STRUCTURE AND TRIBOLOGICAL PROPERTIES OF POST-SPUTTERED ANNEALING NICKEL TITANIUM ALLOY COATINGS ONTO 316L STAINLESS STEEL

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Specially dedicated to my beloved parents, brothers and family who have supported and inspired,

ABDUL AZIZ BIN ABDUL RAHMAN** and **NURAINI BTE ISYA

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ABSTRACT

The purpose of this study is to investigate the effect of the post-sputtering annealing process on the structure and tribological properties of the NiTi shape memory alloy (SMA) coatings. The NiTi SMA coatings were deposited onto the 316L stainless steel substrates using the sputtering PVD technique. The coating thickness was measured at approximately 2μm. The unannealed NiTi SMA coating was determined amorphous based on the differential scanning calorimetry (DSC) and XRD results. The crystallization temperature of the NiTi SMA coating with a composition of Ni 57.89%:Ti 42.11% was determined at a temperature of 519.23°C by the DSC. The post-sputtering annealing process was carried out at the annealing temperatures of 550°C and 600°C and the annealing times for a duration of 30 and 60 minutes. The unannealed and annealed NiTi SMA coatings were then characterized to determine their structure and mechanical properties using various characterization techniques namely optical microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), surface roughness tester, Rockwell C adhesion test, pin-on-disc wear test and nanoindentation test. The post-sputtering annealing process was successful in producing a crystalline Ni-rich NiTi coating with excellent mechanical properties. In this study, the annealing temperature of 600°C for a period of 30 minutes provided the optimum adhesion and mechanical properties of the annealed NiTi SMA coatings. The finding shows the potential of the post-sputtering annealing process to create an excellent structure and tribological properties of NiTi SMA coatings.

ABSTRAK

Tujuan kajian ini adalah untuk menyiasat kesan proses sepuhlindap terhadap struktur dan sifat "tribological" bagi lapisan aloi bentuk memori (SMA) NiTi. Lapisan NiTi SMA telah didepositkan ke atas keluli tahan karat 316L menggunakan teknik "PVD sputtering". Ketebalan lapisan NiTi SMA adalah kira-kira 2μm. Struktur bagi "unannealed" NiTi SMA adalah bersifat "amorphous" berdasarkan keputusan hasil pemeriksaan DSC dan XRD. Suhu penghabluran semula NiTi SMA yang berkomposisi Ni 57.89%, Ti 42.11% telah diperolehi pada suhu 519.23°C menggunakan alat DSC. Proses sepuhlindap telah dijalankan pada suhu sepuh lindap 550°C dan 600°C selama 30 minit dan 60 minit. Lapisan NiTi SMA yang asal dan yang telah di sepuhlindap dikaji bagi menentukan struktur dan sifat-sifat mekanik dengan menggunakan pelbagai teknik pencirian seperti mikroskopi optik, mikroskopi imbasan elektron (SEM), penguji kekasaran permukaan, ujian lekatan "Rockwell", ujian haus "pin-on-disc" dan ujian kekerasan "nanoindentation". Proses sepuhlindap yang di jalankan telah berjaya dalam menghasilkan lapisan NiTi yang berhablur dengan sifat-sifat mekanikal yang baik. Dalam kajian ini, proses sepuh lindap pada suhu 600°C selama 30 minit telah memberikan kesan yang terbaik bagi sifat-sifat mekanikal dan lekatan bagi lapisan NiTi SMA berbanding dengan sampel yang di sepuhlindap pada parameter yang lain. Hasil kajian mendapati bahawa proses sepuhlindap yang dijalankan berpotensi untuk menghasilkan struktur lapisan NiTi SMA dengan sifat-sifat "tribological" yang sangat baik.

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LIST OF SYMBOLS/ABBREVIATIONS

A_f	-	Austenite Finish Temperature
AFM	-	Atomic Force Micriscope
Amrec	-	Advance Materials Research Centre
Ar	-	Argon
A_s	-	Austenite Start Temperature
ASTM	-	American Society for Testing and Materials
BCC	-	Body Centered Cubic
BSE	-	Backscattered Electrons
Cr	-	Chromium
CVD	-	Chemical Vapour Deposition
d	-	Diameter
DC	-	Direct Current
DSC	-	Differential Scanning Calorimetry
E	-	Young's Modulus
EDX/EDAX	-	Energy Dispersive X-ray Spectroscopy
FCC	-	Face Centered Cubic
Fe	-	Iron

GDS	-	Glow Discharge Spectroscopy
GAXRD	-	Grazing Incidence Angle X-ray Diffraction
GPa	-	Giga-Pascal
H	-	Hardness
H/E	-	Ratio of Hardness to Young's Modulus
IBAD	-	Ion-Beam Assisted Deposition
mbar	-	Milibar
M_d	-	Highest Temperature To Strain-Induced Martensite
M_f	-	Martensite Finish Temperature
MEMS	-	Micro-Electro-Mechanical System
MPa	-	Mega-Pascal
M_s	-	Martensite Start Temperature
Ni	-	Nickel
NiTi	-	Nickel Titanium
OM	-	Optical Microscopy
PDF	-	Powder Diffraction File
PECVD	-	Plasma Enhanced Chemical Vapour Deposition
PVD	-	Physical Vapour Deposition
Ra	-	Average Roughness
RF	-	Radio Frequency
RMS	-	Root Mean Square Roughness
SE	-	Superelasticity / Secondary Electrons
SEM	-	Scanning Electron Microscopy

Si	-	Silicon
SiC	-	Silicon Carbide
SMA	-	Shape Memory Alloy
SMAs	-	Shape Memory Alloys
SME	-	Shape Memory Effect
Ti	-	Titanium
TiN	-	Titanium Nitride
TTRs	-	Transformation Temperatures
VDI	-	Verein Deutscher Ingenieure
XRD	-	X-ray Diffraction
2D	-	Two-Dimension
3D	-	Three-Dimension

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Nickel Titanium Shape Memory Alloys (NiTi SMAs) have two unique properties namely shape memory effect and superelasticity [1-3]. Since their first discovery in 1960s, NiTi SMAs have been extensively studied [4]. Both shape memory effect, and superelasticity have been exploited to design functional and smart structures in mechanical and biomedical engineering. For instance, shape memory and superelastic NiTi SMAs have been widely used in medical field and micro-electro-mechanical systems (MEMS). In both applications, the wear performance of the NiTi SMA plays a critical role [5-7].

NiTi SMAs are well-known for their extraordinary shape memory and superelastic properties [8, 9]. These properties are due to the intrinsic thermoelastic martensitic transformation under thermal or mechanical loading conditions at different temperatures. At relatively low temperature and under external force, the initial parent phase (austenite) can transform into a martensite phase accompanied by macroscopic deformation. Upon unloading to zero, the material remains in a martensite state with residual strain. Then, when the material is heated to a certain temperature, the martensite can transform back to the initial austenite phase with the material returning to its initial shape. This is the shape memory effect [10-12]. For the same material, when the load is given at the higher temperature, the martensite structure can transform back to austenite during unloading while recovering a large amount of the prior deformation. This extraordinary recoverable deformation behavior is called superelasticity or pseudoelasticity [13, 14].

However, there are still some concerns for the wide application of SMA coatings because of their unsatisfactory mechanical and tribological performances, chemical resistance and biological reliability. High nickel content in NiTi SMAs often stimulated suspicion for their medical use because of nickel toxicity. The limited hardness and wear resistance of NiTi SMAs make them difficult to be used in orthodontic and MEMS applications [15]. In order to improve surface properties, corrosion resistance and suppression of Ni ions release of NiTi SMAs, through several techniques such as nitrogen ion implantation, laser surface treatment, thermal and anodic oxidation, have been employed. The problems of these surface treatments are high cost, possible surface or ion induced damage, amorphous phase formation, or degradation of shape memory effects. The magnetron sputtering deposition technique has important specific advantages such as low levels of impurities and easy control of the deposition rate and also enables the production of various coatings morphologies and crystallographic structure [3, 4, 10].

The purpose of this study is to investigate the structure and tribological properties of the annealed and unannealed NiTi SMA coatings. A physical vapour deposition (PVD) magnetron sputtering was used to deposit the NiTi SMA coatings onto the 316L stainless steel substrates and the post sputtering annealing process was conducted to crystallise the unannealed NiTi SMA coatings. The mechanical and tribological tests namely; Rockwell C adhesion test, nanoindentation and pin-on-disc wear measurements were conducted to investigate their adhesion and wear properties of the unannealed and annealed NiTi SMA coatings. While the surface characterization equipment namely optical microscopy (OM), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDAX), X-ray diffraction (XRD), atomic force microscope (AFM), surface roughness tester and differential scanning calorimetry (DSC) were used to characterize the structure, surface, composition and thermal analysis of unannealed and annealed NiTi SMA coatings.

1.2 Problem Statement

Shape Memory Alloys (SMAs) are well-known for possessing shape memory effect and superelasticity behaviour due to intrinsic microstructure transition of thermoelastic martensitic transformation. Both shape memory effect and superelastic nickel–titanium alloys are widely used in implants and identified as possible materials for micro-electro mechanical systems (MEMS) [5-7]. In these applications, the wear performance of the material plays a critical role [3]. For instance, medical industries are very interested in the high compliance of NiTi alloy for use in joint replacement, an application where wear plays an important role. Recent research works have shown that NiTi alloys exhibit high resistance to wear. The tribological behavior of NiTi alloys has been investigated and compared to many conventional engineering materials such as steels, Ni-based and Stellite alloys. These investigations have demonstrated higher wear resistance of NiTi compared with many tribological materials. The wear resistance of conventional tribo-materials strongly depends on their mechanical properties such as hardness, toughness, and work-hardening [1-4, 10, 11]. However, it appears that these properties are not the main factors responsible for high wear resistance of NiTi alloys. It is believed that the high wear resistance of shape memory NiTi is mainly due to the recovery of the superelastic deformation. Some researchers indicated that the wear resistance of NiTi SMA was mainly dependent on the recoverable strain limit, for examples the sum of the pseudoplastic and pseudoelastic strain limits. It seems more research is required for fundamental understanding of tribological behavior of the martensite and the austenite phases of NiTi alloys [5, 9, 12,].

1.3 Objective of the Study

To investigate the effect of post sputtered annealing process on structure and tribological properties of the NiTi SMA coatings.

1.4 Scope of the Study

The coated NiTi SMA onto the 316L stainless steel substrates were used in this study. The scope of this study can be divided into three stages as the following:

(i) To conduct the post-sputtered annealing process in a vacuum furnace at various annealing temperatures and annealing times.

(ii) To determine the structure of the unannealed and annealed NiTi SMA coatings.

(iii) To investigate the effect of the post-sputtering annealing process on their structure and tribological properties. The surface morphology, surface roughness, hardness, adhesion and wear properties of the coatings were determined using the selected characterization techniques.

1.5 Structure of the Thesis

Chapter 1 (Introduction)	Describes the background of this study, problem statement, objectives, scope and the project flow chart. This chapter also provides information of the overall study.
Chapter 2 (Literature Review)	Provides information and the theory related to the shape memory alloys (SMAs), types and properties of SMAs. This is followed by a review about the NiTi SMA, production of SMA and the characterization of NiTi SMA coatings.
Chapter 3 (Research Methodology)	Provides the information on the experimental with details of the coating process, the equipment used and the characterization of the coatings.
Chapter 4 (Results and Discussion)	Presents all the results obtained from the study carried out and discusses in detail the results observed for each analysis.
Chapter 5 (Conclusion and Recommendation)	Presents the conclusions and the contributions from the present study. All the experimental data and results to become one short note that briefed completely about the whole project. Besides that it also presents some recommendations for future work in order to improve and enhance the structure and tribological properties of post-sputtered annealing NiTi SMA coatings. The list of references and appendices are presented at the end of this thesis.

Figure 1.1 : Structure of the thesis