EFFECT OF Ni_3Ti FORMATION ON THE OXIDATION KINETICS OF NiTi SHAPE MEMORY ALLOYS

by

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LIST OF ABBREVIATIONS

SEM	Scanning electron microscope
SMA	Shape memory alloy
VPSEM	Variable pressure scanning electron microscopy
EDS	Energy dispersive spectroscopy
DSC	Differential scanning calorimetry
QCA	Quench cooling accessories
TGA	Thermal gravimetric analysis
XPS	X-ray photoelectron spectroscopy
EFTEM	Energy-filtered transmission electron microscopy
HAADF	High-angle annular dark field
BSE	Back scattered electrons
VIM	Vacuum induction melting
PPM	Parts per million
HCP	Hexagonal cubic packing
FCC	Face centred cubic

LIST OF SYMBOLS

M_s	Martensite start
M_f	Martensite finish
A_s	Austenite start
A_f	Austenite finish
ΔH_f	Delta enthalpy formation
T	Temperature
t	time
K	Kelvin
°C	Celsius
J	Joule
Å	Angstrom
k'	parabolic constant
x	thickness

KESAN PERTUMBUHAN Ni_3Ti KE ATAS ANALISA PENGOKSIDAAN ALOI INGATAN BENTUK NiTi

ABSTRAK

Nikel – Titanium (NiTi) aloi ingatan bentuk telah mendapat populariti yang tinggi dalam implan dan peralatan perubatan sejak beberapa dekad yang lalu disebabkan oleh keserasian biologi aloi ini. Keserasian biologi ini dicapai dengan pembentukan lapisan nipis titanium dioxida (TiO_2) di permukaan hasil daripada proses pengoksidaan terkawal. Lapisan ini berkesan menghalang pelepasan nikel ke dalam tubuh manusia. Tindak balas pengoksidaan TiO_2 ini adalah kompleks dan kadar tindakbalas adalah sangat tinggi terutama pada suhu tinggi. Ia melibatkan pembentukan Ni_3Ti dan larutan pepejal $Ni_n(Ti)$ apabila tempoh pengoksidaan dipanjangkan. Kajian ini mengukur kadar pembentukan ketebalan Ni_3Ti untuk mengkaji hubungan pembentukan TiO_2 terhadap variasi suhu dan masa. Sampel aloi diletakkan pada suhu 700 - 900°C pada jangka masa yang berbeza (10 – 200 minit) di dalam persekitaran udara. Didapati bahawa pertumbuhan lapisan Ni_3Ti pada 900°C adalah parabola dan mencapai ketepuan kira-kira 4 µm selepas 60 minit. Pada 700°C, lapisan mencapai ketepuan pada ketebalan kira-kira 1 µm selepas 60 minit. Pada keadaan yang melampau (pada suhu 900°C selama 200 minit) pertumbuhan ketebalan kekal stabil pada ~ 3.5 - 4.0 µm walaupun selepas pengoksidaan dipanjangkan tempohnya. Keputusan Analisis Termogravimetri (TGA) yang dijalankan pada kondisi eksperimen yang sama telah menunjukkan bahawa tingkah laku pertumbuhan TiO_2 adalah faktor penentu pertumbuhan lapisan Ni_3Ti dan lapisan TiO_2 juga memperlihatkan pertumbuhan parabola. Kalorimeter Pengimbasan

Perbezaan (DSC) pengukuran juga menunjukkan bahawa suhu transformasi NiTi mengalami perubahan yang ketara pada suhu 900°C dan 800°C manakala pada suhu 700°C kelakuan tranformasi martensit dilihat stabil. Saiz puncak transformasi pula dilihat menurun pada suhu 900°C dan 800°C dengan peningkatan ketebalan Ni_3Ti.

EFFECT OF Ni_3Ti FORMATION ON THE OXIDATION KINETICS OF NiTi SHAPE MEMORY ALLOYS

ABSTRACT

Nickel - Titanium (NiTi) shape memory alloys have gained its popularity in many medical implants and their apparatus for the past few decades owing to their excellent biocompatibility. This attribute is achieved by the formation of thin layer of titanium dioxide (TiO_2) at the surface from a controlled oxidation process. This layer effectively hinders nickel release into the human body. Oxidation reaction of TiO_2 is complex and the reaction rate is very high especially at elevated temperature. It involves the formation of Ni_3Ti and solid solution $Ni_n(Ti)$ as the oxidation prolongs. This work quantifies the rate of Ni_3Ti formation thickness for establishing a relation in controlling the thickness growth of TiO_2 with respect to temperature and time variations. The alloy was subjected to heat treatment at 700 – 900°C for various times (10 – 200 minutes) in air environment. It was found that the growth of Ni_3Ti layer at 900^{o}C is parabolic and reached saturation at thickness of about 4 μm after 60 minutes. While at 700°C, the layer reached saturation at thickness of about 1 μm after 60 minutes. At the extreme condition (900°C for 200 minutes) the thickness growth remained stable at ~ 3.5 – 4.0 μm although after excessive oxidation treatment. Thermogravimetric Analysis (TGA) results that were ran under same oxidation conditions (700 - 900°C in air at same treatment time) has shown that the TiO_2 growth behaviour is the determining factor for the Ni_3Ti layer and it exhibited parabolic behaviour. Differential Scanning Calorimetry (DSC) measurements also indicated that the transformation temperatures of the NiTi alloy is altered

significantly at 900°C and 800°C while it is seen maintained at 700°C. The size of the transformation peaks is seen decreased with increasing Ni_3Ti thickness at 900°C and 800°C.

CHAPTER 1

INTRODUCTION

1.1 Background

NiTi shape memory alloy has attracted great attention after the discovery of its martensitic phase transformation in 1959 [1]. The martensitic phase transformation allows NiTi to exhibit shape memory effect and superelastic behaviours that produce huge deformation strain without plastic deformation. Thus, these behaviours make it superior as compared to other conventional materials such as stainless steel or cobalt-based alloys. The stainless steel employed limited elastic properties, approximately 1% strain while NiTi alloy can be deformed up to 8% strain for a single cycle making it successfully developed for many applications: e.g., home appliances, medical devices and implants, aerospace engineering as well as actuators in electrical devices and automobiles [2, 3]. Figure 1.1 shows the two possible driving forces for the phase transformation, thermal and mechanical. Thermal phase transformation does not induce any shape and size change because of the self-accommodation of the atoms. On the other hand, transformation induced by mechanical stress produces global shape change because of the reorientation of atoms aligned to the direction of the force. Heating the deformed alloy again provides the atoms with energy to return to its parent phase of austenite.

Thermal oxidation of NiTi is among the most practical technique in the manufacturing of NiTi alloy implants for achieving suitable oxide phase and the thickness of the layer [4]. This technique is normally done via conventional heat treatment process in furnace with controlled flow rate and pressure of the environment gases. Small change in the heat treatment processing procedures such as temperatures, exposure time, oxygen concentration and inert gas mixture will significantly affect the implant crystallic phases, oxides structures, and subsequently the martensitic phase transformation behaviour. Heat treatment in oxygen usually may not only alter the bulk phase composition, but it also modifies the tendencies in the formation of either Ni-rich or Ti-rich surface sub-layers [4]. Other than the conventional heat treatment, there are few other techniques utilized to develop the oxide layer. Among them are laser oxidation [5], oxygen plasma ion implantation [6], anodic oxidation [7], hydrothermal treatment [8], boiling in H_2O_2 aqueous solution [9], advanced oxidation process [10], selective oxidation and nitridation [11], micro-arc oxidation [12], carbon plasma immersion ion implantation and deposition [13], electropolishing and passivation [14]. All these techniques were developed to improve the corrosion resistance of the implant materials as well as its biocompatibility by eliminating the Ni element from the surface in biological environment. [4].

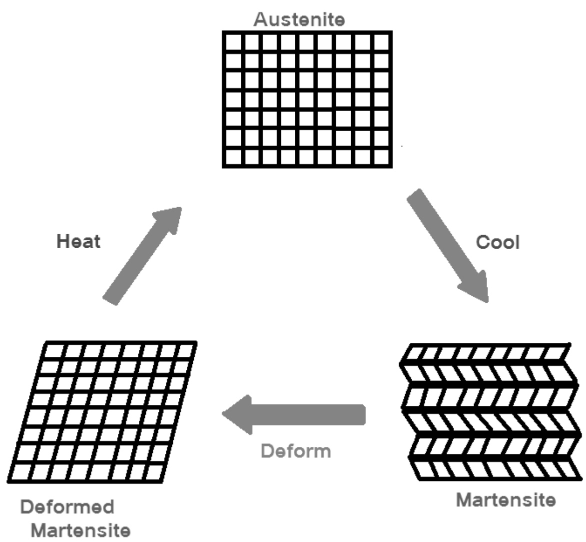

Figure 1.1 Schematic illustration of martensite phase transformation

In thermal oxidation process, materials are oxidized in oxygen environment at elevated temperature. Sufficient energy provided by the heat determines the diffusion rate of oxidation. At room temperature, NiTi atoms remain stable. However, few nanometers of TiO_2 layer will spontaneously form once exposed to the air as a result of Ti atoms availability at the alloy surface [15]. Slow diffusivity may prevent proper crystallization of titanium oxide structure and produce amorphous TiO_2 which is thermodynamically unstable at higher temperature [16]. Faster diffusion rate is achieved at higher temperature, such as 700°C, and it is good for diffusion process whereby a fully stabilized TiO_2 layer can be formed without the formation of TiO [17]. Oxidation at temperature below 500°C produces oxide mixture of both TiO_2 and TiO with some amount of Ni oxides [17, 18]. Oxidation at above 600°C produces almost free Ni surface [18]. The concentration ratio of Ti to Ni has no significant change when heat treated at 400°C, but the ratio reduced to 1:20 Ti:Ni at higher oxidation temperature [19].

Thermal oxidation at low oxygen partial pressure developed thickest oxidation layer with almost Ni-free surface [20], as compared to some other methods such as electropolishing and oxidation boiling in water bath. Basically the oxide layer thickness increases as the oxidation temperatures increase [19]. It has been reported that oxidation at 500°C [16], 600°C [18], 800°C [18] and 1000°C [21] in air is enough to create thick oxide layer (approximately from 1 to 50 µm thickness) and assumed to be sufficient to prevent nickel release. Surprisingly, Tian [17] reported that increasing the oxide thickness did not sufficiently prevent the Ni release. This claim is in agreement with a study by Hesing [22], which found that thick oxidized layer is dense and thus may cause corrosion and surface contaminants in some circumstances. Another important matter to consider beside the oxide thickness is the complete formation of TiO_2 without the formation of TiO during the oxide layer development [17]. In this regard, the surface structural evolution is also an important factor in developing a protective surface. Numbers of studies have been published for each method of oxidation, and all provided diverse variety of surface composition, surface topography, stability and thickness, as well as the depth profile [16-18, 20, 22-31].

1.2 Problem statement and research interest

A recent study of Tian *et. al.* showed oxidation of Ti is the driving force for Ni to diffuse inward the matrix structure. This leads to sequenced layers formation and leaves Ti atom to retain in the oxide structure at the surface. This phenomenon can be described by a chemical sequence starting from the alloy surface as follows: Ti-oxide → Ni_3Ti → NiTi [17]. The formation of Ti-oxide layer at the surface extended inward the matrix structure as the oxidation continues. Finally, a new layer of Ni_3Ti which is rich in Ni is formed beneath the Ti-oxide layer. This clearly shows that reaction of Ti which has high affinity for oxygen atoms at the surface attracts Ti to diffuse outward and creates a Ti-depleted layer as the Ti-oxide layer forms. The higher affinity of Ti for oxygen compared to Ni is a great advantage for NiTi alloy because Ni-oxide could not be a competitor during the alloy oxidation. Moreover, the difference between heat of formation of TiO_2 and NiO are comparatively significant; ΔH_f of TiO_2 is -956 kJ/mol and ΔH_f of NiO is -241 kJ/mol respectively [9]. The larger value of TiO_2 reflects formation of TiO_2 is most favoured.

In deducing the oxidation mechanism of alloys, the information regarding the formation process of the sequenced layers is limited to the extent of diffusion process while thermodynamic approach that usually used to predict the reaction is usually inadequate in complex alloy reaction [32]. In NiTi oxidation, the oxidation process itself has been the driving force for Ni to diffuse inward within the immobile Ti matrix and consequently form the layers sequence as mentioned previously. However, the inward movement of Ni is limited by the maximum concentration of Ni allowed in the growing Ni_3Ti phase. Thus, the migrating Ni started to accumulate in the lower state oxidation layer that is close to the alloy/oxide interphase and form metallic particles within the oxide layer [17]. These sequences of process describe the NiTi oxidation reaction without having a detailed reaction rate. Besides, there is very limited information regarding the Ni_3Ti formation behaviour found in the literature.

The oxidation process happened very fast and complex and the products formation becomes more complex when the alloy oxidation is carried in atmospheric pressure and high pressure. Variety of oxides and intermetallic may formed due to the rapid reaction towards available oxygen including some unwanted species such as $NiTiO_3$ [30], TiO [17], Ti_2O_3 [18], Ni_2O_3 [22] and NiO [27]. However, the appearance of these species could be avoided by adjusting the oxidation temperature and if required, the oxidation pressure especially oxidation at low temperature [27]. On the other hand, although the formation of TiO_2 and Ni_3Ti had been observed in almost all the experimental work done by many researchers [16-18, 23, 26-28, 33], the accurate moment on when the Ni_3Ti started to nucleate is still a big question. The presence of Ni_3Ti has been detected at 600°C and this is the lowest temperature recorded. Oxidation of NiTi at atmospheric pressure below that temperature shows the formation of $NiTiO_3$ instead of Ni_3Ti [16]. However in other works, Xu *et. al*. and Chu *et. al*. showed that the Ni_3Ti is among the main oxidation product at 550°C that formed beneath the oxide layer [26, 28]. Both experiments were carried at atmospheric pressure but different environmental gas; one in flowing pure O_2 and another one was in dry air, respectively.

The Ni_3Ti formation behaviour is another interesting topic that may help researchers to understand the NiTi oxidation mechanism. Until now, the formation behaviour of this intermetallic layer has not been documented and the role played by this layer during the oxidation process is not being explained as well. Since this layer are always observed beneath the oxide layer and at some conditions, it was found beneath the Ni(Ti) layer, it shows that this layer plays an important role during oxidation to produce free-Ni layer surface. Besides, the formation of this layer and its effect on the shape memory behaviour is also not well presented. Shape memory and transformation behaviour of oxidized NiTi alloy has been documented in many studies, i.e. for orthodontic treatment low and constant transformation stresses are sufficient while small changes in transformation temperatures is not critical [34].

1.3 Objectives

The primary objective of this study is to identify the formation behaviour of Ni_3Ti phase after heat treated at high temperatures in oxidizing environment. In specific, these are two objectives to achieve in this study:

a. To study the effect of Ni_3Ti towards shape memory martensitic transformation behaviour.
b. To measure the thickness of Ni_3Ti layer during the oxidation process.

c. To observe and measure the growth of oxidation layer during the oxidation process including its thickness, weight gained and enthalpy change.
d. To determine the suitable oxidation condition that is good for medical application.

1.4 Scope of work

Part of the research work is to evaluate the oxidation behaviour of NiTi alloy at high temperature carried in air. The experimental condition is selected based on the fabrication procedures for medical grades and excludes other commercialization fields such as automobiles and aerospace engineering. The growth behaviour of the oxide is evaluated by running the experiment in a range of time at elevated temperature at constant environmental conditions.

In this study, the weight of oxide growth is assumed to be the representatives to evaluate the oxidation rate. The exact numbers of diffusion coefficients and rate constant are however not calculated in this study since the evaluated temperatures involved only three different temperatures. Besides, the oxide developed in this work is to relate it with the growing behaviour of the Ni_3Ti which will form during the NiTi oxidation at high temperature.

To obtain good information on the Ni_3Ti phase, the thickness of the Ni_3Ti layer is to be measured and thus, observe the effect of this layer towards the transformation behaviour which is important for orthodontic applications. The formation phenomenon of the Ni_3Ti layer is created based on the observations on the oxide growth and the Ni_3Ti thickness.

CHAPTER 2

LITERATURE REVIEW

2.1 NiTi shape memory applications

The unique behaviours of NiTi shape memory alloy render it usefulness in wide range of applications. The successful application of NiTi commonly lies on its two unique ability; superelasticity and shape memory effect. The smart materials are extensively used in engineering applications [35], medicals treatments and devices [36], consumer goods as well as electrical appliances [37]. Among the common application of consumer goods are flexible eye glass frames, headband of headphones and portable cellular telephones. This kind of application requires superelastic behaviour to ensure the stiffness and constant pressure of the material is maintained while the users feel comfort when wearing the eye glass and headphones. In clothing, NiTi alloy can be found in woman lingerie, wedding dress and shoes [3]. For heat recoverable couplings and fasteners, to be specific, in aircraft, the couplings are expanded in liquid nitrogen, and fasten them by bringing them up to the room temperature. The transformation temperature has to be as low as -55°C to prevent the couplings from transformed back to martensite at case lower temperature and this may cause leaking at the titanium hydraulic tubing [3]. The ability of an NiTi alloy to act as actuator make it easily found elsewhere in water kettles, coffee makers, steam traps, over-temperature shut-off valves [3] or anything that requires transformation of heat energy to mechanical work. While in medical applications, historically the superelasticity of NiTi alloy is first used in orthodontic application, replacing the popular usage of gold and stainless steel for the arch wires. In 1970s, the NiTi was introduced due to its exceptional spring back and low elastic modulus [2].

In orthodontic treatment, NiTi superelastic wire is used to develop bone remodelling process [38] due to its durability and low level of continuous recovery force for tooth movement. Light continuous recovery force is essential to reduce pain and tissue destruction as the teeth move or grow in patient's mouth [39]. It is desirable for orthodontist to produce a recent superelastic and effective NiTi wire to minimize pathology aftermath on teeth and the surrounding tissue of the patient. Besides the mechanical aspect of NiTi to provide safety orthodontic treatment, the stability of surface film on the NiTi surface wire is also a controversial requirement. As the wire continuously shift especially when eating, the surface structure which is exposed to temperature and pH change is prone to degrade and affect film stability [38]. The development and advance study on NiTi orthodontic wire remains under attention to ensure safety and effective tooth movement for patient's comfort during the healing period.

Since NiTi shows a good biocompatibility with living tissue [40], plasma treated NiTi alloy has been introduced in orthopedic medication [41]. The alloy helps to straighten patient's spine in the case of severe spinal deformity. Moreover, NiTi elastic modulus is closely similar to human cortical bone compared to other implantable materials like stainless steel and titanium alloy [13]. To fix in rods to the spine, too large force will cause tissue damage while if the force is too low, the medication is under-correction. Therefore, for this case, NiTi rod which is straight is inserted at 15ºC and would progressively bent as the body temperature reaches 37ºC [41]. This constant recovery force makes the surgical procedure become feasible and preferred for most of spine implantation cases. In cardiovascular medicine for severe heart disease, where myocardium; the heart muscle that stimulates contraction to