STRESS CORROSION CRACKING in BIOMEDICAL (METALLIC) IMPLANTS

TITANIUM-NICKEL (TiNi) ALLOY

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ABSTRACT

The potential of TiNi alloy as a material of choice for biomedical devices are still being investigated. This paper reports the unique properties of TiNi as well as the fundamental principles and general roles that mechanical stress plays in corrosion cracking and degradation process of metallic materials in the body environment. Later part of the report discusses the application of TiNi as endovascular stents and some studies and researches on the various methods of improving TiNi device fabrication to achieve longer device lifetime.

1. Introduction

Metals that are currently being used as biomaterials are gold (Au), cobalt-chromium (CoCr) alloys, type 316 stainless steel, titanium (Ti), titanium-nickel alloys (TiNi - Nitinol) and silver-mercury alloys (AgHg). These metals are chosen based on their material properties and biocompatibility. This report focuses on TiNi as a potential material of choice for biomedical implants.

Many factors have to be considered before any particular material can be chosen, fabricated and used as a biomedical material. Biocompatibility and considerations have to be made on how implanted TiNi in the human body will react to the environment it is surrounded in. The human body can be very harsh to the implanted material and though TiNi has relatively good mechanical and chemical properties and is highly corrosion resistant as a material, the environment will slowly but gradually breakdown the TiNi implantations. Reaction and side effects of the products resulted from the material corrosion to the human body has to top the list of considerations during material selection.

Ni ions in TiNi alloy are highly detrimental to the body. However, the many characteristics of TiNi alloy as biomaterial supersedes the consequence that is believe can be controlled. A wide range of unconventional mechanical properties of TiNi can be obtained through modifications to the chemical constitution as well as optimization of the preparation methods using different heat and mechanical treatment.

2. Principle and Mechanism

2.1 Titanium Base Metal

There are 4 grades of unalloyed Ti. These grades are classified by the amount of impurity present in the metal. Among the most common impurity types present are oxygen (O), nitrogen (N) and iron (Fe). O in particular, has a large influence on the ductility and strength of the Ti metal. In the electrochemical series[1], Ti has a potential of –1.63V and is considered a base metal. Ti forms a passivating layer around its surface and thereafter, remains passive and un-reactive under physiological conditions. This passivation gives Ti its very high corrosion resistance property.

2.2 Properties of TiNi

TiNi is a shape memory alloy and has a unique superelastic deformation behavior. It has high ductility and recoverable strain, and good fatigue strength with very high resistance to low-cycle fatigue. These properties can be attributed to the martensitic transformation of TiNi alloy and can be explained as follows.

[1] Electrochemical Series measures the potential difference of the metal against a standard reference hydrogen electrode. he position of a metal in the series indicates the order with which metals displace each other from compounds and a guide to reactivity in aqueous solutions.

The shape memory effect of TiNi is a result of the athermal martensitic transformation that occurs over a temperature range. A uniform lattice shear transformation occurs without a change in the composition of the material. As temperature is increased, loading deformation of TiNi will recover to its original shape through the martensite to austenite transformation.

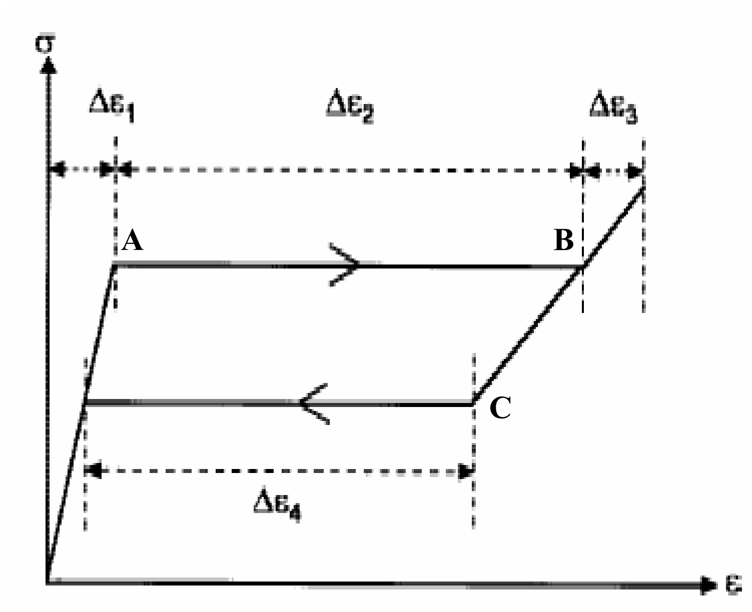

Figure 1: Schematic illustration of superelastic effect

TiNi will exhibit a superelastic effect at temperature slightly above the austenite finish temperature (Figure 1). When stress is first applied on TiNi alloy, a large stress is need to increase a small amount of strain, $\Delta\varepsilon_1$ until point A. Following this transformation, a very small change in stress will cause a large strain, $\Delta\varepsilon_2$ transformation to occur. At this stage, martensite laths nucleate and grow with the preferred martensite variant. Martensitic transformation will complete at the end of this stage at point B after which elastic deformation will continue over the strain range, $\Delta\varepsilon_3$ until yielding or unloading. When stress is decreased, elastic recovery will follow the reverse path along $\Delta\varepsilon_3$ and then continue on the same recovery slope until the point C. Further unloading will see recovering along the previous crystallographic path and volume fraction of martensite decrease over $\Delta\varepsilon_4$ and the parent phase will be recovered and restored to the original undeformed material.

The temperature at which the transformations describe above can be controlled by changing the TiNi alloy composition and the way we process the alloy (prior cold work, heat treatment or quenching cooling rate).

2.3 Corrosion of Metallic Implants

In general, abrasion, wear and tear causes biomaterial implants to breakdown. The other mechanism that can cause implants to fail is aqueous corrosion. Corrosion is unavoidable because the body is an aqueous medium containing various ions and organic substances, forming an electrolyte solution. Depending on the amount and type of ions present and the body temperature, the pH of the aqueous will vary. pH of the body aqueous is typically around 7.4 at normal body temperature of 38^0C. The ions present can be grouped into anions (negative ions) and cations (positive ions). Main anions present are chloride, phosphate, bicarbonate and dissolved oxygen. Cations on the other hand, consists mainly of principle ions Na^+, K^+, Ca^{2+} and Mg^{2+}, and many other cations in smaller amounts. These ions react electrochemically with the surface of metallic biomaterials to cause corrosion.

2 reactions always take place concurrently whenever there is corrosion: the anodic and cathodic reactions. The anodic reaction involves oxidation of the metallic implant and yields metallic ions. The cathodic reaction is dependent on the nature of the electrolyte (the body aqueous). It involves reduction process and reacts with the electrons generated from the anodic reactions. The

rate of anodic reaction must equal the rate of cathodic reaction for electrochemically-based metallic corrosion to occur. With this basic principle in hand, we can prevent corrosion from occurring if we prevent either oxidation or reduction to occur.

Corrosion can be observed on x-ray films as cracking or flaking. The by-product can result in many adverse affects to the region of implant and in some cases, the health of the patient. Some flakes that peel off the metal surface can embed in tissues and cause pain and swelling. Metals chosen for implants must therefore be biocompatible to the human body in order to prevent toxicity.

2.4 Rates of Corrosion

The physiology of the human body functions to prevent and remove any foreign substances that are present in the body. When foreign substances, in this case metallic implants are detected, the body secretes antibodies (proteins) which act as powerful oxidizing agents. These proteins concentrate around the implant material and absorb into the biomaterial. This attacking mechanism results in corrosion rate enhancement of the metallic implants.

Besides the influence of the environment, the rate of corrosion is also dependant on the type of materials used. From thermodynamic point, the position of the metal in the electrochemical series indicates the order with which the metal will be displaced from the compounds. The higher the position of the metal in the series, the more stable and un-reactive, hence the lower the corrosion rate will be.

2.5 Mechanism of Stress Corrosion Cracking

There are many mechanisms of corrosion. Among them are stress corrosion cracking, fatigue corrosion, fretting corrosion, pitting corrosion, localized corrosion, crevice corrosion, intergranular corrosion and galvanic corrosion. This report focuses on the stress corrosion cracking behavior of biomedical implant.

Interactions between corrosion and local crack tip plasticity conditions

Experimentally, stress corrosion cracking can be observed by the decrease in strain to fracture ratio. This experiment can be carried out in a corrosive induced environment using strain tensile test. Hydrogen-dislocation interactions were investigated by Galerie et al. [1] and the corrosion enhanced plasticity model (CEPM) was proposed to describe the elementary mechanisms governing the stress corrosion cracking process (Figure 2) at an intentionally created crack of 1µm length on austenitic stainless steel (face centered cubic structure) surface in $MgCl_2$ solution. It is believed that TiNi behaves the same way as stainless steel but probably at different corrosion rate.

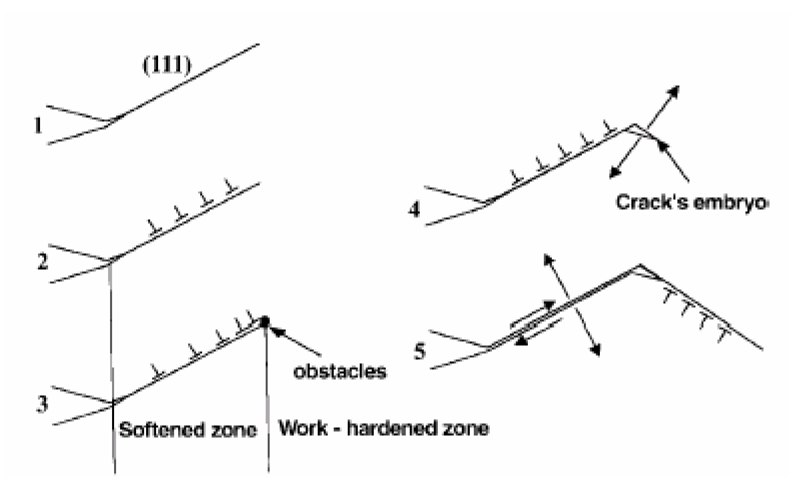

Figure 2: Stages of the corrosion enhanced plasticity model (CEPM)

Referring to 1 in Figure 2, the slip plane at the crack tip is set in motion and acts to depassivate the metal. Localized anodic dissolution takes place on the {111} plane as indicated in the figure and vacancy is generated. Hydrogen is absorbed and corrosion takes place. Enhanced plasticity resulted on the {111} plane and slip activity is localized at the crack tip. As we move further away from the crack tip, dislocation comes into contact with the obstacles that were previously formed when the main stress was applied. Two almost distinct zones are observed along the slip plane: the softened zone (which is also the enhanced plasticity zone), and the previously hardened zone. The interface between the two zones (pointed out by the dot on the figure) can be regarded as a mobile obstacle and this is the area where dislocations gathers, resulting in increased local stress. Hydrogen absorption along the slip plane lowers the cohesion energy of the {111} micro-plane and forms a crack's embryo. When this occurs, a normal amount of stress applied is enough to open the crack along the slip plane. Dislocations will now be distributed along the symmetry of the slip plane to shield the new crack tip and find a new equilibrium position. The entire process leads to periodic changes of the {111} crack plane to create a zigzag micro-cracking (Figure 3).

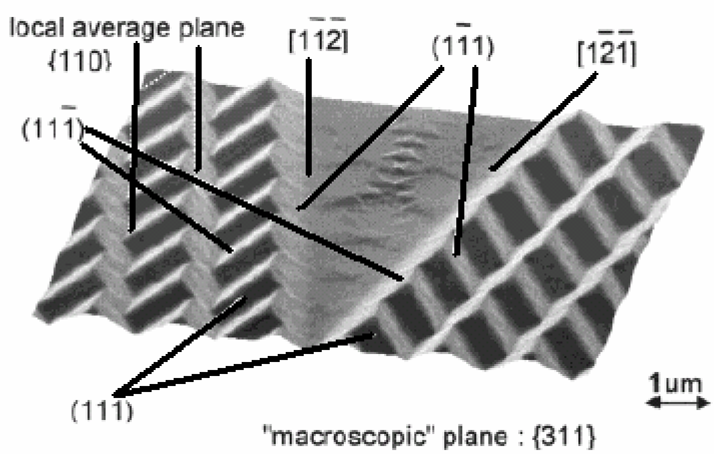

Figure 3: Characteristic features of the stress corrosion cracking fracture crystallography in austenitic stainless steel (face centered cubic structure)

Interaction between corrosion and hydrogen

The mechanism of dislocation gathering at the area at a distance from the crack tip resulted from the existence of microstructure obstacles produced by strain hardening. Hydrogen diffuses towards these obstacles and is expected to reduce the interactions between co-planar dislocations and increase the dislocation density at the area around the obstacles. This mechanism therefore favors the formation of crack nucleus in the symmetric slip plane intersecting the obstacle.

In summary, local softening was observed at the crack tip while dislocation was seen to crowd at a distance around the crack tip. The localized anodic dissolution and cathodic reaction generates hydrogen and vacancies at the crack tip and causes the mechanical property to transition from ductile to brittle.

Stress corrosion cracking formed when an applied stress and a corrosive environment work together will cause complete failure to the implant material. The stress level can be very low but the corrosion may be initiated at a microscopic crack tip that does not passivate rapidly. Incremental crack growth may then occur, resulting in fracture of the implant. Biomaterial implants in the body environment are therefore susceptible to stress corrosion cracking, leading to potential failure of the implanted device.

3 Application

One application of TiNi in the biomedical implant is endovascular stents[2] for constricted coronary and carotid arteries. Existing stents are made from stainless steel but TiNi has been in development to replace stainless steel as biomaterial stents and other medical devices. The superelastic property of TiNi is seen to have much better advantages over existing alloys. TiNi (atomic% –50Ti–50Ni) has approximately 8.0% available elastic strain compared to stainless steel with only 0.5%. TiNi functions almost similarly to stainless steel stents but with some minor differences. Superelasticity effect of TiNi allows it to self-expand and thus it can be inserted into the vessel wall without permanent deformation or cracks on the material. As such, it is expected to have longer fatigue lives and reduced risk of failure.

The other advantage of TiNi as biomedical stents is its biased stiffness. By design using the principles explained in section 2.2, the stent is in a relaxed state when opened. TiNi stent is compressed when it is put into the guide catheter. The compression results in increase in the force on the material (Figure 4). When the stent is in position and deployed or opened, the force reduces along the unloading slope and the stent is in relaxed state.

In the vessel, the stent is acted upon by a constant gentle pressure resulted from the contraction of the blood vessel. This results in some loading resistance and hence, gives rise to biased stiffness as seen along the loading curve 5.

[2] Stent is a hollow tube or helical wire that provides rigid, permanent support to the artery vessel walls. It is permanently left in the body in a fixed position to prevent the artery wall to collapse and block the blood flow. It is also a noninvasive method as compared to the balloon angioplasty technique.

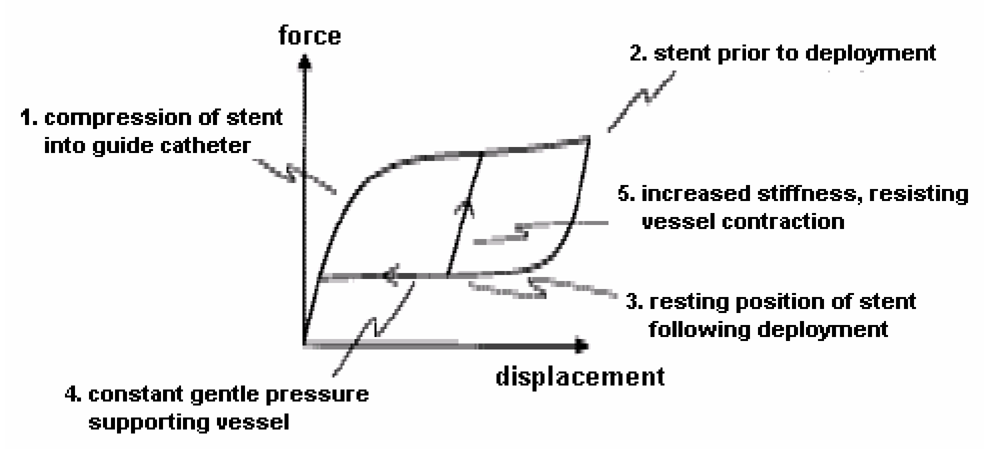

Figure 4: Schematic illustration of biased stiffness in TiNi

The advantages of TiNi discussed above seems to be a breakthrough in the field of biomedical implant but more characterization work of the mechanical and chemical stresses behavior of TiNi in the physiological environment needs to be done.

Fabrication

Laser machining is the known method of fabricating stents. This process produces a small distribution of tiny cracks (sizes ranging 5–20μm) on the material surface. These fabrication cracks are potential stress corrosion cracking sites because cyclic loads arising from the systolic/diastolic blood pressure and the contraction of the heart muscles will result in stresses acting on the TiNi stents. Due to the small size of stent, the lifetime of the stent is largely governed by the fatigue threshold[3] instead of the time it takes for the incipient crack to corrode to failure as described in section 2.5. Thus to predict the expected device lifetime, design of TiNi stents have to take into consideration the fatigue threshold and corrosion rates.

[3] Fatigue threshold, ΔK_{TH} describes stress-intensity range that will start the crack propagation

Presently, a large number of TiNi Stentor devices and aortic endografts implanted in human bodies have been observed to fail or disintegrate within a period of 5–46 months after implantation[3]. New ways of fabricating TiNi devices are still being studied and tested to improve the surface stability of the device in the body environment.

4 Conclusions

Stress corrosion cracking in biomedical implants can lead to loss of structural integrity of the implanted device and its functions. This is highly undesirable especially in the case of stent devices intended for long-term function in the body. The greater significance of the corrosion effect is the reaction of the degradation by-products of metal with the body tissue that leads to toxicity. The discussion in the report concludes that corrosion is a surface phenomenon. The lifetime of the device can be improved by optimizing the surface treatment of the material during processing.

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