Assessment of the Performance of Shape Memory Alloys as Implant Devices

Noura Ali Al-Khalifi

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Assessment of the Performance of Shape Memory Alloys As Implant Devices

By

Noura Ali Al-Khalifi

A Thesis Submitted to the Deanship of Graduate Studies in Partial Fulfillment of the Requirements for the Degree of Master of Science in Materials Science and Engineering

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June 2003
Dedication

To my first valentine ... ... ... How means every thing to me ... ... ...
   To the person ... ... ...
   Who stood beside me throughout
   my toils? and thrills

To Ali Hussein Al-Khalifi
My father ... friend ... and Guide
   Without you ...
None of this could have been possible

Your loving Daughter ...
Noura Ali Al-Khalifi
Acknowledgments

This thesis was carried out at the university of UAE during the years 2000-2003. First of all, I thank Almighty Allah for His Blessings and for providing me the capability to successfully complete this work.

I would like to take this opportunity to thank my senior advisor, Dr. Adel Hammami, who planned and supervised this research project. His sincere guidance, encouragement, fruitful discussions, critical reviewing of the manuscript, unlimited assistance, and providing me the required facilities during the various phases of this work greatly aided its completion.

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I would never forget to thank a great person, Dr. Ahmad Jalal who left the UAE University in the summer of 2002. He gave me great support, great electrochemical information, and great encouragement for the years while he was teaching in the UAE.

Great thanks go to the staff of the central laboratories unit for their cooperation in testing activities. Especially the great help of Mr. Essam Attia in the SEM lab where he gave me good assistance in having excellent and clear SEM micrographs and EDAX analysis for tested shape memory alloys. My thanks also to Mr. Bahaa. He helped me with the chemical analysis of the blood samples.

Special appreciation is expressed to Mr. Singh in the physiological laboratory who implanted tested electrodes in the animals and did muscle contraction test. We have had a good time together. He gave me invaluable technical advice and guidance throughout my master study.

My thanks should be extended to Mr. Saeed Tareq in the electron microscopy laboratories, who worked closely with me to provide necessary guidance and valuable information throughout the TEM ultrastructure examinations.

I am truly grateful to all of those who in some way or other have helped me with the completion of this work. The consummation of this study has been possible with the assistance and support I received from many people.

No words can ever express my great gratitude and special thanks to my great family especially my parents, brothers, and sister who encouraged me in completing my studies after graduation. Thanks to their patience and good care of me.

Finally my greatest deep of gratitude is due to my husband for his unfailing support throughout my study.
Abstract

Shape memory alloys are one class of the family of smart materials. They are considered as biomaterials, since they are well accepted by the human body. One special feature of shape memory alloys (SMA) is their ability to revert to their previous shape. This material is deformed at low temperature and when it is heated, it returns (remember) to its original form. Although, the implant binary NiTi SMA is particularly successful as a biomaterial, our NiTi SMA consist of more that 50% (55.7%) of nickel. The main purpose of this thesis was to evaluate the biological response of the shape memory alloys.

In this project, two classes of shape memory alloys were investigated: Nitinol family (NiTi SMA) and capper based alloys (CuAlNi SMA). A comparison was made between standard NiTi, oxide NiTi, non-oxide NiTi, and CuAlNi SMA. These four materials were subjected to the following experiments. Electrochemical techniques such as potentiodynamic polarization, tafel experiments, and polarization resistance were evaluated to identify the corrosion performance for these alloys. Test specimens from the four materials had been implanted into rat’s left legs and near the sciatic nerve to evaluate the tissue response regarding toxicity of nickel release and biocompatibility in vivo. Muscle contraction measurements were evaluated to study muscle response. The electrodes of SMA were removed after a period of 4, 8, 12, and 16 weeks. The muscles were taken for ultrastructure examination under TEM. In these two main experiments, the materials being used were tested via SEM to analyze the surface conditions and microstructure and EDAX to find chemical composition of the surface. Blood analysis, which was collected from rats, was prepared to evaluate the amount of metal release in the blood sample using ICP-AES.

Electrochemical test was evaluated in the physiological medium to investigate corrosion resistance and therefore corrosion rate of the tested SMA. The main finding was that oxide NiTi SMA has the lowest corrosion rate, which indicated that it has the best corrosion resistance. This is due to the oxide layer acting as a protective layer that defends the NiTi from melting. The resulting micrographs agreed with the electrochemical test. Also, it was found that the surface of non-oxide NiTi SMA had pitting corrosion on its surface. It is founded from blood analysis that the nickel release from Nitinol SMA family was less than CuAlNi SMA regardless of the time of removal of the electrodes from animals.

The effects of these SMA alloys were considered in flexor muscle of implanted animals as a model for studying muscle contraction and neuromuscular ultrastructure. Comparative analysis of in muscle contractile characteristics has been studied (at 1 Hz, 5 Hz, and 30 Hz nerve stimulation) in control and animals that were implanted with tested SMA at four points: 4, 8, 12, and 16 weeks. Twitch tension (evoked directly by muscle stimulation and indirectly by nerve stimulation) and synaptic delay time were recorded in rats via a transducer connected to a computer system. There was a significant increase in synaptic delay time in animals that were implanted with standard NiTi and the electrode was pushed out earlier at the end-of-test point. Compared to control, the muscle of animal that kept non-oxide NiTi showed reduced twitch tension at all three frequencies. However, there was a significant decrease in
twitch tension at the end-of-test point in muscle response of animals that were implanted with CuAlNi SMA. This occurred regardless of whether the electrode was left inside the body.

Ultrastructural alterations were determined via TEM. There was impairment in neuromuscular junctions; nerve terminal, nerve axon, and blood pial microvessels. It seems that standard NiTi did not show significant degree of muscle or nerve impairment. Non-oxide NiTi caused significant damage in blood pial microvessels and intramuscular nerves, where it caused the appearance of thrombi that consisted of platelet aggregates, compared with control. Furthermore, the myelin sheath of the intramuscular nerve was disrupted with the degeneration of microtubules and neurofilaments with mitochondria. This finding demonstrated that non-oxide NiTi caused the most damage in the muscle tissue among other tested alloys. Moreover, CuAlNi altered the nerve terminal and intramuscular nerve. Furthermore, oxide NiTi showed less synaptic vesicles and degenerated mitochondria in the nerve terminal in neuromuscular junction. These changes are possibly related to alteration in Ca\(^{2+}\) mobilization across muscle membrane. The SMA electrodes, which were removed from the animal's body, showed a small degree of corrosion but this relates to a small pits.

It can be concluded from most of the experimental results that oxide NiTi SMA could be represented as superior when compared to the other three tested SMA. Unfortunately at the end of this thesis, the tested SMA was not biocompatible, as one would expect. The reasons could be from the absence of a good surface treatment and high nickel concentration.
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### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Ach</td>
<td>Acetylcholine</td>
</tr>
<tr>
<td>Af</td>
<td>Austenite finish temperature</td>
</tr>
<tr>
<td>AP</td>
<td>Action Potential</td>
</tr>
<tr>
<td>As</td>
<td>Austenite start temperature</td>
</tr>
<tr>
<td>βa</td>
<td>Anodic tafel constant</td>
</tr>
<tr>
<td>βc</td>
<td>Cathodic tafel constant</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>Calcium ions</td>
</tr>
<tr>
<td>C.R.</td>
<td>Corrosion rate</td>
</tr>
<tr>
<td>CuAlNi</td>
<td>Capper-Aluminum-Nickel shape memory alloy</td>
</tr>
<tr>
<td>E&lt;sub&gt;corr&lt;/sub&gt;</td>
<td>Corrosion potential</td>
</tr>
<tr>
<td>EDAX</td>
<td>Electron detection x-ray analysis</td>
</tr>
<tr>
<td>E&lt;sub&gt;oc&lt;/sub&gt;</td>
<td>Open circuit potential</td>
</tr>
<tr>
<td>I&lt;sub&gt;corr&lt;/sub&gt;</td>
<td>Corrosion current density</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>Inductively coupled plasma-atomic emission spectrometry</td>
</tr>
<tr>
<td>Md</td>
<td>Highest temperature to strain-induced martensite</td>
</tr>
<tr>
<td>Mf</td>
<td>Martensite finish</td>
</tr>
<tr>
<td>MPY</td>
<td>Mill inch per year</td>
</tr>
<tr>
<td>Ms</td>
<td>Martensite start</td>
</tr>
<tr>
<td>NiTi</td>
<td>Nickel-Titanium shape memory alloy (also nitinol)</td>
</tr>
<tr>
<td>OWSME</td>
<td>One Way Shape Memory Effect</td>
</tr>
<tr>
<td>R&lt;sub&gt;p&lt;/sub&gt;</td>
<td>Polarization resistance</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SMA</td>
<td>Shape memory alloys</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TWSME</td>
<td>Two Way Shape Memory Effect</td>
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</table>
Chapter One

Thesis

Introduction
1. Thesis Introduction

1.1. Introduction

Shape memory alloys (SMA); because of their unique mechanical characteristics, which include shape, memory effect (SME) and super elasticity have been widely used as biomaterial in medical and dental fields. The shape memory alloys can exist in two different temperature dependent crystal structures (phases): martensite, which is created at low temperature phase, and austenite that appears in high temperature phase. Super elasticity is the ability to recover a shape upon removal of an applied stress over a narrow range of deformation temperature. The strain recovered provided nearly eight times the elastic spring back of ordinary metals. Two systems of shape memory alloys are presented in this thesis, NiTi and CuAlNi. NiTi is known as biomaterial but for the copper-based alloy, it is still under development. In the literature, no information is available regarding the use of this alloy as a biomaterial and probably this work will be among the first attempts to investigate this problem.

1.2. The Objectives and Impact of the Study

Shape memory alloys have unique thermal shape memory, superelasticity and damping properties of a kind not seen in other alloys. The performance and biocompatibility of every new material must be very well confirmed before it can be accepted into use as an implant material. The main purpose of the present study is to evaluate the biocompatibility and corrosion of shape memory alloys for further safe use as implant material and to compare different types of shape memory alloys.

To fulfil this objective, the following items are considered:

- To Study the electrochemical behavior of different types of shape memory alloys in a physiological medium.
- To Study and compare the electrochemical characteristics of shape memory alloys
- To explore the morphological structure of the surface of shape memory alloy specimens needed after polarization in the physiological solution and after implantation in animals.
- To investigate the structural analysis of the surface of the tested specimens in order to understand the chemical composition of the surface.
- To find the corrosion rate of different types of shape memory alloys.
- To investigate the bulk modifications and resulting cellular and tissue response to tested shape memory alloys.
- To evaluate if there is systemic release of trace elements from shape memory alloys to blood and muscle organs.

1.3. Tasks

Several tasks are required in carrying out this study. These include:
- Carrying out a literature review to gather information on the performance of shape memory alloys.
- Studying the characteristics and different properties of the shape memory alloys.
- Devising an experiment to study the corrosion resistance of shape memory alloy using electrochemical tests and to study the biocompatibility of shape memory alloys.
- Analyzing the experimental data and discussing the results in order to select the best alloy among the tested materials.

The tasks of this thesis have been done in four main laboratories, which are (a) Chemical Science Laboratory, UAE University, where the electrochemical measurements have been done and the corrosion rate was determined. (b) Central Laboratories Unit (CLU) where chemical analysis of the blood samples using atomic emission spectrometry (ICP-AES) were done. Also, the morphological characterization of the treated and untreated shape memory alloy electrodes were
taken by using scanning electron microscopy (SEM). (c) Physiological Laboratory, Faculty of Medicine, where the implantation and muscle contraction tests of animals were done. (d) Electron Microscopy Laboratory in the Faculty of Medicine, where the tissues preparation were done with the ultra graph characterization of muscles using transmission electron microscopy (TEM).

1.4. Thesis Organization

This thesis is divided into six chapters. Chapter one includes the general introduction of shape memory alloys. In addition, the purpose and significance of the study with the required tasks to fulfill these objectives are included. Furthermore, the different laboratories where the experiments have been done were mentioned. Also, the outline of the thesis was displayed.

Chapter two includes the major aspect of shape memory alloys. It contains a literature survey on the history, types, the characteristics and the mechanism of transformations of shape memory alloys. Also, it covers thermomechanical and thermoelastic behavior of the system. The main properties that contain shape memory effect and superelasticity were described. The biocompatibility and corrosion aspects were also presented. In addition, the categories and recent applications were included.

The experimental methodology of the thesis is presented in chapter three. It includes electrochemical tests, which analyse the corrosion behavior using different measurements. These tests simulate the material response to the body fluid environment (physiological solution). Moreover, biocompatibility address the issue of using the shape memory alloy as an implant material. This test evaluates the long-term response of surrounding tissues to the implant. This is done by investigating the muscle contraction, tissues collected, and blood analysis. There were many techniques used to investigate the response of the material. They are Scanning Electron Microscopy (SEM), Electron Diffraction X-ray Analysis (EDAX),
Transmission Electron Microscopy (TEM), and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

The reminder of the thesis is organized as follows:

Chapter four presents the results and discussion of corrosion aspects. This was achieved by electrochemical measurements. It contains the corrosion rate determination and the surface microstructure of the tested electrodes. In this context, the results indicate that the oxide NiTi SMA has the best performance against corrosion attacks.

In chapter five, the results and discussion of the biocompatibility aspect was listed. The implantation effect was analyzed. The results of muscle contraction, which included synaptic delay time and twitch tension of muscle were analyzed. Furthermore, blood analysis and ultrastructure of muscle response especially nerve and neuromuscular junction were discussed.

Chapter six reviews the general conclusion with further recommendations of the thesis. It summarizes the results of experiments and presents suggestions for future research on the appropriate use of those materials as biomaterial implants.
Chapter Two

Review of the Literature
2. Review of the Literature

2.1. Introduction

Shape memory alloys (SMA) are special class of superior metallic materials, which can convert thermal energy directly into mechanical work. They are considered as smart materials that can have the ability to return to their original shape prior to the deformation when warmed up above its transformation temperature. Iovine (2000) stated that nitinol SMA could generate a 100x greater thermal movement than standard metal during contraction when heated.

The concept of shape memory alloys is not easy to understand. They exhibit a phase change as they are heated and cooled. The significant characteristics of SMA are found in two different solid phases having the same chemical composition but different crystallographic structure: austenite and martensite, depending on temperature and stress level (Bernardini, 1999). The impressive property of SMA is based on internal transformation of the crystal structure (MMG, 2002).

The phase change is an instantaneous shear transformation between body centered cubic structure called austenite (in NiTi) and a highly twinned martensite structure. This phenomenon causes the specimen to revert completely to the shape it had before the deformation with exerting force. NiTi SMA has the highest energy density for all active materials (AML, 2000). They can be strained (deformed) repeatedly as much as eight times the elastic spring back of other alloys.

The material is easily deformed at low stress to a new shape at a martensitic phase (low temperature), and if it stays cold, it will remain deformed. However, if it is heated the austenitic structure (high temperature) reappears and the material recover to its predetermined shape with a great force. This transformation is responsible for either shape memory or super elasticity being exhibited by the alloy. The temperature
at which the alloys remember their high temperature form when heated can be adjusted by slight change in alloy composition and through heat treatment.

2.2. History

The first recorded observation of the shape memory transformation was in 1932. This transformation was discovered in AuCd through studying metallography (Zhao, 2000). In 1951, the shape memory effect was observed in bent bar of the same alloy. A phase transformation was discovered in Brass (CuZn) in 1938.

Nitinol, which stand for Nickel Titanium Naval Ordnance Laboratory, is a generic name for the family of nickel titanium alloys. At the naval ordnance laboratory (currently the Naval Surface Weapons Center) in Maryland, William Buehler was the one who discovers the shape memory property of equiatomic nickel titanium alloy by accident in 1961. At a laboratory management meeting, a strip of Nitinol was presented that was bent out of shape many times. Potential practical use began and the phenomenon comes to worldwide attention with the announcement in 1962. A group of Brass (CuZnAl) alloys first exhibited shape memory properties in the early 1970's.

Within ten years, the understanding of the effect was much better and a number of commercial products were available on the market. As the understanding of the shape memory effect was better, a number of other alloy systems that exhibited shape memory were investigated. Recently, researches of SMA have been continued at an increasing area.

2.3. Biomaterials Science

Biomaterials science investigates the characteristics of materials such as the mechanical, physical, and chemical properties in addition to the interaction between living and non-living materials. Biomaterial can be defined as an inert material that is in contact with biological environment and they are used to replace part of a living
Biomaterials have contributed significantly to the advances of modern health care in the medical field. The interaction between the material and the body environment with the effect of each one on the other, control the role of materials as biomaterials (1995). The improvement of biomaterials is associated with the development of modern medicine and material science field. The first successful material that was implanted inside the body is a stainless steel and cobalt chromium alloy for fracture fixation in 1960s. After that time better materials were discovered and play a crucial role like titanium and they are classified as “biomaterial” (Ryhanen, 1999b).

The selection of biomaterials is a dangerous decision, which may cause allergic reactions, or kill the surrounding tissue. Thomas (1988) stated that the dependence reaction of tissue and fluids within the body with any foreign implant on a number of variables such as surface chemistry of the implant, the nature of the blood or tissue, the design of the synthetic device, and the care in surgery.

The major factor that determines the convenience of a material inside the body is the biocompatibility of the material. Michael (1999) has officially defined biocompatibility as “the ability of a material to function with a specific host response”. On the other way, Bill (1995) pointed out that “biocompatibility involves the acceptance of an artificial implant by the surrounding tissues and by the body as a whole”. This means absence of inflammatory response, allergic reaction, and does not cause cancer. Hogan (1995) mentioned four conditions that should be considered to accept a biocompatibility of the material: first, the material should not cause harmful reactions. Second, the implant has to be able to withstand the risk of triggering the body's defense mechanisms, which will try to expel the foreign body. Third, the implant should be extremely reliable. Finally, the implant weight is less and durable. This topic will be discussed in more detail in subsequent sections.
2.4. Implantation Effect

According to outstanding properties, biomaterials are superior in load bearing implants. The presence of implant induces reactions in the human body. There are several activities and cellular interactions that are affected by the implant in the physiological environment (Pizzoferrato, 1986). As an example, blood is corrosive due to its high salt content and continuous motion. The environment inside human body attacks any foreign object through immune system, which may cause inflammatory response (Ebsco, 1994). This is depending on patient characteristics and/or implants characteristics.

After implantation, the metal is surrounded by serum ions, proteins, and cells, which may alter the effect on local corrosion reactions. Thus, the characteristics of the material surface may be altered due to the release of agents from the cell or influence of proteins absorbed from plasma. The success of implanted materials relies on its ability to mimic the natural environment of the cell (Ryhanen, 1999b).

2.5. Shape Memory Alloys as Biomaterials

The unique properties such as shape memory, super elastic effect, and high damping make the nitinol to be widely exploited as a biomaterial. Beside these properties the acceptable resistance to corrosion and biocompatibility exhibited by titanium nickel memory alloys has been widely used in the manufacture of biomedical devices. These properties enable the design of implants that change shape or dimensions in response to a temperature dependant increment small enough to be tolerated by the adjacent tissues. Shape memory and super elastic implants have recently aroused large interest in the medical field, and a number of proposed applications will be explained in the following pages.

The research data are still quite deficient in final conclusions about the biocompatibility of nitinol. In particular, the relatively large content of nickel in the alloy gives rise to considerable concern although corrosion studies have demonstrated
that the nitinol alloy approximates the excellent corrosion properties correspond to that of titanium (Rondelli, 1995), (Wever, 1997). Thus, long term in vivo studies in animals are very important before using nitinol implants in humans.

2.6. Shape Memory Systems

2.6.1. Shape Memory Alloys

To date, scientists found shape memory effect in alloys, polymers, and composite. However, shape memory effect is mainly dominant in metallic alloys. Shape memory alloys developed and commercialized are nickel titanium alloys, copper based SMA and iron based SMA alloys. Nitinol is a binary NiTi (50% Ni, 50% Ti); small amount of third element can be added to NiTi to improve its properties like copper, iron, niobium, and hafnium. Example of Cu based SMA such as CuSn, CuZn, MnCu, CuZnAl, CuAlBe and CuAlNi. FeNi, FePt, FeMnSi, FeCrNiMnSi and FeCrNiMnSiIn alloys are some types of Fe based SMA (Li, 1997), (Jin, 1998), (Ullakko, 1996), (Ma, 1998). There are other alloys, which display the shape memory behavior like AuCd, AgCd, Nb-Ru, Ta-Ru, InTi, and InTi (Chiodo, 2000), (NRL, 2001).

2.6.2 Shape Memory Composites

Beside metals, there are shape memory polymers like shape memory Polyurethanes (Hayashi, 1995), (Lendlein, 2001). New applications consist of smart composite shape memory materials, which are defined by thin SMA wires, ribbons, or particles that are embedded into advanced structural matrix (Stalmans, 1995). This will upgrade shape memory characteristics. The matrix can be polymers, epoxy, laminate, fiber-reinforced polymers, metals, or ceramics (Leo, 1995), (Dinah, 1998), (Yang, 2000). NiTi SMA has been distributed throughout an Al matrix to achieve strengthening and improve the fatigue resistance (Porter, 2000). Also, hybrid polymer composites with embedded SMA wire open new perspectives for the development of new engineering
devices with adaptive shape, stiffness, damping, and other properties (Sitter, 2000). Furthermore, SMA wire actuator was incorporated in an epoxy resin reinforced by aramid fibers (Psarras, 2001).

2.7. Manufacturing of NiTi SMA

Processing and shaping of NiTi SMA is not a simple task. The melting of elements should be done in an inert gas because Ti is a very reactive element and to ensure materials quality, purity, and properties. Plasma-arc melting, double vacuum melting, electron beam melting, and vacuum induction melting are some common processing methods (Movroidis, 1999), (SMC, 2000). Yi (1989) used the thermal explosion mode of self-propagating high temperature synthesis (SHS) to produce nitinol SMA. This method provides both time and energy saving and easier processing compared to conventional process.

Work hardening and the convenient heat treatment achieve development of SMA performance. This is because these processes reduce the force needed to de-twin the martensite and increasing the strength in the austenite phase. The wire drawing of NiTi was studied by Wn (1996). He has found that a thin surface oxide film can be used as a lubricant during the drawing process. To create the memory, the alloy is restrained in the desired shape and then it is subjected to heat treatment (annealing) typically between 500 to 800°C. To improve the desired shape, grinding, shearing, and punching can be applied.

2.8. General Characteristics

The martensitic transformation is considered to be a thermoelastic martensite. The shape of martensite is alternately sheared platelets, which is similar to a herringbone structure and is presented as a rhombus. The transformation that occurs in SMA systems is affected by the temperature change, which characterizes the transformation during cooling and heating. The temperature range of transformation is relatively narrow, although the temperature range extends over a much larger than the previous,
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at the beginning and the end of the transformation. The temperature range for the martensite to austenite transformation upon heating is somewhat higher than that for the reverse transformation upon cooling and there is a slight variation in the temperature for the start and finish of each reaction. The difference between the transition temperature upon cooling and heating is called hysteresis. The hysteresis phenomenon will be discussed later.

2.9. The Transformation

The basic idea of the shape memory effect in SMA that they undergo a change in their phase; crystal form as they are heated above their transformation temperature (Hodgson, 2000), (Ashley, 1988). For example, in NiTi alloys, the structure will be formed to an ordered cubic crystal called austenite and to a monoclinic crystal phase called martensite below the transformation temperature. The material forms simple alternating stacks of plates during transformation from high temperature austenite to low temperature martensite. The alternate layer formation is by one layer that is tilted one way while the net it tilted the other (mirror image plates orientation) and so on through the material as shown in figure 2.1.

The overall structure looks like a herringbone structure. This alternate layers or twins cause no net overall shape change. This special transformation is known as thermoelastic martensitic transformation. The transformation occurs because one phase is thermodynamically more stable than another one in specific temperature and stress condition. In addition, one phase can transfer to the other phase by simple shearing motion of the atoms within the crystal structure without resulting in atoms diffusion.
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Figure 2.1: Representation of Transformation from the austenite to the martensite phase which leads to shape memory effect. The high temperature austenite structure undergoes twinning as the temperature is lowered. This twinned structure is called martensite. The martensitic structure is easily deformed by outer stress into a particular shape, and the crystal structure undergoes parallel registry. When heated, the deformed martensite resumes its austenitic form.

2.9.1. Crystal Lattice Structure

Understanding the crystal structure of a SMA is important, in order to give the reader the opportunity to know how the shape memory effect (SME) takes place. This is done in the subsequent section. In general, there are two distinct crystal structures or phases that are exhibited in all SMA. Temperature and the amount of stress being applied to the SMA to control the phase of the structure (Houston, 1992). These two phases are first martensite, which is presents at low temperature and is relatively soft and is common for all types of SMA. Also, its configuration is responsible for shape memory effect in SMA (Schetky, 1979). In contrast, the second phase occurs at high temperature and it is generally called parent phase and it is relatively hard and is either austenite for nitinol SMA or β phase in copper based SMA or FCC γ phase in iron base SMA (Zhao, 1999). The discussion for the high temperature phase will be limited to austenite in this research since it is the most common. The amount of each
crystal phase present in SMA determines its properties. Properties of austenite differ notably from that of martensite.

The structural changes at the atomic level in these alloys are responsible of the unique properties. Nitinol has two states or phase changes, even though it is in a solid state. The crystal structures of nitinol in two phases are depicted in figure 2.2. In figure 2.2a, the martensitic structure is dominant and take a rhombus lattice and the lengths (a, b, and c) of the martensite lattice are different. These sides and angle $\gamma$ will change when load is applied to the lattice.

![Figure 2.2: lattice structure of the martensite and austenite phases of Nitinol](image)

The deformations in various shapes happen easily in the martensite phase due to variability of these lattice parameters (a, b, c, and $\gamma$). Thus, the molecular bonds are not broken. Therefore, causing the SMA to precisely recover its shape when returning to austenite phase as shown in figure 2.2b. Increasing the temperature forces the atoms to arrange themselves into regular pattern resulting in a rigid cubic arrangement known as parent or austenite phase.

### 2.9.2. The Transformation Temperature

When considering only the shape memory effect, and not the superelastic effect, the one thing that causes a SMA to shift from one form to another without the help of any mechanical loading is a change in temperature (lexcellent, 2000). The transformation temperature is the temperature at which a shape memory alloy changes from austenite
to martensite or vice-versa. Or in another way, the transformation temperature is a heating temperature at which the structure is thermodynamically stable to exist as austenite rather than martensite. It is affected by the atomic composition, fabrication, stress, and heat-treated temperature (Hodgson, 2000), (Yoneyama, 1993). There is a slight difference between the temperature rage of forward and reverse transformation due to the energetically dissimilar transformation pathways (Kapanen, 2002). The rate of the transformation from a distorted shape to the original one is very quick less than the one presented in figure 2.3, which portray the elongation under a constant tensile load of SMA versus temperature.

The critical points in the transformation are also appearing. The temperature at which the martensite formed transfers into austenite starts is called austenite start temperature (As). The temperature at which this phenomenon is complete is called austenite finish temperature (Af). Cooling cause's austenite formed changing onto martensite. The temperature at which this phenomena start is called martensite start temperature (Ms). The temperature at which martensite is again completely reverted is called martensite finish temperature (Mf). During heating the specimen from a low temperature, the parent phase starts to form at As. The fraction of parent phase increases as temperature increases until it reaches 100% at Af. The same phenomenon occurs with martensite phase during cooling from Ms to Mf (Xu, 1999).

Figure 2.3: Typical transformation curve for SMA and hysteresis (H) upon a change of temperature under constant stress. Gray area: area of optimal superelasticity.
2.9.3. Hysteresis

Also shown in figure 2.3 is the amount of hysteresis (H) during the cycle, or the difference in temperature between martensite formation and the austenite formation, or in other word, the difference between the temperature at which the material is 50% transformed to austenite upon heating and 50% transformed to martensite upon cooling. Also, hysteresis can be defined as the amount of energy dissipated during one cycle (Strnad, 1995). Mosley (2000) states that this phenomenon occurs because the changes in SMA crystalline structure during SME dissipate energy. This dissipation is due to internal friction. In addition, the hysteresis reflects the amount of irreversible process taking place during the formation of stress-induced martensite (Banks, 2000). Zhao (2000) proved that the relation of elastic energy is for expansion of hysteresis. Also, the transformation temperature region can be calculated as Af-Mf (Jardine, 1989). The width of hysteresis loop of most SMA ranges from 20 to 67.8°C. The range of transformation temperature is changed drastically by small modification in composition of alloy (Planes, 1992).

2.9.4. The Effect of Composition

The addition of ternary alloying alters many characteristics such as the size of Hysteresis, corrosion behavior, transformation temperatures, and fatigue behavior. Thus, a small amount of third element can be added to the binary NiTi to improve its mechanical properties and phase transformation temperature. For instance, extra addition of Ni (up to 1%) to the boundary compound depresses the transformation temperature and increases the yield strength of the austenite. Furthermore, Strnad (1995) found that the cyclic stress-strain curve was stabilized when higher nickel contents added to the binary nitinol.

Drugacz (1995) added Cobalt to the binary NiTi alloy to influence shape recovery temperature and mechanical properties. This improves the plasticity and lowered the strength. Addition of iron or chromium lowers the transformation temperature. Also,
to narrow the hysteresis loop (fast response time) and decrease the deformation stress of the martensite, copper could be added (Mavroidis, 1999). Furthermore, Gil (1999) added copper to NiTi to stabilize the superelasticity characteristics against cyclic deformation.

2.9.5. Characterization of Shape Memory Alloys

The most common method used to characterize transformation temperature (phase transformation) is a Differential Scanning Calorimeter (DSC) (Liu, 1999), (Sabilia, 1996), (Hodgson, 2000). Small amount of sample (<15 mg) is placed in a special test cell and slowly cools and heats the sample at a particular rate. The cell can either giving off heat or absorbing heat via the sample during heating and cooling respectively. This causes the sample to produce either an exothermic reaction (liberates heat) as the material transforms to martensite or endothermic (absorbs heat) as it transforms back to austenite. Delaey (1978) pointed out that the heat transformation of all shape memory alloys has low value and varies from 7 to 6 Jg⁻¹. These reactions generated in DSC curve as a peak in the temperature vs. heat flow curve as shown in figure 2.4. There is also modified DSC, which is Modulated Differential Scanning Calorimetry (MDSC) that can better characterize the thermodynamic, kinetic, and hysteretic features of thermoelastic martensitic transformations (Wei, 1998).

![Figure 2.4: DSC curve record transformation temperature](image-url)
2.10. Thermoelastic Behavior of Shape Memory Alloys

Small changes in temperature or stress drive low energy thermoelastic martensite. These changes cause unsymmetry during transformation, thermoelastic martensite is crystallographically reversible. Thermoelasticity is one of the important characteristics of the martensitic transformation where the new martensite plates form and continue to grow during lowering temperature or applying stress and disappear by the reverse path as the temperature is raised or as stress is released (Perkins, 1992). This mechanism involves heating or cooling to force revision or transformation to proceed (Lovey, 1990). The explanation of thermoelastic martensitic transformation of Cu based SMA is found elsewhere (Novak, 1997).

The structure of thermal martensite is similar to the herringbone. Raboud (1998) states that the structure of thermal martensite consisting mainly of a number of energetically equivalent martensitic variant makes easy the deformation in this phase. “The shape change among the variants tends to cause them to eliminate each other. As a result, little macroscopic strain is generated”. When stressing a self-accommodating structure (stress-induced martensite), yielding of variants transformation in the direction of the applied stress is stabilized and become dominant in the configuration.

A macroscopic strain results from this process, that is recoverable as the crystal structure reverts to austenite (original shape) during reverse transformation. Due to a high degree of crystal symmetry, there are no variants in austenite.

2.11. Thermomechanical behavior

The transformation that occurs due to the temperature range influences the mechanical properties of SMA. The methods that are used to demonstrate the thermomechanical behavior of SMA can be found elsewhere (Huang, 1998), (Lexcellent, 2000). In fact, to produce the two-way behavior, thermomechanical treatment is required usually involving several transformation cycles. For example, figure 2.5 illustrates typical unusual stress stain behavior of tension test for nickel
titanium alloy, below, middle of, and above its transformation temperature range. The austenite (a) has high yield and it behaves like ordinary metals. However, at low stress level (b) represent the shape memory effect where the martensite is easily deformed to several percent strains. During loading (E→F) this stress induces martensite and elastic strain. The formed martensite is still stable when unloading (F→G). Upon heating above Af the material becomes austenite and fully recovers the elastic strain. This is represented in dashed line on the martensite curve (Brocca, 2000). In the austenite phase during heating and staining there is no shape recovery since no phase change occurs.

![Stress-strain curve of SMA](image)

**Figure 2.5:** Typical stress strain behavior of different phases at constant temperature, showing (a) Austenite, (b) Shape Memory Effect, and (c) pseudoelastic behavior.

The stress strain curve of SMA (figure 2.5b) should be understood as follows (Delaey, 1978):

- The purely elastic deformation of the parent phase appears in section EE’.
- The first formation of martensite plates caused by stress-induced occurs at point E’.
- At point F, the transformation is essentially complete.
- On releasing the stress point G will be reached; section EG reflects the irreversible part of the deformation (permanent deformation). As this section decreased, the superelasticity increased.
Alloy composition and temperature control the position of point E', which is yield point.

The interesting part of the material being tested is above its transformation temperature (part in figure 2.5c), where the martensite can be stress induced. Then it immediately strains and exhibits the increasing strain at constant stress behavior, seen in AB. Upon unloading (a reduction of stress not upon heating), the material reverts to austenite at a lower stress and elastic strain therefore recovered, as seen in line CD. This causes the material to be extremely elastic. This behavior is known as Pseudoelasticity or super elasticity (Brocca, 2000).

2.12. Why It Is Repeatable

The shape memory or superelastic effect can be used in a cyclic device up to six million cycles (Shelley, 2000). This is due to the fact that deformation in the martensite is not damaging the crystal structure. These devices require undergoing several percent strain and then return to the original shape many times. In normal metals, atoms are arranged in planes where they slide over one another. During deformation, the atoms move to a new crystal position by the motion of dislocation of atomic slip. Thus, there is no memory in the crystal where the atoms were before they moved. The new movement causes diffusion mixing of atoms and damages the crystalline order as illustrated in figure 2.6.

The reason that the deformation of shape memory alloys in microstructural scale occurs by changing the tilt of twin orientation does not cause any dislocation motion, which does not cause diffusion (Planesm, 1996). It is dominated by coordinated shear displacement of sections of crystal. Therefore, it has been no permanent damage. In addition, the individual plates themselves are internally twinned to help accommodate the transformation strains (Perkins, 1992). Also, the martensite can be deformed by straightening the ‘twins’ out (Shelley, 2000). So, there is only one crystalline direction that the martensite can move in order to restore the austenite structure. Thus, the structure remembers how to return to its original shape.
2.13. Mechanical Properties of SMA

The mechanical properties of SMA depend on its phase state at a certain temperature. At low temperature phase (martensite), the material is soft and ductile while at high temperature form (austenite or parent) the material is rigid (Aerofit, 2001). Mosely and Marroidis (2000) found that the resistance of nitinol wires change with respect to austenite to martensite ratio. Also, the stiffness and elastic modulus change during phase transformation which is useful to absorb vibration (Salichs, 1998), (Stalmans, 1995). From the implantation point of view, the properties of austenitic NiTi is useful for surgical implantation. It is reported that NiTi has high fatigue and ductile properties with very high wear resistance (Ryhanen, 1999b). Liu (2000) observed that the wear resistance of NiTi alloy was two orders of magnitude higher than that of the stainless steel 304 when the alloy behaved pseudoelasticity. Another useful property is that it is non ferromagnetic, so there will be less interference on image of magnetic resonance imaging scanners obtained (Hibbert, 1999).

Yield strength and modulus of elasticity are the basic mechanical properties for SMA. Huang (1999) states that they are strongly temperature dependent, and may be 2 to 3
times different depending on temperature. Stalmans (1995) concluded that many characteristics of SMA change drastically during transformation such as Young’s modulus and electrical resistivity. By coating NiTi SMA by hydroxyapatite (HAP) ceramics, Filip (1997) proved that it increases strength up to 30 Mpa. The force needed to deform the alloy when they are cool is approximately one third of the force that will be generated by the same alloy when it is heated (FTM, 2000).

Generally, the properties have been determined as a function of composition, grain size, grain shape and temperature. McKelvey (1999) found that nitinol have the lowest fatigue-crack growth resistance compared to other biomaterial implant alloys, 316L stainless steel, pure Ti, Ti-7Al-4V and a CoCr.

2.14. Shape Memory Phenomenon

The unusual transformation in SMA, which is thermoelastic martensitic transformation, is responsible for its extraordinary properties. These properties include mainly the Shape Memory Effect (SME), and pseudoelasticity (Hodgson, 2000). The difference between them is that the SME is thermal memory effect while pseudoelasticity is due to the mechanical memory effect (Wayman, 1993). These unique properties resulted from inherent phase transformation (Science Net, 2001). The tilted twins that form martensite can be flipped to the opposite ‘tilt’ by the application deformation. Transformation to martensite by deformation or upon cooling causes most of the martensite variants yield and detwins as the grains reorient such that they are all aligned in the same direction rather than having equal amount of alternate layers (twins) as depicted in figure 2.7 (Mosely, 2000). This phenomenon helps a shape change during deformation. As the martensite twins until back to the cubic austenite form increase during heating, as shape memory arises and generates great force. Byrd (1974) have reported that to remove the shape memory in nitinol wire or to acquire permanent shape by heating the wire to a temperature of about 900F and reshape it under considerable tension.
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![Diagram showing the mechanism of shape memory effect](image)

**Figure 2.7:** Mechanism of shape memory effect (a) Austenite, (b) Twinned Martensite (c) & (d) Deformed Martensite (e) recovered Austenite

### 2.14.1. Shape Memory Effect

A lot of works devoted to the shape memory effect (SME) of SMA can be found in the literature; SME of CuZnAl (Delaey, 1978) or shape mechanism associated with the martensitic transformation in NiTi (Miyazaki, 1989). The shape memory effect is characterized by a phase change in the material (Schoor, 2001). The characterization of SME strongly depends on certain parameters. These parameters are the transformation temperature, the critical stress, which induces martensite and the damping capacity (Delay, 1978). The SME mechanism of Cu based SMA was full understood by Saburi in 1980 with loading, cooling, and heating effect. Also, Miyazaki (1989) was the first researcher who investigates the mechanism of SME of nitinol alloys.

### 2.14.1.1. One Way Shape Memory Effect (OWSME)

SMA is able to convert its shape to a preprogrammed structure. The ability to change shapes by heating or cooling, one can utilize it to push or pull other thing (Raychem, 2001). In most cases, the memory effect is one way that it can recover its shape upon heating above its transformation temperature in only “one way”. When cooling, a SMA does not undergo any shape change, even though; the structure changes to
martensite. In one-way shape memory, it is only the high temperature shape that’s remembered and only one action cycle can be achieved (Leo, 1995).

2.14.1.2. Two Way Shape Memory Effect (TWSME)

If a SMA is repeatedly subjected to the same deformation, heated and then cooled, it will begin to acquire “two way shape memory”. Thus, two-way shape memory has both memorized shapes (high and low temperature). Two way SMA remembers two shapes, which are trained to return to a shape when they are formed into shape restrained, and then continuously heated and cooled for a given number of cycles. The amount of shape recovery in this case is always significantly less than obtained with one-way memory and is in general limited to below 3%. And the amount of exerted stress or force is much little than one-way memory.

To obtain two-way memory effect, a specific thermomechanical treatment called training is applied. To create two way shape memory effect, a number of heat treatment and mechanical training methods have been applied or one way shape memory alloy which is combined with string, weight, or other parts (Sethna, 1994). Liu (1990) reports the factors that influence the magnitude of two-way shape memory of NiTi. These are area-training procedure, the number of training cycles, the training stress and prior heat treatment. Also, Eucken (1989) has found that two-way SME existed in aged NiTi. Cingolani (1999) have studied TWSME of CuAlNi and founds that the efficiency of the alloy is reduced when temperature at training is below room temperature.

2.14.1.3. Training Program of Two Way Shape Memory Effect

A repetitive training regime is subjected to SMA to develop the two-way shape memory alloy with no deformation (Leo, 1995). Simply, elongating (or bending) a wire of the material with constrains in a fixture does this, and increase temperature to converts the martensite to austenite. Then the temperature is lowered for a given
number of cycles after the wire remaining in its new shape. This process is repeated continuously to cycle its structure from austenite to martensite and back. Thus as a result, the wire has a length at the high temperature and an entirely different length (or the wire is bending) at low temperature without the help of any mechanical loading.

2.14.2. Pseudoelasticity Behavior

Pseudoelasticity effect also known as superelasticity refers to the ability of SMA to return to its original shape upon unloading after several deformations. Also, they can withstand huge repetitive deformation without embrittlement (Gopinath, 1999). The pseudoelastic properties are comparable with the elastic properties of rubber and other elastomer. The term pseudoelastic is an elastic behavior due to a phase transformation and the term superelastic is unusual high elastic deformation compared to metallic materials. Stalmans (1996) indicated that a unique combination of high strength, high stiffness, high reliability, and high energy storage produce superelastic effect.

Superelasticity phenomenon appears for constant temperature higher than Af when applying sufficient shear stress to an austenite state to cause it transform to deformed martensite in a way that relieves the applied stress (loading). The temperature of loading and unloading should be kept constant. The deformation disappears and shifts back to austenite as the stress drops to a level when martensite is not stable (unloading) because martensite can exist above Af. Both regions are parts of a hysteresis loop (Vokoun, 1999). The stress strain characteristic of superelastic SMA is obviously different from ordinary spring material as shown in figure 1.8. A superelastic behavior has a highly non-linear stress strain curve with an extensive constant stress plateau and large elastic strains (Melzer, 1994).

The deformed martensite remains as the stress maintained is characterized by a ‘plateau’: i.e., the force remains constant with increasing displacement (Castellano, 1999) as depicted in figure 2.5c. Martensite is formed at temperature higher than Ms and the deformation is occurring at this phase. When the stress is released, the
martensite transforms back into austenite and the specimen reverts to its original shape. This property makes SMA useful for medical and dental applications because the metabolism and temperature of the human body is kept constant (Raychem, 2001). Xu (1999) pointed out that superelastic SMA could be strained about 10% more than conventional elastic material depending on the composition of material, heat treatment, and number of strain cycles.

Yang (2000) stated that this phenomenon is called stress induced martensite (SIM) where the driving force is mechanical opposed to thermal. However, this phenomenon is occurring over a specific temperature range. This required stress to induce martensite increases linearly with temperature (Delaey, 1978).

![Stress Strain Graph](image)

**Figure 2.8:** Stress Strain of conventional elastic (2% elastic strain) and superelastic martensitic materials (10% elastic strain) without permanent set

The highest temperature at which martensite can no longer be stress induced is called Md as shown as gray area in figure 2.3. Applied stress causes the martensite to be stable above Af. Above Md, the SMA becomes ordinary material, which is deformed by slipping (plastic deformation). Also, below As, the material, which is in martensite phase, does not recover. Therefore, superelasticity appears in a temperature range from near Af and up to Md. The largest ability to recover occurs close to Af (Ryhanen, 1999b).
2.14.3. Effects of Cycles

The crucial parameter that controls the life performance of shape memory devices is the amount of transformation cycles. As a consequence, the maximum memory effect, strain and/or stress will be restricted depending on the required amount of cycles. In Table 2.1, is shown the experiments of Humbeek (1999) that can be used to identify the relationship between the % strain and number of cycles. It is noted that the strongly of SMA components is inversely proportional to applied deformation. For instance, the life of SMA may be only few hundred cycles if it is deformed to 8%, whereas for deformations of < 1%, the life continues several million cycles (Tuomien, 1995).

Table 2.1: The allowed maximal strain and stress are affected by number of applied cycles.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Max. Strain</th>
<th>Max. Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8%</td>
<td>500 Mpa</td>
</tr>
<tr>
<td>100</td>
<td>4%</td>
<td>275 Mpa</td>
</tr>
<tr>
<td>10000</td>
<td>2%</td>
<td>140 Mpa</td>
</tr>
<tr>
<td>100000+</td>
<td>1%</td>
<td>70 Mpa</td>
</tr>
</tbody>
</table>

2.15. Categories of Shape Memory Alloys

Shape Memory Alloys (SMA) as engineering materials were known for more than 50 years and understanding of shape memory effect mechanism and crystallography was fully understood. The applications of this memory effect started more that 30 years ago by researchers, designers, and commercial companies.

Generally, the characteristics of these alloys can be divided into six categories: free recovery, constrained recovery, force actuators, proportional control, superelasticity, and high damping capacity (Humbeeck, 1986), (Lin, 1999), (Hodgson, 2000).
2.15.1. Free Recovery

Free recovery of the memory effect is demonstrated when shape memory is deformed at low temperature when the structure is martensite and it fully restores its original shape (with minimal work) above its transition temperature where the structure returns to austenite form. This property is primarily used in blood clot filter. Simon (1989) designs this filter and it is like an umbrella consisting of nitinol wires. It is collapsed in catheter (small insertion tube), which contains cold saline solution and inserting it into the vein of the patient. When reaching the vena cava (the large vein from the lower body to the heart), the catheter is pushed out, then the NiTi wires opens up freely to its previous shape at body temperature to catch passing clots before they can reach the heart and lungs.

2.15.2. Constrained Recovery

This appears in hydraulic couplings such as Coupling NiTi SMA used to joint Ti3Al hydraulic tubing in jet aircraft (Tuominen, 1995). The diameter of the coupling is deformed larger than the metal tube while martensite and diameter become shrink and hold the tube ends when heated to austenite. The tubes prevent the coupling from fully recovering its pre-designed shape and coupling, which may be superior to a weld.

2.15.3. Force Actuators (Work Production)

Shape memory alloy component is shorted when heated and exert force or perform work over a significantly range of motion during many cycles. This is accomplished by applying a voltage drop across the wire causing current to flow (Mosely, 1999). They are able to generate high stress up to 800 MPa and work is generated up to 5 J/g. This is because the stress needed to deform the martensite is much less than the yield strength of the austenite. That is, the force needed to deform a shape memory article during cooling is much less than the force the article can exert (energy) when it is
heated (Hodgson, 2000). The famous application in this category is a circuit board edge connector. It is designed to force open a spring upon heating the connector. This force allows circuit board to insert or leave the connector. However, the spring can deforms the NiTi actuator upon cooling and connects with the circuit board tightly. A fire safety valve made from CuZnAl SMA is another example. It is an actuator used to cutoff toxic or flammable gas flow when fire occurs.

2.15.4. Proportional Control

Because the transformation occurs over a range of temperature, it is possible to utilize this feature to select part of the shape recovery and controlling position mechanism precisely. Adjusting heated valve of SMA will dominate the rate of fluid flow to obtain a desired amount. Also, it is incorporated in cooling circuit valves.

2.15.5. Superelasticity (Energy Stored)

The superelastic alloys have very high energy storage capability (Zhao, 2000). With pseudo-elastic effect, the alloy release stored energy with high strain and no change in temperature. This phenomenon is considered as isothermal process. Superelastic SMA eyeglass frames absorb deformations without breaking themselves when dipped in hot water (Beta, 1986). Also, guide wire of SMA for steering catheters into vessels in the body resist permanent bending.

2.15.6. High Damping Capacity

This new property discovered in SMA especially NiTi, which can dissipate vibrations. Energy is dissipated during superelastic cycling as a result of the stress hysteresis between loading and unloading. This happens by converting part of the unwanted mechanical energy into heat. The forms of this mechanical energy are vibration, impact loading or shock waves (Humbeeck, 2000). Actually, temperature and alloy composition affects obviously the damping capacity of SMA. The major application
of this category is in seismic places to protect architectures against earthquake damages (Liu Y, 2001). SMA can withstand an earthquake 50% stronger than structure reinforced with traditional steel bar (Anonymous, 1999), (Front, 1999). One of the most recent applications is a passive seismic control device, which uses SMA for building a bridge. They have extraordinary fatigue resistance under large strain cycles (Dolco, 2000).

### 2.16. Corrosion Behavior of metallic biomaterial

#### 2.16.1. General

Shape Memory Alloys are widely used in different applications. One particularly attractive use is as implant in the human body. Therefore, the use of NiTi as a new biomaterial imposes a high demand on its corrosion resistance performance. Corrosion is the major responsible for toxic response to implanted material. This is because the migration particles or ions circulate through the body and causes disruptions of the cell structure and function (Rostoker, 1996). Samuel (1986) defined corrosion as “the degradation of a material due to a reaction with its environment”. Degradation implies a reduction in usefulness of the material. Corrosion is influenced by the nature of the environment and the surface treatment; the metal is subject to.

Most of the studies showed that some metallic implant causes some toxic and dissolve in human body due to corrosion. Even though, an extensive understanding of the factors that cause corrosion exist, no real tools exist to control it. The corrosion takes place via an electrochemical mechanism because of the characteristic structure of metals such as free movement of electron through their lattices (Jastrzebski, 1977). There are three mechanisms, which specify the corrosion behavior of the metal; non-physiological in *vitro* studies, physiological in *vitro* studies, and in *vivo* studies. The corrosion resistance of a metallic implant is an important aspect of its biocompatibility.
In the human body, tissue fluid contains water, dissolved oxygen, proteins, and various ions like chloride and hydroxide (Park, 1995). As a result, the human body presents a very aggressive environment to metals used for implantation. Unfortunately, every implant metal is susceptible to corrode inside the human body (Latanision, 1992). Also, the metal concentrations are measured even in distant organs. This is due to ionization with circulation of small metal particles (Ryhanen, 1999a).

Not all forms of corrosion are present within the implant. Pitting corrosion occurs as small points that have small depth on the surface. Crevice corrosion is the same as pitting corrosion but on a larger area. Pitting and crevice are classified as localized corrosion. Galvanic corrosion forms between dissimilar metals; the one which is less noble is corroded and becomes anodic such as SMA plates that encourage healing of the broken bone are screwed with stainless steel.

2.16.2 Electrochemistry of Corrosion

Corrosion in aqueous solutions involves charge transfer. The mechanism of attack during corrosion reactions in aqueous solution will involve some aspects of electrochemistry. The electricity flows from certain areas of a metal surface to other areas through a solution capable of conducting electricity. The circuit contains corroded electrode from which current leaves the metal to the solution and a cathodic electrode from which current leaves the solution and returns to the metal. The electricity, which is, ions flowing in the solution that is called electrolyte from the anode (-ve) to the cathode (+ve) and continue through the metal wires from the cathode to the anode.

2.16.3 Passivation

The passive layer (structure, composition, and thickness) depends on the metal itself and its environment. Also, this layer is affected by impurities or contaminants in the
metal and different heat treatments and working processes. A statement by Zhang (1995) contradicts the above condition since the surface finish does not influence pitting corrosion behavior of NiTi alloy.

The corrosion resistance of metals and alloys is based on a passivation phenomenon. The passivation of metal is the passive layer coated on the surface, which consists of any original metal or a metal oxide layer. The composition of this layer may change from the bulk of the metal. Actually the oxide layer is thicker on implanted metal than on non-implanted metal (Ryhanen, 1999b).

Due to that, the environment of the body is so salty; the metal ions are dissolved when the oxide layer is not fully developed. Therefore, they form metal hydroxide. When there are chloride ions, as in human plasma, they surrounded the passive layer. Immediately, the dissolved metal ions form a metal-chloride complex that causes pitting corrosion to occur when the passive layer is not fully developed. Thus, the implant material contaminates the body fluid.

2.17. Corrosion of NiTi

The corrosion behavior of shape memory alloy has not been adequately investigated so far. Nickel and high nickel alloys have superior corrosion resistance (Jastrzebski, 1977). Also, the results reported by researchers have conflicting views. Most of the studies are concerned with dental arch wire and in vitro conditions. In fact, the knowledge of the corrosion behavior of SMA inside the body is very limited.

2.17.1. In Vitro Corrosion

The in vitro tests evaluate the performance of materials in a simulated physiological environment or in discrete components. The first research that proved good corrosion resistance of NiTi SMA in seawater was done by buehler in 1967. Different methods
Assessment of the Performance of Shape Memory Alloys As Implant Devices
Noura Al-khalifi

of corrosion test have been simulated in artificial physiological solution. Comparison was made between SMA and other metallic implants.

Speck (1980) used hanks’ physiological solution at 37°C and pH 7.4. He pointed out that the corrosion resistance of NiTi is better that CoNiCrMo, CoCrMo, and 316L stainless steel. The addition of cystein amino acid to the solution which represents human blood plasma, lowered pH from 7.4 to 1.5. Although this addition causes a lower breakdown potential for NiTi, this breakdown still was comparable with or higher than other alloys except Ti6Al4V alloy. He defined the breakdown potential as the voltage at which there is a sharp increase in current density or a measurable change in the direction of the curve resulting form increased current density”.

Randi (1988) measured the corrosion resistance of various nickels containing alloys in vitro oxygen-saturated artificial sweat using the tafel extrapolation methods. It was found that the NiTi SMA was in a passive state and the pitting potentials was 1.05 V. The author concluded that the alloy might pit under certain conditions.

Good localized corrosion resistance of NiTi similar to that of Ti6Al4V alloy and better than the types of stainless steels AISI 316L and ASTM F138 at 40°C was evaluated in two studies by Vicentini (1990) and Rondelli (1996). The test was based on potentiodynamic polarization test. Also, potentiostatic scratch test, which determines the potential above which healing of the damaged, passive film does not happen, was done in the same two studies. It showed poor localized corrosion resistance of NiTi where ions releas from NiTi is three times higher than Ti6Al4V and austenitic stainless steel. This confirmed that the re-passivation of the surface film is a slow process. These results encourage using this alloy for long term implantation (Montovani, 2000). In addition, the stability of passive film formed on NiTi alloy is crucial for evaluating biocompatibility of implanted alloy (Rondelli, 2000).

Wever (1998) showed that the NiTi alloy has superior resistance to chemical breakdown of passivity than AISI 316 LVM. This is because the passive film on the
NiTi consists of a mainly TiO$_2$ based oxide with minimal amounts of nickel in the outermost surface layers. This layer is known to resist corrosion efficiently.

### 2.17.2. In Vivo Corrosion

The *vivo* test evaluate the changes occurring in tissues by biomaterials or in biomaterials by tissues. Mori (1995) had placed successfully a urethral SMA stent in 17 depilated patients with various conditions to relieve prostatic obstruction. The period of examination was ranging from 2 to 48 months. The placement and removal of the stent was easy. Neither bleeding nor hematuria occurred during operation. Neither migration nor dislodgement was noted during the indwelling period. The diagnostic on the patients was painless and free of residual urine. Moreover, no prostatism was observed.

Forty four nitinol intravascular stents were implanted in the iliac arteries of 22 sheep for up to six months. The analysis of the studied stents demonstrated a small pitting corrosion. Pit depth was 0.0023 cm. The pitting product was titanium bearing compound, probably the oxide. Even though corrosion was observed after long-term implantation of the stent, this was limited to small pits (Andrew, 1993).

Nitinol rods were implanted to correct spinal deformities in six goats (Sanders, 1993). There was no significant foreign body response. However, there was acute and chronic inflammation and new bone formation compatible with surgical trauma. Nickel and Titanium levels were found only in the surrounded fibrous capsule. Titanium level was 0.48 µg/g of tissue and nickel was 25.6 µg/g.

### 2.17.3. Improving the Corrosion Resistance of NiTi

The surface layer of metallic biomaterials affects their performance significantly (Chen, 1998). The stability of passive oxide layer is responsible for the corrosion resistance of the implanted alloy. This layer acts as a barrier between the alloy itself
and the bioenvironment (Wen, 1996). Some surface treatments have been suggested to improve the corrosion properties of NiTi SMA. This is because some toxic Ni may release from NiTi.

Actually, addition of Copper increases the repassivation potential of NiTi SMA, which improves their corrosion resistance. Wen could not verify this statement in his study in 1997. However, he found that the corrosion potential and corrosion rate of Ti_{50}Ni_{50-x}Cu_x (x = 1, 2, 4, 6, 8) alloys are not related to Cu content. After three months implantation, no corrosion was observed on all alloys surface.

The surface characteristic of electropolishing, heat treatment, and nitric acid passivation improves the corrosion resistance of NiTi alloy (Trepanier, 1998). The removal of the plasticly deformed native oxide layer and its replacement by a more uniform one, contributed to this improvement. The author concluded that the uniformity of the oxide layer seems to control the improvement of corrosion resistance rather than its thickness and composition.

Thierry and others (2000) improved the corrosion resistance of surface of oxide layer (TiO_2) on NiTi after mechanical polishing, electropolishing, and sterilization process. A comparison was done between NiTi, stainless steel, and Ti_6Al_4V. As a preparative surface treatment, electropolishing on NiTi decreased the amount of nickel on the surface, therefore, the corrosion behavior improved by increasing the mean breakdown potential value (0.99±0.05 V/SCE vs. 0.53±0.42). The sterilization technique did not modify the corrosion resistance of electropolished NiTi and the NiTi ranked between 316L stainless steel and Ti_6Al_4V. All alloys were immersed in Hank’s solution maintained at 38°C and the amount of released nickel after few days was similar from electropolished NiTi and 316L stainless steel. Furthermore, this amount of released nickel from passive dissolution was below the expected toxic level in the human body.

In a most recent study by Fu (2000), a pulsed high energy density plasma (PHEDP) coating has been used to improve the corrosion resistance of NiTi by about one order
of magnitude. PHEDP consists mainly of titanium and nitrogen (TiN or Ti$_2$N). In the
PHEDP surface modification, the effects of ion implanting combined with melting
and rapid quenching contribute to the formation of nano crystalline structure of TiN,
which is the main reason behind the corrosion of NiTi alloy.

2.18. Bio compatibility of Implanted Material

The material should remain inert in a biological environment after implantation to be
confirmed as a biocompatible material. This is imperative because local
toxicological, allergic, and/or oncogenic natures are neither wanted nor desirable.
Also, it is preferable to avoid inflammation and cell death of organs in the vicinity of
the implant (Putters, 1992), (Rostoker, 1996). The biocompatible material should be
not degradable or dissolvable which causes releasing of soluble material ions into the
tissue surrounding implants may cause local cytotoxicity affecting the morphology
and structure of the tissue, and may lead to allergic reactions to distant organs
(Mckay, 1996), (Broune, 1994). However, Mohanty (2002) found that long term
implantation, results in wear or corrosion of the materials.


The published knowledge about biocompatibility of SMA is only about NiTi alloy. It
is necessary to review the biocompatibility of NiTi alloy components. This is because
insufficient data of biocompatibility of NiTi. Corrosion causes dissolution of Ni and
Ti induces catastrophic effects and may become toxic to surrounding tissue. To date,
the process of degradation caused by the body’s environment on metal remains
largely speculative. Studying biocompatibility on nitinol is concerned with the
corrosion resistance of the alloy and the toxicity of individual metals, which may
dissolve from NiTi due to corrosion. Thus, it is important to understand the effect of
each one (Ryhanen, 1999b).
2.19.1. Biocompatibility of Nickel

Even though, nickel is an essential element for life, it is a potentially toxic metal for human health. It has been reported that the deficiency of nickel in the animals causes health risk effects. These include reduced growth, weight loss, skin change, and uneven hair development. Further, its deficiency impairs the metabolism of iron, fats, glucose, and calcium. Also, heart, liver, kidneys, and skeletal muscles are malfunctioning due to nickel loss (Ryhanen, 1999b).

In contrast, extra concentration of nickel will cause compatibility problems. The high nickel content of nitinol (54% by weight) may arise abnormality reactions if nickel solute from the alloy. With high concentration nickel damage cells in cell culture and may harm the bone on tissue culture. Many reactions occur in the body after the installation of nickel implants. These reactions are multiple oxidations that nickel undergoes and the many nickel compounds with other ions in the human body. It is known that nickel urges allergic especially on the skin contact with nickel alloy. Extensive amount of nickel would be capable of causing irreversible damage to DNA. There is no sufficient evidence showing the role of nickel to promote or initiate the cancer. Also, immune system is not affected by presence of nickel (Mantovani, 2000), (Ryhanen, 1999b), (Mckay, 1996).

Actually, nickel enters the body via the lungs, oral intake, and skin and is removed by urine and feces. If concentration of nickel is too large, it first accumulates in the pulmonary alveoli and kidney glomerules (Mantovani, 2000).

2.19.2. Biocompatibility of Titanium

Titanium and its alloys opposite to nickel are biocompatible. They are safely stable in the human body and have excellent mechanical properties. No toxic or inflammation response was observed during animal or human implant with titanium (Mantovani, 2000). Stable titanium oxide (TiO₂) film is naturally formed on titanium surface (Chen, 1997). This layer is responsible for good biocompatibility and corrosion
resistance of titanium and titanium alloys. In spite of the fact that breaking the passivation layer causes particles to leave, these particles are insoluble (inert). Also, the passivation layer is healed immediately because titanium has a high oxidation potential (Ryhanen, 1999b).

2.20. Biocompatibility of Nickel Titanium SMA

There are three known biomaterials: austenitic stainless steel Fe-Cr-Ni 316L, Cr-Co alloy, and the titanium alloy Ti-Al-V. Although there are few methodological studies on the biocompatibility of SMA, NiTi alloys show some satisfactory results. Nitinol alloy is offering the best corrosion resistance compared to other shape memory alloys surface (Manitoban, 2000). Compared to other implantable alloys, NiTi is either superior or having the same response on biocompatibility experiments. This is because intermetallic bonds between nickel and titanium are strong and stable, which reduce harmful reaction by surrounding tissue in the body (Hibbert, 1999). Also, nitinol is considered as titanium alloy that has passivation layer of TiO₂. Surface conditions are important to promote biocompatibility of NiTi alloys (Wen, 1995). To maintain passivation film, final treatment must be taken care to prevent small sites to pure Ni at the surface, or compound of NiO and Ti₂O. These results encourage selective dissolution in crystals. Special thermomechanical treatment are applied to NiTi to reach optimal surface performance with warranty to not damage the TiO₂ layer (Humbeeck, 1999)

2.20.1. Biocompatibility of NiTi in Vitro

Only a few in vitro studies of cell response to nitinol, nickel, and titanium have been reported. Putters and others (1992) published a report intending to evaluate the acceptance of NiTi in vitro. Mitosis in human fibroblasts in tissue cultures was used in that study. The results showed that nitinol and titanium induce no significant inhibition of mitosis in human fibroblast, where as nickel induces a significant
inhibition (p<=0.05). These findings confirmed that the biocompatibility of nitinol is comparable to titanium.

Wever and others (1997) evaluated a short-term biological safety of the NiTi alloy. Different tests were used in this paper. The NiTi alloy showed no cytotoxic, allergic, or genotoxic activity and compared to those on AlSi 316 LVM stainless steel. This promising biological behavior release minimal ions and reflects in good corrosion resistance of the NiTi alloy. They suggested NiTi alloy as a biological safe implant material.

Human peripheral blood lymphocytes were cultured in semi physiological medium and used to simulate in vitro genotoxicity of NiTi. A comparison was made with commercially pure titanium and 316L stainless steel. The electron microscopy in situ end-labeling (EM-ISEL) assay then was performed in order to provide quantification of in vitro chromatin DNA single stranded breaks. NiTi, titanium, and stainless steel induced similar DNA strand breaks of inter phase chromatin, but stainless steel induction on metaphase chromatin was more intense than with NiTi or pure titanium. The authors concluded that NiTi genocompatibility is promising in view of its biocompatibility approval (Assad, 1998).

2.20.2. Biocompatibility of NiTi in Vivo

The first attempt to evaluate a profound biocompatibility evaluation of NiTi was made by Castleman (1976). The methods of that study were versatile and the approach was well advised. The study has often been used as a reference study when discussing the biocompatibility. There were three dogs in the NiTi implant group and one Co-Cr implant and was fabricated into prototype bone plates. The examination was exposed for 3, 6, 12, and 17 months. The NiTi was laboratory prepared. Statically tests expected no significant differences between the mean thickness value of the scar cap capsules associated with NiTi and CoCr alloys, although the authors admitted that the capsules of different specimens of same material are inconvenient. The muscle tissue in dogs exposed to NiTi implants for 17 months showed some variability. Overall,
the gross clinical, radiological, and morphological observations of tissue at the implantation sites at autopsy revealed no signs of adverse tissue reactions resulting from the implants. The study warranted further investigation of NiTi alloy potential as a biomaterial even NiTi had no clearly toxic effects.

Andrew and others (1993) evaluated forty four NiTi stents in the iliac arteries of 22 sheep. Follow up was performed with angiography and histological examination for up to 6 months. There was no tissue reaction surrounding the implant site in each animal. However, the vascular wall at the implant sites of several samples contained tiny deposits of nickel-titanium. Even these deposits appeared to represent corrosion products that had undergone phagocytosis; the inflammatory response was mild. The researchers suggested the reliable of nitinol stent to deploy in the vascular system due to minimal corrosion was seen at 6 months, and the stent appears to be biocompatible.

Dai and others (1993) tested 158 NiTi staples in 135 patients for fixation bone fractures for 10 months and subjected to careful investigation by x-ray, histopathological examination, and scanning electron microscopy. It was verified that all fracture healed within two months of operation with complete recovery of the joint motion before fracture and ability to resume work. None of the staple taken out showed any corrosion, or ill effect on the surrounding tissues.

Yang (1994) developed nitinol ring, which was injected into nine dogs. The testing points were at various intervals from 15 to 90 days. The aim of this research is to reconstruct aorta. No complications such as dislodgment, bleeding from the anastomosis, aortic rupture stenosis, or aneurysmal dilation, were observed. These results showed no interstitial corrosion surrounding the tissues.

Drugacz and others (1995) made NiTiCo shape memory clamps and they were placed in seventy-seven patients for joining the bone fragments of mandibular fractures. Clamps were removed after a period of at least 6 weeks and tissue samples were taken for microscopic examination. No complications were found in 72 cases; in five patients infections occurred. Histological examination of tissue taken from 58
patients after removing of the clamps did not indicate any typical tissue reaction or sign of disturbed cell maturation with satisfactory bone healing. The authors concluded that shape memory clamps (Ti$_{50}$Ni$_{48}$Co$_{1.2}$) stabilize the fixation of the bone fragments with no evidence of corrosion.

Wen (1997) reported comparative study investigating the corrosion resistance and tissue biocompatibility of NiTi and Ti$_{50}$Ni$_{50}$xCu$_{x}$ (x = 1, 2, 4, 6, 8) alloys. Electrochemical and quantitative histomorphometric methods were used. After one month, the connective tissue layer covering the Ti$_{50}$Ni$_{42}$Cu$_{8}$ plates was statically significantly thicker than those of the other three types of plates (Ti$_{50}$Ni$_{50}$, Ti$_{50}$Ni$_{48}$Cu$_{2}$, or Ti$_{50}$Ni$_{42}$Cu$_{6}$). There were no significant differences in tissue reaction parameters after two and three months between four alloys. The observation was no corrosion on the plate surfaces of four SMA alloys, which induce good biocompatibility. Surprisingly no further comparative studies on the tissue reaction to NiTi have been published so far.

Neither toxic manifestation nor episodes of an allergic reaction occurred on NiTi clamps. They were used for fixation of small bone fragments in 54 patients during 1993-1995 (Musialek, 1998).

Ryhanen did two studies about biocompatibility of NiTi SMA, one paper was concerned with the implantation into paravertebral muscle and near the sciatic nerve while another was dealing with the placement of an implant in contact with the intact femur periosteum, but it was not fixed inside the bone. Seventy five NiTi wires were implanted in rats; one specimen per rat for both studies. Also, a comparison was made between nitinol, stainless steel, and Ti$_6$Al$_4$V. The testing periods were at 2, 4, 8, 12, and 26 weeks. In the first study (Ryhanen, 1998) light microscopy and semiautomatic computerized image analysis were used. Susceptibility of the muscle tissue to nitinol was non-toxic, no infection, no tumor found, or no abnormal behavior in all time period. The encapsulated membrane of nitinol was thicker than that of stainless steel at 8 weeks. However, the thickness of encapsulate of all tested material was the same at the end of the study. Another study (Ryhanen, 1999a) used
histomorphometry with digital image analysis and field emission scanning electron microscopy (FESEM). At two weeks the new woven bone formulation in the Ti$_6$Al$_4$V is higher than NiTi (P<0.01). At week 8, the NiTi (P<0.05) and stainless steel (P<0.005) alloys had greater cortical bone width. At 12 and 26 weeks no statically difference between them. The histological response of the soft tissues around NiTi implant was obviously non-toxic and non-irritating and similar to other materials. The authors for both studies concluded that nitinol has good biocompatibility in vivo.

Recently, Song and others (2000) inserted expandable nitinol stent in 25 patients with benign esophageal strictures. The stent was left for up to 8 weeks. Esophagogram was performed and stent placement was successful with no procedural complications. The stents were removed successfully and each patient was diagnosed during follow up ranging from 2-25 months. Twelve patients maintained their improvement in dysphagia and needed no further treatment. Thirteen patients with recurrence were treated by means of repeat balloon dilation. It was concluded that nitinol stents seems to be safe and effective method of treatment in selected patients with benign esophageal strictures.

The experiment of Beger-Gorbet and others (1996) has shown that the nitinol is not as biocompatible as one would expect. The biocompatibility of nitinol screws was evaluated using immunohistochemistry. This technique helps to observe the distribution of bone proteins during bone remodeling process around NiTi implant. Results were compared with screws made of vitallium, c. p. titanium, Duplex austenitic-ferritic stainless steel (SAF), and stainless steel 316L. Screws were tested in rabbit for 3, 6, and 12 weeks. The results of the NiTi screws compared with the other screws showed a slower bone remodeling process. Since, NiTi has a certain cytotoxic effect on cell; the authors would try to assess the effect of surface modification of NiTi.
2.21. Applications of Shape Memory Alloys

The unique properties of SMA make them the appropriate choice for different areas. They transpire a lot of fields like aerospace, military, automotive, telecommunication, Household instruments, building construction area, medical and dentistry. But the most notable success of shape memory has been in medicine (Feder, 2002).

2.21.1. Aerospace and Military Field

Tinel-lock rings used in electrical harnessing system as electrical connectors for fighting vehicles. At normal temperature, it can be stored and shipped. While the ring contracts to provide a secure joint when heated (by passing electrical current through the ring) (Raychem, 2000). Also, nitinol wires inside aircraft wing stretch from the trailing edge up to the top of the curve where the bottom is flat and the top is curved. These wires shrink, pulling the trailing edge down like the wing of a bird when heated. The same thing is occurring in smart helicopter blade equipped with nitinol (Williams, 1993). Loth (2001) designed jet engine that contains thousands of thin, small shape memory alloy flaps. This new jet engine fasts flying supersonic aircraft at less cost. In addition, Flexible satellite antennas and satellite release bolts are using shape memory alloys (AML, 1999). US army (1998) has designed a rotor blade technology that uses SMA to make helicopter flight quieter. Improving rotor aerodynamics and decreasing vibration and noise level accomplish this.

2.21.2. Automotive Industry

At higher than 82°C, the sealing nitinol plugs in diesel engine blocks expand and they will be sealed thus resisting high pressure and vibrations (Raychem, 2000). Also, slack adjuster made from CuAlNi SMA was used to compensate the difference between the dilation of steel and Aluminum components in a gearbox (Falcioni, 1992). Car antennas and actuators for central locking system are using SMA (MMG,
2002). Schetky designed Memory spring, which can regulate the radiator fan in an automobile cooling system that serves as a temperature sensor.

### 2.21.3. Household Instruments and Building Construction Area

Intelligent deep fryer has SMA blade that moves when cooking oil reaches 170°C, thereby allowing the fryer basket to descend into the oil. Also, ceiling system has CuZnAl blade that locks the ceiling plates in place upon temperature rises above 60°C. Thus the pipes and cables will be insulated from the fire (Falcioni, 1992). Connor proved that SMA works as temperature sensor in coffeepot thermostats, air conditioner controllers, and showerhead scald protectors. A sturdy shape memory wire, which connects a fishing line to a hook. When the line gets knotted up: warm it and straighten it self-out (Asahi, 1988). One recently deployed nitinol device is a tiny valve for a water sampler in Siemens’s newest dishwashers (Feder, 2002).

SMA can also be used for pipe couplings system and electrical connectors as discussed before. Also, they could be used to automatically open and close green house windows (Mavroidis, 1999). In telecommunication Industries retractable nitinol antennas wire for portable cellular telephones recover their straight shape when bending stresses are removed. In addition, the powerful feature of nitinol urges Mosely and Mavroides (2000) to utilize these wires in microrobotic system in space. Also, the modern heat engines embedded SMA (Iovine, 2001). Heat engine converts low temperature thermal energy to mechanical work. It uses a nitinol loop wrapped around a system of two pulleys; one in cold bath and another in hot bath (George, 1998).

### 2.21.4. Medical and Dental Applications

The versatile SMA rushes into the most commercial products in new medical fields. Duerig (1996) states that, due to their special features such as biocompatibility, kink resistance, constancy of stress, physiological compatibility, shape memory effect,
dynamic interface, and fatigue resistance, SMA penetrate medical and dental field qualification. Beside these properties high wear resistance and corrosion resistance cannot be regardless (IBB, 2001). Also, Stöckel (1996) added that the non-linear elasticity of super elastic provides a ‘physiology’ fell and built in over load protection.

The most dramatic advantage offered by these alloys is superelasticity, which is even superior to shape memory effect. This is due to a combination of high strength, high stiffness, and high reliability, which can not be present at the same time in other materials (Humbeeck, 1999). Among types of SMA, NiTi is dominating because of its biocompatibility feature. Generally SMA can be applied as an implant, in surgery tools, and instruments. In the following some examples of devices that contain SMA.

Superelastic nitinol wire is used in angioplasty guidewire because straightness is required through tortuous vessel paths. HYRL (1986) designed endoscope SMA to be inserted easier into the stomach and colon. Needle is peripherally made from superelastic nitinol because the stress is quite constant for further bending. Therefore, prevention tissues damage (Mekzerm, 1994). Nitinol grasper used to retrieve stones from kidneys, blades, and bile ducts (Suerig, 1997). Mavroidis (1999) stated that a team led by Sawyer developed and tested artificial heart power by SMA electrical actuator.

Nitinol SMA stents help restore blood flow in the artery and blood vessels (Hibbert, 1999), (Tominaga, 1992). Vinograd (1994) developed a new intraluminal nitinol airway stent in pediatric patient to repair of congenital tracheal stenosis and after tracheal resection. Tsugawa (1999) have designed a coil airway stent using a thermal nitinol SMA to relieve airway collapse in children. Thermal expandable NiTi stents are used instead of stainless steel balloon because they provide effective palliation of malignant esophageal obstructions with low risk (Kulkarni, 1999). Recently, Chen (2002) has used NiTi SMA mesh stent for correction of adult cleft nose deformities.

In orthopedic sector, SMA plates or staples implanted on both sides of broken bones. They contract at body temperature of the patient and fit between two parts of the
bone. This will accelerate healing because they provide a constant torque (Allsopp, 1997). With the same process, a SMA spacing disc or rod is inserted between two vertebrae, which straighten crooked spines more effectively and more safely than current surgical tools to reinforce the spinal column. Also, this process is used to correct scoliosis and reinforcement of the spinal column. (Leo, 1995), (Veldhuizen, 1997), (Mantovani, 2000).

Porous nitinol in skull plates promotes bone ingrowth because it is similar to the mechanics of biological materials by sharing loads with the surrounding tissue (Duerig, 1997). A thin needle or hook of SMA is used to locate and isolate a beast cancer during the surgical operation. Thus the operation can be more precise and less invasive (Stöckel, 1996).

The most famous role of SMA is in orthodontic treatment by superelastic SMA archwires. NiTi wire moves teeth under uniform low and constant force at mouth temperature (37°C) during tooth movement (Raboud, 1998). Consequently, gaps between healthy teeth would be closed (Glendenning, 2000). This will relatively eliminate retighten again over along treatment time and a much larger teeth displacement. These reduce visiting orthodontist because the increased elastic range reduces the need for wire retightens with less pain.

Suerig (1997) showed that the newest product that utilizes the advantage of elastic deployment is the arterial septal defect occlusion system (ASDOS), which avoids surgery. It is used to repair or seal occlusions or holes in the arterial wall of the heart. Beside these, other applications are still in the research stage like hip prostheses (Mantovani, 2000). By its shortening, when electricity go through it, a shape memory alloy wire could be used to improve the self-sufficiency of people handicapped by pretension difficulties (Nicolas, 1999)
2.21.5. Other Fields

Thermo-O-Disc battery, which utilizes nitinol SMA, is used to power a variety of portable devices such as laptop computers and cell phones. It is used instead of lithium-ion battery cells because it enhances battery performance (Babyak, 1999), (Knott, 2000). Wn (2000) suggested that NiTi wire be utilized as strain sensors in actuator intelligent systems. Furthermore, Pfeiffer and others designed SMA artificial muscles as actuators in artificial limbs in robotics at Rutgers University. Also, they developed a finger prototype to test actuation schemes with SMA in multifingered hands. Also, Brown (2001) used SMA as read/write head mechanisms in disk drives and disk ejection mechanisms in computers.
Chapter Three

Materials and Methods
3. Materials and Methods

3.1. Introduction

Studying the biocompatibility and corrosion resistance is a very important aspect before applying the shape memory alloys as a biomaterial. Two types of shape memory alloys have been studied, nitinol alloys (NiTi SMA) and copper based alloy (CuAlNi SMA). Different techniques were used to check the performance of the shape memory alloys.

Biocompatibility testing and evaluation of medical devices is performed to determine the potential toxicity resulting from contact of the device with the body. The materials should not, either directly or through the release of their material constituents, produce adverse local or systemic effects, be carcinogenic, or produce adverse reproductive and developmental effects. In this work, three tests have been done to evaluate the biocompatibility of tested SMA alloys. They are animal blood analysis, muscle contraction measurements, and ultrastructural evaluation of blood capillaries and nerves that connect to the muscle.

Since corrosion is an electrochemical process, it follows that electrochemical techniques and electrochemical instrumentation can be used to study the corrosion process. The electrochemical techniques measure the corrosion resistance of the tested alloys. Several techniques were utilized in polarization of specimens for corrosion testing. Polarization resistance monitors the resistance of the material to corrosion. Polarization resistance test, tafel measurement and potentiodynamic polarization are techniques where the potential of the electrode is varied at a selected rate while monitoring the current response through the electrolyte.
3.2. Test Implants

The materials tested were three types of nitinol and copper based alloys. The nitinol alloy is a NiTi family that is composed mainly of nickel and titanium. The NiTi alloys were obtained from medical technologies n.v and their composition is shown in table 3.1. Three different sizes of NiTi were available; one with a diameter of 1mm, which represent standard oxide free, while the other two have 0.25 mm. One of the wires of 0.25 mm is provided with an oxide-coated surface while the other one is not. CuAlNi alloy is part of the copper based alloy family. The material information and chemical composition CuAlNi alloy according to the data sheet provided by the supplier are listed in table 3.2. The company is United Finance Group Inc. The diameter of CuAlNi is 1mm. All the materials were in cylindrical form (rods).

Table 3.1: Chemical composition (weight %) of NiTi family alloys and their mechanical properties.

<table>
<thead>
<tr>
<th>Chemical composition:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel (%wt.)</td>
<td>55.7 nom.</td>
</tr>
<tr>
<td>Titanium (%wt.)</td>
<td>Balance</td>
</tr>
<tr>
<td>Carbon (ppm)</td>
<td>500 max.</td>
</tr>
<tr>
<td>Oxygen (ppm)</td>
<td>500 max.</td>
</tr>
<tr>
<td>Any single trace element (%wt.)</td>
<td>0.1 max.</td>
</tr>
<tr>
<td>Total trace elements (%wt)</td>
<td>0.4 max.</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1,250</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mechanical properties:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total elongation</td>
<td>10% min.</td>
</tr>
<tr>
<td>Ultimate tensile strength</td>
<td>1137.8 Mpa min.</td>
</tr>
<tr>
<td>Plateau stress at 4% strain</td>
<td>413.8 Mpa min.</td>
</tr>
<tr>
<td>Ar</td>
<td>-5°C to 10°C</td>
</tr>
<tr>
<td>Density (g/cm3)</td>
<td>6.45</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>80x 10⁻⁶ ohm nom. Martensite</td>
</tr>
<tr>
<td>Corrosion Resistance</td>
<td>Excellent</td>
</tr>
</tbody>
</table>
Table 3.2: Material information and chemical composition (weight %) of CuAlNi alloy.

<table>
<thead>
<tr>
<th>Chemical composition:</th>
<th>Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (%wt.)</td>
<td>13.0-13.5</td>
</tr>
<tr>
<td>Aluminum (%wt.)</td>
<td>4.0-5.0</td>
</tr>
<tr>
<td>Nickel (%wt.)</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Oxygen (%wt.)</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Total all others (%wt.)</td>
<td>1.050</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Transformation temperature:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_s$</td>
<td>72°C</td>
</tr>
<tr>
<td>$M_f$</td>
<td>55°C</td>
</tr>
<tr>
<td>$A_s$</td>
<td>67°C</td>
</tr>
<tr>
<td>$A_f$</td>
<td>86°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mechanical properties:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovery strain (%)</td>
<td>Not less 8</td>
</tr>
<tr>
<td>Condition</td>
<td>As heat treatment</td>
</tr>
<tr>
<td>Surface</td>
<td>As grow</td>
</tr>
<tr>
<td>Diameter</td>
<td>1.0 mm</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>7.150</td>
</tr>
<tr>
<td>Corrosion Resistance</td>
<td>Good</td>
</tr>
</tbody>
</table>

In this project, four types of different SMA electrodes were implanted in the mice. A standard oxide-free NiTi alloy with a diameter of 1 mm, CuAlNi alloy with a diameter of 1 mm. The other two are from NiTi alloys having an oxide and non-oxide layer respectively with 0.25 mm diameter. Metal test implants of 40-mm length were taken from longer wire by cutting them with clippers. Special metallurgical surface preparations were not made; the material surfaces were as received. The test implants were degreased in ethanol and was thoroughly rinsed with distilled water and dried.
3.3. Animals

All the animals used were male mice TO strain and Wistar rats from the laboratory animal center after being approved by the faculty of medicine (UAE University). The ages of the mice ranged between 12 and 13 weeks with a weight range of 32 to 35 g. The rats age are close to 8 weeks with a weight from 150 to 180g. All the animals were housed in groups; each ten mice or four rats were kept in polycarbonate cages in a thermostatically controlled room at 25 ±1°C. The room was artificially illuminated on a schedule of 12 h of light and 12 h of darkness. Wooden chewing was used as bedding, pelleted mouse feed (Abu Dhabi National Hotels Company, Abu Dhabi) and tap water ad libitum was available. The animals were divided into four groups. These were treated after implantation up to 4, 8, 12 and 16 weeks respectively. A fifth group served as a control.

3.3.1. Mice Implantation

Previously, one hundred and seventy mice were injected in four times as shown in table 3.3. One implant (electrode) was implanted per animal. In the first time of surgical implantation, 20 mice were implanted; 10 electrodes of oxide NiTi SMA were fixed in 10 mice and another 10 mice with non-oxide NiTi electrodes. There were 40 mice in the second surgical operation, which was done after six weeks from the first implantation. Each ten mice were implanted with one of the four types of our electrode. In the third operation after fourteen weeks from the second implantation, 5 mice were implanted with a standard NiTi electrode, 10 mice with a CuAlNi electrode, 20 mice with an oxide NiTi electrode, and 15 mice with a non-oxide NiTi electrode. After four weeks, the forth implantation was decided. The electrodes were 20 for each group except standard NiTi electrode.
Table 3.3: The number of implanted animals in each group.

<table>
<thead>
<tr>
<th>Implantation</th>
<th>Standard NiTi (1 mm)</th>
<th>CuAlNi (1 mm)</th>
<th>Oxide NiTi (0.25 mm)</th>
<th>Non Oxide NiTi (0.25 mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>19</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>10</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>

### 3.3.2. Problems Faced With the Experiments

For the first three implantations, the length of the electrode was 4 cm. In the first examination, in a sample of 19 mice with different types, only two electrodes were found. One was injected with a thick electrode of CuAlNi and one was injected with a thin electrode of oxide NiTi. Following this, it was decided to shorten the length of the electrode from 4 cm to 2 cm in the fourth implantation.

The problem remains unsolved and electrodes were still pushed away from the body. The mice were selected first because most of the equipment and drugs in the faculty of medicine are suitable for the mouse. Also, they are available in the animal house. Furthermore, due to the small size of the mouse, the implantation operation procedure was easy to manage.

### 3.3.3. Rats Implantation

The rats were selected as a tested animal after the failure of finding electrodes in the mice because rats are less active than mice. Since the quantity of available electrodes decreased, the number of tested animals was smaller than the previous cases. In the fifth implantation, 12 rats were used for electrodes of standard NiTi, oxide NiTi and...
non-oxide NiTi, as described in table 3.3, while 10 rats were injected with electrode of CuAlNi. Beside these rats, eight control rats were kept untreated.

### 3.4. Biocompatibility Test Procedure

#### 3.4.1. Surgical Procedure

The animal was anaesthetized with diethyl-ether (BDH Library Service, England). Diethyl-ether is a solvent, which is used for short term anesthesia. The animal was put in a beaker containing cotton gauze soaked with diethyl-ether as shown in figure 3.1. Breathing in this beaker makes the animal sleep. As soon as the animal was asleep, it was putted on the dissection board. Care was taken not to over drug the animal, which may result in killing the animal. Animals' legs were fixed on the dissection board with pins as shown in figure 3.2.

![Figure 3.1: Animal in the beaker during anesthesia](image)
For inserting 1 mm diameter electrode, a hole was made in the left leg with the help of a sterile hypodermic needle (Becton Dickinson S.A., Spain) and the electrode was
slowly pushed through this hole subcutaneously after removing the needle as shown in figure 3.3. For 0.25 mm electrode, the electrode was pushed through the needle into the skin with the help of a forceps. Before insertion, all electrodes were cleaned with deionized water and dried. The whole process had to be done quickly before the animal recovered from anesthesia. Animals were put back in the cage for recovery and no drug was used against inflammation or infection.

3.4.2. Muscle Preparation for Contraction Studies

The animals were anaesthetized with urethane (25%). The dose is calculated according to the weight of the animal (0.1ml/30gm body weight). Urethane causes the animal to sleep. Then the animals were secured on the dissection board and legs were fixed with the pins to prevent interfering movements. The skin of the left leg was removed and then the implant was carefully removed. The flexor muscle was cut carefully to avoid any bleeding and damaging the muscle. The tendon of the muscle was fixed with a thread tightly and the tendon was cut to free the flexor muscle from the connective tissues as shown in figure 3.4. This muscle contains predominantly fast twitch muscle fibers. The flexor muscle was selected because its location makes in situ recording possible and it contained predominantly fast-twitch muscle fibers (Hasan, 2002).

Table 3.4: Compositional elements of Kreb's solution

<table>
<thead>
<tr>
<th>Elements</th>
<th>g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>7.88</td>
</tr>
<tr>
<td>KCl</td>
<td>0.3725</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>0.246</td>
</tr>
<tr>
<td>Glucose</td>
<td>2.17998</td>
</tr>
<tr>
<td>Na₂HPO₄</td>
<td>0.14196</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>1.266</td>
</tr>
<tr>
<td>Cagluronate</td>
<td>1.0759</td>
</tr>
<tr>
<td>PH</td>
<td>7.4</td>
</tr>
</tbody>
</table>
Another incision was made to expose the sciatic nerve, which supplies the flexor muscle. The exposed nerve and muscle should be kept moist throughout the experiment with normal Kreb’s solution at room temperature (25°C). The composition of the kreb’s solution is listed in the table 3.4. The above process was repeated for exposing the right flexor muscle.

![Figure 3.4: Prepared process of the muscle for muscle contraction measurement. The sciatic nerve of the rat is shown as a white line.](image)

### 3.4.3. Muscle Contraction Measurements

Immediately, the muscle contraction test was verified. The muscle contraction was applied because the electrode was implanted inside the left leg near the flexor muscle. The other end of the flexor muscle was tied to the transducer as shown in figure 3.5. The stimulation was given indirectly (through sciatic nerve) and directly through the muscle. Direct and indirect isometric twitch tension was measured after the tendinous insertion was attached to a force-displacement transducer (model FT-03C; Grass Instrument Co., Quincy, MA), and the output was amplified differentially and displayed on a chart recorder on the computer for further analysis.
The muscle contraction charts were performed via Intracel software (Intracept physiology teaching system, England) attached with a transducer that is used to stimulate the muscle. A stimulator (Grass S44, USA) was used to evoke twitches either directly or indirectly, delivering 5 volt, 0.5 msec duration. (DC wave pulses). In direct muscle stimulation, two wide platinum wires were placing underneath the muscle. The tension-time curves obtained from the groups studied were displayed as twitch tension (g) on the y-axis and time on the x-axis. The frequency relationship was tested using a train of stimulation at the single twitch (1Hz), 5Hz, and 30Hz for 10 seconds each separated by a one-minute rest. Trains of 30Hz stimuli were applied to assess muscle fatigability (Nakahata, 2001).

Figure 3.5: The stimulation of flexor muscle via the transducer to prepare the muscle contraction measurements.
3.4.4. **Tissue Collections and Specimen Processing Evaluation**

After finishing the muscle contraction measurement, the flexor muscle of the left legs was removed and weighted and was put in the McDowell & Trump prefixative solution for one day either in the refrigerator (4°C) or at room temperature. The chemical composition of the fixative solution is presented in table 3.5. The fixative solution is useful to preserve the structure and relationships of cells and the intracellular substances of tissues. Similarly, tissues from liver, heart, spleen, and kidney were collected and put in the fixative for one day.

Blood was collected from the carotid artery as shown in figure 3.6 and serum was split for analysis after centrifuging the blood. The serum samples were kept in the fridge at about -80°C until sending them to chemical testing. Tissue samples were washed on the next day with the buffer for the couple of times and sent for TEM (Transmission Electron Microscope) preparation.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde (37%)</td>
<td>50 ml</td>
</tr>
<tr>
<td>Glutaraldehyde (25%)</td>
<td>20 ml</td>
</tr>
<tr>
<td>0.1 M monobasic phosphate buffer</td>
<td>430ml</td>
</tr>
<tr>
<td>• KH₂PO₄</td>
<td>3.4 g</td>
</tr>
<tr>
<td>• NaH₂PO₄.H₂O</td>
<td>10.4g</td>
</tr>
<tr>
<td>• Distilled water</td>
<td>1000 ml</td>
</tr>
<tr>
<td>• PH 7.2</td>
<td>*36 mls of 2M NaOH into final 1000 mls</td>
</tr>
</tbody>
</table>

Table 3.5: Chemical composition of fixative solution (McDowell and Trump Fixative), source: Arch. Pathol. Lab. Med., 100:405, 1976. * 2M --> 80g of NaOH /1000 ml distilled water
3.4.5. Analysis of Animal Blood

Wet digestion was done before analyzing blood to transfer the blood serum into inorganic form (Manning T, 1997). The samples were weighted in the 150 ml beaker. A 25 ml of concentrated nitric acid (HNO₃) was added. Covered with a watch glass and boiled for 30-45 minutes. The solution was cooled to oxidize all easily oxidizable material and added 10 ml 72% HClO₄. Boiled very gently until the solution was nearly colorless. The solution was not be allowed to go to dryness. Left the solution to cool and added distilled water and dilute to 10 ml with distilled water in 10 ml volumetric flask. The samples became digested samples in inorganic form. Blank was prepared at the same time and the same condition. The prepared samples were sent to Inductivity Coupled Plasma Atomic Emission Spectrometry (VISTA, Australia) to determine the metal contents of Ni, Cu, and Al.
3.4.6. Samples Processing and Embedding Protocols for TEM Studies

3.4.6.1. Thin Sectioning

At the termination of the muscle contraction experiment of each group, the tissues, which were dissected out from the animals, were cut into small pieces having the size of 1x1x3 mm maximum. These specimens were then transferred into prefixative solution (McDowell+ Trump) immediately, in 7 ml glass bottles and were left for four hours at room temperature. This mixture of glutaraldehyde and formaldehyde fixative was used to fix and stiffen the tissues, so they are capable of bearing up against a sharp cutting edge. Then the samples were washed in phosphate buffer (G. Millonigs phosphate buffer 0.1 M, Ph 7.2) three times for five minutes each and stored at 4°C until being ready for post fixation. The usefulness of the buffer is to preserve the details of molecular architecture and maintain osmotic pressure of tissues (PH 7.2).

3.4.6.2. Fixation

After that, 2 ml of buffered 1% osmium tetroxide aqueous (R1023, Agar Scientific Limited, Standard Essex England, U.K.) was added to each bottle and mixed for 90 minutes on a Rotamix (Agar Scientific Ltd 66a, Essex CM24 8DA, England) at room temperature. A 2 ml of osmium tetraoxide 4% solution; OsO₄ was prepared in 6 ml of phosphate buffer at near neutral pH. This solution represents a secondary fixative solution that keeps the morphology of the tissues (internal organisms), so they can resist the effects of subsequent steps (dehydration, embedding, and electron microscopy). The osmium solution was removed and the samples were rinsing three times in distilled water to remove the excessive osmotic acid.
3.4.6.3. Dehydration

The dehydration process was carried out via a graded alcohol series (Panreac, Panreac Quimica SA, E.U.) to dehydrate the specimen and decrease the water concentration in the tissue samples according to the following procedure:

- 50% ethanol (CH₃CH₂OH) – 15 minutes
- 70% ethanol – samples could be stored at 4°C until they were ready for further processing.
- 95% ethanol – 15 minutes
- 100% ethanol I – 15 minutes
- 100% ethanol II – 15 minutes
- Propylene oxide I (CH₃CH.CH₂O) – 15 minutes
- Propylene oxide II – 15 minutes

Propylene oxide was used because it evaporates the water more easily than alcohol. Also, it prepares the samples for epoxy resin, which is used for embedding purposes.

3.4.6.4. Embedding

The Epon812 resin (Agar Scientific limited, Stansted England, U.K.) was prepared carefully in a plastic disposable beaker and made up using a balance in a fume hood. The chemical composition of resin is presented in table 3.6. Thoroughly the resin components with a wooden tongue depressor was mixed. The samples were infiltrated where the final dehydrating fluid, which is propylene oxide was mixed with resin together in a 3:1 ratio respectively, allowing 3 ml per bottle and these mixture was left one hour. Then mixture was replaced with a 1:1 ratio of resin with propylene oxide for one hour. After that, the samples were transferred to pure resin and were left overnight in the refrigerator.
Table 3.6: Chemical compositions of resin

<table>
<thead>
<tr>
<th>Contents</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agar 100 epoxy resin</td>
<td>R1043</td>
</tr>
<tr>
<td>DDDSA (C₁₆H₂₆O₃)</td>
<td>R1051</td>
</tr>
<tr>
<td>MNA (C₁₀H₁₀O₃)</td>
<td>R1081</td>
</tr>
<tr>
<td>DMP-30 (C₁₅H₇N₃O)</td>
<td>R1065</td>
</tr>
</tbody>
</table>

The next day, a second resin replaced the older one and left it for three hours. Resin II was changed with a fresh resin III and embedded samples in small blocks by transferring samples with the tip of a wooden toothpick to the bottom of the cavity in flat embedding mold and overlaid with the embedding mixture. The blocks were then hardened and polymerized in an oven (Agar Scientific, Stansted Essex England) set at 65°C for 24 hours. The usefulness of resin is to permit cutting the samples into ultra thin sections.

3.4.6.5. Microtomy

3.4.6.5.1. Block Trimming

The blocks were removed from the oven and were started rough block trimming by removing the hard resin around the surface of the sample to became a pyramid shape with stainless steel razer blade and glass knife before starting the sectioning of the samples. The rounded end of the embedded block which was mounted in the was trimmed freehand with a razor blade to a four-sided truncated pyramid of about 45° angle and about 0.5 mm square face.

3.4.6.5.2. Semithin Sectioning

The block is trimmed to semithin sections (2-3 microns). The semithin sections were cut with glass knife (LKB, Sweden) then transferred with forcep and mounted on a drop of distilled water on glass slides, then heated on a hot plate at 80°C for a few
minutes to induce spreading and sticking with the glass slide. Sections were stained with aqueous 1% toluidine blue to get the contrast for a few seconds and washed by distilled water and then left to evaporate on the slide warmer. Thick sections taken on glass slides were covered with cover slips and observed under the light microscope (Microthek Medical Inc. Washington, USA) to get tissue orientation for ultrathin sections and light microscopic studies.

3.4.6.5.3. Ultrathin Sectioning

The trimmed blocks were finally remounted in the automatic rotary ultra microtome chuck (Reichert Ultracut Leica, Wein-Austria). A diamond knife (Polyscience Inc. Warrington PA UK) is triangular in shape and is obtained by breaking a square piece of glass along a diagonal line scored into its surface. The cutting edge should be straight and even and the front surface (facing the specimen) very flat and smooth. With a diamond knife, ultrathin sections were cut and floated on the surface of water in the form of ribbon (distilled water) filled in truf. The floating ultrathin sections of golden color (70-90 nm) were collected on 300 mesh Cu grids with the help of metallic loop. The grids were kept on 11mm whatmann filter paper in a petriplate to dry them properly.

3.4.6.6. Contrasting the Ultrathin sections (grids)

The ultrathin sections were contrasted by using the saturated heavy metallic stains; i.e. uranyle acetate (BDH Chemicals Ltd Pool England) and lead citrate (Agar Scientific Ltd Essex, England), which were freshly prepared in the laboratory. These stains was used to enhance the scattering contrast of specimens by increasing the mass density differences of various components of tissue and cells, thus increasing the scattering of electron outside the objective aperture (YUN, 2001). The metal ions of the staining solutions form complexes with certain components of cells, thus increasing their density.
The first staining step was to float the sections mounted on the grid on the surface of 13% uranyle acetate in distilled water for 25-30 minutes under a glass chamber with NaOH pellets. The single droplet of staining solution was placed on the surface of wax and the grid was placed with the sections facing the surface of the drop. The grids were then removed and washed with distilled water and transferred to the droplet of lead citrate for 10-12 minutes. After the second staining, the grids were removed and washed with distilled water and transferred to the filter paper in a glass chamber to dry them. Then the grids were ready to observe under transmission electron microscope.

Lead citrate was prepared by adding 1.3 g of lead citrate in 15 ml of distilled water and 1.76 g of sodium citrate in 15 ml distilled water. Each solution was dissolved separately and they were mixed to form the milky solution and mixed by hand vigorously to homogenize them. Then 8 ml of 1N sodium hydroxide was added. The milky mixture was turned into the transparent solution and then it was filtrated and made up to 15 ml distilled water.

3.5. Electrochemical Techniques

3.5.1. Electrochemical cells

The main cell used as the electrolyte consist of three electrodes that were immersed in physiological solution and one compartment glass cell as shown in figure 3.7. The working electrode, which is a tested electrode, was inserted in the glass tube 3 cm long and having an inner diameter of 0.8 cm. Their terminals were outside the tube. An epoxy resin was used in one terminal to protect the sample and its holder from the solution except for a length of 1 cm. The second terminal was connected to the circuit. This specimen configuration was used for electrochemical measurements. The second electrode was a reference electrode that was a saturated Ag/AgCl reference electrode. The third electrode was an auxiliary electrode that completes the circuit and it was made of platinum sheet (2 x 2 cm²) counter electrode, which serves as
a catalyst to measure the potential. The surface potential of the working electrode was measured with respect to a reference electrode. Experiments were carried out at room temperature (25°C).

![One compartment cell of electrochemical measurement](image)

**Figure 3.7:** One compartment cell of electrochemical measurement, where R: Reference electrode, W: Working electrode, C: Counter electrode which is platinum electrode.

### 3.5.2. Solution Preparation

The physiological solution was prepared from reagent chemicals and distilled water in the physiological laboratory at the College of Medicine. Ringer's solution is a special type of physiological solution that was selected in this thesis, which simulates the muscle as presented in table 3.7. This solution was used as electrolyte in electrochemical measurements.
3.5.3. Experimental Electrochemical Measurements

Polarization resistance, Tafel experiments and Potentiodynamic tests are the most commonly used electrochemical techniques that have been performed to study the corrosion rates in physiological solutions. These methods were applied to study the corrosion resistance of SMA in physiological solutions. All measurements were carried out with Gamry CMS 100 software. Before doing these tests, the open circuit condition was applied to identify the open circuit potential ($E_{\text{open}}$) of the specimen that represents the equilibrium potential for 300s. It measures the potential versus time until a steady potential was obtained ca. ±0.001 V variation.

Table 3.7: Chemical Composition of Ringer' solution

<table>
<thead>
<tr>
<th>Composition</th>
<th>Concentration</th>
<th>Molecular Weight</th>
<th>Liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>135 mM</td>
<td>58.44</td>
<td>7.55</td>
</tr>
<tr>
<td>KCl</td>
<td>5 mM</td>
<td>74.50</td>
<td>0.3725</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>1 mM</td>
<td>246.48</td>
<td>0.24648</td>
</tr>
<tr>
<td>Glucose</td>
<td>11 mM</td>
<td>198.18</td>
<td>2.17998</td>
</tr>
<tr>
<td>Na₂HPO₄</td>
<td>1 mM</td>
<td>141.96</td>
<td>0.14196</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>15 mM</td>
<td>84.0</td>
<td>1.266</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>25 mM</td>
<td>430.38</td>
<td>1.0759</td>
</tr>
</tbody>
</table>

3.5.3.1. Linear Polarization Resistance (LPR)

Linear polarization resistance (LPR) measurement was generally followed according to ASTM G59 (conducting potentiodynamic polarization resistance measurements). The corrosion potential of the specimen tended to become more negative after immersion, and reached a relatively steady state after 10 minutes. The response of the curve rapidly increased during the first few seconds after immersion and then stabilized much slower with time. Once the steady state free corrosion potential ($E_{\text{open}}$) was achieved, the specimen was polarized to 20 mV more negative than the
Asessment of the Performance of Shape Memory Alloys As Implant Devices
Noura Al-Khalifi

recorded corrosion potential. Then the anodic potential scan was started at a sweep rate of 1 mV/sec.

The potential sweep was terminated when a potential of 20 mV was reached. Thus, the aim of polarization resistance measurement is to change the potential around the equilibrium potential with a range of ±20 mV. The polarization resistance is the ratio of the applied potential and the resulting current response. This "resistance" is inversely related to the uniform corrosion ($R_p = \frac{V}{I}$). The polarization resistance can be determined from a plot of polarization data near the freely corroding potential ($E_{corr}$). The accuracy of LPR measurements is most likely to be affected at higher corrosion rates (lower polarization resistance) where the resistance is inversely related to the corrosion rate. Polarization experiments were conducted according to the conditions listed in table 3.8.

3.5.3.2. Tafel Extrapolation Measurements

In this method, once the steady-state free corrosion potential was achieved, the specimen was polarized to 250 mV more negative than the recorded corrosion potential. Then the potential scan was started in the anodic direction at a sweep rate of 1 mV/sec. The scan direction was reversed when the current density reached a value 1.5 to 2 decades higher than the passive current density. The scan was terminated when the current density after reversal decreased to the passive value. Thus, the range of applied potential was increased to ±250 mV versus equilibrium potential.

The polarization behavior is reflected in a linear plot of potential vs. the logarithm of current. The resultant current is consequently increased and the surface on the specimen will be affected. Two lines are obtained (one for anodic and the other for cathodic) as a result between potential current relationships. To determine the corrosion current ($I_{corr}$) form the plots of the polarization curve is by extrapolating the anodic and cathodic tafel region to the corrosion potential ($E_{corr}$) and they have intersect at the corrosion potential. By definition, corrosion potentials usually refer to
open circuit (no current flow) measurement (Tullmin, 2000). From the value of the corrosion current \( I_{\text{corr}} \), the corrosion rate can be expressed as an average penetration rate. Tafel measurement conditions are listed in table 3.8.

### 3.5.3.3. Potentiodynamic Polarization Measurements

The aim of the Potentiodynamic Polarization Measurement is to examine the corrosion behavior over a broader range of polarization. The test was conducted in the range of potential that is far away from the equilibrium point (-0.5 to 1.5V) and scan rate of 5 mV/sec. Table 3.8 lists the experimental conditions for potentiodynamic experiments. First, the current density is decreased while increasing the potential that causes cathodic reaction start and which is located under the equilibrium point. When reaching the corrosion potential \( E_{\text{corr}} \) the current density is suddenly increased thus result in an anodic reaction. The corrosion current \( I_{\text{corr}} \) represents the current density that corresponds to the corrosion potential \( E_{\text{corr}} \).

**Table 3.8: Electrochemical measurement conditions**

<table>
<thead>
<tr>
<th>Electrochemical Tests</th>
<th>Initial Potential</th>
<th>Final Potential</th>
<th>Scan Rate</th>
<th>Initial Delay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polarization Resistance</td>
<td>-0.02V vs. ( E_{\text{open cir.}} )</td>
<td>+0.02V vs. ( E_{\text{open cir.}} )</td>
<td>1 mV/s</td>
<td>300 s</td>
</tr>
<tr>
<td>Experiments</td>
<td>-0.250V vs. ( E_{\text{open cir.}} )</td>
<td>+0.250V vs. ( E_{\text{open cir.}} )</td>
<td>1 mV/s</td>
<td>300 s</td>
</tr>
<tr>
<td>Tafel Experiments</td>
<td>-0.5V vs. ( *E_{\text{reference}} )</td>
<td>+1.5V vs. ( *E_{\text{reference}} )</td>
<td>5 mV/s</td>
<td>300 s</td>
</tr>
<tr>
<td>Potentiodynamic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiments</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(*E_{\text{reference}}: \text{Ag/AgCl}.*\)
3.6. Equipments and Instrumentations

3.6.1. Electrochemical Equipments

Electrochemical measurement analysis; polarization resistance, tafel, and potentiodynamic measurements were performed using Gamry CMS system equipped with an IBM computer and Gamry control/analysis software (Gamry, Inc., USA).

3.6.2. Surface Analysis Instrumentation (SEM & EDXA)

The specimen surface was characterized using scanning electron microscopy (SEM) equipped with an energy dispersive x-ray analyzer (EDXA). The surface morphology was determined by using a Jeol Model JSM-5600 SEM attached with EDXA capability. The instrument has a magnification range from 18 xs to 300,000 xs with a resolution of 3.5 nanometers. Some of the samples were coated with a very thin layer of gold to eliminate the effect of charging during measurements. A Jeol JFC-1200 fine coater was used for this purpose. Quantitative elemental analysis of a tested alloy was detected by EDXA.

3.6.3. Muscle Contraction Equipment’s

The flexor muscle contraction was performed using Intracetae physiology teaching system (Intracet, Inc., England) equipped with an IBM computer and Intracetae software attached to a transducer (Grass S44, USA) which was used to stimulate the muscle in 1, 5, 30 Hz.

3.6.4. Light Microscopy

The semithin sections of tissues were observed under the light microscope (Microthek Medical Inc. Washenton DC, USA) for morphological and histological studies of the tissues. The magnification could reach up to 1,800x. The semithin sections on slides
were explored under light microscope to select interest area before testing under the transmission electron microscope (Meek, 2001).

3.6.5. Ultra Microtome

The samples were prepared into semithin (1-10 micron) for examination with the light microscope and ultrathin (order of 10 nanometers) sections for TEM. These sections can be easily obtained under microtome instruments (Reichert Ultracut, GA.A-1091, Leica Wein-Austria). Very small samples of tissue are usually embedded in hard resin before cutting. They can cut uniformly ultrathin sections for detailed microscopic examination.

3.6.6. Structure Examination Instruments (TEM)

Ultrathin sections of tissue samples were studied by transmission electron microscopy (TEM). The internal structure and morphological details were studied by TEM. (Phillips CM10, M/S FEI Company, The Netherland) operating at accelerating voltages of up to 80 kV at different magnification. The specific areas were selected and photographed for the results; the EM film negatives were developed in the dark room of the electron microscopy facility and printed on the automatic paper processor (Ilford 2150RC, UK).

3.6.7. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Serum blood samples were investigated using inductively coupled plasma-atomic emission spectrometry (ICP-AES) (VISTA, Australia). It was used to identify elements and qualify their concentration in serum blood. Its speed of operation can accurately measure 30 or 40 elements in a matter of minutes. Samples require special preparation steps including treatment with acids, heating, and microwave digestion.
Chapter Four

Corrosion Performance of SMA: Results and Discussion
4. Corrosion Performance of SMA: Results and Discussion

4.1. Electrochemical Measurements

Electrochemical principles are very useful for understanding the factors affecting corrosion resistance (Bundy, 1994). Identifying the corrosion resistance phenomena of Shape Memory Alloys is crucial before applying it in the biomedical field. The corrosion behavior of non-oxide NiTi SMA (0.25 mm), oxide NiTi SMA (0.25 mm), standard NiTi SMA (1mm), and CuAlNi SMA (1mm) was studied via these electrochemical tests: tafel constant measurement, polarization resistance measurement, and potentiodynamic scanning measurement with SEM, and EDAX methods. They allow detailed information about the reaction that occurs on the electrode. The results of laboratory tests conducted under controlled conditions were examined and different types of SMA alloys were compared to each other. The tests were fully automated with a computer-based, menu selectable program of Gamry CMS 100 software to establish test parameters.

4.1.1. Tafel Constant Behavior

The electrochemical data of the tafel constant for non-oxide NiTi SMA (0.25 mm), oxide NiTi SMA (0.25 mm), standard NiTi SMA (1mm), and CuAlNi SMA (1mm) were conducted. Figure 4.1 depicts anodic and cathodic polarization tafel curves for four tested SMA alloys in artificial ringers’ physiological solution. The
scanning potential was ranged between ±150 mV close to \( E_{oc} \) or \( E_{corr} \). The general tafel curves for all types were similar.

The tafel slopes of the anodic and cathodic reactions was obtained from the linear portions of the scan and together with corrosion current, \( I_{corr} \), the corrosion rate could be calculated. The slopes of the cathodic and anodic branches were comparable in four tested materials. It could be observed that anodic and cathodic tafel constants (\( \beta_a \) and \( \beta_c \)) showed different trends. Anodic tafel constant (\( \beta_a \)) values for non-oxide NiTi SMA (0.25 mm), oxide NiTi SMA (0.25 mm), standard NiTi SMA (1 mm), and CuAlNi SMA (1 mm) were 454.4, 1938.5, 174.4, and 49.8 mV/Decade respectively. Cathodic tafel constant (\( \beta_c \)) were 125.1, 204.0, 219.1, and 166.8 mV/Decade respectively.

At this stage, the extrapolation of the region of tafel line gives the corrosion current, \( I_{corr} \) at \( E_{corr} \). Thus, the corrosion rate can be calculated from polarization data, as discussed further in section 4.2. Moreover, corrosion potential (\( E_{corr} \)) can provide a useful indication of active passive behavior of the electrode. Despite the difference in \( E_{corr} \), the curves were had similar behavior. Corrosion potential (\( E_{corr} \)) values were -162, -346.3, -272.4, and -190.1 mV for non-oxide NiTi SMA (0.25 mm), oxide NiTi SMA (0.25 mm), standard NiTi SMA (1 mm), and CuAlNi SMA (1 mm), respectively. Therefore, oxide NiTi SMA (0.25 mm) has the largest \( E_{corr} \) while non-oxide NiTi SMA (0.25 mm) has the lowest value. However, \( E_{corr} \) of the oxide NiTi SMA specimen shifted to more negative value, indicating stronger surface activation.
Figure 4.1: Schematic Tafel plots for non-oxide NiTi SMA (0.25 mm), oxide NiTi SMA (0.25 mm), standard NiTi SMA (1 mm), CuAlNi SMA (1 mm) tested in artificial physiological ringer’s solution.
Table 4.1: Electrochemical polarization resistance measurement for non-oxide NiTi SMA (0.25 mm), oxide NiTi SMA (0.25 mm), standard NiTi SMA (1 mm), and CuAlNi SMA (1 mm) in artificial ringers' physiological solution.

<table>
<thead>
<tr>
<th>Tested Alloys</th>
<th>Non oxide NiTi SMA (0.25 mm)</th>
<th>Oxide NiTi SMA (0.25 mm)</th>
<th>Standard NiTi SMA (1 mm)</th>
<th>CuAlNi SMA (1 mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E&lt;sub&gt;oc&lt;/sub&gt; T. *</td>
<td>-0.098</td>
<td>-0.287</td>
<td>-0.279</td>
<td>-0.18</td>
</tr>
<tr>
<td>P.R. **</td>
<td>-0.246</td>
<td>-0.182</td>
<td>-0.345</td>
<td>-0.174</td>
</tr>
<tr>
<td>P.S. ***</td>
<td>-0.075</td>
<td>-0.392</td>
<td>-0.307</td>
<td>-0.179</td>
</tr>
<tr>
<td>E&lt;sub&gt;corr&lt;/sub&gt; (mV)</td>
<td>-162</td>
<td>-346.3</td>
<td>-272.4</td>
<td>-190.1</td>
</tr>
<tr>
<td>I&lt;sub&gt;corr&lt;/sub&gt; (A.cm&lt;sup&gt;-2&lt;/sup&gt;)</td>
<td>5.132x10&lt;sup&gt;-8&lt;/sup&gt;</td>
<td>7.29x10&lt;sup&gt;-9&lt;/sup&gt;</td>
<td>1.567x10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td>1.467x10&lt;sup&gt;-7&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ba (mV/Dec)</td>
<td>454.4</td>
<td>1938.5</td>
<td>174.4</td>
<td>49.8</td>
</tr>
<tr>
<td>Be (mV/Dec)</td>
<td>125.1</td>
<td>204.0</td>
<td>219.1</td>
<td>166.8</td>
</tr>
<tr>
<td>Rp T. * (Ω.cm&lt;sup&gt;2&lt;/sup&gt;) R. **</td>
<td>8.3x10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>1.099x10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>2.691x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>1.135x10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

* T = Tafel measurement
** P.R. = Polarization Resistance measurement
*** P.S. = Potensiodynamic scanning measurement
The data summarized in table 3.1 including the corrosion current density, $I_{corr}$, varied relatively from one alloy to the other. Oxide NiTi SMA (0.25 mm) had the lowest corrosion current density ($I_{corr}$) value of $7.29 \times 10^{-9}$ A.cm² which indicates that this alloy can resist corrosion better while standard NiTi SMA (1 mm) had the highest $I_{corr}$ value of $1.567 \times 10^{-6}$ A.cm². Electrochemical parameters for polarization data of tested shape memory alloys are reported in table 4.1.

### 4.1.2. Polarization Resistance Measurement

Another electrochemical method has been selected for further investigation. Testing of the four shape memory alloys was performed using the polarization resistance measurement. The polarization resistance of non-oxide NiTi SMA (0.25 mm), oxide NiTi SMA (0.25 mm), standard NiTi SMA (1 mm), and CuAlNi SMA (1 mm) in artificial ringers' solution has been drawn in figure 3.2. The actual data points are shown as well as the line determined by linear region. The potential was scanned through a potential ranging between ±20 mV close to $E_{oc}$ or $E_{corr}$ and the scan rate used was 1 mV/s.

As shown by figure 4.2, the resulting current plotted versus potential is a straight line. The slope of the line, which is the polarization resistance ($R_p$), represents the resistance of the current to pass. In other words, it indicates resistance to dissolution. The polarization resistance ($R_p$) can be calculated from the derived stern-Geary relation
\[ R_p = \frac{\Delta E}{\Delta i} = \frac{\beta a \beta c}{2.3(I_{corr})(\beta a + \beta c)} \] 

Where \( R_p \) is a polarization resistance expressed in ohm.cm\(^2\)

\( \Delta E \) is a potential expressed in mV

\( \Delta i \) is a current expressed in \( \mu \)A

\( \beta_a, \beta_c \) are anodic and cathodic tafel constants, respectively expressed in mV/Decade

\( I_{corr} \) is a corrosion current density expressed in A.cm\(^2\)

The polarization resistance values, extracted form the slope of the polarization resistance plot were \( 1.008 \times 10^5 \), \( 4.213 \times 10^7 \), \( 1.685 \times 10^4 \), and \( 9.477 \times 10^4 \) ohm.cm\(^2\) for non oxide NiTi SMA (0.25 mm), oxide NiTi SMA (0.25 mm), standard NiTi SMA (1 mm), and CuAlNi SMA (1 mm), respectively.

However, the polarization resistance value, calculated from the tafel measurement for non-oxide NiTi SMA (0.25 mm), oxide NiTi SMA (0.25 mm), standard NiTi SMA (1 mm), and CuAlNi SMA (1 mm), were \( 8.3 \times 10^5 \), \( 1.099 \times 10^7 \), \( 2.691 \times 10^4 \), and \( 1.135 \times 10^5 \) ohm.cm\(^2\), respectively. Both values have the same trend. Therefore, oxide NiTi SMA (0.25 mm) has the highest resistance to dissolution.
Polarization Resistance plots for Tested Shape Memory Alloys

Figure 4.2: Polarization resistance behavior of non-oxide NiTi SMA (0.25 mm), oxide NiTi SMA (0.25 mm), standard NiTi SMA (1 mm), CuAlNi SMA (1 mm) in artificial ringer's physiological solution.
4.1.3. Potentiodynamic Polarization Behavior

The importance of potentiodynamic experiments is to show the characteristics of the tendency to corrosion. The potentiodynamic anodic plot is practically useful to determine important information such as (i) the ability of the material to spontaneously passive in the particular medium, (ii) the potential region over which the specimen remains passive, and (iii) the corrosion rate of the material. The typical potentiodynamic scanning curves for non-oxide NiTi SMA (0.25 mm), oxide NiTi SMA (0.25 mm), standard NiTi SMA (1 mm), and CuAlNi SMA (1 mm) in artificial physiological ringer’s solution were sketched in figure 3.3 where the current was varies logarithmically with potential.

The following observation could be drawn from the data shown in figure 4.3.

- The general shape of the polarization curves of all types of tested shape memory alloys is comparable among the different types.
- It is clear from the plot that the corrosion potential were displayed in a negative sense by up to 162 mV. Where, it has been the lowest value in oxide NiTi SMA, about −346 mV, due to the oxide layer. As furthermore, the corrosion current increased, the protective film on the surface was weakened. These behavior are attributable to the increased corrosion. Standard NiTi SMA has the highest corrosion current density of $1.567 \times 10^{-6}$ A.cm$^2$
- On the polarization curve of non-oxide NiTi SMA, the linear anodic tafel region appeared extended over the wider current range when compared to the other SMAs.
The first region on the anodic curve of non-oxide SMA where the anodic current density in the passive state slightly increased indicates the formation of an oxide film on the surface. Then the high plateau was established where large current densities are produced at low potential. The increase of the anodic current observed at the potential more positive than 0.27 V indicated a breakdown of passivity. Thus the specimen was dissolved and the anodic current density rapidly increased with potential in the second region. The alloy was trying to heal the passive film on the surface but the passivity layer was broken and dissolution occurred.

The polarization curve of oxide NiTi SMA starts at the low corrosion potential then the phenomenon goes to very low anodic current density at the high range of scanning potential. Therefore, the oxide film was produced on the surface, which increased the passivity of the surface. Moreover, the oxide layer was relatively maintained although the potential scan was increased.

On the standard NiTi SMA, there was noise spikes found in the anodic polarization region due to meta stable pitting, where oxide layer was formed and dissolved repeatedly. Therefore, anodic current density increased relatively in a wide range that caused the alloy to be corroded easily.

In the polarization curve of CuAlNi, the anodic current density in the anodic tafel plot increased with increasing potential. Then the current density rapidly increased which produced a small plateau at a point where the surface starts to dissolve. This point has a breakdown potential of close to 50 mV.
Figure 4.3: Potentiodynamic polarization scanning curves of non-oxide NiTi SMA (0.25 mm), oxide NiTi SMA (0.25 mm), standard NiTi SMA (1 mm), and CuAlNi SMA (1 mm) in artificial physiological ringer’s solution.
One can notice that the anodic behavior of all shape memory alloys could be described as passive because the level of corrosion potential is relatively normal. Unfortunately, the anodic current density in the passive state increased rapidly in non-oxide NiTi and standard NiTi, indicating a decrease in protective properties of the surface film. Also, the surface of CuAlNi shows signs of dissolution before entering the passive region. However, oxide NiTi was passive with very low anodic current observed. This observation will be supported in the subsequent section of corrosion rate, SEM, and EDAX experiments.

4.2. Calculation of Corrosion Rate From Current Density

The corrosion rate can be expressed as an average penetration per unit time period by using the modification of Faraday’s law. Faraday’s law gives the relationship between current and corrosion rate (CR). Calculation of the corrosion rate or penetration rate for an alloy requires identification of the corrosion current density. The current $I_{\text{corr}}$ can be calculated from the polarization resistance and tafel constant values, through equation 4.1. This equation is rearranged to yield $I_{\text{corr}}$.

$$I_{\text{corr}} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)R_p}$$

Therefore, the corrosion rate can be directly related to the corrosion current density through the following equation.
\[ C.R. = \frac{0.13 I_{corr} \cdot E.W.}{d} \]  

(4.3)

Where C.R. = corrosion rate, mpy; mils per year.
E.W. = equivalent weight of the corroding species, g.
d = density of the corroding species, g/cm³.

The determination of equivalent weight (E.W.) requires identifying the number of equivalents. The total number of equivalents, \( N_{\text{EQ}} \) that results from dissolving unit mass of the alloy is:

\[ N_{\text{EQ}} = \sum \frac{f_i n_i}{a_i} \]  

(4.4)

Where \( f_i \), \( n_i \), and \( a_i \) are the mass fraction, the electron exchange, and atomic mass, respectively of the alloying element. Equivalent weight E.W., is then the reciprocal of \( N_{\text{EQ}} \), i.e., E.W. = \( N_{\text{EQ}}^{-1} \).

The values of slope (\( R_p \)), tafel constants (\( \beta_a \) and \( \beta_c \)) were obtained from the polarization resistance curve and tafel plot, respectively. The corrosion current values (\( I_{\text{cor}} \)) were calculated from equation 4.2. Then the corrosion rate for the examined four alloys was calculated from equation 4.3. The polarization values of calculated current corrosion (\( I_{\text{cor}} \)) and the corrosion rate for the tested specimens are presented in table 3.2.

It can be concluded from table 4.2 that oxide NiTi SMA (0.25mm) has the lowest corresponding calculated corrosion rate (0.00205 mpy). Moreover, the calculated
corrosion rates for CuAlNi SMA (1mm), non-oxide NiTi SMA (0.25mm), standard NiTi SMA (1mm) are 0.1928, 0.455, and 2.695 mpy, respectively. Although, the corrosion rate of standard NiTi SMA (1mm) has the highest corrosion rate, its value is comparable to its higher diameter. Also, CuAlNi SMA has a lower corrosion rate compared to standard NiTi SMA when compared with two different types of SMA with the same diameter.

Table 4.2: Calculated electrochemical parameters for non-oxide NiTi SMA (0.25 mm), oxide NiTi SMA (0.25 mm), NiTi SMA (1mm), and CuAlNi SMA (1mm)

<table>
<thead>
<tr>
<th>Tested Alloys</th>
<th>Rp</th>
<th>Ba</th>
<th>Bc</th>
<th>I_corr</th>
<th>Corrosion Rate (mpy*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non oxide NiTi SMA</td>
<td>1.008x10^5</td>
<td>454.4</td>
<td>125.1</td>
<td>4.231x10^-7</td>
<td>0.455</td>
</tr>
<tr>
<td>Oxide NiTi SMA</td>
<td>4.213x10^7</td>
<td>1938.5</td>
<td>204.0</td>
<td>1.905x10^-9</td>
<td>0.00205</td>
</tr>
<tr>
<td>Standard NiTi SMA</td>
<td>1.685x10^4</td>
<td>174.4</td>
<td>219.1</td>
<td>2.506x10^-6</td>
<td>2.695</td>
</tr>
<tr>
<td>CuAlNi SMA</td>
<td>9.477x10^4</td>
<td>49.8</td>
<td>166.8</td>
<td>1.759x10^-7</td>
<td>0.1928</td>
</tr>
</tbody>
</table>

* mpy= milli inch per year (mm/y=mpy*0.0254)

From the preceding results, one can conclude that the NiTi SMA covered with oxide layer offers a higher resistance to corrosion. According to Fontana’s classification (Shabalovskaya, 2002), the 0.02 and 0.0006 mm/year (0.79 and 0.024 mpy) corrosion rates in aerated and de-aerated solutions, respectively, oxide NiTi SMA can be defined as excellent (0.00205 mpy) in de-aerated solution. The oxide layer plays a role in protecting the surface from the environment. The results obtained for corrosion potential (E_corr), polarization resistance (R_p), corrosion current density (I_corr), and corrosion rate (C.R.) of oxide NiTi SMA are consistent, where its polarization resistance has the highest value and the
corrosion potential, corrosion current density, and corrosion rate have the lowest value.

### 4.3. Scanning Electron Microscopy (SEM)-Energy Dispersive x-Ray Analysis (EDAX)

In addition to the electrochemical data, the images of the corresponded surfaces from scanning electron microscope can be used to indicate the quality of the alloy (Vepulanout, 1998). Surface morphology of non-oxide NiTi SMA, oxide NiTi SMA, standard NiTi SMA, and CuAlNi SMA samples was examined to study the effect of the corrosion on the surface. Scanning electron microscopy studies of the shape memory alloys surface showed that the surface morphology is characterized by different elements.

The microstructure of untreated specimens of non-oxide NiTi SMA and its polarized specimen in ringer’s physiological solution is depicted in figure 4.4a and figure 4.4b, respectively. The pitting corrosion is clearly observed in figure 4.4b because the diameter of the pits is very large. This is because the amount of Ni and Ti was relatively decreased from 42 to 40%wt for Ti and 58 to 50%wt for Ni accompanied with precipitate of Na, Cl, and the small amount of Ca. This is proved via energy-dispersive x-ray analysis (EDAX), as reported in figure 4.5b compared with untreated sample of non-oxide NiTi SMA as shown in figure 4.5a.
Figure 4.4a: SEM micrograph of untreated non-oxide NiTi SMA (0.25 mm)

Figure 4.4b: SEM observation of non-oxide NiTi SMA (0.25 mm) after polarization in ringer’s artificial physiological solution.
Figure 4.5a: EDAX spectra of untreated non-oxide NiTi SMA (0.25 mm)

Figure 4.5b: EDAX analysis of non-oxide NiTi SMA (0.25 mm) after polarization in ringer’s artificial physiological solution.
Figures 4.6a: SEM micrograph of untreated oxide NiTi SMA (0.25 mm)
Figure 4.6b: SEM observation of oxide NiTi SMA (0.25 mm) after polarization in ringer's artificial physiological solution.
Figure 4.7a: EDAX spectra of untreated oxide NiTi SMA (0.25 mm)
Figure 4.7b: EDAX analysis of oxide NiTi SMA (0.25 mm) after polarization in ringer's artificial physiological solution.
Figure 4.8a: SEM micrograph of untreated standard NiTi SMA (1 mm)
Figure 4.8b: SEM observation of standard NiTi SMA (1 mm) after polarization in ringer’s artificial physiological solution.
Figure 4.8c: Magnified SEM micrograph of figure 3.7b for the polarized standard NiTi SMA (1 mm).

It could be noticed from the micrograph depicted in figure 4.6a, which describes the surface of a standard specimen of oxide NiTi SMA. On the other hand, the micrograph of figure 4.6b, describes the surface of the same alloy after polarization in ringers physiological solution. The important feature for the micrograph of figure 4.6b, that there is an appearance of small cracks on the surface of the layer. This is proved by EDAX spectra which was given in figures 4.7a and 4.7b for standard specimen and polarized specimen for non-oxide NiTi SMA, respectively. As seen from the results, the relative decrease of oxygen (O) contents from 9%wt to 8.7%wt with the appearance of the small amount of calcium (Ca) and chloride (Cl) (0.13%wt and 0.17%wt, respectively) after applied the specimen to the electrochemical test, caused the oxide layer to crack in small areas.
Figure 4.8a and figure 4.8b show the micrograph SEM of untreated standard NiTi SMA and polarized specimen, respectively. The few large pits are visible on the specimen surface after exposure to the electrochemical test in ringer’s solution as detected in figure 4.8b. The detailed structure of the corroded area is depicted in the micrograph of figure 4.8c that clearly shows the occurrence of moderately pitting corrosion. EDAX analysis was performed to prove this phenomenon as reported in figure 4.9b compared to figure 4.9a. The general features of the spectra are similar in both cases except the appearance of Ca and S peaks. This is because the processing eliminates metallic Ni from the surface and CaS salt as precipitate (Al-Kaabi, 2001), which was represented as the white line in figure 3.8b.

The capper based alloy surface is relatively smooth; however, some negligible roughness could be identified for the untreated sample of CuAlNi SMA as seen in figure 4.10a. Figure 4.10b shows the surface feature of CuAlNi SMA after polarization in ringer’s solution. As can be noticed by comparing the two figures, the crevice corrosion was established. The white spots at the surface of the polarized specimen were found to be due to precipitation of Cl. These areas were indicated by quantitative EDAX analysis as reported in figure 4.11b compared to figure 4.11a of untreated sample. They mainly contained Cu, Al, and Ni. When the amount of Cu, Al, and Ni decreased in case of the polarized specimen, the evident appearance of the Cl peak that caused removal of the dissolved area on the surface.
Figure 4.9a: EDAX spectra of untreated standard NiTi SMA (1 mm)

Figure 4.9b: EDAX analysis of standard NiTi SMA (1 mm) after polarization in ringer’s artificial physiological solution.
Figure 4.10a: SEM micrograph of untreated CuAlNi SMA (1 mm)
Figure 4.10b: SEM observation of CuAlNi SMA (1 mm) after polarization in ringer’s artificial physiological solution
Figure 4.11a: EDAX spectra of untreated CuAlNi SMA (1 mm)
Figure 4.11b: EDAX analysis of CuAlNi SMA (1 mm) after polarization in ringer’s artificial physiological solution.
4.4. Discussion

Passal (1974) pointed that even though shape memory alloys are operating in the passive state under most circumstances with the body, there will still be a release of material into the tissue that could cause tissue damage. Electrochemical test techniques are useful in the study of corrosion resistance of alloys. These tests typically can control the potential on the specimen by accelerating or retarding electrochemical reactions related to corrosion on the surface. The results from the electrochemical tests were compared with the results obtained with SEM micrographs and EDAX spectra’s.

The experimental results obtained in electrochemical tests showed the superiority of oxide NiTi SMA when compared to other alloys because in the physiological solution environment, oxide NiTi was reasonably immune from corrosion attack. Furthermore, it has the lowest corrosion rate, which is consistent with the results shown in SEM and EDAX, where only the oxide layer on the surface exhibited small cracks. Also, the results found in electrochemical tests and SEM microstructure of CuAlNi SMA were consistent, since there was small crevice corrosion happening only on the surface and the corrosion rate was moderately low.

The results showed that in these particular experiments, all methods agree on the alloy that exhibits the highest resistance to corrosion. It can be concluded that corrosion studies based on polarization resistance measurement, tafel extrapolation method, potensiodynamic scanning method, and surface
microstructure, indicated that the oxide NiTi SMA exhibits good corrosion resistance compared to the other three alloys, although it has a small diameter.

Some special treatments have been reported to improve SMA’s corrosion behavior. Tan (2002) has improved corrosion resistance of NiTi SMA by applying ion implantation with oxygen, which alters the surface structure, composition, and morphology of NiTi. Surface modification with the Plasma Source Ion Implantation (PSII) technique has been used by Crone (2000) to improve the biocompatibility of NiTi SMA without negatively affecting its mechanical behavior.

In conclusion, it is suggested to add an oxide layer on the surface of shape memory alloys to improve their corrosion resistance and decrease their corrosion rate (Al-Hassan, 2001). Also, the thin oxide film should be very stable in order for the shape memory alloy to resist corrosion.
Chapter Five

Biocompatibility Behavior of SMA: Results and Discussion
5. Biocompatibility Behavior of SMA: 
Results and Discussion

5.1. Introduction

There has been a substantial lack of evidence on the biocompatibility of SMA and the role of nickel in the alloy. When a material is intended for safe use inside the body, its in vivo performance and biocompatibility must be very well verified. There is still a lack of evidence must be very well verified. This still is a lack of evidence on shape memory alloy’s biocompatibility. Biocompatibility problems might arise, since the SMA used in this study contain nearly 55.7% nickel in NiTi SMA family and 4-5% in CuAlNi SMA. At high concentrations, nickel is the major cause of allergic contact dermatitis. Thus the aim of the intramuscular implantation study was to clarify the detailed muscle tissue response to tested SMA.

The animals were subject to the muscle contraction test at four periods; 4, 8, 12, and 16 weeks. At four weeks, three animals from each group of standard NiTi SMA and CuAlNi SMA were taken to experiment. The electrode was found in only one animal from each group. At 8 weeks, two animals kept the electrodes: one was the oxide NiTi electrode and the other one was non-oxide electrode. The other tested animals having the four types of SMA electrode lost their electrodes. Each group consisted of two animals, except the group having CuAlNi implant, which was made up of three. At 12 weeks, only one animal kept a non-oxide NiTi SMA. Also, the other two animals from each group who lost their electrode were subject to testing. For the 16 weeks period, no electrode from each of the four SMA was found in tested animals. Furthermore, the numbers of tested animals were two in each group. In addition to tested animals, there were two animals considered as controls (untreated) for each period. Three types of tests were performed to investigate the biocompatibility performance of nitinol SMA (standard NiTi, oxide NiTi, and non-oxide NiTi) and CuAlNi SMA. They were blood analysis, muscle contraction, and ultrastructure
investigation. In addition surface microstructures of implanted electrodes were investigated using SEM and EDAX.

5.2. Blood Analysis

Blood analysis of the implanted animal with NiTi SMA and CuAlNi SMA has not been investigated extensively for the impact of using these materials as a biocompatible material. The amounts of metals that are present in serum blood were examined via inductively coupled plasma-atomic emission spectrometry (ICP-AES). They are aluminum, copper, and nickel. The titanium was not displayed because its standard was not included in the instrument.

5.2.1. Results

The blood analysis contents were summarized in table 5.1. Figure 5.1 shows the contents of Al, Cu, and Ni in rat serum after 8, 12, and 16 weeks of implantation. The observation was taken by comparing the values of Al, Cu, and Ni in implanted animals with the control animal, which represented the untreated animal. At 8 weeks, it was found that the amount of Al and Ni increased after the electrode was removed, 447 and 163 ppm for the treated animal, 389 and 146 ppm for the untreated animal for Al and Ni, respectively. Also, Cu amount remains the same in both animals. However, in the case of the animals that were implanted with standard NiTi SMA and the electrode was not found, the amount of Ni drastically decreased from 146 to 49 ppm. The same response was observed in animals that were implanted with oxide and non-oxide NiTi SMA. The values were 42 and 45 ppm in oxide and non-oxide NiTi SMA, respectively. Furthermore, when the electrode was found inside the two animals that were implanted with oxide and non-oxide NITI SMA, Ni contents were 22 and 28 ppm, respectively.

When comparing these values, it is clear that the nickel content within the implanted region is less than the control sample. An explanation for this is that nickel reacts with titanium to form compounds that are not detected by the measuring device. This
Assessment of the Performance of Shape Memory Alloys As Implant Devices
Noura Al-Khalifi

assumption is confirmed by the nickel contents, i.e. when the implant was lost, the higher nickel content was found.

Table 5.1: Typical composition of the blood serum investigated of control animals with four implanted alloys.

<table>
<thead>
<tr>
<th>Animals</th>
<th>Al (ppm)</th>
<th>Cu (ppm)</th>
<th>Ni (ppm)</th>
<th>Period (week)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>389</td>
<td>15</td>
<td>146</td>
<td>8</td>
<td>electrode was not found</td>
</tr>
<tr>
<td></td>
<td>522</td>
<td>25</td>
<td>195</td>
<td>12</td>
<td>electrode was not found</td>
</tr>
<tr>
<td></td>
<td>107</td>
<td>16</td>
<td>50</td>
<td>16</td>
<td>electrode was not found</td>
</tr>
<tr>
<td>CuAlNi</td>
<td>447</td>
<td>15</td>
<td>163</td>
<td>8</td>
<td>electrode was not found</td>
</tr>
<tr>
<td></td>
<td>186</td>
<td>12</td>
<td>85</td>
<td>12</td>
<td>electrode was not found</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>10</td>
<td>41</td>
<td>16</td>
<td>electrode was not found</td>
</tr>
<tr>
<td>Standard NiTi</td>
<td>49</td>
<td></td>
<td></td>
<td>8</td>
<td>electrode was not found</td>
</tr>
<tr>
<td></td>
<td>139</td>
<td></td>
<td></td>
<td>12</td>
<td>electrode was not found</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td></td>
<td></td>
<td>16</td>
<td>electrode was not found</td>
</tr>
<tr>
<td>Oxide NiTi</td>
<td>42</td>
<td></td>
<td></td>
<td>8</td>
<td>electrode was not found</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td></td>
<td></td>
<td>8</td>
<td>electrode was found</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td></td>
<td></td>
<td>12</td>
<td>electrode was not found</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td></td>
<td></td>
<td>16</td>
<td>electrode was not found</td>
</tr>
<tr>
<td>Non-oxide NiTi</td>
<td>45</td>
<td></td>
<td></td>
<td>8</td>
<td>electrode was not found</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td></td>
<td></td>
<td>8</td>
<td>electrode was found</td>
</tr>
<tr>
<td></td>
<td>47</td>
<td></td>
<td></td>
<td>12</td>
<td>electrode was not found</td>
</tr>
<tr>
<td></td>
<td>29</td>
<td></td>
<td></td>
<td>12</td>
<td>electrode was found</td>
</tr>
<tr>
<td></td>
<td>141.5</td>
<td></td>
<td></td>
<td>16</td>
<td>electrode was not found</td>
</tr>
</tbody>
</table>
Figure 5.1: The amounts of Al, Cu, and Ni in the implanted animals with standard NiTi SMA, CuAlNi SMA, Oxide NiTi SMA, and Non-oxide NiTi SMA and control animals after 8, 12, and 16 weeks of implantation.

At 12 weeks, the opposite was found in CuAlNi SMA where the electrode was not found. The contents of Al, Cu, and Ni in animal implanted with CuAlNi SMA decreased as shown in figure 5.1. It was also observed that in animals, which were implanted with the three types of NiTi SMA and the electrode was missing, the contents of Ni decreased compared to the control animal. Moreover, the Ni contents in both oxide and non-oxide NiTi SMA animals were much lower than standard NiTi SMA animals. The corresponding values in the oxide, non-oxide, standard NiTi SMA...
and control were 38, 47, 139, and 195 ppm, respectively. Only one animal preserved non-oxide NiTi SMA in this period. Their corresponding Ni content was 29 ppm compared to 47 and 50 ppm founded in the same missed alloy and control animal, respectively.

At 16 weeks, all implanted animals did not keep any of the tested electrodes. The Al, Cu, and Ni amounts decreased when the electrode was not found in animals that were implanted with CuAlNi SMA when compared to control animals. The values were 107, 16, and 50 ppm, respectively in control animals for Al, Cu, and Ni, while the values were 95, 10, and 41 ppm, respectively, in CuAlNi alloy animals. The same case happens in animals that were implanted with standard NiTi SMA, where the value was 35 ppm. However, the amount of Ni increased sharply in oxide NiTi and non-oxide NiTi SMA, which have 128 and 141.5 ppm, respectively compared to 50 ppm in control specimens.

5.2.2. Discussion

In the three periods the amounts of Al, Cu, and Ni were investigated. The presence of CuAlNi alloy causes the amount of Al and Ni to increase in the blood at 8 weeks and the copper amount did not change in that period, while at 12 and 16 weeks the amount of three metals decreased. A possible explanation for this is that the implanted alloy was probably removed close to week 8, thus explaining the high metal content. Following this, the amount of the implanted metals in the blood decreased caused by ions releasing in the animal’s body.

Ni contents in NiTi SMA of three types decreased at 8, 12, and 16 weeks except in animals that were implanted with oxide NiTi, where the Ni content increased after 16 weeks. For example, in standard NiTi, the amount of Ni decreased at 12 and 16 weeks. However for 8 weeks, the rate was higher. The Ni content was lower in the blood of the implanted animal when compared to the control specimen. It is possible that since the electrode was removed earlier, the specimens checked close to this period would showed higher metal contents. Then metals would be dissolved in the
blood through ion release. Ryhanen (1999a) mentioned that the Ni release from nitinol during the first day of immersion in vitro was higher than that from stainless steel. After a few days, it becomes similar to that and later drops to undetectable levels.

It is concluded that from this analysis, the NiTi alloy family are better than capper based alloys because the amount of metals did not increase regardless of implant duration. Also, standard NiTi is better than oxide and non-oxide NiTi because the amount of Ni in the animal implanted with oxide and non-oxide NiTi is larger than the amount found in control specimen at 16 weeks. Shabalovskaya (2002) pointed out that the absolute values of Ni concentrations with or without implants differ from one animal to another by as much of a factor of ten. Thus, it would be reasonable to compare the results of different experiments.

5.3. Muscle Contraction

Muscle contraction measurements of animals, which were implanted with NiTi SMA and CuAlNi SMA, have not been studied before for their effectiveness on the muscle work. Skeletal muscle was selected because the electrode was implanted in the left leg of the animal. Thus, the aim of this study was to clarify muscle response to SMA. The dissected flexor muscle was stimulated and tight to a force-displacement transducer. This transducer converts mechanical response of the muscle to electrical signal. Electric shocks provided stimulus. The produced output chart recorder was analyzed to measure synaptic time delay and twitch tension for single twitch (1Hz), 5 Hz, and 30 Hz. In each frequency, the stimulation test was done in two ways, directly on the flexor muscle and indirectly on the sciatic nerve, which was connected to that muscle. Figures 5.2 (a, b, c) show an example of the output chart recorder for single twitch (figure 5.2a), 5 Hz (figure 5.2b), and 30 Hz (figure 5.2c). The time between stimuli and start of developed tension represents the synaptic time delay (latent phase) while twitch tension of the muscle is the height of the curve, which is the maximum amplitude. Notably that when the electrode was found in the tested animal, the muscle contraction tests were done before removing the electrode from the leg.
Figure 5.2: Output chart for muscle contraction for (a) 1 Hz, (b) 5 Hz, and (c) 30 Hz where (1) stimulus (2) synaptic delay time (3) twitch tension of the muscle

5.3.1. Results

The values are expressed as mean ± standard deviation. The differences in standard deviations were not found to be statistically different as the number of animals in each group was not sufficient. In synaptic time delay, the stimulation was done indirectly through the nerve to evaluate the effect of the electrode on the time of signals that pass through the sciatic nerve to reach the muscle. Table 5.2 shows the synaptic delay time of treated animals with control rats in four different periods. It can be observed
that, the synaptic delay time of control animals was decreased as the animal age increased. After 4 weeks of implantation in animals that were implanted with standard NiTi and CuAlNi SMA, and the electrode was found in both animals, the synaptic delay time was relatively less than in the control (7.6 msec and 7 msec, respectively, compared with 8.3 msec). At 8 weeks, the synaptic delay time in all treated animals was normal compared to that in the control except in animals that did not have the electrode. Their corresponding values were 9.1 ± 0.4 msec and 9.3 ± 2.5 msec, respectively compared with 7.6 ± 1.2 msec in control animals. All animals that lost their electrode had longer synaptic delay time compared to control animals at 12 weeks. The exception to this occurred in animals that were implanted with standard NiTi where the time was faster than normal (6.3 ± 0.1 msec and 7.1 ± 0.2 msec, respectively). However, the synaptic delay time in animal that kept the non-oxide NiTi was relatively extended time, 7.4 msec. After 16 weeks of implantation, only animals that were implanted with missed standard NiTi showed longer synaptic delay time compared with the control. The values were 7.5 ± 0.4 msec and 5.5 ± 0.7 msec, respectively.

Table 5.2: Synaptic delay time in indirect muscle stimulation through the sciatic nerve at 1 Hz for animals that were implanted with standard NiTi, CuAlNi, oxide NiTi, and non-oxide NiTi SMA.

<table>
<thead>
<tr>
<th>Animals</th>
<th>4 wks (msec)</th>
<th>8 wks (msec)</th>
<th>12 wks (msec)</th>
<th>16 wks (msec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>8.3 ± 0</td>
<td>7.6 ± 1.2</td>
<td>7.1 ± 0.2</td>
<td>5.5 ± 0.7</td>
</tr>
<tr>
<td>Standard NiTi</td>
<td>8.6 ± 1.3</td>
<td>6.3 ± 0.1</td>
<td>7.5 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>Standard NiTi, elec.</td>
<td>7.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuAlNi</td>
<td>9.1 ± 0.4</td>
<td>7.6 ± 0</td>
<td>5.04 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>CuAlNi, elec.</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxide NiTi</td>
<td>9.3 ± 2.5</td>
<td>7.9 ± 0.2</td>
<td>5.9 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>Oxide NiTi, elec.</td>
<td>6.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-oxide NiTi</td>
<td>8.7 ± 0</td>
<td>7.6</td>
<td>6.9 ± 1</td>
<td></td>
</tr>
<tr>
<td>Non-oxide NiTi, elec.</td>
<td>8.7</td>
<td>7.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The measured twitch tension from the output record was multiplied by the muscle weight to get the gram tension per unit tissue although tension is proportional to the size of the muscle. Table 5.3 presents single twitch tension at 1 Hz for direct and indirect stimulation, respectively, for control and tested animals. In the direct stimulation test, which was applied directly to the muscle, the twitch tension decreased significantly in muscle obtained from animals that kept their standard NiTi electrodes and increased in animal that kept their CuAlNi at 4 weeks. Their values were 2.2 g and 3.9 g, respectively. At 8 weeks, the twitch tension did not change drastically for all tested animals compared to the control except the flexor muscle of animal that kept the oxide NiTi electrode, where the twitch was lower (3.4±0.6 g compared with 4±0.5 g in control). The twitch tension of muscle obtained from animals that were implanted with non-oxide NiTi SMA- whether the electrode was found or not- decreased after 12 weeks of implantation. Their corresponding values were 3.7 g and 3.6 g, respectively, compared with 4.4±0.2 g in normal level. Moreover, no effect was observed in other tested animals. At 16 weeks, the twitch tension of muscles that were obtained from all tested animals was reasonably normal.

However, in the indirect stimulation test, which was applied through the sciatic nerve, the twitch tension of muscles that were obtained from animals that kept the standard NiTi electrode and the CuAlNi SMA electrode was valid value at 4 weeks. After 8 weeks of implantation, the twitch tension of muscles from animals with non-oxide NiTi SMA electrode was higher compared with control animals. The twitch tension was 4.6 g in that animals compared with 3.7±0.3 g in the control specimen. The twitch tension of muscle obtained from animal that contained non-oxide NiTi electrode was relatively low at 12 weeks. However, the twitch tension was significantly low in muscle obtained from animal where the electrode was lost. Their corresponding values were 3.6 g and 3 g, respectively compared with 3.9±0.1 g in control animals. Moreover, the twitch tension of muscle in all tested animals at 16 weeks was in the accepted range.
Table 5.3: Twitch tension in direct and indirect muscle stimulation at 1 Hz for animals that were implanted with standard NiTi, CuAlNi, oxide NiTi, and non-oxide NiTi SMA.

<table>
<thead>
<tr>
<th>Animals</th>
<th>Direct Muscle Stimulation</th>
<th>Indirect Stimulation through Nerve</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4 wks</td>
<td>8 wks</td>
</tr>
<tr>
<td></td>
<td>N*</td>
<td>N*</td>
</tr>
<tr>
<td>Control</td>
<td>3.4±0.3</td>
<td>4±0.5</td>
</tr>
<tr>
<td>Standard NiTi</td>
<td>3.9±0.7</td>
<td>3.7±0.6</td>
</tr>
<tr>
<td>Standard NiTi, elec.</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>CuAlNi</td>
<td>3.9±0.8</td>
<td>3.8±0.3</td>
</tr>
<tr>
<td>CuAlNi, elec.</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>Oxide NiTi</td>
<td>3.4±0.6</td>
<td>4.1±0.4</td>
</tr>
<tr>
<td>Oxide NiTi, elec.</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>Non-oxide NiTi</td>
<td>4.3±0.7</td>
<td>3.6</td>
</tr>
<tr>
<td>Non-oxide NiTi, elec.</td>
<td>4</td>
<td>3.7</td>
</tr>
</tbody>
</table>

* The unit of twitch tension is gram tension per gram tissue.

Table 5.4 shows the twitch tension of control and treated animals at 5 Hz for direct muscle stimulation and indirect stimulation through nerve. At 4 weeks, the twitch tension of muscle obtained from animals where the standard NiTi electrode was found significantly decreased from the control in direct stimulation and increased in indirect stimulation test. The values were 1.9 g and 2.8±0.1 g in direct stimulation and 2.9 g and 2.4±0.02g in indirect stimulation for implanted NiTi SMA and control specimen, respectively. In the muscle measured in animal where the implanted CuAlNi SMA electrode was found, the twitch tension increased significantly in indirect stimulation (3.2 g). At 8 weeks, in muscle obtained from animals where the oxide NiTi SMA electrode was found, the twitch tension was low in direct stimulation and high in indirect stimulation. Their corresponding values were 2.6 g and 4.1 g for oxide NiTi SMA compared to 3.4±0.4 g and 3.8±0.1 g in control specimens in direct and indirect stimulation, respectively. In addition to that, in indirect stimulation, the twitch tension of muscles obtained from animals with the oxide NiTi electrode was had a
significantly low value (3.3±0.1 g). The twitch tension on muscle of animal where the non-oxide NiTi was found had the higher value (4.2 g) compared to control animals (3.8±0.1). At 12 weeks, the twitch tension of muscle in all tested animals was significantly lower than the control specimen in direct stimulation. Even though, the twitch tension of muscles in animals where the oxide NiTi electrode was lost had the normal value. Moreover, in the indirect stimulation test only in muscles obtained from all animals with or without non-oxide NiTi, the twitch tension was drastically low. Their values were 3.2 g and 3.4 g respectively, compared to 3.9±0.7 g in control animals. At 16 weeks in both stimulation tests, the twitch tension for all treated animals did not exceed that in control animals. However, the exception to this occurred in muscle obtained from animals that were implanted with CuAlNi electrode and the electrode was lost, where the twitch tension had a smaller value than that in control animals (3.7±0.1 g and 3.5±0.2 g for missed CuAlNi SMA compared to 4.2±0.2 g and 4.3±0.2 g in the control in direct and indirect stimulation, respectively).

Table 5.4: Twitch tension in direct and indirect muscle stimulation at 5 Hz for animals that were implanted with standard NiTi, CuAlNi, oxide NiTi, and non-oxide NiTi SMA.

<table>
<thead>
<tr>
<th>Animals</th>
<th>Direct Muscle Stimulation</th>
<th>Indirect Stimulation through Nerve</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4 wks N*</td>
<td>8 wks N*</td>
</tr>
<tr>
<td>Control</td>
<td>2.8±0.1</td>
<td>3.4±0.4</td>
</tr>
<tr>
<td>Standard NiTi</td>
<td>3.8±0.9</td>
<td>3.2±0.01</td>
</tr>
<tr>
<td>Standard NiTi, elec.</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>CuAlNi</td>
<td>3.9±0.7</td>
<td>3.5±0.1</td>
</tr>
<tr>
<td>CuAlNi, elec.</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>Oxide NiTi</td>
<td>3.4±0.1</td>
<td>4.1±0.2</td>
</tr>
<tr>
<td>Oxide NiTi, elec.</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>Non-oxide NiTi</td>
<td>3.7±0.5</td>
<td>3.4</td>
</tr>
<tr>
<td>Non-oxide NiTi, elec.</td>
<td>3.3</td>
<td>3.4</td>
</tr>
</tbody>
</table>

* The unit of twitch tension is gram tension per gram tissue
The twitch tension of both direct and indirect stimulation at 30Hz for control and tested animals are presented in table 5.5. It can be noticed that in muscle obtained from animal where the CuAlNi SMA electrode was found, the twitch tension decreased compared to the control specimen in both stimulation tests; direct and indirect stimulation at 4 weeks. The values were 4.1 g and 4 g in CuAlNi SMA and 3.7±0.1 g and 3.5±0.02 g in the control in direct and indirect stimulation tests, respectively. The animals where the standard NiTi SMA was found, the twitch tension was normal in both stimulation tests. At 8 weeks, the twitch tension of muscle in animal that kept the oxide NiTi SMA in direct muscle stimulation decreased significantly compared to control animals (2.5 g and 4±0.04 g in kept oxide NiTi SMA and control, respectively. Also, the twitch tension decreased relatively in animals that lost the electrode (3.8±0.03 g). In addition, in the muscle obtained from animal that was implanted with the found non-oxide NiTi SMA electrode, the twitch tension increased relatively in indirect stimulation during the same period. The corresponding values for found non-oxide NiTi and control were 4.5 g and 4.1±0.3 g, respectively.

Furthermore, at 12 weeks, in the muscle from animals that were implanted with non-oxide NiTi SMA, the twitch tension was much lower than the control in both tests; direct and indirect stimulation. Their values were 3.8 g and 3.5 g for the non-oxide NiTi found and lost respectively compared to 4.5±0.2 g for the control in indirect stimulation. Moreover, the same muscle response occurred in animals that were implanted with lost CuAlNi SMA although it had relatively small value in direct stimulation (3.8±0.1 g and 4.3±0.2 g in lost CuAlNi electrode and control, respectively). At 16 weeks, in direct and indirect stimulation tests, the twitch tension of muscle obtained from all tested animals was close to that in control animals.
Table 5.5: Twitch tension in direct and indirect muscle stimulation at 30 Hz for animals that were implanted with standard NiTi, CuAlNi, oxide NiTi, and non-oxide NiTi SMA.

<table>
<thead>
<tr>
<th>Animals</th>
<th>Direct Muscle Stimulation</th>
<th></th>
<th></th>
<th></th>
<th>Indirect Stimulation through Nerve</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4 wks</td>
<td>8 wks</td>
<td>12 wks</td>
<td>16 wks</td>
<td>4 wks</td>
<td>8 wks</td>
<td>12 wks</td>
<td>16 wks</td>
</tr>
<tr>
<td></td>
<td>N*</td>
<td>N*</td>
<td>N*</td>
<td>N*</td>
<td>N*</td>
<td>N*</td>
<td>N*</td>
<td>N*</td>
</tr>
<tr>
<td>Control</td>
<td>3.7±0.1</td>
<td>4±0.04</td>
<td>4.3±0.2</td>
<td>4.7±0.2</td>
<td>3.5±0.02</td>
<td>4.1±0.3</td>
<td>4.5±0.2</td>
<td>4.6±0.3</td>
</tr>
<tr>
<td>Standard NiTi</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.1±0.5</td>
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<td></td>
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</tr>
<tr>
<td>Standard NiTi, elec.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4±0.3</td>
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<tr>
<td>CuAlNi</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4±0.6</td>
<td>3.8±0.1</td>
<td>4.4±0.5</td>
<td>3.9±0.6</td>
</tr>
<tr>
<td>CuAlNi, elec.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxide NiTi</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.8±0.03</td>
<td>4.2±0.1</td>
<td>4.8±0.2</td>
<td>3.9±0.2</td>
</tr>
<tr>
<td>Oxide NiTi, elec.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-oxide NiTi</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.3±0.9</td>
<td>3.6</td>
<td>4.9±0.3</td>
<td>4.4±0.9</td>
</tr>
<tr>
<td>Non-oxide NiTi, elec.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.3</td>
<td>3.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The unit of twitch tension is gram tension per gram tissue

5.3.2. Muscle Contraction Discussion

5.3.2.1. Muscle Contraction Mechanism Overview

It is relevant to discuss the mechanisms of muscle contraction before analyzing the results. Muscle is an excitable tissue which can be stimulated mechanically, chemically, or electrically to produce an action potential. An action potential is an electrical charge across a cell membrane due to changes in the conduction of ions across the membrane. The smallest unit of information that nerve axons deal with is the action potential. And so the smallest functional unit of tension is the contraction initiated by a single action potential in a motor axon. Such contraction is the twitch of the single motor unit. Thus a muscle contraction results in tension. The skeletal muscle is stimulated by nerves and contraction begins with an action potential in the muscular fiber.
The nerve is connected to the muscle fibers by neuromuscular junctions. The produced stimulation in our experiment represents the signal that comes from the brain. The signal transmitted through the nerve as action potential (AP) and action potential propagate to the axon terminals of a motor neuron. The neuron ends in the terminal button of the nerve, contains small vesicles filled with the neurotransmitter acetylcholine (Ach). When the AP reaches the axon terminal button, the vesicles are released and the Ach diffuses across a narrow space (the space between the nerve axon terminal and the receptors on the muscle cell) to bind to receptors on the muscle fibers cell membrane, as shown in figure 5.3. When the Ach binds to the receptors, the local permeability of the muscle cell membrane is altered so that an AP is initiated on the muscle cell. This action potential then spreads over the muscle cell membrane to initiate the contractile process (Puura, 2001).

![Figure 5.3: Neuromuscular junction between nerve axon terminals and muscle cell](image)

Calcium ions ($Ca^{2+}$) link action potentials in a muscle fiber to contraction. In resting muscle fiber, $Ca^{2+}$ is stored in the sarcoplasmic reticulum. Each action potential created at the neuromuscular junction sweeps quickly along the sarcolemma and is carried into the T or transverse tubules system that are formed in the muscle fibers as depicted in figure 5.4.

The beginning of action potential at the ends of the T system causes the release of $Ca^{2+}$ from the sarcoplasmic reticulum. The $Ca^{2+}$ diffuses among the thick and thin filaments where it binds to troponin on the thin filaments. This turns on the interaction between actin and myosin and the sarcomere contracts. Therefore, the initiated action potential spreads toward the ends of the fiber making it possible for all
sarcomeres to contract at the same time. When the process is over, the Ca\(^{2+}\) is pumped back into the sarcoplasmic reticulum to levels below those needed to activate the contractile process. Muscle contraction continues as long as Ca\(^{2+}\) concentration remains high.

![Diagram of T system and sarcoplasmic reticulum](image)

**Figure 5.4:** The T system and sarcoplasmic reticulum in plasma membrane of muscle fibers

### 5.3.2.2. Discussion of Muscle Contraction Results

A single muscle action potential produces a brief contraction of the muscle fiber called a twitch (Rastogi, 1982). Single twitch stimulation can be repeated at slow frequency (1 Hz i.e. one cycle per sec.). Muscle fibers are organized so they can cooperatively function to produce contractions stronger than a twitch.

However, no previous investigation has examined the mechanisms of muscle caused by implantation of shape memory alloys in vivo. Thus the aim of our muscle contraction test was to study nerve action potential with muscle action potential. It included measuring the conductivity of the nerve and connecting the nerve to the muscle. Two parameters were studied; synaptic delay time and twitch tension. Synaptic delay time is the time between arrival of a neural stimulus through the nerve
and tension developed by the muscle or it is a brief period that exists between application of the stimulus and the beginning of the contraction. The twitch tension was described earlier in this section.

The importance of studying synaptic delay time is related to the nerve action potential. When the synaptic delay time is higher than normal level that means that the implanted alloy affects the nerve. The synaptic delay time was enhanced where it goes lower to the level of normal as the time period increased after the following electrodes left the animals that were implanted with CuAlNi, oxide NiTi, and non oxide NiTi. Unfortunately, the synaptic delay time was prolonged up to the normal as age increase of the animals pushed out the standard NiTi. The nerve was not affected with found alloys of standard NiTi, CuAlNi, and oxide NiTi because the synaptic delay time was relatively the same as in control animals. In found non-oxide NiTi, the time was relatively prolonged which delayed the signal to the muscle. It can be concluded that, the nerve was not affected by implantation of CuAlNi and oxide NiTi SMA at all. On the other hand, it was relatively affected with the existence of non-oxide NiTi and after removing standard NiTi electrodes.

Frequency tension relationship was tested by using the pattern of stimulation at 1 Hz, 5 Hz, and 30 Hz. They were applied as direct twitch tension to the flexor muscle and indirect to the sciatic nerve. Single twitch tension was represented as 1 Hz that produced single action potential while 5 Hz and 30 Hz were applied to study the Ca$^{2+}$ release that connected the action potential through muscle membrane and the fatigue of the flexor muscle, respectively.

At single twitch tension (1 Hz), the muscle responded to the single stimuli, since the twitch tension is proportional to the animal age. To overcome this, the twitch tension was multiplied by muscle weight to get gram tension per gram tissue. In general, after the tested shape memory alloys were pushed out from the body, the direct and indirect muscle response through the nerve returned to the normal level. The exception to these occurred in animals that were implanted with CuAlNi at 16 weeks in the indirect stimulation test and non-oxide NiTi SMA of both tests at 12 weeks. The
possible explanation of lower twitch tension for animals that were implanted with the CuAlNi electrode at 16 weeks is that the electrode may push out recently, which injured the nerve. However, when the electrode was still in the muscle, the muscle response decreased in animals that were implanted with standard NiTi, oxide NiTi, and non-oxide NiTi.

The 5 Hz represents the facilitation of the response of the muscle contraction. In this test, the muscle response of animals that lost standard NiTi and non-oxide NiTi was low at 12 weeks even though it improved at 16 weeks. Unfortunately, in animals that pushed out the CuAlNi electrode, the muscle contraction was not as good as in the control in some periods, especially at 16 weeks. The muscle response with the aid of the nerve was worse in animals that were implanted with oxide NiTi at 8 weeks. In contrast, the animals that kept standard NiTi and oxide NiTi were poor in muscle response although muscle response of animal that were implanted with oxide NiTi SMA exceeded the level of control muscle response with the aid of the nerve stimuli. The response of muscle in the animals that kept the CuAlNi electrode was good in spite of the fact that it was strengthened with the aid of the nerve stimuli. Also, the muscle response was low in animal that kept non-oxide electrodes at 12 weeks even though it was fine at 8 weeks.

Fatigability is one of the most important properties of muscle. This is loaded by repeated activation on the muscle that causes prolonged strong contractions (Bichler, 2001). However, the maximum firing rates (the frequency of activation of the nerve connected to the muscle fibers) that can be achieved during steady contractions are considerably lower and generally not exceeding 30 Hz. Silverthorn (2001) states that these rates are sufficiently high that several action potentials can occur before the twitch force from the first action potential has dropped to zero. The nerve continues to function properly passing the action potential onto the muscle fibers but the contraction becomes weaker and weaker because the muscle force decreases and its response is slow. Therefore, the muscle will go into a smooth continuous contraction.
The 30 Hz corresponds to the fatigue behavior of the muscle response for the extended time. In animal that kept the CuAlNi electrode, the muscle contraction was stronger than the normal level while the muscle contraction of animal that kept the non-oxide NiTi was weaker. Only the muscle response of animals that kept standard NiTi and oxide NiTi was within the accepted range. The same response occurred in the muscle of animals that lost these electrodes. However, the muscle response decreased relatively in animal that lost the CuAlNi electrode and significantly decreased in animal that lost non-oxide NiTi at 12 weeks.

The standard deviation in some times was large because the number of tested animals was between two and three. The electrodes were removed from animals due to the high rate of motion activity of the animals. It can be noticed that, at some period of time for some electrodes, the nerve and/or the muscle was weakened. This could be because when the electrode was taken out close to the test period, they caused injury to the muscles, thus not leaving enough time for them to heal. It is possible that improper electrode implantation causes injury to the muscle tissue. Actually the muscle response in animals that lost and kept non-oxide was relatively similar to each other. Also with the presence of the electrode inside the leg, the muscle response with the nerve was better than the muscle response alone. This because the nerve assists the muscle to contract and the stimulus was spread outside the muscle.

It can be concluded that the response of the muscle contraction was enhanced after the SMA electrodes were removed from the body, where it reached normal levels. The exception occurred in the animal that was implanted with CuAlNi where the muscle contraction did not improve at the longer time. In contrast, in the animal that kept the non-oxide NiTi, the muscle contraction increased at 8 weeks and became lower at 16 weeks.

In general, with the presence of the electrode in the muscle, the muscle contraction of animals that were implanted with standard NiTi, and oxide NiTi SMA would be good. On the other hand, the muscle contraction of animals that were implanted with CuAlNi SMA will be high and low in muscle of animal that were implanted with non-
oxide NiTi SMA. However, after removing the SMA electrode from the body, the muscle contraction of the animals that were implanted with standard NiTi, oxide NiTi, and non-oxide NiTi would be according to normal muscle response. However, the muscle contraction of animal that was implanted with CuAlNi would be good at first, and then became worse at the longer time.

The synaptic delay time stands for latent period where it represents the conduction velocity of action potentials. When this time is slow this could be caused by the reduction in nerve fiber dimension, which was in agreement with previously reported changes in extracellular muscle (Fahim, 1998) in diabetic mice. This may be the cause of the synaptic delay observed in some tested electrodes in some periods in the present study.

The Ni release from some tested SMA electrodes may affect neuromuscular function, which reduces or increases flexor muscle twitch tension that leads to muscle impairment. It can be caused by Ca^{2+} mobilization, which has been proposed as a contributing mechanism to the neuromuscular of implanted animals. Additionally, the decrement in muscle contractility could be due to muscle membrane damage (Hasan, 2002). It is possible that excessive Ni release acting through disruption of Ca^{2+} handling which controls the tension production capability in fast muscles of implanted animals was reported to result in loss of tension production capability in fast muscles (Fahim, 1998) of diabetic mice. Furthermore, he pointed out that the muscle twitch response after transmitter release from nerve terminals could be changed significantly by changing sarcoplasmic reticulum function. Moreover, it is known that muscle twitch responses can be altered drastically by changing the sarcoplasmic reticulum function, because the physiological role of skeletal muscle sarcoplasmic reticulum is the release and sequestration of Ca^{2+} during the contraction relaxation cycle, thus regulating the level of contractile apparatus activation. Thus, the extracellular Ca^{2+} concentration appears to be involved in altered muscle contraction (Hattam, 2001). Modification of Ca^{2+} overload has also been shown to induce rapid swelling and disruption of mitochondria (Fahim, 2000)
Flexor muscles from the rats that kept or lost the SMA electrode in some period, especially those implanted with non-oxide NiTi SMA, depicted a decreased ability to maintain tension during a regimen of stimulation that was designed to demonstrate muscle fatigue characteristics. Under repetitive stimulation, the nerve terminal synaptic vesicle deficit could be enhanced by the muscle’s role in sustaining the contraction (Fahim, 1998).

5.4. Ultrastructure Studies

5.4.1. Results

The biocompatibility of a material in vivo can be evaluated by analyzing the morphological characteristics of the tissue around the implant. Normal morphological in vivo examinations with animals give reasonably reliable results and belong to the basic protocol used to estimate the biocompatibility of a new material. However, the release of nickel ions into tissues surrounding implants may cause cytotoxicity affecting the morphology and structure of the tissue. It is important to examine whether ultrastructure abnormalities of neuromuscular junction are present in animals that were implanted with shape memory alloys. The muscles of animals that kept the SMA electrode were investigated via transmission electron microscope (TEM). The ultrastructure features of the neuromuscular junction of the control rats have been shown in figure 5.5. It shows the normal organization of the nerve terminals. Briefly, nerve terminals contain synaptic vesicles and intact mitochondria inside the nerve terminals. Synaptic vesicles were covered by a schwann cell and were found to lie within a depression of the muscle fibers. It is well established that Schwann cells play a critical role in degeneration and regeneration of axons (Ansselin, 1998). Mitochondria are the cell’s power source. The muscle sarcolemma as shown in figure 5.5 extended inward to form junctional folds underneath the nerve terminals.
Figure 5.5: Electron photomicrograph of a control rat neuromuscular junction demonstrating normative appearance with depiction of numerous synaptic vesicles and intact mitochondria inside the nerve terminal, which is lying in a depression on the postsynaptic muscle cell. A Schwann cell at the top of the photomicrograph caps the nerve terminal. Magnification x7000.

The ordinary axonal cytoplasm and axonal cytoskeletal elements are shown in figure 5.6. The cytoskeletal elements contain microtubules and neurofilaments. They translate synaptic vesicles, which hold Ach through axons to nerve terminals that connect to muscle fibers. Also, the normal myelin sheath and mitochondria, are well organized and can be observed in figure 5.6. Also, the ultrastructure of pial microvessels in control animal shows the ordinary lumen shape with red blood cells as shown in figure 5.7.
Figure 5.6: Electron photomicrograph of control rat axonal cytoplasm. It contains normative axonal cytoskeletal elements, microtubules and neurofilaments with intact mitochondria. Magnification x14000.

Figure 5.7: Electron photomicrograph depicting normal pial microvessels ultrastructure with no evidence of cellular damage taken from control rat. Magnification x4900.
Figure 5.8: Electron photomicrograph of a typical neuromuscular junction after 4 weeks of implantation of CuAlNi SMA. Nerve terminal appears to have degenerated almost completely (star) where the junctional folds are clearly visible, but there is no intact presynaptic terminal. Magnification x2700.

After four weeks of implantation, animals with standard NiTi SMA did not affect the neuromuscular junction significantly. However, there were significant alterations at neuromuscular junctions at four weeks of implantation of CuAlNi SMA in rat animal as shown in figure 5.8 compared to control in figure 5.5.

There were four nerve terminals; one of them is not completed (degenerated) with the abnormality of postsynaptic junctional fold to the left of the photomicrograph. This electrode induced ultrastructural changes that were also seen in the peripheral intramuscular myelinated axons as shown in figure 5.9. The intramuscular axon has been destroyed. There is obvious demyelination in the myelin sheath of nerve axonal cytoplasm, which affected intramuscular axon. Also, there is an appearance of abnormal vacuoles compared to the control specimen as shown in figure 5.6. Therefore, these changes in the axon affected neuromuscular junction, which has some remodeling changes as shown previously in figure 5.8.
Figure 5.9: Alterations occurred at intramuscular axons after 4 weeks of the implantation of CuAlNi SMA. There is signs of demyelination and appearance of abnormal vacuole (star) occurring at the axon. Magnification x7000.

Figure 5.10 illustrates the neuromuscular junction in the animal that was implanted with oxide NiTi SMA after 8 weeks of implantation. The oxide NiTi affected the neuromuscular junction. The nerve terminal showed a decrease in the number of synaptic vesicles and debris of mitochondria compared to the control specimen, as shown in figure 5.5. Some nerve terminals were completely devoid of synaptic vesicles with electron dense bodies and myelin like figures. Also, mitochondria were swollen, with clear disorganization of their cristae. Despite the degeneration of synaptic vesicles and mitochondria, junctional folds were often intact and segments of plasma membrane remained. Moreover, despite the damage of nerve terminal, there was no morphological evidence of damage to most underlying muscle fibers.

At 8 weeks there was also another animal that kept non-oxide SMA. There was impairment in pial microvessels, as illustrated in figure 5.11 compared to figure 5.7 of the control. Non-oxide NiTi SMA caused dilation and narrowed down endothelium were also seen protruding into the lumen of the pial vessels. Moreover, there were three platelets observed in the lumen area. The importance of the platelet is that it hinders blood flow. The platelets displayed a variety of forms consistent with the
onset of platelet aggregation i.e. discoid platelets containing granules, spheroid degranulated platelets. Fortunately, the non-oxide NiTi electrode was also found in the animal after 12 weeks of implantation.

Figure 5.10: Changes of neuromuscular junction after 8 weeks of implantation of oxide NiTi SMA. Nerve terminals showed decreased number of synaptic vesicles. Disorganization of mitochondrial cristae that usually appear swollen is present at the nerve terminal. Magnification x14000.

Figure 5.12 shows the alterations were occurred at intramuscular axons of animals that were implanted with non-oxide NiTi SAM at 12 weeks. It can be noticed that, the axon has some morphological differences where the myelin sheath is abnormal compared to the control in figure 5.6. There are disorganized axonal cytoskeletal elements; microtubules and neurofilaments. Obviously, there were demyelination and disruption of mitochondria occurring at the axon. The mitochondria were swollen. Also, the axonal cytoplasm contained an increased number of membranous materials.

In addition, there is appearance of vacuolization inside axonal cytoplasm.
Figure 5.11: Electron photomicrograph of a pail microvessels from rats that were implanted with non-oxide NiTi SMA, after 8 weeks of implantation. It demonstrates aggregation of many platelets with dilated endothelium that protruded into the lumen of the vessel. Magnification x4900.

Figure 5.12: Alterations occurred at the intramuscular axon after 12 weeks of implantation of non-oxide NiTi SMA. There were signs of demyelination and disruption of axonal skeletal elements at the axon. There are considerable swollen mitochondria with the appearance of vacuolization (star). Magnification x14000. M: mitochondria; V: synaptic vesicles; JF: junctional folds; PS: post-synaptic; N: nucleus; SCH: Schwann cell; MY: myelin sheath; ASE: axonal cytoskeletal elements VA: vacuole; MF: muscle fibers; NT: nerve terminal; R: red blood cell; L: lumen; E: endothelium; P: platelet.
5.4.2. Discussion

The animals that were implanted with SMA may produce Ni release that caused the observed neuromuscular impairment and muscle weakness. The ultrastructural data presented in this thesis support such an assumption; a neuromuscular impairment could have resulted at several levels. First, the demyelination and the reduction of fiber dimension that are present in muscles of animals that were implanted with non-oxide and CuAlNi SMA in peripheral nerves could represent causal factors in slowing the conduction velocity of action potentials (Hasan, 2002). Second, the significant reduction of synaptic vesicles at nerve terminal levels in the muscle of animal that was implanted with oxide NiTi SMA supports the notion of direct interference with the process of neuromuscular release. Third, the weak tension in the fast muscle of that occurred in some periods imply muscular morphological changes. Indeed, intracellular Ca\(^{2+}\) overload has been shown to cause rapid swelling and disruption of mitochondria and sacroplasmic reticulum (Fahim, 2000). Flexor muscle that shows fatigue characteristics resulting in swollen mitochondria with disorganized cristae suggest that there is a postsynaptic element of muscle of animals that were implanted with CuAlNi SMA. However, there is certainly evidence for a presynaptic contribution, including remodeling of some of the nerve terminal population and reduction in capacity of sustained neuromuscular transmission (Hasan, 2002).

Some alterations shown by the ultrastructure of nerves are related to the functional modifications observed in muscle contractile properties (Bruce, 1998). The muscle weakness can be attributed to changes in the intramuscular nerves and in the neuromuscular junction. Morphologically, mitochondrial degeneration, electron dense bodies, myelin figures, irregular synaptic vesicles were all observed in animal that were implanted with CuAlNi, oxide NiTi, and non-oxide NiTi SMA. The ultrastructures seen in this study appear to be consistent with altered Ca\(^{2+}\) mobilization across muscle membrane, is the most obvious possibility (Fahim, 2000). Also, the disordered events through the plasma membrane of the nerve terminal would also explain the degeneration of the nerve terminal (Harris, 2000). The uncontrolled entry of Ca\(^{2+}\) would not only enhance transmitter release but would lead
to mitochondrial damage (Wrogeeman, 1976). Stool (1999) stated that there are two principal targets of peripheral nerve damage: the axon and the Schwann cells with their myelin sheaths. Attacks on myelin sheaths or myelinating Schwann cells as often seen in inflammatory neuropathies lead to focal demyelination with relative preservation of the axon. In addition, extreme swelling can hamper the nerve regeneration (Meek, 2001).

This study reports the ultrastructural evidence that non-oxide NiTi SMA could caused platelet aggregation. The observed endothelial abnormalities and platelet aggregates in animal that was implanted with non-oxide NiTi SMA reflect true changes and not fixative artifacts because control samples were prepared in the same manner and no such changes were seen (Fahim, 2001). Fixation has been reported to produce a small number of discoid platelets with no degranulation in control animals, but never platelet aggregation. The Ni release from non-oxide NiTi may have a direct noxious effect on causing endothelial abnormalities, which increases susceptibility to thrombosis. The mechanism underlying the observed thrombogenic effect of Ni release was not fully understood. It is possible that the Ni element released arachidonic acid and this could result in alteration of endothelial cell structure and function and hence accelerating platelet aggregation (Fahim, 2001). Shabalovskaya (2002) observed that electropholished NiTi surfaces significantly activate platelet spreading, and therefore, would have a tendency to induce thrombosis. This results in deterioration of corrosion resistance of Nitinol. The authors concluded that platelet spreading greatly depends on the surface conditions.

In conclusion, the data in this study show that, degeneration of the motor nerve terminal, intramuscular axon, and platelet aggregation may be the common response to implantation of shape memory alloys in the muscle.

5.6. Implanted Electrodes Surface Measurements

There were five implanted electrodes, which were presented in animals during different test points. They were standard NiTi SMA and CuAlNi SMA at 4 weeks,
oxide NiTi SMA and non-oxide NiTi SMA at 8 weeks, and another non-oxide NiTi SMA at 12 weeks. These electrodes with the untreated electrodes were subject to scanning electron microscopy (SEM) and electron diffraction x-ray analysis (EDAX) to study the surface topography and chemical composition of the surface, respectively.

Figure 5.13a and figure 5.13b show the surface features of untreated standard NiTi SMA and the implanted one after 4 weeks, respectively. The surface of implanted standard NiTi had some changes where some areas were quite affected. Energy dispersive X-ray analysis (EDAX) was also performed on this alloy as depicted in figure 5.14a and figure 5.14b for untreated and implanted standard NiTi SMA, respectively. It can be noticed that a sulfur peak (0.07%) and calcium peak (0.11%) clearly appeared in the case of implanted standard NiTi SMA. However, the amount of nickel decreased by 2.8% and titanium by 1.5%. The appearance of the sulfur and calcium peak could be precipitated from the surrounding blood. Moreover, the decrease in the amount of nickel and titanium is a clear sign that the surface of the standard NiTi was affected.

The CuAlNi SMA electrode, which was found at 4 weeks, was analyzed using SEM as shown in figure 5.15b and compared to untreated CuAlNi SMA as shown in figure 5.15a. Some corrosion pits are visible on the implanted CuAlNi SMA surface. The pits were uniformly distributed over the implant at the magnification of x250 or higher. Also, EDAX was performed on untreated and implanted CuAlNi SMA as depicted in figure 5.16a and figure 5.16b, respectively. The amounts of copper and nickel were affected when comparing the two graphs since the amount of copper and nickel decreased by 1.5% and 0.4%, respectively in the implanted alloy. The decrease in the amount of copper and nickel indicated that the dissolution of implanted CuAlNi SMA has already occurred.
Figure 5.13a: SEM micrograph of untreated standard NiTi SMA
Figure 5.13b: SEM micrograph of implanted NiTi SMA after 4 weeks of implantation in the rat.

Figure 5.14a: EDAX spectra of untreated standard NiTi SMA
Figure 5.14b: EDAX spectra of implanted standard NiTi SMA after 4 weeks of implantation in the rat.

In figure 5.17a, a micrograph shows the untreated surface of oxide NiTi SMA. On the other hand, the micrograph of figure 5.17b shows the surface of oxide NiTi SMA after 8 weeks of implantation. The important feature for the micrograph of figure 5.17b is the presence of visible white contaminants. The white contaminants on the surface of oxide NiTi SMA were found to be due to precipitation of calcium (0.08%) with the decrease of the oxide layer by 0.7%. This result was also confirmed by EDAX analysis as shown in figure 5.18a and figure 5.18b. Also, the amount of Ni increased by 2.3%. Blood analysis provides the same results where the amount of nickel in the serum blood was decreased than the normal animals at 8 weeks.

Figures 5.19 (a, b, and c) show the SEM micrographs of untreated non-oxide NiTi, implanted non-oxide NiTi after 8 weeks, and implanted non-oxide NiTi after 12 weeks of implantation, respectively. The surface of the specimen was almost clean and there was no evidence of corrosion on visual inspection in implanted non-oxide NiTi SMA at 8 weeks. No such pits were seen as compared to untreated non-oxide SMA. However, the implanted non-oxide NiTi SMA, after 12 weeks of implantation, shows minor pitting corrosion, which in turns contained small, irregular pits distributed on the surface, which can be considered as localized attacks on the surface.
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Figure 5.15a: SEM micrograph of untreated CuAlNi SMA
Figure 5.15b: SEM micrograph of implanted CuAlNi SMA after 4 weeks of implantation in the rat.

Figure 5.16a: EDAX spectra of untreated CuAlNi NiTi SMA
Moreover, EDAX spectra of untreated non-oxide NiTi, implanted non-oxide NiTi at 8 weeks and implanted NiTi SMA at 12 weeks are displayed in figure 5.20a, figure 5.20b, and figure 5.20c, respectively. As seen from the data displayed, the general features of the spectra of untreated non-oxide NiTi and implanted non-oxide NiTi at 8 weeks are similar except that the amount of nickel increased by 2.9% in implanted non-oxide NiTi SMA. This result affected the serum blood analysis where the nickel amount decreased in the blood. Nickel ions are thought to be attracted to the surface of implanted non-oxide NiTi SMA. On the other hand, the important feature difference between the data shown in figure 5.20b and figure 5.20c is the appearance of the calcium peak. As could be noticed by comparing the two figures, the amount of nickel decreased by 0.8% but still it is higher than untreated non-oxide NiTi by 2%. These results indicated that nickel dissolved and caused the appearance of small pits. Therefore, the development of pits took place preferentially, which could become a crack initiation site (Montero, 1996)

In conclusion, the general morphology of implanted electrodes studied at different periods was found to be similar. They demonstrated a small degree of corrosion. Pitting was the predominant type of corrosion. Also, EDAX data helped to describe
the decrease in nickel in the serum blood compared to the normal level.

**Figure 5.17a:** SEM micrograph of untreated oxide NiTi SMA

**Figure 5.17b:** SEM micrograph of implanted oxide NiTi SMA after 8 weeks of implantation in the rat.

**Figure 5.18a:** EDAX spectra of untreated oxide NiTi SMA
Figure 5.18b: EDAX analysis of implanted oxide NiTi SMA after 8 weeks of implantation in rat.

Figure 5.19a: SEM micrograph of untreated non-oxide NiTi SMA

Figure 5.19b: SEM micrograph of implanted non-oxide NiTi SMA after 8 weeks of implantation in the rat.
Figure 5.19c: SEM micrograph of implanted non-oxide NiTi SMA after 12 weeks of implantation in the rat.

Figure 5.20a: EDAX spectra of untreated non-oxide NiTi SMA
Figure 5.20b: EDAX analysis of implanted non-oxide NiTi SMA after 8 weeks of implantation in the rat.

Figure 5.20c: EDAX analysis of implanted non-oxide NiTi SMA after 12 weeks of implantation in the rat.
Chapter Six

Conclusions and
Conclusion
6. Conclusions and Recommendations

6.1. Summary and Conclusion

The combination of shape memory effect and superelasticity with good biocompatibility could make shape memory alloy especially suited for medical applications. Most of the data accumulated or published to date regarding NiTi as a medical material was concerned with binary NiTi alloy only. In spite of the satisfactory clinical use of NiTi SMA in some situations, its corrosion resistance and therefore its biocompatibility are still being questioned. In particular, the relatively large content of nickel in our tested NiTi alloy was 55.7\% that gives rise to considerable concern. Another kind of shape memory alloy that was also studied in this thesis was CuAlNi SMA to find out its corrosion resistance and biocompatibility in addition to three types of NiTi SMA, which contain high nickel contents: standard NiTi SMA, oxide NiTi SMA, and non-oxide NiTi SMA. The main objective of this thesis is to compare corrosion resistance performance and biocompatibility behavior of nitinol SMA and CuAlNi SMA.

Although, we found statistically significant differences in every study, the methods, results, and above all, the implantation implications merit discussion. Several experimental settings were considered to study the performance of tested shape memory alloys. They were divided into two sections. First, quantitative analysis, which includes the electrochemical test, blood analysis and muscle contraction measurements. Then a qualitative analysis, which contains the investigation of the surface of tested shape memory alloy electrodes under SEM as well as chemical analysis with EDAX, in addition to studying the biological response of muscle to tested SMA electrode under TEM.
The results obtained from the electrochemical test showed that oxide NiTi had the lowest corrosion rate while the standard NiTi had the highest corrosion rate. This is due to the oxide layer acting as a protective layer that protects the NiTi from dissolution. The apprehension about NiTi biocompatibility is based on the relatively large nickel content in the NiTi family. Although nickel is nutritionally essential, it is well known that nickel is capable of eliciting toxic and allergic response. However, the laboratory results of serum blood analysis indicated that the NiTi SMA family was better than CuAlNi SMA because Ni release in the blood did not increase regardless of the time of removal of the electrode compared to the blood of implanted CuAlNi SMA.

Moreover, the data collected from muscle contraction measurements showed the same response, where the muscle contraction response of the animals that were implanted with NiTi family was better than that with implanted of CuAlNi SMA when the electrode was pushed out from the body. Also, non-oxide NiTi SMA affected the muscle response in the mid-test-point period but it overcame this problem at the end-of-test point. Although the NiTi SMA family was better than CuAlNi SMA in the muscle contraction test of the removed electrode, non-oxide NiTi from NiTi SMA family with CuAlNi SMA weakened the strength of the muscle. On the other hand, when the electrodes was still in the muscle, the nerve conduction worked properly except in the animal that was implanted with non-oxide NiTi SMA. The following conclusions have been drawn from this study: Non-oxide NiTi SMA affected the work of the nerves and muscles when the electrode was still in the muscle. Also, standard NiTi SMA affected the nerve after this electrode was left the body. In the case of CuAlNi and regardless of whether the electrode was inside the body or not, the muscle response was affected.

Local tissue response is the most important aspect of biocompatibility. The implantation of the shape memory alloy object into the rat’s body inevitably leads to some degree of local muscle response or systemic toxicity related to the implants. It seems likely that, the muscle of animal that was implanted with standard NiTi did not show any muscle or
nerve destruction. However, the other three SMA electrodes showed some degree of damage occurring in the nerve axon, nerve terminal, and blood pial microvessels. The most local severe damage occurs in the muscle of the animal that was implanted with non-oxide NiTi SMA. This is because this electrode created activated platelets aggregation that causes obstruction to blood flow and then leads to thrombosis, while the nerve was impaired of the animals that were implanted with non-oxide NiTi SMA and CuAlNi SMA. This is because of the appearance of the abnormal vacuoles in the myelin sheath of the nerve axon.

Surface morphology of tested shape memory alloy electrodes, which were removed from animals after the test-point period and that were polarized via electrochemical test, were examined to study if there was corrosion on the electrode surface. Although corrosion was observed on some surfaces of polarized and implanted SMA electrodes, this was limited to small pits.

As expected, most of the results showed that oxide NiTi SMA could be represented as superior when compared to the other three shape memory alloys. Unfortunately, from most of the experimental results it seems obvious that the tested shape memory alloys were not biocompatible, as one would expect. This is because the high content of nickel in the NiTi SMA and the surface treatment did not provide a good surface polish.

The use of shape memory alloy as biomaterial has several possible advantages. Its shape memory property and superelasticity are unique characteristics and totally new in the medical field. The possibility to make self-locking, self-expanding, and self-compressing thermally activated implants is fascinating. As far as good biocompatibility of binary NiTi SMA is concerned, it is anticipated that NiTi SMA has the potential to be a clinical success in several applications in the future.
6.2. **Recommendations For Future Study**

It is well known that nickel released from electrode is capable of eliciting toxic and allergic responses with subsequent cell disruption. Consequently, the release of nickel from shape memory alloy implants may have relative implications on local tissue response. Various approaches are currently under development to prevent undesirable nickel release and ensure implant safety. There are some recommendations that have been drawn to minimize the nickel release from shape memory alloys.

The biological response to implant material is a property directly related to their surface condition. Therefore, the amount of dissolved metal especially nickel is highly dependent on surface treatment. Surface layers of tested SMA especially NiTi SMA family have been observed to have irregular features on the surface. To make the surface more biocompatible, it would be beneficial to apply a preventive surface treatment that leaches the surface, since corrosion resistance relies on protective oxide films. The study revealed that, surface oxide film formation is of great importance for SMA corrosion performance. Thus it will ultimately determine the long-term biological response to the implant (Kraft, 2001). It is also recommended to reduce the amount of nickel in the NiTi SMA family by 1% to 5% to keep a good yield strength with lowered transformation temperature to be in line with the temperature of the body’s environment.

It is suggested to do studies with several animal species and in several tissues. It would be beneficial if the sufficient number of further studies are continued to prove final conclusions about the biocompatibility of shape memory alloys in the longer term. Furthermore, insight can be gained into the corrosion behavior of shape memory alloys in order to optimize their field of biocompatibility application. Finally, surface treatment, compositional degree in the shape memory alloy, and the thermal treatment may all notably affect the biocompatibility of a specific implant application.
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النيكل تيتانيوم العادية المزروعة في نهاية نفق الاختبار، وعِضلة الحيوان الذي أحتفظ
بسببية النيكل تيتانيوم الغير مؤكسدة كانت خصائصها منخفضة في الثلاث ذئاب، ولكن كان هناك
انخفاض هام في توزع الارتعاش في نهاية نفق الاختبار لعِضلة الحيوان المزروع بسبيكة الكوير
النيوم نيك. وهذا التأثير كان واحدا سواء بقيت السبيكة أو خرجت من الجسم.

العِضلات التي حدثت في العضلات درست عن طريق جهاز ميكروسكوب الأرسال الإلكتروني.
على ما يبدو أن سبيكة النيكل تيتانيوم العادية لم تؤثر على العضلات والأعصاب. سبيكة النيكل
تيتانيوم الغير مؤكسدة سببت دمار واضح في الأوعية الدموية والأعصاب، حيث سببت ظهور
جلطة المكونة من تجمع الصفائح الدموية وتمزق الغطاء الميلين للعصب مع اضمحلال
الشعرات العصبية. من هذا التلفبين أن سبيكة النيكل تيتانيوم الغير مؤكسدة سببت أكثر دمار
في العضلة من بين الأنواع الأخرى. أيضا السبيكة النحاسية غيرت من شكل العصب وسبيكة
النيكل تيتانيوم المؤكسدة قلت من عدد الحويصلات في طرف العصب. هذه التغييرات ربما
سببها تغير في حركة أيونات الكالسيوم خلال أغشية العضلة. السبانك المزروعة التي أزيلت من
الجسم ظهر فيها نسبة قليلة من التآكل لكنها عبارة عن حفر صغيرة. من معظم النتائج التجريبيّة
يمكن استنتاج أن سبيكة النيكل نيتانيوم المؤكسدة تعتبر متفقة على السبانك الأخرى. لسوء
الحظ في نهاية هذه الأطراف، السبانك الذكية المستخدمة لم تكن متوافقة حبيبا كما كان متوقعا.
الأسباب يمكن أن تكون من عدم معالجة السطح جيدا وتركيز النيكل العادي.
الخلاصة

السائبات التي لها خصائص ذكاء الشكل هي واحدة من عائلة المواد الذكية. وهي تعتبر المواد الحيوية لتمثيل الجسم لها. أحد المميزات الخاصة أن لها الفترة للحول إلى شكلها السابق. هذه المادة تشكل في درجة الحرارة المنخفضة. وعندما تسخن (تتكرر) إلى شكلها الأصلي. بالرغم من نجاح زراعة سبعة نباتات ثنائية أن السائبات المستخدمة في هذه الأطروحة تتكون من أكثر من 65% من النبات (75.7%) والعرض الرئيسي من هذه الأطروحة هو تقييم القد البيولوجي لسباك التي لها خصائص ذكاء الشكل.

في هذا المشروع تم استعمال صنف من سباقات التي لها خصائص ذكاء الشكل. عائلة نيتول (نورتك، نيتول) وعائلة السائبات الحساسية (كوبير نيتول، نيتول). المقارنة تم بين سبعة نباتات نيتول، سبعة نباتات النيتول المعدة وسبعة نباتات النيتول المعدة لزراعة النباتات الثانوية. أظهر النتائج أن النباتات التي استخدمت عائلة النيتول كانت أكثر فعالية من النباتات الأخرى. ومع ذلك، فإن النباتات التي استخدمت في هذه التجربتين كانت بنفس القياسات والمعدلات المعتادة في النباتات الحساسية. النباتات المستخدمة في هذه التجربتين كانت من نباتات النيتول المعدة لزراعة النباتات الثانوية. حيث أنه بالنسبة للنظام البيولوجي النباتات المعدة لزراعة النباتات الثانوية، فإن النباتات التي استخدمت عدد أعلى من النباتات.’

التجارب الكهروكيماوية نفذت في وسط فسيولوجي للتحقيق في مقاومة النبات الكل وتحديدا معرفة معدل النبات لكل مادة. وقد وجد أن معدل النبات لكل سبعة نباتات المعدة هو الأكثر انخفاضاً الذي بين أن لهذه المادة أفضل مقاومة للناتج، وهذا بسبب البطين الأسود التي تعمل كطبقة واقي للتفاعل ضد ديوان المادة. اقتدى الصور المجهرية السطحية للمادة المعتادة مع النباتات الكهروكيماوية. حيث يوجد أن سبعة نباتات النيتول المعدة تعرست لتجارب الكهروكيماوية. ومن خلال هذه التجربة، وجد أن كمية النباتات المعتادة من عائلة النيتول أقل من السبعة النباتات.

تأثرات هذه السائبات الذكية درست على عضلة القاضية كنموذج لدراسة استجابة العضلة ودراسة التراكيز الداخلي للعضاة والأعراض. خصائص انقباض العضلة قوة وسرعة في (1 و 8 و 16 أسبوع). التوتر (التردد) عضلة المعتادة عضلة نباتات النيتول. وعندما وصل الإشارات من النباتات إلى العضلة، سجلت عن طريق محاكاة مكون الأكياس. كان هناك زيادة في وقت وصول الإشارات في الحيوانات التي زرعت

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دراسة أداء السبائك الذكية في التطبيقات الطبية

إعداد
نورة علي حسين الخليفي

رسالة مقدمة لعمادة الدراسات العليا
ضمن متطلبات الحصول على درجة الماجستير
في علوم و هندسة المواد

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