (left) and a TiAlV implant for autologous bone filling (right) [77]. Data are reproduced with permission of the authors.

230±130 µm and a porosity of 65±10% has a breakdown potential of 270±70 mV. Moreover, the passive current density values measured from the PTN specimen are higher than those from the dense metal. The complicated intertwined three-dimensional permeable porous structure results in a larger true surface area compared to solid NiTi. The corrosion behavior may involve corrosion between crevices in the form of pores and restrictions to the flow of fluids can cause an autocatalytic process by which localized corrosion propagates. Compared to the PTN specimens produced by self-propagating high-temperature synthesis with pore size of 100 µm, the latter shows a lower breakdown potential of 173 mV [78]. The synthesis technique also influences the corrosion resistance of porous NiTi. The samples produced by powder sintering show the lowest breakdown potential of 60 mV in 0.9% NaCl and it is probably due to the complex surface [79]. The mass loss from sintered NiTi is indeed a few times higher than that from the as-cast alloy (Fig. 13, curve 1). Itin relates the high corrosion rate of porous NiTi to the larger surface area of porous samples and their specific surface morphology [80]. However, there is a large difference between the corrosion rates of sintered NiTi samples and ones manufactured using ignition synthesis, as shown in Fig. 15. The latter shows corrosion rate almost similar to that of as-cast NiTi alloy (curves 2 and 3). The better corrosion performance of porous NiTi by ignition synthesis is attributed to higher concentrations of gaseous admixtures like 0.15 weight % of oxygen, 0.14 weight % carbon and 0.02 weight % nitrogen compared to sintered alloy. These elements are present in the alloy basically in the form of surface films like Ti₄Ni₂O(C,N). Another factor that may reduce the corrosion rate in an alloy synthesized by ignition is related to its lower surface area due to the higher portion of big pores [1, 80]. Although the breakdown potentials are different, the $E_{corr}$ values of PTN are lower in stimulated fluids, especially for the PTN by Schrooten which is around -670 mV in HBSS. All the PTN
Figure 15. Corrosion rate (loss of the mass, Δ m/mo, %) of various NiTi alloys. 1-interred, 2-btained using ignition synthesis, 3-as cast alloy [59]. Data are reproduced with permission of the authors.

samples show instant repassivation and a protection potential that is nobler than the $E_{\text{corr}}$. The PTN corrosion rate (<0.02 mm/year) is regarded to be excellent. The galvanic (direct coupling) corrosion between PTN and Ti6Al4V devices (surface ratios 2/1 and 1/1) has also been investigated. The PTN-Ti6Al4V couple shows a steady-state value around -220 mV ($E_{\text{couple}}$) and a current density of <10^{-7} A/cm^2 ($I_{\text{couple}}$). No specific increase in the current density due to galvanic coupling is indicated confirming the stable behavior of the PTN-Ti6Al4V coupled device.

Assad has reported Ni ion release from PTN implanted in the lumbar region of sheep after 3, 6, and 12 months. No evidence of surface corrosion is observed either pre- or post-implantation. Using inductively-coupled plasma mass spectrometry (ICPMS), the amounts of released nickel ions are determined and displayed in Fig. 16. The nickel levels in blood are observed to be within acceptable levels at all times. The nickel contents in tissues adjacent to the PTN implant as well as in the detoxification and remote organs are found to be similar to those in the PTN-treated and control sheep. Furthermore, the classical skin sensitization assay (Buehler patch test) in guinea pigs, rabbit intracutaneous test, and systematic injection test in mice show good results. The Buehler patch test in guinea pigs reveals no significant change in skin reactions such as erythema or swelling between the induction and the challenge period. In the rabbit intracutaneous irritation test, no irritation or sensitization reactions are observed in the saline-extracted PTN samples. Negligible to slight irritation is observed at some of the sites involving PTEN samples extracted in cottonseed oil, but the resulting primary irritation index is similar to the one elicited by the blank solution itself. Finally, no toxic symptoms are observed with any of the mice injected with
Figure 16. Ni contents at different regions over the 12-month post-surgery recovery time: (a) PTN-adjacent tissue; (b) Remote organ; (c) Blood; (d) Detoxification organ [81]. Data are reproduced with permission of the authors.

porous titanium-nickel extracts during the acute systemic toxicity test. Based on these results, porous titanium-nickel is considered to be a non-sensitizing, non-irritant, and non-toxic biomaterial for medical applications [77, 81].

6. Conclusion and outlook

More than twenty years ago, Castleman suggested that the development of NiTi as a biomaterial may take a long but its future looks bright [82]. In the following twenty years, a large number of papers on its biomechanical properties, biocompatibility, and biofunctionality from the perspective of orthopedic and orthodontic implants have been published. Based on the physical-chemical and corrosion performance, it can be concluded that NiTi is indeed a superior biomaterial possessing good biomechanical functionality and biocompatibility. The surface oxide layer plays an important role in determining the corrosion performance of NiTi alloy. Surface treatment falls into three categories. Removal of the surface and oxide yields smooth surfaces. Chemical, electrochemical, or thermal oxidation produces passive films of desired thickness, structure and composition making the material corrosion resistant in a biological environment. The layers also act as barriers impeding release of toxic nickel ions. However, the results produced by different treatments demonstrate that our understanding of NiTi surfaces is still preliminary. Electropolishing for selective elemental dissolution of Ni from
NiTi or smart anodization to form pure TiO$_2$ are presently under investigation. Chemical deposition of highly protective layers using organic solutions or ionic liquids is also under development [83].

In ambients of different physiological media that are neutral or close to neutral at a moderate temperature (37 °C), NiTi alloy shows extremely low corrosion rate that is excellent according to Fontana’s classification [70]. However, most tests have been carried out under static conditions but the \textit{in vivo} conditions are dynamic. Hence, successful development and application require dynamic tests under simulated conditions. However, the corrosion behavior of NiTi under dynamic conditions including stress, after deformation, and under loading/unloading conditions has not been investigated extensively. For example, NiTi vascular implants inserted in the heart may be subjected to ~30 million loading/unloading cycles annually. It is not certain whether currently available materials have the proper properties such as corrosion resistance. In addition, Ni ion release under such dynamic conditions must be controlled.

The effect of solution composition on the breakdown behavior under physiological conditions depends primarily on the chloride concentration. Bicarbonate is known to shift the breakdown potential, and fluoride ions cause rapid breakdown of the protective passivation layer on titanium and its alloys [84, 85]. Body fluids consist of water, complex compounds, dissolved oxygen, large amounts of sodium (Na$^+$), chloride (Cl$^-$) ions, and other electrolytes like bicarbonate and small amounts of potassium, calcium, magnesium, phosphate, sulphate and amino acids, proteins, plasma, lymph, etc [7, 16]. The corrosion mechanism of NiTi in body fluids of different compositions and proteins should be studied.

Porous superelastic NiTi developed for medical applications is an attractive implant material in orthopedics, spine surgery, soft tissue reconstructive surgery, and maxillofacial surgery [1]. Recent studies on implantation of porous NiTi indicate good biocompatibility and biofunctionality [1, 86, 87]. The requirements for early bone ingrowth, reliable fixation, modulus matching, and need to eliminate the brittleness of ceramic implants continue to spur the development of new NiTi -based composite materials like porous NiTi/porcelain and porous NiTi /hydroxylapatite [1,88]. However, the corrosion behavior of porous NiTi materials must be studied in details under stimulated or real body fluids.

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