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Surface Nitriding and Oxidation of Nitinol

Edin Bazochaharbakhsh
San Jose State University

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SURFACE NITRIDING AND OXIDATION OF NITINOL

A Thesis

Presented to

The Faculty of the Department of Chemical and Materials Engineering

San José State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Edin Bazochaharbakhsh

August 2011

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The Designated Thesis Committee Approves the Thesis Titled

SURFACE NITRIDING AND OXIDATION OF NITINOL

by

Edin Bazochaharbakhsh

APPROVED FOR THE DEPARTMENT OF CHEMICAL AND MATERIALS
ENGINEERING

SAN JOSÉ STATE UNIVERSITY

August 2011

Dr. Guna Selvaduray Department of Chemical and Materials Engineering

Dr. Melanie McNeil Department of Chemical and Materials Engineering

Dr. Gregory Young Department of Chemical and Materials Engineering

ABSTRACT

SURFACE NITRIDING AND OXIDATION OF NITINOL

By Edin Bazochaharbakhsh

Nitinol has been widely employed in biomedical devices due to its unique mechanical properties such as superelasticity, shape memory, and good biocompatibility. However, nickel ion release from the surface of the Nitinol is an issue. Surface nitriding and oxidation was performed on the Nitinol specimens to develop a nickel-free oxide layer on the surface. Nitinol specimens were nitrided in nitrogen + 4% hydrogen at 800 - 1000°C for 10 - 30 min and further nitrided in nitrogen + 5% ammonia at 500 - 675°C for 0 - 30 min. The thickness and chemical composition, specifically the nickel content of the surface layer, were determined by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. The effect of the nitriding time and temperature on the thickness and chemical composition of the nitride layer was evaluated. Nitriding temperature was found to be more effective than nitriding time on the thickness of TiN layer. Titanium nitride, the dominant phase on the surface of the nitrided specimens, was nickel free. The nitrided Nitinol specimens were then oxidized at 675°C and 700°C for 30 and 60 min, respectively. The chemical composition and elemental depth profile showed that oxidizing Nitinol specimens with a 0.4 μm thick nitride layer on the surface did not provide a nickel-free oxide layer on the surface of the Nitinol. However, oxidizing the Nitinol specimens with a surface nitride layer that was thicker than 6 μm resulted in a nickel-free oxide layer.

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This thesis is dedicated to the author's family, who have supported him throughout his education.

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CHAPTER ONE

INTRODUCTION

Shape memory alloys are widely used in medical devices. The most widely used shape memory alloy today is Nitinol which has excellent biocompatibility [1].

1.1 History and Background

Nitinol is a family of equiatomic intermetallic compounds of nickel and titanium. The term “alloy” is used loosely to describe the combination of these two elements. “Nitinol” is an acronym for Nickel and Titanium Naval Ordnance Laboratory [2]. The discovery of Nitinol is credited to William J. Buehler who was investigating nickel and titanium alloys as candidate materials for the nose cone of the U.S. Navy Polaris reentry vehicle. However, Nitinol was not found to be useful in the Polaris project. After further research by Buehler and others, more information was gathered about Nitinol’s phase transformation at room temperature, and this raised the interests of many researchers. A detailed history of the discovery of Nitinol is well described by Kauffman and Mayo [2].

1.2 Properties of Nitinol

Nitinol undergoes a martensite-to-austenite phase transformation during heating over a temperature range close to room temperature. This phase transformation in Nitinol is the cause of its unique mechanical properties such as shape memory and superelasticity.

The term “shape memory” is used to characterize the group of metallic materials that demonstrate the ability to return to a previously defined shape or size when heated. As shown in Figure 1, when Nitinol is in its twinned martensite phase, the phase changes to deformed de-twinned martensite when deformed. After heating the Nitinol to a temperature higher than the austenite finish temperature, the phase changes to austenite, and the shape returns to its original configuration. As shown in Figure 2, austenitic Nitinol shows superelastic behavior and has an elastic deformation range of approximately 8%, which is very high compared to other metallic materials which have elastic deformation ranges that typically do not exceed 1% [3, 4].

Figure 1. Schematic diagram of shape memory effect in Nitinol [5]. Reproduced with permission from John Wiley and Sons.

The elastic deformation in Nitinol can be caused not only by atomic bond stretching, but also by the martensitic transformation induced by stress. Martensitic

Nitinol is more stable under applied stress. When a stress is applied to Nitinol, it changes from austenite to martensite, and when the applied stress is removed, the phase returns to austenite. This phenomenon is represented in Figure 3 [3, 4].

Figure 2. Engineering stress-strain curve of Nitinol and stainless steel 316 [1]. Reproduced with permission from Elsevier.

Figure 3. Martensitic transformation of superelastic Nitinol [5]. Reproduced with permission from John Wiley and Sons.

Nitinol is also a corrosion resistant and biocompatible material due to the formation of a passive oxide layer on the surface. Thermodynamically, TiO_2 is a very stable compound due to its extremely low standard Gibbs free energy of formation of -889 kJ/mol at room temperature. Therefore, when in contact with oxygen, the titanium in Nitinol forms a TiO_2 layer on the surface. Titanium dioxide is inert in the human body [6, 7].

1.3 Applications of Nitinol

At the time of the discovery of Nitinol, it did not receive much attention from research institutes and manufacturers due to its unconventional properties and sensitivity to temperature and composition; it was difficult for designers to employ Nitinol in their designs. After further research on some specific compositions, designers found some applications for which Nitinol's properties could to be employed. The first successful application of Nitinol was as a pipe coupler in U.S. Navy F-14 jet fighters [2].

The excellent corrosion resistance and biocompatibility of Nitinol made it desirable for implanted biomedical devices. The combination of superelasticity, shape memory, kink resistance, and lack of hysteresis during cyclic loading make Nitinol unique; this combination is not offered by typical biomaterials like 316L stainless steel, commercially pure (C.P.) titanium, or cobalt chromium alloys. The combination of its unique mechanical properties, with good corrosion resistance and biocompatibility, has

resulted in Nitinol being an attractive choice for implantable biomedical devices such as catheters, stents, inferior vena cava filters [1], and orthodontic arch wires [5].

Angiography is an interventional radiology procedure. A catheter (a tube) is inserted into the body, passing through arteries and veins, to perform advanced medical procedures such as re-establishing blood flow in blocked arteries or implanting filters to prevent blood clots from reaching the lungs. From the insertion point to the desired delivery point, the catheter needs to pass through very small vessels and some tortuous regions. Superelasticity (high recoverable strain), good kink resistance, steerability, and torquability of Nitinol make it a good candidate for this device [1].

Stents are permanently implantable metal scaffolds used to support the wall of the blood vessel during angioplasty, a technique employed to restore blood flow in the treatment of coronary heart diseases [1]. Conventional stents are made of Stainless Steel 316LVM™. A balloon is used to expand these stents to match the blood vessel's diameter. Self-expanding stents, made of Nitinol, expand to their original shape when they reach body temperature, taking advantage of the shape memory character of Nitinol. The lack of hysteresis in superelastic stress-strain behavior also makes it a good choice for use in stents.

Another Nitinol application is for inferior vena cava filters (IVC) [1]. Pulmonary embolism occurs when one or more blood clots move to the lungs. This can be fatal. In conventional approaches, medicines such as Warfarine are employed to decrease the clotting ability of blood. Another method is to employ IVC filters in the vein to block blood clots before they reach the lungs. This biomedical device needs to be removed

after a period of time. A small insertion profile is also required during the installation of IVC. Nitinol, due to its superelasticity, is a good candidate to be employed in IVC filters.

Nitinol is also widely used in dentistry [7]. Superelasticity makes Nitinol a good material to be used in root canal tools. To clean and expand curved canals, Nitinol files are used with an extremely low risk of breaking the tool. Orthodontic arch wires are also made of Nitinol. The high spring-back property due to the superelastic behavior of Nitinol as well as good biocompatibility and corrosion resistance make Nitinol a good candidate to be employed in this application.

Application of Nitinol as a biomaterial is not limited to the applications listed above, and new uses continue to be developed. However, the potential allergic reaction to nickel, particularly in women, continues to be a problem with implantation of Nitinol in the human body [8].

1.4 Nickel Toxicity

The presence of nickel in metallic and oxide forms on the surface layer is of considerable concern. Nickel ion leaching from Nitinol specimens has been reported [9-11]. Compared to nickel in the oxide form, elemental nickel leaches more easily into body fluids. The amount and rate of the nickel ion release varies with exposure time and surface treatments on the Nitinol specimens. Generally, the nickel ion release rate has been found to decrease with time due to nickel depletion from the surface as a result of the leaching. In most of the cases reported in the literature, a mechanically polished specimen was considered as the control specimen and was compared with other

specimens that were surface treated with methods like thermal oxidation, electropolishing, chemical etching, pickling and/or boiling in water. For the mechanically polished samples, the nickel ion release rate decreased with exposure time to undetectable amounts after 10 days [12]; however, in some cases nickel ion release was reported even after 10 days or more of exposure in simulated body environments [13]. Surface treatments on Nitinol samples decreased the amount of released nickel ions, with the decrease varying with the surface treatment method [9-13]. To eliminate the presence of nickel on the surface, different surface treatments have been studied and/or are under investigation.

1.5 Scope of Research

The widespread use of Nitinol in biomedical devices, due to its unique mechanical properties such as shape memory and superelasticity, as well as good biocompatibility and corrosion resistance of Nitinol, coupled with the requirement of a surface treatment to eliminate the nickel ion release, led to this research effort. Therefore, the objective of this research was to study the effects of surface nitriding and oxidation, separately and sequentially, on the surface chemistry of Nitinol, and evaluate the ability of this surface treatment to form a nickel-free oxide layer on the surface.

Previous studies on different surface treatment methods such as thermal oxidation, mechanical surface treatment, aqueous surface treatment methods and surface nitriding are reviewed and presented in Chapter Two. In Chapter Three the research objectives of this work are described. The experimental procedures and the research approaches to

fulfill the research objective are described in Chapter Four. The results of the experiments are in Chapter Five, followed by the discussion of these results in Chapter Six. Chapter Seven contains the conclusion of this research and recommendations for future work are in Chapter Eight.

CHAPTER TWO

LITERATURE REVIEW

2.1 Background

Previous studies on different surface treatment techniques on Nitinol were reviewed and are presented in this chapter. The surface treatment methods reviewed were all related to reducing nickel ion release and improving corrosion resistance. Surface treatments of Nitinol include mechanical polishing, electropolishing, chemical etching, boiling in water, thermal oxidation, laser surface melting and ion implantation. A combination of two or more of the techniques listed above could potentially be employed to form a nickel depleted TiO_2 layer on the surface. Methods to form a TiN layer on the Nitinol's surface, such as thermal nitriding, laser nitriding, and PIRAC nitriding (Powder Immersion Reaction Assisted Coating) have also been studied. After surface treatments, the surface of the Nitinol samples have been characterized by different surface characterization methods like X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) to obtain data on the thickness of the surface layer as well as its chemical composition.

The most appropriate surface treatment method is usually selected according to the performance expectation of Nitinol, as well as the cost of the part and the process [7]. For each surface treatment process, there are many different variables affecting the

outcome of the treatment. For nitriding and oxidizing the important process factors are temperature, time and the surface treatment atmosphere [7].

The nickel content of the passive film on the surface determines the nickel release rate of the part during service [14].

2.2 Mechanical Surface Treatment Methods

Mechanically polished Nitinol has been used in biological studies. In most cases mechanically polished specimens were used as the base-case and were compared with specimens treated with other techniques. Mechanical polishing has also been used as a specimen preparation step before other surface treatment and/or coating methods.

Mechanically polished Nitinol specimens have poor corrosion resistance [15, 16].

One reason for the low corrosion resistance is surface damage during polishing, which increases the risk of pitting corrosion. Another cause of the corrosion is the stored energy on the surface in plastically deformed micro-zones [15]. Contaminants absorbed from polishing particles and/or during handling and cleaning also potentially decrease the corrosion resistance. The surface elemental composition of the mechanically polished Nitinol depends on polishing method and materials, cleaning technique and the drying and handling process of the specimen. The presence of different surface contaminants such as Ca, Cl, P, Si, Mg and Na has been reported. The concentrations of these contaminants on the surface were 1 – 8% (at.%) [17].

While the surface of the mechanically polished Nitinol is predominantly TiO_2 , the presence of significant amounts of nickel in metallic and/or oxide forms has been

reported [15, 18]. The nickel concentration on the surface was not consistent and different values varying from 0.9 - 20% (at.%) has been reported. This inconsistency was most probably due to the presence of the surface defects, formed during the mechanical polishing procedures [19, 20]. The amount of the released nickel has also been reported. It was $200 \mu\text{g l}^{-1} \text{cm}^{-2}$ from a mechanically polished sample after five days immersion in simulated body fluid, which was high compared to $50 \mu\text{g l}^{-1} \text{cm}^{-2}$ from electropolished specimens and $15 \mu\text{g l}^{-1} \text{cm}^{-2}$ from specimens oxidized at 600°C with an oxygen partial pressure of 1 atmosphere [21]. Sources of the released nickel are nickel concentration on the surface and corrosion sites.

2.3 Thermal Oxidation

When in contact with oxygen, TiO_2 forms on the surface of Nitinol due to the high thermodynamic stability of TiO_2 . The standard Gibbs free energy of formation for TiO_2 is lower than that for nickel oxides. As shown in Figure 4, titanium in different oxidation states is more stable than nickel oxide, over the temperature range of 298 K (25°C) to 1800 K (1527°C). At room temperature the standard Gibbs free energy of formation for TiO_2 is -889 kJ/mol, lower than the value for NiO which is -212 kJ/mol [6]. Titanium dioxide is therefore the dominant phase on the surface of Nitinol. The TiO_2 layer thickness increases with increase in the oxidation temperature, which facilitates the diffusion of oxygen into the Nitinol surface and diffusion of titanium from the bulk toward the outer surface. The presence of nickel in elemental and oxide forms on, and nickel ion release from, the surface of thermally oxidized Nitinol has been reported [7].

Figure 4. Standard Gibbs free energy of formation of NiO, TiO, TiO₂, Ti₂O₃ and Ti₃O₅ for 298 K to 1700 K, Data from [6].

The standard Gibbs free energy of formation of TiO₂ from TiO, Ti₂O₃, Ti₃O₅ and oxygen is negative; therefore, when in contact with oxygen all forms of titanium oxide tend to form TiO₂ [6]. At higher oxidation temperatures diffusion of oxygen into the Nitinol surface layer and titanium migration from the Nitinol bulk toward the outer surface become easier; therefore, the oxide layer on the surface of the Nitinol becomes thicker with an increase in oxidation temperature. Increase in the oxidation time also increases the thickness of the oxide layer on the surface of Nitinol.

The kinetics of formation of TiO₂ on the surface of the Nitinol has also been studied [22]. The oxide layer thickness increases with increase in oxidation temperature and time; however, oxidation temperature was found to be more controlling than oxidation time. There was a change in the oxidation behavior of Nitinol at temperatures close to 600°C. In the temperature range of 600 to 1000°C the growth rate of the oxide

layer on the surface of the Nitinol was parabolic with an activation energy of 203 kJ/mol. However, in the temperature range of 400 to 600°C the oxide layer thickness fits a logarithmic growth rate, for which the activation energy value is 22 kJ/mol. This change in the surface oxidation behavior of Nitinol has also been reported by others [18]. At oxidation temperatures below 500°C an inward growth of the TiO_2 on the surface of Nitinol has been reported.

When oxidized at 400°C for 30 min TiO_2 formed, based on the diffusion of the oxygen into the surface of Nitinol. This conclusion was based on the observation that there was practically no change in the Ti/Ni ratio after oxidation. If the titanium had diffused out toward the surface, then the Ti/Ni ratio would have changed, with the titanium concentration being greater than what was started with. In contrast, at higher oxidation temperatures, like 500 and 600°C, the nickel content in the TiO_2 dropped significantly. This was interpreted as evidence of the outward diffusion of titanium toward the surface/atmosphere interface.

As shown in Figure 5, at low oxidation temperatures like 400°C where only inward diffusion of oxygen occurs (not outward titanium diffusion), oxygen can diffuse into the surface of the Nitinol, react with titanium and form TiO_2 . Insufficient amounts of oxygen can lead to the formation of other titanium oxides like TiO , Ti_2O_3 and Ti_3O_5 in the inner layers; nevertheless, the nickel from the Nitinol is still present in the TiO_2 layer. When in contact with oxygen where there is no titanium available, nickel can oxidize and form NiO and other oxides such as NiTiO_3 [23]. Some elemental nickel can be expected to be present in the oxide layer. At higher oxidation temperatures such as 600°C,

titanium diffuses toward the outermost surface, reacts with oxygen and forms TiO_2 . As shown in Figure 6, under the TiO_2 layer a nickel rich zone forms. The dominant phase in this zone is reported as being Ni_3Ti [22-24]. Also, at oxidation temperature above 600°C nickel was present on the outermost surface and in the TiO_2 layer in the form of particles of Ni and NiO [19, 20, 22]. These particles most probably are formed during the outward diffusion of titanium. It is possible that the nickel was trapped on the surface and/or in the middle of the TiO_2 layer. It is also possible that the nickel diffuses into the oxide layer after completion of the surface oxidation, due to the thermodynamic activity difference between the nickel in the nickel-rich zone and the nickel in the nickel-free oxide layer.

Figure 5. Schematic of the oxidation process on the surface of Nitinol at oxidation temperature $< 500^\circ\text{C}$.

Figure 6. Schematic of the oxidation process on the surface of Nitinol oxidation temperature $> 600^{\circ}\text{C}$.

The presence of the nickel-rich zone under a thick TiO_2 layer can lead to problems such as high nickel release rates and low corrosion resistance. Titanium dioxide is brittle and it can break during deformation or fabrication [25]. If the oxide layer on the surface of the Nitinol breaks, the nickel rich zone will be exposed to the environment. This phenomenon is considered as a potential cause for nickel ion release. Also, due to the difference in the electrochemical potential of the TiO_2 and the nickel-rich zone, corrosion may happen. Low corrosion resistance and high nickel ion release rate in thermally oxidized Nitinol samples is also caused by the presence of voids in the oxide layer on the surface. Voids and/or pores were detected close to the oxide-metal interface with the suggestion that these voids and pores are created due to the Kirkendall effect

[24]. Many studies were performed on the surface modification of the Nitinol with thermal oxidation, and some of them are described in more detail in this review. In most of the thermal oxidation processes, the shape setting process conditions were mimicked. The oxidation of the Nitinol specimens was performed in the temperature range of 400°C to 600°C, for different lengths of time.

In 2002 Firstov *et al.* [23] studied the effect of the oxidation temperature on Nitinol, using 1.5 mm x 1.5 mm x 5 mm samples, which were polished with emery paper to a mirror surface. The samples were first ultrasonically cleaned in DI water and ethanol and then isothermally oxidized at several temperatures between 300°C to 800°C for 30 min, with 50 ml/min air flow. To prevent oxidation during heating, an argon flow of 50 ml/min was used. The samples were studied with SEM, XRD, XPS, Raman spectroscopy and thermogravimetry. Samples oxidized at temperatures below 500°C had a smooth oxide (TiO₂) layer. Oxidization at temperatures above 600°C resulted in a rough final surface for the oxide (TiO₂). Using an XPS depth profile, Firstov found that the oxide layer thickness increased with the increase of the oxidation temperature. Firstov used changes in sputtering time versus concentration to obtain the depth profile. The concentration of the oxygen dropped to ½ of its maximum value after approximately 3,000 s of ion etch for the specimen oxidized at 500°C for 30 min, but it took about 13,000 s for the ion etching to reach this region for the specimen oxidized at 600°C for 30 min.

Firstov *et al.* did not clarify their sample size and number of runs for each condition. The temperature gap between processes was 100°C and for a wide range of

temperatures (300°C to 800°C) it is a good choice. Thermogravimetry results indicated that the oxidation rate increased with an increase in oxidation temperature, but isothermal data was presented only for oxidation at 300°C and 800°C. The XPS depth profile was presented in terms of sputtering time versus concentration and the interpretation for the actual depths was not presented.

Michiardi *et al.* [26] studied the effects of different oxidizing methods on the nickel concentration on the surface, as well as nickel ion release. Michiardi investigated the effects of oxidizing of Nitinol's surface at 400°C, with an air pressure of 3×10^{-2} mbar for 150 min. The samples were 8 mm diameter and 2 mm thick discs. Specimens were annealed and mechanically polished with 1 μm alumina to a mirror-like surface.

On the surface of the heat treated sample there was no metallic nickel present. X-ray photoelectron spectroscopy detected approximately 2% (at.%) of Ni^{2+} on the surface of the heat treated sample. Michiardi did not report the type of nickel oxide that was present on the surface of the heat treated sample. The Ti/Ni ratio, obtained from the XPS, was 14. For the mechanically polished sample the Ti/Ni ratio was one. Metallic nickel was observed on the mechanically polished sample. For the oxidized sample 100% of the titanium on the surface was TiO_2 (Ti^{4+}). At a depth of 6 nm from the surface 63% of the titanium was Ti^{3+} and the rest was Ti^{4+} . Argon ion beam with a 4 keV energy source was used for the purpose of sputtering the surface. A standard TiO_2 sample was used to calibrate the instrument. There were no clear data for nickel and its oxides on the surface. Leaching tests showed that the oxidation process decreased the amount of nickel released from the surface of the Nitinol from 100 ng/cm^2 for the mechanically polished specimen

to 32 ng/cm² after 30 days of exposure to simulated body fluid. During the first hour nickel release from the thermally oxidized sample was 27% of the nickel release from the mechanically polished sample. The nickel ion release test was performed in simulated body fluid (SBF) [26]. Michiardi did not investigate heat treatments at other temperatures and different times. It was not clarified why 400°C was chosen for oxidation of Nitinol.

To activate the shape memory property of Nitinol, the part needs to be “Shape-Set” using a mandrel, at moderate temperatures of approximately 500°C for 10 min. Vojtech *et al.* [27] studied the effects of surface oxidation under similar conditions. The surface oxidizing process was performed on 0.2 mm diameter Nitinol wires which were chemically etched in a solution of 30 ml HF (30 ml), HCl (20 ml), HNO₃ (20 ml) and H₂O (100 ml) for 30 min to remove surface impurities from previous processes, then washed with DI water and dried. The samples were then oxidized at 480°C and 530°C for 10 min. This group of researchers also performed a similar process at 530°C, 580°C, 600°C and 650°C for up to 240 min in air [27]. The oxidation of the Nitinol surface as a result of cyclic heat treatment was also studied. For the cyclic oxidation and isothermal oxidation the heating and cooling rate was 250°C /min. The cyclic oxidized specimens were held at the dwell temperature for 30 min and then cooled down to room temperature. The second cycle was 210 min at dwell temperature before cooling the specimens down to room temperature. Cyclic oxidation did not lead to a big difference in oxidation kinetics compared to isothermal oxidation and after 240 min of oxidation at 600°C. The

oxide layer thickness changed from 1.2 μm for the isothermally oxidized Nitinol to 1.1 μm for the cyclically oxidized Nitinol.

Plant, Grant and Leach [28] also studied the effects of oxidizing the surface at 300°C, 400°C and 600°C, for 30 min. The atmosphere of the oxidation furnace was air at one atmosphere pressure. The surface of the oxidized specimen was mainly TiO_2 . However, on the surface of the specimens oxidized at 300°C and 400°C for 30 min minor amounts of elemental Ti, Ni and NiO were detected, based on XPS analysis, but the surface of the specimen oxidized at 600°C for 30 min was nickel-free and all of the titanium was oxidized. The authors state that at the oxidation temperature of 600°C titanium diffuses from the bulk toward the outermost surface, but at 300°C and 400°C there is only inward diffusion of oxygen. As a result there was a nickel-free TiO_2 oxide layer observed on the surface of the specimen oxidized at 600°C for 30 min, but on the surface of the specimens oxidized at 300°C and 400°C there was some nickel detected.

Zhu *et al.* [24] investigated the oxidation process using a wider range of time and temperature. Three millimeter diameter Nitinol wire samples were annealed at 1000°C for thirty min. The atmosphere of the annealing process was not indicated. Then the oxide layer was removed by polishing. The details of the polishing procedure were not reported. After mechanical polishing, the specimens were electropolished, but there is no detailed description about the electropolishing process. The heat treatment was performed in air. Heat treatment temperatures were 400°C to 1000°C in 100°C increments. The heat treatment times were 3, 10, 30, 100 and 300 min. Using AES, the oxide layer thickness was measured, which was the distance from the surface to the depth

at which the oxygen concentration drops to one half of its maximum value. Several voids were observed inside the oxide layer. These voids increased in size and/or quantity with increase in oxidation temperature and/or time, implying that a thicker oxide layer is more porous.

In all of the studies reviewed above, thermal oxidation formed a titanium oxide layer on the surface, with TiO_2 being the dominant phase. However, in some cases minor amounts of nickel was detected in the oxide layer in either elemental and/or oxide forms. Nickel release from the surface of the Nitinol decreased after thermal oxidation, and it was lower than that for mechanically polished specimens, but it was still observed. To obtain complete nickel depletion in the oxide layer, different oxidation atmospheres have been studied. These studies were based on thermodynamic reasoning and selective oxidation of titanium, with the expectation that nickel can thus be removed.

Hassel *et al.* [29] studied the effects of thermal oxidation at 600°C to 800°C in a mixture of argon and HCl vapor. The partial pressure of the HCl was 7.5×10^{-3} atmospheres. Impurities in the gas were used as the source of the oxygen. After mechanically polishing and cleaning the specimens, thermal oxidation was carried out in the HCl and Ar mixture. It was claimed that the presence of chlorine in the atmosphere forms NiCl_2 , and by evaporation of NiCl_2 the oxide layer would be nickel depleted. Due to the lower standard Gibbs free energy of formation, TiCl_4 is more stable than NiCl_2 . For example, the standard Gibbs free energy of formation of NiCl_2 at 298 K is -259 kJ/mol which is higher than -736 kJ/mol for TiCl_4 . However, since TiO_2 is more stable than TiCl_4 , there will be no titanium available to form TiCl_4 , and the chlorine will be

consumed to form NiCl_2 . The standard Gibbs free energy of formation of NiCl_2 is lower than that for NiO ; for example, at room temperature the standard Gibbs free energy of formation of NiCl_2 is -260 kJ/mol which is lower than -212 kJ/mol for NiO . Therefore, the formation of NiO would not be favored due to the lower standard Gibbs free energy of formation of NiCl_2 compared to that for NiO . Based on this theory, TiO_2 can form on the surface of Nitinol, and nickel will be depleted from the oxide layer by evaporation of NiCl_2 . However, Hassel *et al.* [29] did not provide evidence of the presence of a nickel-free TiO_2 layer on the surface. Also, nickel leaching tests were not performed to prove the depletion of nickel on the surface.

Another thermodynamics-based selective oxidation study was reported by Hessing *et al.* [21]. In this research, thermal oxidation was performed at 600°C in an environment where the oxygen partial pressure was below 3.58×10^{-33} atmosphere. At 600°C and oxygen partial pressures below 6.61×10^{-20} atmosphere nickel oxide is not stable. Under this condition the Gibbs free energy of formation of NiO is not negative. With a decrease in the oxygen partial pressure the thermodynamic activity of oxygen decreases, resulting in the Gibbs free energy of formation of NiO increasing to zero. For example, at 600°C the Gibbs free energy of formation of nickel oxide increases from -159 kJ/mol at an oxygen partial pressure of 1 atmosphere to zero at an oxygen partial pressure of 3.58×10^{-33} atmosphere. However, the Gibbs free energy of formation of TiO_2 is negative at an oxygen partial pressure of 3.58×10^{-33} , and titanium in contact with oxygen can form TiO_2 . To reach very low partial pressure values for oxygen, water was used as the oxygen source. The partial pressure of the water vapor was kept below $2.6 \times$

10^{-6} atmosphere by passing the N_2 gas with 3 ppm water through an aluminosilicate molecular sieve. The partial pressure of the water was calculated from the dew point* of the gas mixture, which was 203 K. The dissociation constant of water at 600°C is 1.37×10^{-24} atmosphere. From the partial pressure of water and dissociation constant of water the oxygen partial pressure was calculated as 3.58×10^{-33} atmosphere. The oxidation time was one min. From the XPS analysis data the Ti/Ni ratio was measured. After the selective oxidation, the Ti/Ni ratio on the surface increased from 16 for the specimen oxidized in dry air at 600°C to 320. An XPS spectrum from the surface of the selectively oxidized Nitinol specimen showed a 7.5 nm thick TiO_2 layer. This oxide layer was nickel-free. Also, the selectively oxidized specimen had the lowest nickel ion release compared to thermally oxidized, mechanically polished and electropolished samples. With low oxygen partial pressure at 600°C, Hessing *et al.* were able to form a nickel-free oxide layer on the surface [21].

Neelakantan *et al.* [30] performed thermal oxidation in a low oxygen partial pressure in a reducing environment. The oxidizing gas was a mixture of 10% H_2 + 90% N_2 . The partial pressure of the oxygen was $1 \times 10^{-41.9}$ atmosphere at 600°C and $1 \times 10^{-31.5}$ atmosphere at 800°C. The extremely low oxygen partial pressure was reached by an approach similar to that used by Hessing *et al.* [21]. The heat treatment was performed at 600°C and 800°C for 5 min. The oxygen partial pressure was controlled by using water vapor as the source of the oxygen. The samples were 10 mm diameter and 2 mm thick discs. They were mechanically polished, rinsed in DI water, ultrasonically cleaned in

* Dew point is the temperature at which water vapor in a humid gas will condense to water.

ethanol, and dried. The specimens were heated to 600°C and 800°C in the reducing atmosphere. The heating and cooling rates were 300°C per min. X-ray photoelectron spectroscopy and SEM were employed to analyze the surface. An XPS depth profile was collected by Ar⁺ sputtering. The sputter rate was calibrated using a standard silicon wafer with a known oxide layer thickness. X-ray photoelectron spectroscopy data indicated the presence of TiO₂ on the surface of the sample heat treated at 600°C. Titanium nitride was detected on the surface of the specimen heat treated at 800°C for 5 min. It was claimed that the TiN formation on the surface of Nitinol was due to the TiN's lower Gibbs free energy of formation compared to TiO₂ at the low oxygen partial pressure. On the surface of the sample heat treated at 800°C, TiN was the dominant compound. According to the XPS data the TiN layer on the surface was nickel-free. Also, after treatment at 600°C for five min, the TiO₂ layer on the surface of Nitinol was also nickel-free. In this research the number of samples was not clarified and only two runs were performed on Nitinol. There were no transverse section images to show if the layer on the surface was porous or not. The thickness of the TiN layer on Nitinol's surface was 175 nm, but there was no depth profile showing it.

Nickel removal during surface oxidation processes can potentially form a nickel-free oxide layer on the surface. However, nickel ion release has been reported from the surface of the thermally oxidized Nitinol.

2.4 Aqueous-based Surface Treatment

Different surface treatment techniques in aqueous solutions were also studied as a means to provide a corrosion resistant and nickel-free oxide layer on the surface. Some of them were as simple as boiling in DI water. In these methods water was considered as the source of oxygen and the temperature was higher than room temperature. One advantage of these methods is simultaneous nickel removal. Since the nickel ion release rate increases with temperature, some nickel can be expected to be removed from the surface during the surface oxidation. Oxidation of titanium and the nickel removal rate increase during chemical etching. Some etchants, such as HF and HNO₃ aqueous solutions, have the potential to oxidize the titanium on the surface and simultaneously remove the nickel atoms from the surface. In some studies chemical etching was introduced as chemical polishing and passivation. Some electrochemical methods like electropolishing have also been employed to provide a smooth and homogenous surface on Nitinol. After the completion of passivation, there should be no elemental titanium and/or nickel present on the surface of the Nitinol.

Michiardi *et al.* [26] investigated the effects of boiling Nitinol in water. Nitinol specimens were polished with SiC paper and alumina to a mirror surface (1 μ m finish). Then they were ultrasonically cleaned in DI water, IPA and acetone followed by surface treatment in boiling water for 30 min. X-ray photoelectron spectroscopy data showed a three nanometer thick oxide layer on the surface. The Ti/Ni ratio was 4.0. The nickel concentration on the surface was lower than that for mechanically polished specimens. Michiardi *et al.* also studied the effect of autoclaving at 121°C for 30 min. The humidity

and the pressure of the autoclave were not specified. The titanium on the surface was present in the form of Ti_2O_3 . The oxide layer thickness was 2.4 nm, and the Ti/Ni ratio was 1.6, which was low compared to chemically etched specimens.

Chemical etching in $\text{HF} + \text{HNO}_3$ has also been studied and in some cases has been considered as a specimen preparation method prior to other surface treatment methods, like boiling in water, thermal oxidation, and electropolishing [11, 20, 25, 31]. To remove defects from the surface the chemical etch solution was 10% $\text{HF} + 40\%$ $\text{HNO}_3 + 50\%$ H_2O , for 30 min. It also removes the nickel from the surface and oxidizes the titanium on the surface, at room temperature. Nickel removal was proved by the color of the etchant changing to green. Also, some carbon removal and cleaning of the surface was reported. The presence of 4% [26], 6% [32], 9% [21] and 11% [15] nickel on the surface of the chemically etched Nitinol was reported; these values decreased to 0.4% after boiling in water for 30 min and 1.3% after steam autoclaving for 2 h [31]. The high roughness on the surface is caused by material removal from the surface during chemical etching. Selective oxidation of titanium and removal of nickel forms a disordered oxide layer on the surface. A rough surface on the chemically etched Nitinol can result in low corrosion resistance and high nickel release. To form a smooth surface, electropolishing has been studied.

Electropolishing is the dominant treatment to modify the surface of Nitinol. This technique also has been used to treat other metallic biomaterials like stainless steel 316 and cobalt-chromium alloys [32, 33]. Different electrolytes, times, temperatures, and DC voltages have been used. These are summarized in Table 1.

Electropolishing with 4.7% acetic acid and 95.3% perchloric acid at room temperature for 2 min and 15 s with a 30 volts DC potential formed a 6 nm thick oxide layer on the surface of mechanically polished Nitinol. The Ti/Ni ratio was 12.3 which was higher than the Ti/Ni ratio for the water boiled Nitinol specimen (4) and the autoclaved Nitinol (1.6), and it was lower than that for Nitinol thermally oxidized at 400°C in air (14) [26].

Table 1. Electropolishing parameters.

Method #	Electrolyte	Electropolishing Time (min)	Electropolishing Temperature (C)	DC Voltage (V)	Reference
1	10% Perchloric Acid + 90% Acetic Acid	6	Room Temperature	20	[11, 25]
2	70% Methanol + 30% Nitric Acid	6	-45	20	[11]
3	4.7% Acetic Acid + 95.3% Perchloric Acid	2.25	Room Temperature	30	[26]

Electropolishing at room temperature in 10% perchloric acid + 90% acetic acid for 6 min resulted in a smooth surface on a Nitinol specimen, which was in its austenite phase; however, electropolishing at -45°C in methanol and nitric acid solution formed a surface with a higher roughness. The Nitinol specimen was in its martensite phase during the electropolishing process, but transformed to austenite at room temperature, and this increased the roughness on the surface [11]. The nickel concentration was 2.5% (at.%)

on the outer surface of the Nitinol electropolished in 10% perchloric acid + 90% acetic acid. This value was lower than that for mechanically polished Nitinol (3%) and Nitinol heat treated at 520°C for 15 min in air (8.2%). Also, the Ti/Ni ratio was 6 on the outer surface of the electropolished specimen, higher than that for mechanically polished Nitinol (3.4) and Nitinol heat treated at 520°C for 15 min in air (2.2).

2.5 Summary of Oxidation

Different oxidation methods and their effects on the surface of the Nitinol are based on the high thermodynamic stability of the TiO_2 . The nickel concentration on the surface, the TiO_2 layer thickness and its chemical composition, the surface roughness and presence of voids and pores are the properties of the surface of Nitinol which are of interest. Nickel ion release in biological solutions, and the presence of nickel in oxide and elemental form on the surface of the Nitinol is of particular interest. By using different surface treatment techniques, the properties of the oxide layer on the surface of the Nitinol can be changed.

In all of these studies, the main purpose was to form a nickel-free TiO_2 layer on the surface. For thermal oxidation all reviewed articles agreed that the oxide layer thickness on Nitinol increases with oxidation time and/or temperature, but the thickness was more dependent on the oxidation temperature rather than time. At oxidation temperatures over 500°C, the oxide layer's roughness increased. The oxide layer's porosity, detected by SEM images from the transverse section of specimens, also increased in this temperature range. At lower temperatures the oxide layer had a

smoother surface compared to Nitinol oxidized at temperatures over 500°C. X-ray photoelectron spectroscopy and AES depth profiles showed that the oxide layer was relatively thin and the nickel concentration, close to the surface, was relatively high. Also, Neelakantan *et al.* [30] proved that with heat treatment at 800°C for 5 min in a nitrogen-containing reducing atmosphere, a TiN layer formed on the surface of the Nitinol. Thermodynamically, nickel oxide is less stable than TiO₂, but it can exist, and its presence on the surface of the oxidized Nitinol has been reported.

2.6 Surface Nitriding of Nitinol

Because nickel cannot form a nitride compound, nitriding is another possible surface treatment method that removes the nickel from the surface. It is a promising surface treatment method to form a protective and wear resistant TiN layer on the surface of Nitinol. An advantage of nitriding is the formation of a nickel depleted surface. Thermodynamically nickel does not form a nitride [6]. Therefore, the formation of a TiN that is nickel-free can be expected.

As shown in Figure 7, over the temperature range of 298 K (25°C) to 1773 K (1500°C) TiN is thermodynamically stable due to its negative standard Gibbs free energy of formation [6]. Values for the standard Gibbs free energy of formation are applicable when pure titanium is exposed to nitrogen at one atmosphere partial pressure, but there are various factors that can affect the reaction conditions. Only 50% of Nitinol is titanium and the remaining is nickel, so the thermodynamic activity of titanium is less than one. According to Equation 1, a decrease in the thermodynamic activity of titanium

increases the Gibbs free energy of reaction. However, as shown in Figure 8, the Gibbs free energy of formation of TiN is negative for titanium activities above 0.00001, in the temperature range of 400 K (127°C) to 1400 K (1127°C), and TiN is thermodynamically stable [6, 34].

$$\Delta G_{f,TiN} = \Delta G_{f,TiN}^0 + RT \ln \frac{a_{TiN}}{a_{Ti} a_{N_2}^{1/2}} \quad \text{Equation 1. [34]}$$

Figure 7. Standard Gibbs free energy of formation of TiN as a function of temperature [6].

A problem associated with the nitriding of the titanium in Nitinol is its sensitivity to the presence of oxygen. Residual oxygen during the process and the presence of an oxide layer on the surface of Nitinol from specimen preparation can affect the formation of TiN. To prevent the formation of TiO_2 , oxygen should be removed from the system. This means the oxygen partial pressure should be low enough to increase the Gibbs free energy of formation of TiO_2 to values higher than Gibbs free energy for formation of TiN.

Figure 8. Gibbs free energy of formation of TiN as the function of titanium activity at different temperatures [6].

Surface nitriding of Nitinol has been reported by various investigators. The source of the nitrogen varied from pure N_2 [35, 36] to a partially reducing atmosphere consisting of 90% N_2 and 10% H_2 [29], or nitrogen in a monoatomic state, formed by Powder Immersion Reaction Assisted Coating (PIRAC nitriding) [37-39]. Plasma Gas Nitriding (PGN) is another method that has been used to form TiN on the surface of the Nitinol [40, 41]. An important factor about the nitrogen source is the concentration of the monoatomic nitrogen content.

Neelakantan *et al.* [30] has reported the formation a nickel-free TiN layer on the surface of Nitinol after annealing at 800°C for 300 s, with an atmosphere of $N_2+10\% H_2$, as discussed in Section 2.4.

Surface nitriding of Nitinol in an atmosphere of pure nitrogen has also been reported. Gil *et al.* [35, 36] investigated the effects of nitriding time and temperature, using Nitinol wires. The Nitinol samples were introduced into a tubular furnace having a pure nitrogen environment. It was not clear if there was any surface treatment performed on the wires before heat treatment. The samples were heat treated at 800°C, 900°C and 1000°C for 5, 7, 10, 15, 20, 25, and 30 min. Leaching tests in artificial saliva were then performed at 37°C. Nickel release was found to decrease after nitriding the sample. After the initial release of nickel, which was approximately 60 ppb, no nickel release was observed for up to 200 h. X-ray diffraction was performed, but no data were presented, so there were no data for the composition of the surface. A nanohardness test was performed on the Nitinol wires with a 1 gram load for 15 s. The procedure explaining how the nanohardness test was performed on wires was not reported. The hardness increased with increase of the TiN layer thickness. In this research Gil *et al.* used Nitinol with a composition of 56% nickel and 44% titanium. According to the Ni-Ti phase diagram there will be some nickel rich zones present in the bulk [42]. This high nickel concentration changes some properties such as the austenite and martensite start and finish temperatures. Nickel release would be higher in this combination compared to other combinations of nickel and titanium with lower nickel concentrations. Pure nitrogen, which is primarily N₂, was used. Since the N-N bond in N₂ is very strong, the probability of the presence of atomic nitrogen on the surface of the Nitinol is relatively low.

To increase the amount of monoatomic nitrogen on the surface of Nitinol, different methods have been studied. Powder Immersion Reaction Assisted Coating (PIRAC) was used to provide nitrogen in the monoatomic form. In this method, nitrogen atoms were supplied from unstable nitride powders or by selective diffusion of the atmospheric nitrogen through a high chromium stainless steel foil. During the diffusion of air through the foil oxygen atoms will form chromium oxide. However, nitrogen in the monoatomic form will diffuse throughout the stainless steel foil without reacting with chromium, nickel and/or iron. Nitinol specimens were thermally nitrided, in contact with monoatomic nitrogen, at temperatures of 850°C to 1100°C for up to 24 h.

Starosvetsky and Gotman [37, 38] performed the PIRAC nitriding at 850°C to 1100°C on mechanically polished and cleaned Nitinol coupons. The method of providing the monoatomic nitrogen was the selective diffusion of atmospheric nitrogen. Nitinol specimens were placed in sealed containers which were made of high chromium stainless steel foils. The presence of TiN was detected by the golden color of the surface of the specimen as well as by XRD. Also, a titanium-rich layer under the TiN layer was detected by XRD. The dominant phase in this layer was NiTi₂. The presence of the NiTi₂ layer, under the TiN layer has been reported elsewhere as well [30]. The thickness of the TiN layer on the surface was measured by SEM images of the transverse section of specimens. The thickness of the nitride layer varied from 0.1 µm for specimens nitrided at 900°C for 30 min to 5 µm for those nitrided at 1050°C for 24 h. There were no data about the nickel concentration in the TiN layer, but Zorn *et al.* [39] performed a similar process and using XPS detected no nickel on the TiN layer.

Another method of creating a TiN layer on Nitinol's surface is plasma gas nitriding (PGN). A laser beam melts the surface in a nitrogen environment, and TiN forms on the surface. The factors that affect the properties of the TiN layer include the nitrogen gas purity and flow rate inside the chamber, the width of the laser pulses, voltage, frequency, and laser scanning speed.

Cui *et al.* [40] investigated the effects of PGN on the properties of the TiN layer formed on Nitinol. Nitinol samples were mechanically polished and rinsed with DI water. The laser parameters were 500 W, 2 mm beam diameter, 5 mm/s for scanning speed and 50% overlap in width. The nitrogen flow rate in the chamber was not specified. A nickel ion release test was performed in Hank's solution at 37°C. The surface characteristics were investigated using SEM, XRD and XPS. After the PGN process the nickel release for the first day was reduced from $3.6 \mu\text{g day}^{-1}\text{cm}^{-2}$ for the mechanically polished specimen to $1 \mu\text{g day}^{-1}\text{cm}^{-2}$. The effects of nitrogen gas flow were investigated by Zhao *et al.* [41]. The laser parameters were similar to the research by Cui *et al.* [40]. The molten line's overlap after each pass changed from 50% to 25%. Nitrogen gas with 99.9% purity flowed during the PGN was at 10, 30, and 40 L per min. Using nanohardness tests, the TiN layer thickness on the surface of Nitinol specimens was estimated. The nanohardness increased with increase in nitrogen gas flow. This was interpreted as being evidence of an increase in the TiN layer thickness. However, with an increase in the nitrogen gas flow from 10 to 40 L per min TiO_2 was detected by XRD, as the TiO_2 peaks became larger. This was caused by the presence of oxygen as an impurity in the nitrogen.

2.7 Summary of Nitriding

Surface nitriding of the Nitinol forms a protective and wear resistant TiN layer. Titanium nitride is the only phase in this layer and there were no data indicating the presence of other phases on the surface; so surface nitriding formed a nickel-free TiN layer on the surface. However, TiN is very brittle and breaks if it is deformed. Formation of cracks on the surface of the nitrided Nitinol can lead to the exposure of the inner layers to the environment. This exposure can potentially cause nickel ion release. Also, in contact with oxygen, titanium from the inner layers forms TiO_2 . More investigations are required on the corrosion and nickel release behaviors of surface nitrided Nitinol after deformation.

2.8 Summary of Literature Review

In contact with oxygen, a TiO_2 layer can form on the surface of Nitinol. This phenomenon can happen even at room temperature. With different surface treatment techniques, the oxide layer's properties like thickness, chemical composition, porosity and roughness change. In the research reviewed the effects of different surface treatment methods on the properties of the Nitinol's surface were investigated.

Mechanical polishing was generally used to remove the oxide layers from the surface of the Nitinol. This method was used to prepare a base-case to be compared with other Nitinol specimens which are surface treated with other methods. However, due to high nickel release and low corrosion resistance, mechanical polishing cannot be used as the only surface treatment method for the Nitinol used in implantable devices. However,

mechanical polishing can be used as a surface preparation method for other surface treatments.

All articles related to thermal oxidation agreed that the oxide layer thickness on Nitinol increases with oxidation time and/or temperature, and it is more sensitive to the oxidation temperature than time. At oxidation temperatures over 500°C the oxide layer's roughness increased, and a nickel-rich zone with Ni_3Ti as the dominant phase formed under the TiO_2 layer. Also, some nickel was detected in the oxide and/or elemental forms at the TiO_2 /atmosphere interface. With the presence of cracks on the surface of the thermally oxidized Nitinol, the nickel-rich zone will be exposed to the environment and can lead to nickel ion release. At oxidation temperatures lower than 500°C, a relatively smooth surface was reported, but the thickness of the oxide layer was significantly lower than that for specimens oxidized at high temperatures. The oxide layer's pores and size and quantity of voids also increased at oxidation temperatures higher than 600°C, and nickel content in the oxide layer was reported. Selective thermal oxidation methods lead to very low nickel ion release.

Surface nitriding formed a protective and wear resistant TiN layer on the surface of Nitinol. Formation of a NiTi_2 layer under the TiN layer after thermal nitriding was reported. Titanium nitride is corrosion resistant and very hard, but it is very brittle and will break if subjected to deformation. The breakage of TiN potentially leads to nickel release and decrease in the corrosion resistance, which is not desirable.

CHAPTER THREE

RESEARCH HYPOTHESIS AND OBJECTIVES

The hypothesis for this study is that thermal oxidation subsequent to nitriding the surface of Nitinol can result in a TiO_2 layer that is free of nickel. This hypothesis is based on the fact that nickel does not form a nitride. As such, when nitrided, only the titanium on the surface of the Nitinol will form TiN ; this is expected to be nickel-free. Subsequent oxidation of the nickel-free TiN layer is expected to result in a TiO_2 layer that is also nickel-free.

The overall objective of this research was to determine if surface nitriding, followed by oxidation, can result in a nickel-free oxide layer on the surface. The specific objectives of this research were:

- Study the oxidation of the Nitinol as a function of time and temperature.
- Study the nitriding of Nitinol in N_2 , 96% $\text{N}_2 + 4\% \text{H}_2$, and 95% $\text{N}_2 + 5\% \text{NH}_3$ as a function of time and temperature.
- Study the nitriding followed by oxidation of Nitinol as a function of time and temperature.

Thermodynamically, TiN formation from the titanium on the surface of Nitinol and nitrogen is spontaneous. Nickel nitride is not stable and there is no driving force for nickel to diffuse toward the surface. Therefore, the surface of the nitrided Nitinol will be nickel depleted TiN . Since TiO_2 is thermodynamically more stable than TiN , TiN will oxidize when in contact with oxygen, and form TiO_2 . By forming a nickel-free TiN layer

on the surface of the Nitinol as a precursor for TiO_2 , the surface of the Nitinol will be nickel-free. Since TiN is being used as the precursor and oxidized right after formation, the mechanical properties and issues associated with brittleness of TiN are not of concern.

CHAPTER FOUR

MATERIALS AND METHODS

An overview of the experimental conditions and processes is shown in Figure 9. Specimens were cut from a 1.5 mm thick Nitinol sheet having a composition of 50.8% Ni + 49.2% Ti (at.%). The specimens were mechanically polished to a mirror-like finish. The specimens were then washed and dried.

After surface preparation the specimens were nitrided in pure N₂, 96% N₂ + 4% H₂, and 95% N₂ + 5% NH₃. The golden color of specimens was considered as initial evidence for the presence of TiN on the surface. The surface properties were studied using Glancing Incidence X-ray Diffraction (GI-XRD) and X-ray Photoelectron Spectroscopy (XPS). The thickness of the nitride layer was measured from Scanning Electron Microscopy (SEM) images of transverse sections of specimens. One group of specimens was oxidized at 600 - 700°C for 30 - 60 min. This group was considered to be the base-case and the chemical composition of the surface of these specimens was compared with the surface of nitrided and oxidized specimens. Nitriding was followed by oxidation under two conditions, namely nitriding in 96% N₂ + 4% H₂ at 1000°C for 20 min followed by oxidation in air at 700°C for 60 min and nitriding in 95% N₂ + 5% NH₃ at 675°C for 5 min followed by oxidation in air at 675°C for 30 min.

Analytical methods, namely XPS, XRD, and SEM were used to analyze the nickel concentration, elemental depth profiles, the nitride and oxide layer thickness, and oxidation state of the elements on the surface.

Figure 9. An overview of surface treatment processes on the Nitinol specimens.

4.1 Specimen Preparation

One and half millimeters thick Nitinol sheet with a composition of 50.8% (at.%) Ni and 49.2% (at.%) Ti was obtained from Nitinol Technology Inc. (Mountain View, CA). The composition was verified by EDS and is presented in Section 5.1.1. Specimens (20 x 10 mm) were cut from the sheet. The surface of the specimens was mechanically ground using 600 grit silicon carbide papers and then polished using 1 μm Al_2O_3 paste, followed by 0.3 μm Al_2O_3 paste to a mirror finish. After polishing, the specimens were rinsed with DI water, cleaned ultrasonically in deionized (DI) water, and air-dried.

To study the effects of washing with deaerated DI water and argon on the removal of the native oxide from the surface of the specimen, one set of specimens was washed with deaerated DI water and argon dried. Argon with 99.999% purity (grade 5), was purchased from Praxair Inc. (San Jose, CA) to dry Nitinol specimens. To deaerate the DI water, argon gas was bubbled through it for 12 h. Another specimen, after mechanical polishing, was washed with DI water, air dried, and chemically etched in 10% HF + 40% HNO_3 + 50% H_2O (Kroll solution) at room temperature for 4 min.

4.2 Tube Furnace and Gas Delivery System Setup

The nitriding and oxidation processes were performed in a Lindberg 55035 tube furnace with a Mullite tube of inner diameter of 1 inch. The temperature profile along the tube furnace was measured with an R-type thermocouple in the temperature range of 500 - 1100°C in 100°C increments. As shown in Figure 10, the temperature at the two

ends of the tube was approximately 400°C lower than at the center of the tube. However, at the middle of the tube (6 inches from two ends), the temperature was similar to the nominal temperature from the temperature controller. Because the thermocouple connected to the temperature controller was in the middle of the tube, there was no difference between the actual temperature in the middle of the tube and the temperature displayed by the temperature controller.

Figure 10. Temperature profile along the tube furnace at 500°C to 1100°C.

The tube was sealed, with only one gas inlet and one outlet. For accurate control of the temperature an R-type thermocouple was placed above the specimen. Figure 11 is a schematic diagram of the transverse section of the tube with fittings made of Teflon on both ends, a thermocouple in the middle, and a Nitinol specimen inside. The specimen was seated on a quartz boat in the middle of the tube. A schematic and an image of the specimen on a quartz boat in the tube are shown in Figure 12 and 13.

Figure 11. Schematic of the tube with fittings and thermocouple.

Figure 12. Schematic of Nitinol specimen on quartz boat in tube furnace.

Figure 13. Image of Nitinol specimen on quartz boat in tube furnace.

Oxidation was performed in dry air. Air was flowed into the tube furnace by an Elite 802 aquarium pump. The flow rates of argon, air, a 96% N_2 + 4% H_2 mix and a 95% N_2 + 5% NH_3 mix were nominally one L per min. All processes with ammonia were performed under a laboratory fume hood, with a ¼ inch Teflon tube used for gas delivery. All connections, valves and fittings were made of stainless steel 316 for the ammonia experiments.

To remove residual moisture from argon, nitrogen, 96% N_2 + 4% H_2 , and air a moisture trap was purchased from Agilent Technologies (Santa Clara, CA).

Specifications of the moisture trap are listed below:

- Removal capacity: 130 g H_2O
- Performance: 5 ppb
- Not refillable

An oxygen trap for removal of residual oxygen in the argon, nitrogen, and 96% N_2 + 4% H_2 was also purchased from Agilent Technologies Incorporated and had the following specifications:

- Removal capacity: 2400 mg O_2
- Performance: 1 ppb
- Not refillable

Ammonia and nitrogen gas mixture was not passed through any moisture and/or oxygen trap due to the corrosive nature of ammonia. Figure 14 is a schematic of the gas delivery system, to the tube furnace, for nitriding with pure nitrogen, 96% N_2 + 4% H_2 and oxidation with air.

Figure 14. Schematic of tube furnace and gas delivery system set up for gas nitriding with pure N_2 or 96% $N_2 + 4\% H_2$, followed by oxidation.

After nitriding with ammonia, the gas was disposed of by bubbling into DI water in a bubbling flask. The ammonium hydroxide in the bubbling flask was disposed as a hazardous waste and was replaced with DI water. This procedure was performed after each nitriding process with ammonia. To prevent the water being sucked back into the tube furnace due to low pressure during furnace cool-down, an empty and sealed container was placed between the tube furnace and the bubbling flask. Figure 15 is a schematic diagram of the gas delivery system to the tube furnace and ammonia gas disposal.

Figure 15. Schematic diagram of tube furnace and gas delivery system set up for gas nitriding with a 95% $N_2 + 5\% NH_3$ mix.

4.3 Nitriding

4.3.1 Nitriding in Pure Nitrogen

Nitinol specimens were heated to $1000^{\circ}C$ or $1100^{\circ}C$ for a dwell time of 60 min. Pure N_2 after passing the moisture and oxygen traps was flowed through the tube furnace at a flow rate of 1 L per min. Grade 5 nitrogen (99.999% purity) was purchased from Praxair Inc. (San Jose, CA). The heating ramp to the dwell temperature was $50^{\circ}C/min$, and the specimens were furnace cooled to room temperature after nitriding. During heat-up and cool-down pure argon was passed through the moisture and oxygen traps and

flowed through the tube furnace at a flow rate of 1 L per min. The experimental design and values for each parameter are represented in Table 2.

Table 2. Experimental design matrix and specimen numbers for specimens nitrided in pure N₂.

Specimen Number	Nitriding Temperature (°C)	Nitriding Time (min)
P-1000-60	1000	60
P-1100-30	1000	60

4.3.2 Nitriding in 96% N₂ + 4% H₂

Mixture of 96% N₂ + 4% H₂ was flowed through the tube furnace at 1 L per min during the high temperature dwell time. Grade 4.8 gas mix of 95% N₂ + 4% H₂ (99.998% purity) was purchased from Praxair Inc. (San Jose, CA). During heating and cooling argon gas was flowed through the tube furnace. The heating ramp rate was 50°C/min. Gas nitriding was performed at 800°C, 900°C, and 1000°C for dwell times of 10, 20, and 30 min, followed by furnace cooling of the specimens.

Investigation of nitriding with 96% N₂ + 4% H₂ was restricted to two parameters, namely nitriding time and temperature. To test the effects of changing these factors on the chemical composition of the surface and the nitride layer thickness, an experimental design with three levels for each parameter was utilized. The experimental design and values for each parameter are shown in Table 3. The values of each level were selected base on observations from the trial tests.

Table 3. Experimental design matrix and specimen numbers for specimens nitrided in 96% N_2 + 4% H_2 .

Specimen Number	Nitriding Temperature ($^{\circ}C$)	Nitriding Time (min)
N-800-30	800	30
N-900-20	900	20
N-900-30	900	30
N-1000-10	1000	10
N-1000-20	1000	20
N-1000-30	1000	30

4.3.3 Nitriding in 95% N_2 + 5% NH_3

Gas nitriding with 95% N_2 + 5% NH_3 was performed at 500 $^{\circ}C$ and 675 $^{\circ}C$ for 5, 10, and 30 min. Grade 4.8 gas mix of 95% N_2 + 5% NH_3 (99.998% purity) was purchased from Praxair Inc. The heating ramp rate was 50 $^{\circ}C$ per min and after nitriding the specimens were furnace-cooled to room temperature. During heating and cooling argon gas was flowed through the tube furnace. The gas flow rate for the 95% N_2 + 5% NH_3 and the argon was 1 L per min. Argon gas was passed through the moisture and oxygen traps. Due to concerns with corrosion by ammonia, 95% N_2 + 5% NH_3 was not passed through the oxygen and/or moisture trap. Because there was no previous study performed on surface nitriding of Nitinol with ammonia, the experimental design was based on observations during a trial run which was performed at 400 $^{\circ}C$ for 60 min. The experimental design and values for each parameter are represented in Table 4.

Table 4. Experimental design matrix and specimen numbers for specimens nitrided in 95% $N_2 + 5\% NH_3$.

Specimen Number	Nitriding Temperature ($^{\circ}C$)	Nitriding Time (min)
A-500-5	500	5
A-500-30	500	30
A-675-5	675	5
A-675-30	675	30

4.4 Oxidation

One group of specimens, after being mechanically polished to a mirror finish and washed, was thermally oxidized in air with a flow rate of 1 L per min at 675 $^{\circ}C$ for 30 min and 700 $^{\circ}C$ for 60 min.

4.5 Nitriding and Oxidation

One set of specimens were nitrided and subsequently oxidized. The values of the parameters for the nitriding and oxidation process were based on observations from the preceding nitriding and oxidation experiments. Completion of the oxidation of the nitride layer first was visually evaluated from the Nitinol specimen's color change from golden, indicating the presence of TiN on the surface, to black which is a sign of the presence of TiO_2 on the surface. Nitriding followed by oxidation was done under two conditions, namely, (a) nitride in 96% $N_2 + 4\% H_2$ at 1000 $^{\circ}C$ for 20 min, then oxidize with air at 700 $^{\circ}C$ for 60 min (N-1000-20-O-700-60) and (b) nitride in 95% $N_2 + 5\% NH_3$ at 675 $^{\circ}C$

for 5 min, then oxidize with air at 675°C for 30 min (A-675-5-O-675-30). The experimental design and values for each parameter are shown in Table 5.

Table 5. Experimental design matrix and specimen numbers for nitrided and oxidized specimens.

Specimen Number	Nitriding Atmosphere	Nitriding Temp. (°C)	Nitriding Time (min)	Oxidation Temp. (°C)	Oxidation Time (min)
A-675-5-O-675-30	95% N ₂ + 5% NH ₃	675	5	675	30
N-1000-20-O-700-60	96% N ₂ + 4% H ₂	1000	20	700	60

4.6 Surface Characterization

The surfaces of the untreated, oxidized, nitrided and nitrided and oxidized specimens were characterized by XRD, SEM, EDS and XPS.

4.6.1 X-ray Diffraction

To characterize the phases present on the surface of the specimens, Glancing Incidence X-ray Diffraction with Cu K α X-rays ($\lambda = 1.542 \text{ \AA}$) was performed, using a Rigaku X-ray diffractometer, model Ultima III. The grazing angle was five degrees. The specimens characterized with XRD were:

- a) An untreated specimen.
- b) A specimen oxidized in air at 700°C for 60 min.

- c) A nitrided- oxidized specimen nitrided in 96% N₂ + 4% H₂ at 1000°C for 20 min, followed by oxidation in air at 700°C for 60 min.
- d) A specimen nitrided in 96% N₂ + 4% H₂ at 800°C for 30 min.

4.6.2 X-ray Photoelectron Spectroscopy

To determine the chemical composition of the surface and the depth profile, surface analysis was performed using a Thermo Scientific K-Alpha XPS. The acceptance angle was 60°, and the take-off angle was 90°. High resolution XPS depth profiles were also obtained. Ion etching during the depth profiling was done using a 3 kV argon ion etch.

4.6.3 Atomic Force Microscopy

The thickness of the nitride layers was measured from the elemental depth profiles based on the distance from the surface to where the nitrogen concentration drops to one half of its maximum concentration value.

Since the nitride layer thickness from the XPS depth profiles was in terms of argon ion etching time, the ion etch rate of the nitride layer was also measured using Atomic Force Microscope (AFM).

As shown in Figure 16, ion etching of the surface of a Nitinol specimen was artificially blocked with silicon and the step height was measured by a Pacific Nanotechnology model Nano-I AFM (San Jose, CA). The ion etch rate was measured at 12 points for three different ion etching times yielding a total of 36 points. The ion etch

rate, as shown in Appendix B, was determined to be 0.91 nm/s for 3kV argon ion etching, with a standard deviation of 0.12 nm/s.

Figure 16. Measurement of the ion etch rate using AFM.

4.6.4 Scanning Electron Microscopy

To measure the nitride layer thickness, SEM images of the transverse sections of specimens were prepared. The specimens were cold mounted and polished with 120 - 600 grit silicon carbide followed by 1 μm and 0.3 μm Al_2O_3 paste. An FEI Quanta 200 scanning electron microscope was used. Images from the specimens were obtained at an accelerating voltage of 20kV, and the nitride layer thickness was measured from the images.

Another set of SEM images were taken at the surface of specimens after preparation and chemical etching to investigate the effect of chemical etching on the surface roughness. The elemental composition of specimens was confirmed by Energy-dispersive X-ray Spectroscopy (EDS) analysis of the mechanically polished specimens.

CHAPTER FIVE

RESULTS

In this chapter the characteristics of the surfaces resulting from the various oxidation, nitriding and nitriding and oxidation experiments are described. The surface characterization techniques employed were XPS, SEM, GI-XRD and AFM. Overall, the surface oxidation of the nitrided Nitinol with a thick nitride layer was found to be capable of forming a nickel-free TiO_2 layer on the surface. However, when Nitinol specimens with a thin nitride layer were oxidized, some nickel was found on the surface/atmosphere interface.

5.1 Untreated Specimens

The surface composition of the mechanically polished specimen, washed and dried specimen and chemically etched specimen are presented in this section. This analysis was done to determine the chemical composition of the Nitinol used, and the potential effect of sample preparation technique on the surface of the Nitinol samples, prior to nitriding and/or oxidation.

5.1.1 Nominal Composition of Nitinol Specimens

The composition of a mechanically polished specimen was measured by EDS. As shown in Figure 17, the composition of Nitinol specimen was 50.81% Ni and 49.19% (at.%) Ti. As shown in Figure 18, Nitinol was the only phase detected by XRD.

Figure 17. Energy-dispersive X-ray spectroscopy spectrum from the mechanically polished Nitinol after the polishing.

Figure 18. X-ray diffraction pattern from the mechanically polished Nitinol.

5.1.2 Specimen Preparation

In order to determine the effects of sample preparation on the oxidation state of the surface of the Nitinol specimen, one set of specimens were washed with deaerated DI water and dried with argon and compared with the specimens which were washed with DI water and air-dried. As shown in Figure 19 (a), there was a peak in the oxygen concentration on the surface of the sample that was mechanically polished, washed with DI water and air-dried. As shown in Figure 19 (b), oxygen was detected on the surface of the argon-dried specimen as well. Washing with deaerated DI water and argon-drying was not effective in preventing of the formation of the oxide layer on the surface.

Figure 19. X-ray photoelectron spectroscopy elemental depth profile of (a) air-dried and (b) argon-dried specimens.

Scanning electron microscopy images from the surface of the chemically etched specimen, shown in Figure 20, showed a dramatic increase in the surface roughness as compared to mechanical polishing. Chemical etching also increased the concentration of oxygen on the specimen since 13.39% oxygen was detected by EDS, as shown in Figure 21.

Figure 20. Scanning electron microscope images from (a) mechanically polished and (b) mechanically polished and chemically etched specimens.

As was shown in Figure 17, oxygen was not detected, by EDS, on the mechanically polished specimen; however, 13.39% oxygen was detected on the chemically etched specimen. Since washing with deaerated DI water and argon-drying did not reduce the oxygen concentration on the surface, as shown in Figure 19, and chemical etching increased the surface roughness and increased the oxygen concentration

on the surface, the specimen preparation was restricted to mechanical polishing and washing with DI water, followed by air-drying.

Figure 21. Energy-dispersive X-ray spectroscopy spectrum from the chemically etched Nitinol.

5.2 Nitrided Nitinol

After mechanical polishing, the Nitinol specimens were thermally nitrided in a tube furnace. Three different atmospheres, pure nitrogen, nitrogen/hydrogen mixture, and nitrogen/ammonia mixture were used. The presence of a golden color was the first indicator of the presence of nitride on the surface of the Nitinol. After visual inspection, the assumed presence of the TiN was confirmed with XPS and/or GIXRD. Using these characterization methods, the chemical state, elemental depth profile, and crystal

structure of the surfaces were studied. The thickness of the TiN layers on the surfaces was measured from the SEM images of the transverse sections of specimens.

5.2.1 Nitinol Nitrided With Pure Nitrogen

The color of the specimens at nitrided at 1000°C and 1100°C for 60 min was dark blue, indicating there was no TiN on the surface. This was most probably due to the lack of atomic nitrogen. Since the golden color indicating formation of TiN was not observed, these specimens were not analyzed further.

5.2.2 Nitinol Nitrided With Nitrogen + 4% Hydrogen

Nitriding in 96% N₂ + 4% H₂ was performed at 700°C for 60 min and 800°C to 1000°C for 10 to 30 min. Nitriding at 700°C for 60 min did not result in the formation of a nitride layer on the surface. The color of the specimen remained dark blue. However, at temperatures above 800°C the surface color of the specimens changed to golden, indicating the presence of TiN. X-ray diffraction analysis of the specimen nitrided at 800°C for 30 min, as shown in Figure 22, indicated that the surface was primarily TiN, with minor amounts of NiTi₂. Also, as shown in Figure 23 (a) and (b), a layer with a Ti/Ni ratio of 2 was detected at a depth of 1.2 and 2.75 µm from the surface of the specimens nitrided at 800°C for 30 min and at 900°C for 30 min, under the TiN layer. This indicates that the peaks of NiTi₂ detected by XRD are potentially from the layers under the TiN layer on the surface. The presence of a NiTi₂ layer under the TiN layer after the gas nitriding has been reported elsewhere as well [37, 39].

Figure 22. X-ray diffraction results from the specimen nitrided at 800°C for 30 min.

Figure 23. Elemental depth profile of specimens nitrided in 96% N_2 + 4% H_2 at (a) 800°C for 30 min, (b) 900°C for 30 min and (c) 1000°C for 30 min.

As shown in Figure 23 (a) and (b), for specimens nitrided at 800°C and 900°C for 30 min (N-800-30 and N-900-30) the nickel concentration increased to almost one half of the titanium concentration when the concentration of the nitrogen dropped to zero. The nitrogen concentration dropped to zero at approximately 1.2 μm from the surface for specimen nitrided at 800°C for 30 min and 2.75 μm from the surface for the specimen nitrided at 900°C for 30 min. For the specimen nitrided at 1000°C for 30 min (N-1000-30), the nitride layer on the surface was very thick, and the depth profile was not able to reach the NiTi_2 zone, as a result of which the thickness of the nitride layer could not be estimated from the XPS depth profile. Based on 0.91 nm/s ion etch rate for TiN, as discussed in Appendix B, the TiN layer thickness on the specimen nitrided at 1000°C for 30 min was found to be greater than 2.75 μm .

Nickel was not detected in the TiN layer. As shown in Figure 24, the nickel depletion on the outmost surface was confirmed by XPS survey spectra for the surface of all 6 nitrided specimens. There was no peak in the range of 800 to 900 eV of binding energy, indicating the presence of nickel and/or its compounds. In Figure 23 it can be seen that the nickel concentration increases only at distances, from the surface, where the nitrogen concentration starts to decrease. For example, for the specimen nitrided at 900°C for 30 min, the nitrogen concentration starts to drop at approximately 1 μm from the surface and in this region the nickel concentration starts to rise. This indicates that the nitriding process formed a nickel-free TiN layer on the surface. The titanium concentration remained constant at approximately 50% (at.%).

Oxygen and carbon were detected on the surface. These were most probably adsorbed on the surface during the post-nitriding handling. An increase in the oxygen concentration was observed at a distance from the surface where the nickel concentration starts increasing. The reasons for this were not explored further.

Figure 24. X-ray photoelectron spectroscopy survey scan of specimens nitrided in 96% N_2 + 4% H_2 at (a) 800°C for 30 min, (b) 900°C for 20 min, (c) 900°C for 30 min, (d) 1000°C for 10 min, (e) 1000°C for 20 min, and (f) 1000°C for 30 min.

At a distance from the surface where the nickel concentration starts increasing, nickel was in the oxide form (NiO) with a binding energy of 854 eV, as shown by the XPS high resolution scans for the range of 845 to 865 eV in Figure 25. No peaks were observed in the range of 852 to 853.8 eV, where the peak of elemental nickel is located.

Figure 25. High resolution XPS spectra for Ni₂p from (a) specimen nitrided at 800°C for 30 min and (b) specimen nitrided at 900°C for 30 min.

5.2.2.1 Nitride Layer Thickness

By using the ion etch rate, determined from AFM measurements, the thickness of the nitride layer was determined from XPS depth profiles. Measured values for the nitride layer thickness are represented in Table 6. The nitride layers on the surfaces of specimens nitrided at 1000°C for 20 and 30 min (N-1000-20 and N-1000-30) were very thick, and the elemental depth profile could not reach the end of the nitride layer. Based on the measurements taken, the TiN layer thicknesses were determined to be greater than 2.75 μm for specimens nitrided at 1000°C for 20 and 30 min.

The thickness of the nitride layer was also measured from SEM images of cross-sections. Measured values of the TiN layer thickness are listed in Table 6. As shown in Figure 26 there was some electron charging on the TiN layer, due to the low electrical conductivity of TiN. At low nitride layer thicknesses the measured values for the thickness of the nitride layer by SEM was relatively close to the values measured from the XPS, but for specimen nitrided at 1000°C for 10 min it was not the case.

Table 6. Thickness of the nitride layer on the surface of the Nitinol.

Specimen Number	Nitriding Temperature (C)	Nitriding Time (min)	Nitride Layer thickness From SEM (μ)	Nitride Layer thickness From XPS (μ)
N-800-30	800	30	0.69	0.82
N-900-20	900	20	1.42	1.32
N-900-30	900	30	2.52	1.70
N-1000-10	1000	10	6.11	2.60
N-1000-20	1000	20	6.43	-
N-1000-30	1000	30	6.32	-

Figure 26. Scanning electron microscope images from the transverse section of specimens nitrided in 96% N_2 + 4% H_2 .

Nitriding in 96% N_2 + 4% H_2 at temperatures above 800°C resulted in the formation of nickel-free TiN layers on the surfaces of the Nitinol specimens. The nickel concentration was zero in the nitride layer and started to increase at depth where the nitrogen concentration started to decrease. X-ray diffraction and XPS results showed a

NiTi₂ zone under the nitride layer after nitriding. The TiN layer thicknesses were measured from the SEM images of the transverse section of specimens. They varied from 0.7 μm for the specimen nitrided at 800°C for 30 min to 6.3 μm for the specimen nitrided at 1000°C for 30 min.

5.2.2.2 Effect of the Nitriding Time and Temperature

Nitriding temperature was found to be more effective in determining the nitride layer thickness, as compared to nitriding time. As shown in Figure 27 the thickness of the nitride layer on the surface increased dramatically with nitriding temperature, from less than 1 μm at 800°C to 6.2 μm at 1000°C. This is due to the fact that diffusion of nitrogen into the surface is faster at higher temperatures. However, the nitriding time did not affect the nitride layer thickness. As shown in Figure 28, the nitride layer thickness at 1000°C was not statistically different for specimens nitrided for 10, 20, and 30 min.

Figure 27. Nitride layer thickness on the surface of the Nitinol as a function of nitriding temperature.

Figure 28. Nitride layer thickness on the surface of the Nitinol as a function of nitriding time.

5.2.3 Nitinol Nitrided With Nitrogen + 5% Ammonia

Nitinol specimens were nitrided in 95% N_2 + 5% NH_3 at 450°C for 60 min and at 500°C and 675°C for 5 and 30 min. At the nitriding temperature of 450°C there were no signs of nitriding occurring. The surface was oxidized, as there was no golden color on the surface and it was black. At nitriding temperatures of 500°C and 675°C the surface color turned to golden. The presence of TiN on the surface was confirmed by XPS analysis. As shown in Figure 29 (a) and (b), the surface of both specimens, nitrided at 500°C and 675°C for 5 min was nickel-free TiN. X-ray photoelectron spectroscopy depth profiles also detected a nickel-rich zone under the nitride layer, with a nickel concentration of 65% (at.%). Oxygen at relatively high concentrations was detected in the nitride layer on the surface of both specimens. The oxygen concentration in the nitride layer, after nitriding with 95% N_2 + 5% NH_3 , was higher than that for specimen nitrided in the 96% N_2 + 4% H_2 . Oxygen was most probably present in the 95% N_2 + 5%

NH₃ as an impurity. It is also possible that the presence of oxygen in the nitride layer, at such high levels, was potentially due to accumulation by absorbing oxygen during the XPS analysis. With increase in the nitriding time from 5 to 30 min at 500°C and 675°C the surface color of the specimen became dark. It is most probably due to the absorption of more oxygen from the 95% N₂ + 5% NH₃ and subsequent oxidization of the nitride layer on the surface during the longer nitriding times.

The SEM image from the transverse section of specimens nitrided in 95% N₂ + 5% NH₃ at 500°C for 5 min, as shown in Figure 30, showed a 0.52 μm thick nitride layer on the surface.

Figure 29. X-ray photoelectron spectroscopy depth profile of specimens nitrided in 95% N₂ + 5% NH₃ at (a) 500°C for 5 min and (b) 675°C for 5 min.

Figure 30. Scanning electron microscope image from the transverse section of specimen nitrided in 95% N_2 + 5% NH_3 at 500°C for 5 min.

5.2.4 Summary of Nitriding

Overall, nitriding in 96% N_2 + 4% H_2 in the temperature range of 800°C to 1000°C and in 95% N_2 + 5% NH_3 in the temperature range of 500°C to 675°C resulted in the formation of nickel-free TiN layers on the surface of the Nitinol specimens. The nitride layer's crystal structure, chemical composition and thickness were studied by XRD, XPS and SEM. The Nickel concentration was zero in the nitride layer and started to increase at depths where the nitrogen concentration started to decrease. For example, this distance for the specimen nitrided in a 96% N_2 + 4% H_2 mix at 900°C for 30 min was

1 μm . A nickel-rich zone with a nickel concentration of 60 to 70% (at.%) was observed under the nitride layer, after nitriding with 95% N_2 + 5% NH_3 . X-ray diffraction and x-ray photoelectron spectroscopy results showed a NiTi_2 zone under the nitride layer after nitriding with the 96% N_2 + 4% H_2 . Both nitriding processes were sensitive to the presence of oxygen as an impurity in the gases and/or as native oxide on the surface after specimen preparation. Based on the results two nitriding conditions were selected for nitriding the Nitinol specimens before oxidation. These two conditions were nitriding in a 96% N_2 + 4% H_2 mix at 1000°C for 20 min (N-1000-20) and nitriding in 95% N_2 + 5% NH_3 at 675°C for 5 min (A-675-5). These two conditions were selected because they were able to form a relatively thick (6.4 μm for N-1000-20 and 0.5 μm for A-675-5) and nickel-free nitride layer on the surface.

5.3 Oxidized Nitinol

One set of Nitinol specimens was oxidized after specimen preparation. The oxidation process was performed with a one L per min flow rate of dry air, at 675°C for 30 min (O-675-30) and 700°C for 60 min (O-700-60). After oxidation, the surface color of the specimens changed to black; this was interpreted as evidence of the presence of TiO_2 . As shown in Figure 31, GIXRD showed the presence of TiO_2 (Rutile). Also, some Ni_3Ti was detected by GIXRD, presumably due to the formation of a nickel-rich zone under the TiO_2 layer. However, the major peaks were from TiO_2 , indicating the presence of a thick TiO_2 layer on the surface. The XPS depth profile was not able to reach the Nitinol bulk after 3,000 s of 3 kV ion etching, so it was not possible to estimate the

thickness of the oxide layer. Based on 0.91 nm/s of ion etch rate, the TiO₂ layer thickness was higher than 2.75 μ m.

X-ray photoelectron spectroscopy results, as shown in Figure 32, confirmed the presence of TiO₂ on the surface. On the surface of the specimen oxidized in air at 675°C for 30 min 1.75% (at.%) of nickel was detected. High resolution XPS spectra indicated that the nickel was in the form of NiO (Ni2p binding energy = 854.5). As shown in Figure 33, there was no peak in the 850 to 853 eV range, which represents elemental nickel. At approximately 0.5 μ m from the outermost surface (based on 0.91 nm/s ion etch rate), there was no nickel detected.

Figure 31. X-ray diffraction results from the oxidized Nitinol in air at 700°C for 60 min.

Figure 32. X-ray photoelectron spectroscopy depth profile of specimen oxidized at 675°C for 30 min.

Figure 33. Nickel high resolution XPS scan results for specimen oxidized at 675°C for 30 min.

Nickel was also detected on the outmost surface of the specimen oxidized in air at 700°C for 60 min. As shown in Figures 34 and 35, for the specimen oxidized at 700°C for 60 min the nickel concentration dropped to zero at a distance greater than 1.8 μm from the surface, compared to 0.5 μm for the specimen oxidized at 675°C for 30 min.

Figure 34. X-ray photoelectron spectroscopy depth profile of specimen oxidized in air at 700°C for 60 min.

Figure 35. Nickel high resolution XPS scan results for specimen oxidized at 675°C for 30 min.

Oxidation in air at 675°C for 30 min and at 700°C for 60 min formed a surface layer with TiO₂ as the dominant phase. X-ray photoelectron spectroscopy analysis detected nickel on the surface/atmosphere interface for specimens oxidized in air at 700°C for 60 min and 675°C for 30 min. Therefore, oxidation did not result in the formation of a nickel-free oxide layer on the surface.

5.4 Nitrided and Oxidized Nitinol Specimens

Thermodynamically, oxidation of TiN is a spontaneous reaction. Surface nitriding followed by oxidation was performed on Nitinol specimens under two conditions. The first condition was nitriding in 96% N₂ + 4% H₂ at 1000°C for 20 min and then oxidizing in air at 700°C for 60 min (N-1000-20-O-700-60). The second condition was nitriding in 95% N₂ + 5% NH₃ at 675°C for 5 min and then oxidizing in air at 675°C for 30 min (A-675-10-O-675-30). The values of the parameters for the nitriding and oxidation process were selected based on the findings from earlier nitriding experiments, the thickness of the nitride layer with undetectable amounts of nickel on the surface, and the Nitinol specimen's color change from gold to black, an indication of the completion of the oxidation of the nitride layer.

X-ray diffraction analysis was performed on the specimen nitrided at 1000°C for 20 min, followed by oxidation at 700°C for 60 min (N-1000-20-O-700-60). As shown in Figure 36, the surface was only TiO₂. Other phases such as TiN and Ni₃Ti were not detected. This is evidence that the nitrided layer was completely oxidized. Also, the oxide layer was thick enough that no Nitinol, Ni₃Ti, or other phases were detected. The

presence of the thick oxide layer with a thickness greater than 2.75 μm (based on 0.91 nm/s of ion etch rate) on the surface was confirmed by XPS depth profiles. As shown in Figure 37, there was a TiO_2 layer on the surface, with no detectable nickel.

Figure 36. X-ray diffraction results from N-1000-20-O-700-30.

Figure 37. X-ray photoelectron spectroscopy depth profile of N-1000-20-O-700-30.

Nitriding in the 96% N₂ + 4% H₂ atmosphere formed a 6.43 μm thick TiN layer with undetectable amounts of nickel on the surface. Oxidation of this TiN layer resulted in the formation of a TiO₂ layer with undetectable amounts of nickel on the surface. Also, no nitrogen was detected in the oxide layer, indicating that oxidation of the nitride layer was complete.

Nitriding in 95% N₂ + 5% NH₃ at 675°C for 5 min, followed by oxidation at 675°C for 30 min formed a TiO₂ layer which was not nickel-free on the surface. As shown in Figure 38, XPS results detected 0.6% (at.%) of nickel on the surface.

Figure 38. X-ray photoelectron spectroscopy depth profile of A-675-5-O-675-30.

Nitrided specimens were oxidized in air at 675°C for 30 min and 700°C for 60 min. The surface oxidation of the nitrided Nitinol with a 6.4 μm thick TiN layer with undetectable nickel was found to be capable of forming a TiO_2 layer in which nickel was undetectable. However, after oxidation of Nitinol specimens with a 0.25 μm thick nitride layer, some nickel was found on the surface/atmosphere interface. It was most probably caused by an outward diffusion of nickel, due to the thermodynamic activity difference of nickel present in the nickel-rich zone and the nickel-depleted zone. Also, presence of oxygen on the surface and the thermodynamic stability of NiO was a driving force for nickel to diffuse toward the surface.

CHAPTER SIX

DISCUSSION

6.1 Surface Chemical Composition

Based on the results in Chapter Five, surface nitriding followed by oxidation was found to be an effective technique to form a TiO_2 layer with no detectable nickel on the surface. The nickel concentration on the outermost surface of the Nitinol specimen dropped to zero, from about 20% (at.%) for the mechanically polished specimen and 1.5% (at.%) for the Nitinol specimens that were oxidized only. The fundamental reason for this drop in the nickel concentration was surface nitriding prior to oxidation. Nitriding formed a TiN layer on the surface of the Nitinol, and by oxidation of the TiN, a TiO_2 layer with no detectable nickel was formed on the surface.

6.1.1 Bare Nitinol

After specimen preparation, the surface of the Nitinol specimens was analyzed by XPS. The nickel concentration value dropped from 50.8% (at.%) in the bulk to approximately 20% (at.%) on the surface. By XPS 50% oxygen and 25% (at.%) titanium was also detected. These results indicate the spontaneous oxidation of titanium and the formation of TiO_2 on the surface/atmosphere interface on the Nitinol specimen. This oxidation occurred while titanium was in contact with atmospheric oxygen at room temperature. According to thermodynamic data, this phenomena is predictable due to a very low standard Gibbs free energy of formation for TiO_2 . The oxidation of titanium on

the surface of the Nitinol has been reported repeatedly in other research [16-20]. In other work, the value of the nickel concentration on the surface varied from 0.9% to 20% (at.%). The amount of nickel detected on the surface in this work was in this range.

6.1.2 Nitrided Nitinol

Nitinol specimens were surface nitrided in three different atmospheres, pure N_2 , a 96% N_2 + 4% H_2 mix, and a 95% N_2 + 5% NH_3 mix. Surface nitriding of Nitinol in pure nitrogen and in a nitrogen/hydrogen gas mix has been reported by other researchers [30, 35, 36], and these two atmospheres were selected based on previous work. Ammonia is also a source of nitrogen. Although there was no report for the surface nitriding of Nitinol in a nitrogen/ammonia gas mixture, it was selected to nitride the Nitinol based on ammonia being a source of atomic nitrogen.

Since there was no golden color observed on the surface of the Nitinol specimen nitrided in pure nitrogen, nitriding in pure nitrogen did not result in the formation of a TiN layer on the surface. It was most likely due to the lack of atomic nitrogen in the atmosphere. Pure nitrogen is in the form of N_2 . Breaking the N-N bond is required to provide atomic nitrogen for the nitriding reaction. The observation that the Nitinol specimen was not nitrided was probably due to insufficient energy to break the N-N bonds. Although nitriding of the Nitinol in pure nitrogen was reported in other research at 800 - 1000°C for 5 - 30 min [35, 36], in this work, nitriding with pure nitrogen was unsuccessful for reasons that need further exploration.

Another technique to nitride Nitinol, adopted from previous works, was nitriding in a 90% N₂ + 10% H₂ gas mix. After nitriding at 800°C for 300 s TiN was detected on the surface of the Nitinol [30]. In this work specimens were nitrided in a 96% N₂ + 5% H₂ mix. The gas with a lower percentage of hydrogen was selected due to safety concerns and availability. Based on XRD and XPS analysis, after nitriding of Nitinol in 96% N₂ + 5% H₂, TiN was formed on the surface of the Nitinol. The effect of the presence of 4% H₂ in the nitrogen on the formation of atomic nitrogen was not investigated in this research.

Another set of specimens were nitrided in a 96% N₂ + 4% H₂ mix at 700 - 1000°C. At nitriding temperatures below 800°C, nitriding was not observed, probably due to the lack of energy to break N-N bonds and provide atomic nitrogen at the surface of the Nitinol. The nitride layer thickness increased dramatically from 0.75 - 6 µm with an increase in nitriding temperature from 800 - 1000°C. It was most likely due to the fact that the increase in the nitriding temperature can accelerate the diffusion of nitrogen into the surface and titanium from the bulk toward the surface. Also, at higher nitriding temperatures more atomic nitrogen is available due to more energy available to break the N-N bonds. No nickel was detected in the TiN layer on the surface, and the nickel concentration began to rise when the nitrogen concentration began to drop. Based on thermodynamic data this was predictable. Nickel does not form a nitride, due to the positive standard Gibbs free energy of formation; the surface will therefore be predominantly TiN. The presence of a nickel-free TiN layer has been reported in previous research on the nitriding of the Nitinol [30, 35-41].

The third atmosphere selected to nitride the Nitinol was 95% N_2 + 5% NH_3 , with ammonia as the source of atomic nitrogen. There was no previous study performed on the nitriding of Nitinol in ammonia, so the nitriding conditions were selected based on the observations from the experiments in this investigation. However, due to being corrosive and flammable, ammonia was not deoxidized before the nitriding process, as a result of which considerable amounts of oxygen (56 - 60%) was detected on the surface of the Nitinol which was nitrized in the ammonia-containing atmosphere. No nickel was detected in TiN layer on the surface of the Nitinol. The thickness of the layer on the surface was approximately 0.25 μm which was thinner than the nitride layer on the surface of the Nitinol specimens nitrized in a 96% N_2 + 4% H_2 mix. This was most probably due to the lower nitriding temperature which limited the diffusion of the nitrogen into the surface of the Nitinol and titanium towards the surface.

Overall, nitriding was capable of forming a TiN layer on the surface of the Nitinol with no nickel being detected. Two nitriding conditions were selected for nitriding prior to oxidation. They were nitriding in 96% N_2 + 4% H_2 at 1000°C for 20 min and nitriding in 95% N_2 + 5% NH_3 at 675°C for 5 min.

These two processes were selected based on their capability of the formation of a uniform and nickel-depleted TiN layer on the surface. After nitriding under these conditions the specimens were oxidized in air. The oxidation conditions were selected based on color change from gold to black, indicating the completion of the oxidation of the TiN layer on the surface. To study the effect of the nitriding prior to the oxidation

process, one set of specimens were oxidized only in air to be compared with the nitrated and oxidized specimens.

6.1.3 Oxidized Nitinol

Nitinol specimens were oxidized in air at 675°C for 30 min and 700°C for 60 min. These two conditions were selected to mimic the oxidation process after the nitrating for the nitrated and oxidized specimens. After oxidation, based on the XRD results, the dominant phase was TiO₂ as expected. The formation of TiO₂ after oxidation has been reported repeatedly [19-31]. However, the TiO₂ layer was not nickel-free, and based on XPS results 1.5 to 1.7% (at.%) of nickel was detected on the outermost surface of the oxidized specimen. The presence of nickel in the form of NiO on the surface/atmosphere interface has also been reported by others [19, 20, 22]. Two phenomena are suggested to be responsible for the presence of the nickel on the outermost surface of the Nitinol specimen.

- Availability of oxygen for the nickel to form NiO on the surface is a driving force for nickel to diffuse toward the outer surface.
- After completion of the surface oxidation and formation of a nickel-rich zone under the TiO₂ layer, nickel diffuses into the oxide layer toward the outermost surface due to the thermodynamic activity difference of nickel in the nickel-rich zone and the nickel in the nickel-free oxide layer.

6.1.4 Nitrided and Oxidized Nitinol

Nitriding and oxidation processes were performed on the Nitinol specimens under two conditions:

- Nitriding in a 96% N_2 + 4% H_2 at 1000°C for 20 min and then oxidizing in air at 700°C for 60 min (N-1000-20-O-700-60).
- Nitriding in 95% N_2 + 5% NH_3 at 675°C for 5 min and then oxidizing in air at 675°C for 30 min (A-675-10-O-675-30).

The values of the parameters for the nitriding and oxidation process were based on observations from the nitrided specimens, which had a relatively thick and uniform nitride layer on the surface with no detectable nickel. Also, the completion of the oxidation of the nitrided layer was another factor for the selection of the oxidation parameters. The first nitriding and oxidation process, which was nitriding in a 96% N_2 + 4% H_2 mix at 1000°C for 20 min followed by oxidation in air at 700°C for 60 min, resulted in a TiO_2 layer on the surface with no detectable nickel. Nitriding in 96% N_2 + 4% H_2 prior to the oxidation of the Nitinol and formation of a relatively thick TiN layer (6 μm) eliminated the presence of the nickel on the outermost surface. Nitinol specimens which were only oxidized under the similar oxidation condition (in air at 700°C for 60 min) had a nickel concentration of 1.5% (at.%) on the outermost surface of them. Based on the observations nitriding prior to the oxidation eliminated the presence of the nickel on the surface. However, nitriding in 95% N_2 + 5% NH_3 at 675°C for 5 min and then oxidizing in air at 675°C for 30 min did not eliminate the nickel on the outermost surface

of the specimen. 0.62% (at.%) nickel was detected on the outermost surface of the specimen nitrided in ammonia and then oxidized.

Based on these observations, an outward diffusion of the nickel from the nickel-rich region, under the nickel-free region, toward the nickel-free zone on the surface is suggested as the responsible factor for the presence of the nickel on the outermost surface of the Nitinol. This phenomenon is most probably due to the difference of the thermodynamic activity of the nickel in nickel-rich zone and the nickel-free zone. Also, availability of oxygen for the nickel to form NiO on the surface is another driving force for nickel to diffuse toward the surface. However, for the nitrided Nitinol in a 96% N₂ + 4% H₂ mix at 1000°C for 20 min and then oxidized in air at 700°C for 60 min, the TiN layer was very thick, and nickel was not able to diffuse through the TiN and/or TiO₂ layer, and a TiO₂ layer with undetectable amounts of nickel was observed on the surface of this specimen.

6.2 Sources of Error and Confidence of Results

There were at least five specimens surface treated per condition. XPS and XRD analysis was performed only on one specimen, and were verified only in some cases. Analysis of more samples was not possible within the scope and resources available for this research. The fundamental purpose of this research was to test the validity of the research hypothesis presented in Chapter Three. Since investigation of process parameters and kinetics was not part of the scope of this research, the lack of analysis of more than one specimen per condition does not distract from the validity of the findings.

The temperature in the tube furnace was calibrated, and a thermocouple was placed right on the top of the specimens, but small variations in the temperature due to the accuracy of the thermocouple ($\pm 1^\circ\text{C}$) and temperature difference between the surface of the specimen and the tip of the thermocouple could be a source of error.

Another process related source of error was the gas composition. This is considered as a source of error only for the nitriding process since the oxidation was performed in air. The ratio of the 96% N_2 + 4% H_2 was considered to be 96/4, but there was the possibility of minor changes in this ratio.

Errors in the XPS, SEM, and XRD analysis could also be sources of error. Since TiN's electrical conductivity is low, charging was observed during the SEM analysis. The charging potentially can decrease the accuracy of the TiN layer thickness measurements from the SEM images.

Interpretation of the ion etch time to the actual distance from the surface in μm required another ion etch rate measurement experiment, using AFM. The accuracy of the AFM as well as the accuracy of the XPS depth profile affected the accuracy of the TiN layer thickness, as measured by XPS.

Another analysis based error is from the detection limit of XRD, which is 1% (wt.%). This means if the concentration of a phase, for example NiO, is less than 1% (wt.%), XRD could not detect it.

CHAPTER SEVEN

CONCLUSIONS

Due to its good biocompatibility, corrosion resistance, and unique mechanical properties such as superelasticity and shape memory, Nitinol has been used in several biomedical devices. However, Nitinol contains 50% nickel, a toxic material, which can cause severe allergic reactions in the human body. Nickel can leach out from the surface of Nitinol into the human body, and nickel ion release from Nitinol has been reported repeatedly.

Different surface treatment methods like thermal oxidation, electropolishing, passivation, and boiling in water have been used to provide a protective and nickel-free TiO₂ layer on the surface of Nitinol.

During this investigation, it was found that nitriding followed by thermal oxidation is capable of forming an oxide layer on the surface with undetectable amounts of nickel. Nitriding in 96% N₂ + 4% H₂ at 1000°C for 20 min followed by oxidation in air at 700°C for 60 min formed a TiO₂ layer on the surface, and no nickel was detected in the TiO₂ layer. The nitride layer should also be thick enough to prevent the nickel atoms from outward diffusion due to the thermodynamic activity difference. Monitoring the surface properties during the nitriding and oxidation process, provide these findings:

- Washing with deaerated DI water and argon-drying instead of washing with DI water and air-drying was not an effective surface preparation technique to prevent

Nitinol surface oxidation. Chemical etching in 10% HF + 40% HNO₃ + 50% H₂O (Kroll solution) formed more oxides on the surface of Nitinol.

- Nitriding in pure nitrogen at 1000°C and 1100°C, in 96% N₂ + 4% H₂ at temperatures below 800°C, and in 95% N₂ + 5% NH₃ at temperatures below 500°C did not form a nitride layer on the surface of Nitinol.
- The nitriding process was very sensitive to the presence of oxygen, and small amounts of oxygen as an impurity in nitrogen sources, or other gases, can cause surface oxidation instead of nitriding.
- TiN was the predominant phase on the surface of nitrided specimens.
- The TiN layer thickness, on the surface of specimens which were nitrided in 96% N₂ + 4% H₂ at 800°C to 1000°C, was strongly affected by nitriding temperature and increased dramatically at higher temperatures. However, nitriding time was not as effective as nitriding temperature in affecting the thickness of the nitride layer.
- Nickel was present on the outmost surface of the specimens oxidized in air at 675°C for 30 min and 700°C for 60 min.

CHAPTER EIGHT

RECOMMENDATIONS FOR FUTURE WORK

Biocompatibility tests, other performance tests like nickel ion leaching and corrosion resistance, and effects of the nitriding and oxidation on the surface roughness would be helpful to refine the data obtained from this study. Also, investigation of the nitriding kinetics with 95% N_2 + 5% NH_3 and 96% N_2 + 4% H_2 and kinetics of oxidation of the TiN would be helpful to control the oxidation-nitriding process. Corrosion resistance and nickel ion release as a result of deformation is recommended to be studied to mimic the performance of nitrided and oxidized Nitinol in its actual applications. A broader scope with more replications is also recommended.

In this work nitriding in 96% N_2 + 4% H_2 at 800°C to 1000°C for 10 to 30 min was performed. Studies of the effects of nitriding for longer and/or shorter periods of time are recommended. Also, measuring the nitride layer using a field emission SEM will provide better images from the transverse sections and ultimately more accurate measurements of the nitride layer thickness. Using data of the nitride layer thickness, the kinetics of nitriding could be studied. Similar research on kinetics of nitriding with 95% N_2 + 5% NH_3 is also recommended.

Oxidation of the nitrided surface was performed at 675°C and 700°C for 30 and 60 min. This process needs to be investigated in greater detail, and the effects of the oxidation time and temperature on the completion of oxidation, the nickel content on the surface and surface morphology is recommended to be studied in greater detail.

The primary objective of the surface treatments on Nitinol is to reduce and ideally eliminate the nickel ion release. Surface nitriding and oxidation formed a nickel-depleted oxide layer on the surface, but nickel ion release is possible from cracks and/or corrosion spots, so nickel ion release tests would provide valuable data on the effectiveness of surface nitriding and oxidation processes. Also, studying the effects of nitriding and oxidation on the corrosion resistance of Nitinol is recommended. Ultimately, high corrosion resistance and low nickel ion release lead to improved biocompatibility, which is recommended to be studied by *in vitro*, and ideally, *in vivo* research. Corrosion resistance, nickel release and biocompatibility depend on the surface roughness; therefore, studying the effects of nitriding and oxidation process on the surface roughness will also be useful.

In most of the previous works, the corrosion resistance and nickel release tests were performed on undeformed Nitinol samples. Investigations of Nitinol's corrosion resistance under a constant and/or variable load will provide information which is closer to reality.

The fatigue life of a part most probably decreases dramatically with the presence of cracks on the surface. Titanium dioxide and titanium nitride are known to be brittle, so fatigue tests on Nitinol specimens after any type of surface treatment is recommended. Resistance to fretting corrosion would also be a valuable evaluation tool for the performance of Nitinol.

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APPENDIX A THERMODYNAMIC CALCULATIONS

$$\Delta G_T^0 (\text{J/mol}) = -523,000 + 151.1T \quad (600 \text{ K} < T < 2000 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -523,209 + 91.2T \quad (1150 \text{ K} < T < 1264 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -524,025 + 128.9T \quad (1264 \text{ K} < T < 1800 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -754,438 + 36.4T \quad (298 \text{ K} < T < 1150 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -773,245 + 341.2T \quad (1150 \text{ K} < T < 1264 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -773,475 + 280.05T \quad (1264 \text{ K} < T < 1800 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -820,161 + 182.3T \quad (298 \text{ K} < T < 1150 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -817,735 + 222.5T \quad (1150 \text{ K} < T < 1264 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -817,916 + 162.1T \quad (1264 \text{ K} < T < 1800 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -956,128 + 345.8T \quad (298 \text{ K} < T < 1150 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -956,337 + 287.6T \quad (1150 \text{ K} < T < 1800 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -223,844 + 231.7T \quad (298 \text{ K} < T < 525 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -246,730 + 266.3T \quad (525 \text{ K} < T < 565 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -241,869 + 184.0T \quad (565 \text{ K} < T < 633 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -240,998 + 137.3T \quad (633 \text{ K} < T < 1725 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -345,560 + 193.0T \quad (298 \text{ K} < T < 1150 \text{ K})$$

$$\Delta G_T^0 (\text{J/mol}) = -345,800 + 133.3T \quad (1150 \text{ K} < T < 1800 \text{ K})$$

Table A-1. Calculated ΔG_f^0 values for NiO, TiO, Ti₂O₃, Ti₃O₅, TiO₂ and TiN

T (K)	Standard Gibbs free energy of formation (kJ/mol)					
	NiO	TiO	Ti ₂ O ₃	Ti ₃ O ₅	TiO ₂	TiN
298	-215.19	-489.11	-711.81	-769.41	-888.68	-308.09
400	-205.14	-475.09	-698.92	-755.14	-869.85	-298.61
500	-195.29	-469.65	-686.02	-740.86	-851.86	-289.32
600	-185.43	-460.24	-673.12	-726.59	-833.87	-280.04
700	-175.58	-450.62	-660.22	-712.32	-815.67	-270.75
800	-165.73	-441.41	-647.33	-698.05	-798.1	-261.46
900	-155.87	-432.21	-634.43	-683.78	-780.53	-252.17
1000	-146.02	-423	-621.53	-669.51	-762.95	-242.88
1100	-136.17	-413.8	-608.64	-655.24	-744.75	-233.59
1200	-126.31	-404.59	-595.74	-640.97	-727.56	-224.18
1300	-116.46	-395.39	-582.84	-626.7	-709.4	-214.67
1400	-106.61	-387.02	-569.94	-612.43	-692.24	-205.16
1500	-96.755	-378.02	-557.05	-598.16	-674.46	-195.65
1600	-86.902	-369.66	-544.15	-583.88	-657.93	-186.15
1700	-77.048	-361.5	-531.25	-569.61	-640.57	-176.64
1800	-66.467	-354.59	-518.36	-555.34	-624.88	-167.13

$$\Delta G_{f,TiN} = \Delta G_{f,TiN}^0 + RT \ln \frac{a_{TiN}}{a_{Ti} a_{N_2}^{1/2}}$$

Table A-2. Gibbs free energy of formation of TiN as a function of thermodynamic activity of Ti and temperature.

Temperature (K)		400	600	800	1000	1200	1400
		Gibbs free energy of formation of TiN (kJ/mol)					
Thermodynamic Activity of Ti	0.0001	-245.01	-199.63	-154.25	-108.88	-63.372	-17.554
	0.1001	-290.95	-268.55	-246.14	-223.74	-201.21	-178.36
	0.2001	-293.26	-272.01	-250.75	-229.5	-208.12	-186.43
	0.3001	-294.61	-274.03	-253.45	-232.87	-212.17	-191.15
	0.4001	-295.56	-275.46	-255.36	-235.26	-215.04	-194.5
	0.5001	-296.31	-276.58	-256.85	-237.12	-217.26	-197.09
	0.6001	-296.91	-277.49	-258.06	-238.63	-219.08	-199.22
	0.7001	-297.43	-278.26	-259.09	-239.92	-220.62	-201.01
	0.8001	-297.87	-278.92	-259.97	-241.03	-221.95	-202.56
	0.9001	-298.26	-279.51	-260.76	-242.01	-223.13	-203.94
	1	-298.61	-280.04	-261.46	-242.88	-224.18	-205.16

APPENDIX B DETERMINATION OF THE ION ETCH RATE BY AFM

The ion etch rate was measured at 12 points for three different ion etching times, 200, 700, and 1,100 s of 3 kV argon ion etch on TiN, yielding a total of 36 points. The ion etch rate was determined to be 0.91 nm/s for 3kV argon ion etching with a standard deviation of 0.12 nm/s. Atomic force microscopy images from the surface topography images and the transverse section images from the surface of the Nitinol specimens are presented in Figures B-1 to B-6. The step height of the ion etched region was measured and the average ion etch rate was determined. Step heights values and the ion etch rate values are presented in Tables B-1 and B-2.

Figure B-1. Topography of the surface of the nitrided specimen, ion etched for 200 s.

Figure B-2. Transverse section and the measured step height from 12 points on the surface of nitrided specimen, ion etched for 200 s.

Figure B-3. Topography of the surface of the nitrided specimen, ion etched for 700 s.

Figure B-4. Transverse section and the measured step height from 12 points on the surface of nitrided specimen, ion etched for 700 s.

Figure B-5. Topography of the surface of the nitrided specimen, ion etched for 1100 s.

Figure B-6. Transverse section and the measured step height from 12 points on the surface of nitrided specimen, ion etched for 1100 s.

Table B-1. Step heights, measured by AFM.

Data point	Step Height		
	Data Points From 200 s of ion etch	Data Points From 700 s of ion etch	Data Points From 1100 s of ion etch
1	112.04	597.55	790.00
2	149.57	622.62	811.32
3	167.11	653.74	815.25
4	171.17	667.60	884.46
5	181.72	679.66	891.65
6	183.79	680.86	910.90
7	186.91	681.21	911.01
8	188.32	681.62	912.86
9	207.90	697.97	939.78
10	210.25	714.92	940.04
11	229.54	734.91	964.86
12	265.86	812.65	982.43
Mean	187.81	685.83	894.87
Std. dev.	40.87	57.20	64.53
Median	183.79	680.86	910.00

Table B-2. Calculated values for ion etch rate.

	Ion Etch Rate (nm/s)			
	Data Points From 200 s of ion etch	Data Points From 700 s of ion etch	Data Points From 1100 s of ion etch	Average
Mean	0.94	0.98	0.81	0.91
Std. dev.	0.20	0.08	0.06	0.11
Median	0.92	0.97	0.83	0.91

APPENDIX C XPS ANALYSIS

C.1 Mechanically Polished Specimens

Figure C-1. X-ray photoelectron spectroscopy depth profile of the mechanically polished specimen, washed with DI water and air dried.

Figure C-2. X-ray photoelectron spectroscopy high resolution scans of the mechanically polished specimen, washed with DI water and air dried.

Figure C-3. X-ray photoelectron spectroscopy depth profile of the mechanically polished specimen, washed with deaerated DI water and argon dried.

Figure C-4. X-ray photoelectron spectroscopy high resolution scans of the mechanically polished specimen, washed with deaerated DI water and argon dried.

C.2 Specimens Nitrided in 96% N₂ + 4% H₂

Figure C-5. X-ray photoelectron spectroscopy depth profile of the specimen nitrided in 96% N₂ + 4% H₂ at 800°C for 30 min.

Figure C-6. X-ray photoelectron spectroscopy high resolution scans of the specimen nitrided in 96% N₂ + 4% H₂ at 800°C for 30 min.

Figure C-7. X-ray photoelectron spectroscopy depth profile of the specimen nitrided in 96% N₂ + 4% H₂ at 900°C for 20 min.

Figure C-8. X-ray photoelectron spectroscopy high resolution scans of the specimen nitrided in 96% N₂ + 4% H₂ at 900°C for 20 min.

Figure C-9. X-ray photoelectron spectroscopy depth profile of the specimen nitrided in 96% N₂ + 4% H₂ at 900°C for 30 min.

Figure C-10. X-ray photoelectron spectroscopy high resolution scans of the specimen nitrided in 96% N₂ + 4% H₂ at 900°C for 30 min.

Figure C-11. X-ray photoelectron spectroscopy depth profile of the specimen nitrided in 96% N₂ + 4% H₂ at 1000°C for 10 min.

Figure C-12. X-ray photoelectron spectroscopy high resolution scans of the specimen nitrided in 96% N₂ + 4% H₂ at 1000°C for 10 min.

Figure C-13. X-ray photoelectron spectroscopy depth profile of the specimen nitrided in 96% N₂ + 4% H₂ at 1000°C for 20 min.

Figure C-14. X-ray photoelectron spectroscopy high resolution scans of the specimen nitrided in 96% $N_2 + 4\%$ H_2 at $1000^{\circ}C$ for 20 min.

Figure C-15. X-ray photoelectron spectroscopy depth profile of the specimen nitrided in 96% N₂ + 4% H₂ at 1000°C for 30 min.

Figure C-16. X-ray photoelectron spectroscopy high resolution scans of the specimen nitrided in 96% N_2 + 4% H_2 at 1000°C for 20 min.

C.3 Specimens Nitrided in 95% N₂ + 5% NH₃

Figure C-17. X-ray photoelectron spectroscopy depth profile of the specimen nitrided in 95% N₂ + 5% NH₃ at 500°C for 5 min.

Figure C-18. X-ray photoelectron spectroscopy high resolution scans of the specimen nitrified in 95% N₂ + 5% NH₃ at 500°C for 5 min.

Figure C-19. X-ray photoelectron spectroscopy depth profile of the specimen nitrided in 95% N₂ + 5% NH₃ at 675°C for 5 min.

Figure C-20. X-ray photoelectron spectroscopy high resolution scans of the specimen nitrided in 95% N_2 + 5% NH_3 at 675°C for 5 min.

C.4 Oxidized Specimens

Figure C-21. X-ray photoelectron spectroscopy depth profile of the specimen oxidized in air at 675°C for 30 min.

Figure C-22. X-ray photoelectron spectroscopy high resolution scans of the specimen oxidized in air at 675°C for 30 min.

Figure C-23. X-ray photoelectron spectroscopy depth profile of the specimen oxidized in air at 700°C for 60 min.

Figure C-24. X-ray photoelectron spectroscopy high resolution scans of the specimen oxidized in air at 675°C for 30 min.

C.5 Nitrided and Oxidized Specimens

Figure C-25. X-ray photoelectron spectroscopy depth profile of the specimen nitrided in 95% N_2 + 5% NH_3 at 675°C for 5 min and oxidized in air at 675°C for 30 min.

Figure C-26. X-ray photoelectron spectroscopy high resolution scans of the specimen nitrided in 95% N_2 + 5% NH_3 at 675°C for 5 min and oxidized in air at 675°C for 30 min.

Figure C-27. X-ray photoelectron spectroscopy depth profile of the specimen nitrided in 96% N₂ + 4% H₂ at 1000°C for 20 min and oxidized in air at 700°C for 60 min.

Figure C-28. X-ray photoelectron spectroscopy high resolution scans of the specimen nitrided in 96% N₂ + 4% H₂ at 1000°C for 20 min and oxidized in air at 700°C for 60 min.