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#### INDENTATION AND TRIBOLOGICAL BEHAVIOR OF NITI ALLOYS AND STUDY OF INSTRUMENTED SPHERICAL INDENTATION

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### INDENTATION AND TRIBOLOGICAL BEHAVIOR OF NITI ALLOYS AND STUDY OF INSTRUMENTED SPHERICAL INDENTATION

By

Wangyang Ni

### A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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### ABSTRACT

## INDENTATION AND TRIBOLOGICAL BEHAVIOR OF NITI ALLOYS AND STUDY OF INSTRUMENTED SPHERICAL INDENTATION

By

### Wangyang Ni

In this work, microscopic shape memory (SME) and superelastic (SE) effects in martensitic and austenitic NiTi alloys were probed by instrumented indentation techniques. Both pyramidal and spherical indenters were used to study the mechanical response of the NiTi alloys. It was found that deformation due to indentation was recoverable by the shape memory or superelastic effect and that the magnitude of indent recovery can be rationalized using the concept of the representative strain and maximum strain. Instrumented indentation techniques, especially using spherical indenters, are shown to be useful in quantifying shape memory and superelastic effects at micron and nanometer length scales.

Novel tribological applications of superelastic NiTi thin films suggested by these results were also studied. A novel composite coating, with a superelastic NiTi interlayer betweers soft aluminum substrate and hard CrN coating, was studied using instrumented indentation, scratch, and pin-on-disk wear tests. It was found that a superelastic NiTi interlayer can dramatically improve hard-coating adhesion and wear resistance. The improved coating performance is attributed to the large elastic recovery ratio and strain tolerance of the superelastic NiTi interlayer.

It was demonstrated that spherical indentation is very useful in the characterization of the mechanical properties of NiTi shape memory alloys. To further understand the spherical indentation process, a general study of spherical indentation in elastic-plastic materials was carried out. Two previously unknown relationships between hardness, reduced modulus, indentation depth, indenter radius, and work of indentation were found. Based on these relationships a novel energy-based method for determining contact area, reduced modulus, and hardness of materials from instrumented spherical indentation measurements was proposed. This method also provides a new way of calibrating the effective radius of imperfectly shaped spherical indenters.

To my Parents and Wife with Great Appreciation

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## TABLE OF CONTENTS

LIST OF TABLES	ix
LIST OF FIGURES	x
INTRODUCTION	1
CHAPERT 1: LITERUATURE REVIEW	4
1 1 NiTi shape memory alloys	4
1 1 1 Shape memory and superelastic effects	4
1.1.2 Sliding wear and indentation behavior of NiTi allovs	8
1.1.3 Processing and characterization of NiTi thin films	12
1.2 Tribalogical coatings	15
1.2.1 Hand coating materials	15
1.2.2 Characterization of tribological costings	16
1.2.2 Unaracterization of the totogical coatings	16
1.2.2.1 Residual successes	17
1.2.2.2 Adhesion strength	18
1.2.2.3 Hardness	19
1.2.2.4 Friction and wear.	21
1.2.3 Inbological coating with interlayers	
1.2. Instrumented indeptetion experiments	23
1.3 Instrumented Borkevich indeptetion experiments	22
1.3.1 Instrumented Derkovich indentation experiments	25
1.3.1.1 Onver-Phart's method for hardness and modulus measurement	23
1.3.1.2 Piling-up and sinking-in	27
1.3.1.3 Scaling relationships	28
1.3.1.4 Correlation between indentation and uniaxial tensile experiments	29
1.3.2 Instrumented spherical indentation experiments	30
1.3.2.1 Analyzing methods	30
1.3.2.2 Representative strain for spherical indentation experiments	32
CHAPTER 2: ON THE STUDY OF MICROSCOPIC SHAPE MEMORY	
EFFECT, SUPERELASTIC EFFECT AND WEAR BEHAVIOR OF NITI	
ALLOYS	35
2.1 Introduction	35
2.2 Instrumented indentation experiments	37
2.2.1 Sample preparation and experimental methods	37
2.2.2 Results and discussion	38
2.2.2 1 Transformation temperatures and structures	28
2.2.2.1 Transformation temperatures and structures	20
2.2.2.2 Shape memory energy of machines	JY 40
2.2.2.2.1 Berkovich and vickers indenis	40

2222 Spherical indents	40
2.2.2.2.2 Spherical medicity under indentation	40
2 2 2 3 1 Berkovich inden tation	43
2 2 2 3 2 Spherical indentation	43
2.2.3.2 Ophenical indentation distribution under indenters	45
2.2.5 Representative strain and strain distribution under indenters	47
2.5 Dry shulling wear beliavior or there anolys	47
2.3.1 Sample preparation and experimental methods	48
2.5.2 Results and discussion	50
CHARTER 2. IMPROVE THE ADHESION AND WEAR DESISTANCE OF	
CHROMER S. INTROVE THE ADJIESTON AND WEAR RESISTANCE -	
SUDEDEL ACTIC INTEDI AVED	52
SUPERELASTIC INTERLATER	
2.1 Introduction	52
2.2 Some lo propagation and experimental methods	53
2.2 Benutes and discussion	56
2.2.1. Comparison of the second secon	56
2.2.2. Must evided properties	57
3.3.2 Mechanical properties	57
	59
3.3.2.2 Adhesion test	61
3.3.2.3 Dry sliding wear test	65
3.4 Conclusions	05
CHAPTER 4: INSTRUMENTED SPHERICAL INDEN TATION	67
4.1 Introduction	67
4.2 Dimensional analysis	20
4.2.1 Dimensional analysis of loading	00
4.2.2 Dimensional analysis of including	69
4 2 3 Scaling relationships from dimensional analysis	71
4.3 Finite element analysis	71
4.3.1 Diling_un/sinking_in in suberical indentation	73
4.3.2 Delationship between $h_c/h_{c}$ and $(WW_{c})/W_{c}$	74
4.3.2 Relationship between $H/F^*$ and $(W_1 - W_2)/W_1$	76
4.5.5 Relationship between $\Pi L$ and $(\Pi P W_{W}) \Pi_{1}$	77
4.4.1 Sample preparation and experimental methods	79
4.4.1 Sample proparation and experimental methods	79
4.4.2 All experimental proof of the relationship between $n_f/n_{max}$ and $(W, W)/W$	0.0
$(M_1 - M_W)$ $(M_1 - M_W)$ $(M_1 - M_1)$	80
A A Hordness and Young's modulus man surger that the approximation	80
T.T.T MATCHICSS AND I OWING S MODULIUS MEASUREMENT BY THE ENERGY-DASED	~ ~
A 5 Constraint fortune for only when in largest in the state in the sector	81
4.6 Conclusions	84
	87
CHAPTER 5: SUMMARY AND FUTURE WORK	88

. .

APPENDIX: FUNDAMENTALS OF DIMENSIONAL ANALYSIS AND Π	02
	92
REFERENCES	163

## LIST OF TABLES

Table 1.1.1 Crystal Structure and lattice parameters of NiTi alloys	95
Table 1.2.1 Properties of metallic hard materials	96
Table 1.2.2 Properties of covalent hard materials	97
Table 1.2.3 Properties of ionic hard materials	98
<b>Table 2.1</b> Phase transformation temperatures and structures of specimen BH and         BS	99
Table 2.2 Mechanical Properties of martensitic (specimen BH), austenitic         (specimen BS), and amorphous NiTi thin film obtained from nanoindentation test	99
Table 3.1 Description of specimens	100
Table 3.2 Composition and phase transformation temperatures of NiTi thin films	100
Table 3.3 Nanoindentation properties of aluminum substrate, interlayer materials         (S1, S2 and Cr) and CrN hard coating.	101
Table 3.4 A comparison of the mechanical properties of between superelastic NiTi and polyisoprene.	101
Table 4.1 Mechanical properties of the tested materials.	102
<b>Table 4.2</b> Relationship between Poisson's ratio and constraint factor for elastic           contact with a rigid spherical indenter	102

## LIST OF FIGURES

Figure 1.1.1 DSC test shows characteristic phase transformation temperatures of NiTi shape memory alloy	103
Figure 1.1.2 A schematic representation of the shape memory effect of NiTi alloy	103
Figure 1.1.3 A schematic representation of superelasticity of NiTi alloy	104
Figure 1.1.4 Representative stress-strain curves of shape memory and superelastic NiTi alloys	104
Figure 1.1.5 Phase diagram of binary NiTi alloy	105
Figure 1.1.6 NiTi shape memory alloy: dependence of martensite start temperature on composition	105
Figure 1.1.7 A comparison of wear rates between Ti50Ni47Fe3 and SAE 52100 steel.	106
Figure 1.1.8 A schematic representation of sputtering process	106
Figure 1.2.1 Residual stresses in thin films cause bending of the specimen	107
<b>Figure 1.2.2</b> Schematic representation of coating failure modes in the scratch test in profile and plan view: spalling failure (a); buckling failure (b); chipping failure (c); conformal cracking (d), and tensile cracking (e)	108
Figure 1.3.1 A schematic illustration of the load-displacement curve of instrumented indentation test and the graphical interpretation of contact depth	109
Figure 1.3.2 Illustration of conical indentation experiment	109
Figure 1.3.3 Degree of piling-up and sinking-in, $h_c/h$ , as a function of the ratio of yield stress to Young's modulus, $Y/E$ , and work hardening exponent, $n$ , in conical indentation experiments.	110
Figure 1.3.4 The top-point, instead of the cross point, defines the contact perimeter when piling-up occurs	110
Figure 1.3.5 A relationship between the ratio of irreversible work to total work, $W_p/W_i$ , and ratio of residual depth to maximum indentation depth, $h_f/h_m$ , in conical indentation experiments.	111

Figure 1.3.6 A relationship between the ratio of residual indentation depth to maximum indentation depth, $h_f/h_m$ , and ratio of harness to reduced modulus, $H/E^*$ , in conical indentation experiments	112
<b>Figure 1.3.7</b> Different combination of <i>Y/E</i> and <i>n</i> can lead to the same load- displacement curve in conical indentation experiments: Highly elastic materials (a), and high plastic materials (b)	113
<b>Figure 1.3.8</b> Relationship between representative strain ~ hardness and true strain ~ true stress. Curve A, mild steel. Curve B, annealed copper. O × hardness measurement. — stress-strain curve. ( $P_m$ stands for the hardness in this figure)	114
<b>Figure 1.3.9</b> A schematic illustration of the evolution of plastic zone during spherical indentation process: elastic (a), elastic-plastic (b), and fully-plastic (c)	115
Figure 2.1 DSC curves of specimen BH (a) and BS (b)	116
Figure 2.2 XRD patterns of specimen BH and BS	117
Figure 2.3 A schematic illust ration of thermally activated recovery of indent on shape memory alloy (specimen BH)	117
<b>Figure 2.4</b> Change of residual indentation depth was observed for Berkovich indent (a) and Vickers indent (b) on a NiTi shape memory alloy (specimen BH) after heating above to austenite finish temperature.	118
<b>Figure 2.5</b> Relationship between recovery ratio and residual indentation depth for Berkovich and Vickers indents on a NiTi shape memory alloy (sample BH)	119
<b>Figure 2.6</b> Geometry of the spherical indenters measured by SEM: R=213.4μm (a), and R=106.7μm (b)	120
<b>Figure 2.7</b> Spherical indents on a NiTi shape memory alloy (specimen BH): before heating (a), after heating (b), 3D profile of indent before heating (c), 3D profile of indent after heating (d), and recovery ratio as a function of residual indentation depth (e).	121
Figure 2.8 Cross-section profile of the spherical indents on specimen BH shows that no piling-up occurs	122
Figure 2.9 A schematic illustration of indentation sinking-in for spherical indentation experiments	122

Figure 2.10 Relationship between thermally activated recovery ratio and representative strain, and the relationship between the true stress and true strain of a NiTi shape memory alloy (specifien BH). The recovery ratio starts to decrease	
when the representative strain exceeds the critical strain in the stress-strain curve	123
Figure 2.11 A schematic representation of the elastic recovery of indents after removal of the load	124
<b>Figure 2.12</b> Berkovich indentation of a superelastic NiTi alloy (specimen BS) and copper: load-displacement curves (a), and depth (squares) and work (triangles) recovery ratios upon unloading at various depths (b). Filled symbols for NiTi and unfilled symbols for copper.	125
<b>Figure 2.13</b> Comparison between spherical indentation on a superelastic NiTi alloy (specimen BS) and copper ( $R=213.4\mu m$ ) (a), and relationship between the depth recovery ratio and representative strain, and the relationship between the true stress and true strain of a superelastic NiTi alloy (specimen BS) (b). The	
strain in the stress-strain curve	126
Figure 2.14 XRD shows indentation induced austenite $\rightarrow$ martensite transformation in specimen BS: non-indented area (a) and inside the indent (b)	127
Figure 2.15 Finite element modeling of strain distribution under sharp indenter (a) and spherical indenter (b). The white region right under the conical indenter has a minimum strain larger than the maximum strain under the spherical indenter. Regions with the same color have a plastic strain of the same value in (a) and (b)	128
Figure 2.16 A schematic figure of the target for the deposition of amorphous NiTi	•
film	129
Figure 2.17 XRD of amorphous NiTi thin film	130
Figure 2.18 Load-displacement curves of martensitic (specimen BH), austenitic (specimen BS) and amorphous NiTi	130
Figure 2.19 Dry sliding wear rate of martensitic (specimen BH), austenitic (specimen BS) and amorphous NiTi	131
Figure 2.20 XRD spectra show wear-induced austenite $\rightarrow$ martensite transformation in specimen BS: outside the wear track (a) and inside the wear track (b)	131
Figure 3.1 A schematic illustration of the structure of sputtering equipment for deposition NiTi thin films	132

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.

Figure 3.2 DSC curves of post-annealed NiTi thin films show that, at room temperature, specimen S1 is austenitic (a), while specimen S2 is martensitic (b)	133
Figure 3.3 XRD patterns of post-annealed NiTi thin films: S1 (a), and S2 (b)	134
Figure 3.4 XRD pattern of 5µm thick CrN coating on aluminum substrate (specimen CrN5-Al)	134
<b>Figure 3.5</b> Berkovich indentation test on various materials: load-displacement curves (a) and the relationship between $H/E^*$ and depth recovery ratio (b)	135
<b>Figure 3.6</b> Berkovich indentation tests at various depths: composite hardness (a), and depth recovery ratio (b)	136
<b>Figure 3.7</b> SEM images of the end of scratches on CrN1-Al (a), CrN5-Al (b), CrN-S1-Al (c), CrN-S2-Al (d), and CrN-Cr-Al (e). The arrow indicates the scratch direction	137
Figure 3.8 A schematic illust ration of the stress-strain curves of superelastic NiTi (a) and elastomeric polymer (b)	140
Figure 3.9 Friction coefficient and durability of coatings obtained by pin-on-disk test: specimen CrN1-A land CrN-S2-Al (a), and specimern CrN-Cr-Al, CrN5-Al and CrN-S1-Al.	141
Figure 3.10 Friction coefficient of specimen CrN-S1-A1 and CrN-Cr-A1 measured by scratch test using progressive load up to 2N	. 142
<b>Figure 3.11</b> Illustration of a spherical indenter sliding on a material: without elastic recovery in wear track (a) and with elastic recovery in the wear track (b)	- 143
<b>Figure 3.12</b> Illustration of a spherical indenter sliding on a material: piling-up (a) and sinking-in (b)	144
<b>Figure 3.13</b> Extent of material piling-up around a scratch made by a progressive load up to 6N: 3D profile of CrN-Cr-Al (a), 3D profile of CrN-S1-Al (b), cross- section profile of CrN-Cr-Al (c), and cross section profile of CrN-S1-Al (d). Note that dash lines in (a) an (b) indicate the locations for cross section profile	145
Figure 3.14 Wear rate of the specimens. Note that the Y-axis is in logarithm scale.	145 146
<b>Figure 4.1</b> Schematic illustration of indentation load-displacement curve and definition of the irreversible work, $W_t$ - $W_u$ , and reversible work, $W_u$	147

Figure 4.2 Finite element modeling: overall mesh and contact counterparts (a), and magnified image of the top-left part of the overall mesh (b)	148
Figure 4.3 A schematic illustration of indentation piling-up for spherical indentation experiment.	149
<b>Figure 4.4</b> Extent of piling-up $(h_c/h_{max}>1)$ and sinking-in $(h_c/h_{max}<1)$ as a function of $h_{max}/R$ (a-c), Y/E (d), and strain-hardening exponent n (e), in spherical indentation simulations. Note that (a), (b) and (c) represent materials with strain-hardening exponent n=0.1, 0.3 and 0.5, respectively, (d) represents material with n=0.1, $h_{max}/R=0.05$ , 0.2 and 0.4, (e) represents materials with Y/E=0.05, $h_{max}/R=0.05$ , 0.2 and 0.4. PU stands for piling-up and SI stands for sinking-in	150
Figure 4.5 Calculated load-displacement curves of a material with $Y/E=0.025$ , $\nu=0.2$ , and $n=0.5$ at various indentation depths	152
Figure 4.6 Finite element result shows that, for all the materials studied, a linear relationship exists between $h_f / h_{max}$ and $(W_t - W_u)/W_t$	153
<b>Figure 4.7</b> For each fixed $h_{max}/R$ , a linear relationship exists between $H/E^*$ and $(W_r - W_u)/W_t$ for spherical inderstation in elastic-plastic solids with work-hardening	154
Figure 4.8 A linear relationship between $ln(h_{max}/R)$ and $ln(-B)$	154
Figure 4.9 Spherical indentation experiments show that a linear relationship exists between $h_f / h_{max}$ and $(W_t - W_u)/W_t$ . The finite element results are also shown in this figure.	155
Figure 4.10 Experimental load-displacement curves for spherical indentation in a copper sample	156
<b>Figure 4.11</b> Effective indenter radius, $R_{eff}$ , as a function of indentation depth, $h_{max}$ for an imperfect spherical diamond indenter	157
<b>Figure 4.12</b> Experimental load-displacement curves obtained from instrumented spherical indentation experiments in aluminum (a), tungsten (b), and fused silica (c).	158
<b>Figure 4.13</b> Measured composite reduced modulus (a) and hardness (b) using the energy-based method together with indenter shape calibration. The error bar indicates the standard deviation of the measured values	159

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\_\_\_\_

Figure 4.14 Relationship between hardness and true stress for spherical indentation in elastic material (a), material with $Y/E=0.002$ , $n=0.3$ , and (c) material with $Y/E=0.025$ , $n=0.3$ . The horizontal axis represents true strain or representative strain of the same value.	
Figure 4.15 Constraint factors for various materials at different indentation dent $n=0.1$ (a), $n=0.3$ (b) and $n=0.5$ (c). Note that the scale for x-axis is different in (b) and (c).	epths: 1 (a), 161

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## **TRODUCTION**

NiTi alloys are well known for the shape memory and superelastic effects. Since their first discovery in 1960's, NiTi alloys have been extensively studied. Recent years have seen an increasing interest in the application of sputtered NiTi thin films, as both actuators and as tribological coating materials, which calls for a new method to characterize shape memory and superelastic effects at the microscopic scale. The approach taken in this study has been instrumented indentation experiments. Two types of recovery effects have been observed for indents in NiTi: one is the isothermal strain recovery upon unloading due to superelasticity, and the other is the strain recovery on heating due to the shape memory effect. Influences of indenter geometry and indentation depth on the recovery effects were studied. It was found that instrumented indentation experiments, especially using spherical indenters, are useful to quantitatively characterize the shape memory and superelastic effects at the microscopic scale. In addition, the maximum recoverable strain can be measured in spherical indentation experiments.

In this study, the wear behavior of martensitic, austenitic and amorphous NiTi were compared by dry sliding wear tests. It is found that superelastic NiTi is less wear resistant than amorphous NiTi, although the former has a higher elastic recovery ratio. To make superelastic NiTi a good wear resistant material, ploughing during sliding should be prevented. This can be achieved by depositing a hard coating on the top of the NiTi.

Base on the above observations, a novel composite tribological coating, using Superelastic NiTi as an interlayer material between hard CrN coating and soft aluminum Substrate, was developed. The indentation, adhesion, friction, and wear behavior were

studied. It is found that the superelastic NiTi interlayer can dramatically improve the adhesion, decrease the friction coefficient and increase wear resistance due to its large strain tolerance and elastic recovery effect.

To further understand the spherical indentation process, dimensional and finite element analysis were conducted to study spherical indentation in elastic-plastic solids with work hardening. Scaling relationships between hardness, reduced modulus, indentation depth, indenter radius, and work of indentation were studied. Based on the scaling relationships revealed by finite element modeling, an energy-based analysis method for instrumented spherical indentation measurements was proposed. This method applies for both piling-up and sinking-in of the materials around the indenter. It also provides a way of calibrating the effective radius of imperfectly shaped spherical indenters. The validity of this new method was tested by instrumented spherical indentation experiments on copper, aluminum, tungsten, and fused silica. Finally, constraint factors, defined as the ratio of indentation hardness to uniaxial true stress, for different stage of spherical indentation were studied using finite element analysis. The feasibility of using constraint factor to derive stress-strain curves was studied.

The main body of this dissertation is organized into four chapters. Chapter 1 reviews the literature on topics related to this dissertation work. Chapters 2-4 provide detailed descriptions of the sample preparation, experimental methods, experimental results, discussion, and conclusions of the dissertation work in three self-contained parts: Chapter 2 reports on the study of microscopic shape memory effect, superelastic effect and wear behavior of NiTi alloys. Chapter 3 describes experiments on improving the adhesion and wear resistance of chromium nitride coating on an aluminum substrate using superelastic NiTi interlayer. Chapter 4 details on the study of instrumented spherical indentation experiments. F inally, Chapter 5 provides a general conclusions and comments on possible directions for future research.

## CHAPTER 1

## LITE RATURE REVIEW

This chapter will introduce NiTi shape memory and superelastic alloys and  $v_{in}$  films, provide background on issues related to tribological coatings, and review previous work on and study of instrumented indentation experiments.

#### **1.1 IN ITI SHAPE MEMORY ALLOYS**

### 1.1. 1 Shape Memory and Superelastic Effects

NiTi alloys are well known for the shape memory effect (SME) and superelasticity (SE). Since the discovery of the shape memory effect in NiTi alloys in 1960's, [1-3] they have become increasingly important materials with wide applications. [4-6] NiTi alloys have a low temperature phase (the martensite), an intermediate phase (R-phase), and a high temperature phase (the austenite). The crystal structure and lattice parameters of these phases are shown in Table 1.1.1. [7-9] A schematic of the differential scanning calorimetry (DSC) response of NiTi is shown in Figure 1.1.1. [10] When temperature increases NiTi transforms from martensite into austenite; when temperature decreases the austenite phase transforms into martensite phase. Sometimes, during the <sup>C</sup>ooling, there exists a R-phase before martensite is formed. The formation of martensite and austernite is characterized by a start and finish temperature. Both shape memory and superelastic effects are closely related to the martensitic transformation. The martensitic transformation is a diffusionless phase transformation in solids, in which atoms move collectively, and often by a shear-like mechanism.

When NiTi is deformed in the martensitic phase, it recovers to its original shape by reverse transformation upon heating to above the austenite finish temperature,  $A_f$ . This effect is called the shape memory effect. The deformation may be in tension. compression, or bending, [11] as long as the strain is below some critical value. The mechanism of shape memory is illustrated in Figure 1.1.2. [5] When a single crystal parent phase, the austenite, is cooled to a temperature below the martensite finish temperature,  $M_{f_i}$  martensite is formed in a self-accommodating way by internal twining. as shown in Figure 1.1.2(a) and (b). In this process, the shape of the specimen does not charge because the phase transformation occurs in a self-accommodating manner. When an external stress is applied, the twin boundaries moves so as to accommodate the applied stress, as shown in Figure 1.1.2(c) and 1.1.2(d), and if the stress is high enough it will become a single variant of martensite under stress. When the deformed specimen in Figure 1.1.2(d) is heated to a temperature above austenite start temperature,  $A_s$ , the reverse phase transformation occurs. The shape recovery begins at  $A_s$  and the original shape is regained at austenite finish temperature,  $A_f$ , as shown in Figure 1.1.2(e). Once the shape has recovered at  $A_f$ , there is no change in shape when the specimen is cooled to below  $M_{f}$ . In the above explanation, it is assumed that the deformation proceeds solely by twin boundary movement and the transformation is crystallographically reversible. If either of the conditions is not satisfied, complete shape memory effect can not be Obtained.

When NiTi is deformed at a temperature slightly above the austenite finish temperature, it recovers to its original shape when the load is removed. This effect is called superelasticity, and it is related to the transformation of stress-induced martens it. For the austenite  $\rightarrow$  martensite transformation in NiTi alloy, there is a coupling effect between the transformation temperature and applied stress. If a stress is applied, martensite can form above the normal martensite start temperature,  $M_{s}$ , and martensite so formed is termed stress-induced-martensite (SIM), which has been observed by in-stitu TEM experiment. [12] Stress-induced-martensite is reversible upon unloading. The transformation mechanism is schematically shown in Figure 1.1.3. The stress needed to produce SIM obeys a uniaxial version of the Clausius-Clapeyron equation

$$\frac{d\sigma}{dM_{\star}} = -\frac{\Delta H}{T\varepsilon_0},$$
(1.1.1)

where  $\Delta H$  is the transformation latent heat; T is the temperature;  $\sigma$  is the applied stress;  $M_s$  is the martensite start temperature, and  $\varepsilon_0$  is the transformation strain resolved along the direction of the applied stress. The formation of stress-induced martensite may compete with the plastic deformation of austenite phase. If the dislocation movement is activated before stress-induced-martensite is formed surperelasticity can be inhibited.

Representative stress-strain curves of NiTi alloys are shown in Figure 1.1.4. When the test temperature is below the martensite finish temperature,  $M_f$ , a residual strain is left after the removal of the load, as shown in Figure 1.1.4(a). The residual deformation is recoverable by heating to above  $A_f$ . The initial plateau arises from the stress-induced growth of some martensite variants at the expense of others. When the test temperature is slightly higher than  $A_f$ , Figure 1.1.4(b), it is possible for little or no residual deformation to be left after removal of the load. It has been demonstrated by tensile tests that the

recoverable strain may reach 0.08, depending on the composition and thermo-mechanical history. [13] The initial stress plateau results from the stress-induced martensite transformation. For both shape memory and superelastic alloys, the recovery becomes incomplete when the stress is high begins when the strain exceeds the critical strain defined by the end of the stress plateau. begins when use such 113 Sher than  $A_f$ , Figure 1.1.4(c), dislocation slip is activated before the formation of stress-induced martensite can begin and no stress plateau is observed. The deformation becomes irreversible, and no shape memory effect

or superelasticity will be observed.

NiTi alloys are ordered intermetallic compounds based on near equiatomic compositions. According to the phase diagram, Figure 1.1.5, this compound exists as a stable phase down to room temperature. The NiTi single phase region becomes very narrow at temperatures below 923K, and the alloys often contain precipitates of a second

Figure 1.1.6 shows that the phase transformation temperatures are strongly phase. dependent on composition. [4] The martensite start temperature,  $M_s$ , decreases dramatically from 100°C to -100°C when Ni content increases from 49at.% to 51at.%. Phase transformation temperatures and transformation hysteresis are also dependent on the thermal and mechanical history. [14-16] Deformation can stabilize the stress-induced marter si te and increase the transformation temperature. [17] Precise composition control and care ful heat treatment are therefore required in the processing of NiTi alloys.

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1.1.2 Sliding Wear and Indentation Behavior of NiTi Alloys Good wear resistance of NiTi alloys has been reported by a number of experiments. Good wear resistance of NiTi alloys with commercial wear lin and Wang [10] count commercial weat that the NiTi alloys are more wear resistant than Co45 and 38CrM Alalloys, although they have lower hardness. Clayton [19] studied the sliding wear resistance of Ti<sub>48.1</sub>Ni<sub>47.9</sub>Fe<sub>3.6</sub> using pin-on-ring sliding wear test, where a Ti<sub>48.1</sub>Ni<sub>47.9</sub>FC<sup>3.6</sup> pin slides against D5594 steel. The wear rate was obtained by measuring the weight 10ss of the pin. It was revealed that the wear rate of  $Ti_{48.1}Ni_{47.9}Fe_{3.6}$  is lower than that of K44 pearlitic steel. Clayton suggested that the good wear resistance of  $Ti_{48,1}Ni_{47,9}Fe_{3,6}$  was due to the hardening of the alloy during the sliding wear process. Singh and Alpas [20] investigated the dry sliding wear resistance of  $Ti_{50}Ni_{47}Fe_3$  alloy against a SAE 52100 steel under a wide range of load and sliding speed conditions. Figure 1.1.7 shows that the intermetallic  $Ti_{50}Ni_{47}Fe_3$  has 2-5% as much wear as SAE 52100 steel during dry sliding wear, although Ti<sub>50</sub>Ni<sub>47</sub>Fe<sub>3</sub> has a lower bulk hardness (300kg/mm<sup>2</sup>) in comparison to that of the SAE 52100 bearing steel (9OOkg/mm<sup>2</sup>). [20] Microhardness measurement on the worn surface of Ti<sub>50</sub>Ni<sub>47</sub>Fe<sub>3</sub> alloy showed that surface hardness can reach up to 400 kg/mm<sup>2</sup>, an increase of about 30%relative to the bulk hardness. Nevertheless, surface hardening of NiTi may not be the main factor responsible for the good wear resistance of NiTi since even the hardness of

the **worn** surface is lower than the bulk hardness of 52100 steel. **I** [21] investigated the wear behavior of  $Ni_{51.5}Ti$  alloy subject to 1.5 and 24.5 hour

aging at 500°C and found that the 1.5 hours aging leads to better wear resistance. Li [21] attributed the difference to the precipitation hardening of the  $Ni_{14}Ti_{11}$  precipitate. The

8

precipitates gradually lose the coherence with the matrix with increasing aging time. which causes a decrease in hardness. The change of transformation temperature due to different aging and its influence on wear behavior were not reported. It is possible that the transformation temperature of Ni<sub>51.5</sub>Ti<sub>48.5</sub> increases with aging time since precipitation of nickel rich Ni<sub>14</sub>Ti<sub>11</sub> will decrease the nickel content in matrix, and the stress-stain relationship and wear behavior will change accordingly. The wear resistance of a shape memory Ni<sub>50,3</sub>Ti with a superelastic Ni<sub>51,5</sub>Ti<sub>48,5</sub> was compared. Li [21] found that the wear resistance of the superelastic Ni<sub>51.5</sub>Ti<sub>48.5</sub> is superior to that of shape memory Ni<sub>50,3</sub>Ti<sub>49,7</sub>. [21] Similiarly, Lin [22] found that the austenitic Ni<sub>51</sub>Ti<sub>49</sub> alloy exhibits better wear resistance than the martensitic Ni<sub>50</sub>Ti<sub>50</sub> alloy in the dry sliding wear against a SUJ-2 Cr-steel ball. Liang et. al. [23] compared the wear behavior of superelastic and shape memory NiTi and argue that the wear resistance of NiTi is mainly dependent on the recoverable strain limit, i.e. the sum of the pseudoelastic strain (also termed as superelastic strain) and pseudoplastic strain limit, where the pseudoelastic strain is the recoverable strain after unloading and the pseudoplastic strain is the recoverable strain on heating. Liang [23] argued that, in essence, wear is fracture at small scale, which is nucleated at locations where the dislocation density increases obviously. In wear of a superelastic alloy, deformation occurs at contacts by transformation of austenite to me artensite. It will recover immediately by reverse transformation on unloading. Stressinduced martensite has been found in the sliding wear tracks of otherwise austenitic NiTi, which indicates that stress-induced martensite does occur under this complex loading condition. [22] For shape memory NiTi, psuedoplastic deformation occurs, and it will remain even after the load is removed, but permanent defects, such as dislocation, can not

be created because the deformation is only through the reorientation of the selfaccommodating martensite. In addition, as demonstrated by finite element modeling between two spherical asperities, [24, 25] the low stress-plateau related to shape memory and superelastic NiTi makes the materials deform easily, which can increase asperity contact area and consequently decrease contact stresses. Both superelasticity and shape memory effect are responsible for the good wear resistance of the NiTi alloy. The better wear resistance exhibited by the superelastic NiTi might be due to its higher hardness. Under the same applied load it is more difficult to generate dislocations in superelastic NiTi than in shape memory NiTi, since the former is stronger. Furthermore, for superelastic NiTi, there is no accumulative deformation under the cyclic wear test loading since the deformation is recoverable when the load is removed. However, for shape memory NiTi, the deformation is cumulative since the deformation is irreversible when the load is removed. An extra deformation is generated in each loading cycle, which will deteriorate the shape memory ability and wear resistance. The cyclic loading condition exists when NiTi alloys serve as the disk in pin-on-disk wear test. Theses investigations demonstrate that NiTi alloys, especially the superelstic NiTi, are promising as novel tribological materials. However, there has been no reported research on the tribological application of NiTi thin films.

Because the loading conditions in wear tests are very similar to those in indentation experiments, efforts have been conducted to correlate the wear resistance of NiTi alloys with their indentation behavior. [26-28] Mechanical properties, such as hardness, modulus, work recovery ratio and depth recovery ratio, can be obtained by instrumented indentation experiments. [28-31] A detailed description of the indentation experiment and analysis methods used to calculate hardness, Young's modulus, work recovery ratio, and depth recovery ratio will be presented in section 1.3. It was reported that superelastic  $Ni_{51}Ti$  alloy exhibits an energy recovery ratio as high as 47%, in contrast to the 304 stainless steel which has an energy recovery ratio of 11%. [28, 32] The energy recovery ratio is defined as the ratio of elastic work to total work in the indentation experiment, and the depth recovery ratio is defined as the ratio of reversible indentation depth to total indentation depth. The high recovery ratio of  $Ni_{51}Ti$  alloy was attributed to the reversible stress-induced martensite transformation under the indenter, which has been verified by TEM observation. [29]

The shape memory effect under indentation loading has been studied as well using Rockwell indenter. [26] Recovery of the Rockwell indents upon heating were observed in NiTi alloy. It was found that the ratio of indentation depth after heating to indentation depth before heating is a function of the amount of martensite present. It was suggested that, for NiTi alloys, the deformation under indenters can be divided into three types: [26, 29] (i) elastic deformation, which includes both linear elasticity and superelasticity arising from the stress-induced martensitic transformation (ii) pseudoplastic deformation arising from the reorientation of martensite variants, and (iii) unrecoverable deformation due to generation of permanent defects, such as dislocations. The contribution of each the total deformation may depend on the indenter geometry and applied load.  $H_{O}$  wever, no systematic study on shape memory effect and superelasticity using insternamented indentation techniques has been reported, which take into account of indeer tation load and indenter geometry.

#### 1.1.3 Processing and Characterization of NiTi Thin Films

The microstructure and mechanical behavior of NiTi thin films have been extensively studied since 1990. [7, 33-45] NiTi thin films are interesting because they have the potential to be high performance actuating materials for photolithographically micromachined systems. NiTi shape memory alloys have the largest actuation force and displacement among many actuator materials. [7, 46-49]

NiTi thin films have been successfully processed by the sputtering method. A schematic representation of the sputtering process is shown in Figure 1.1.8. A glow discharge is generated first and the working gas is ionized. The working species is accelerated toward the target due to the potential difference between the target and plasma, which cause the atoms come off the target and finally deposit on the substrate.

It has been generally found that Ti content in sputtered NiTi thin films is lower than that in target. [7] This composition shift may arise from differential sputtering yield, [7] difference in angular flux distribution, [50-52] or by differential lateral drift caused by flux thermalization. [53, 54] It has been shown that the polar angular distribution of Ti is wider than that of Ni during sputtering. [50] This means that Ti:Ni ratio is larger at low angle from the target surface and is smaller at normal direction of the target surface. The *c* ffect of angular distribution on film composition is more pronounced at larger distance fm on the target.

Thermalization of the deposition flux is caused by collision of the deposited species with the working species. The thermalization is controlled by the parameter of  $P \times d$ , where P is the working pressure and d is the working distance. [53] More sputtered atoms are diverted by the collision with the working gas species when  $P \times d$  value

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The h Ti<sub>3</sub>Ni<sub>4</sub> increases. The diversion of the deposited species depends on their mass. A concentration shift occurs due to the mass difference in the deposition flux, and it will affect the transformation temperature and mechanical properties of the thin films.

The as-deposited NiTi thin films are amorphous if the substrate temperature is kept low. Crystalline NiTi thin films can be obtained by subsequent annealing after deposition. It was reported that the crystallization temperature of  $Ni_{48.9}Ti_{51.1}$  thin film is about 500°C. [55]

Careful control of the annealing temperature and time is required to make shape memory and superelastic NiTi films since the transformation temperatures are closely related to the annealing method. Two types of annealing methods have been used to make good crystalline films: (i) two-step annealing method: the as-deposited film is solution treated at 973 K followed by aging at temperatures from 573K to 773K; [56] (ii) one-step annealing method: the as-deposited film is annealed at a temperature between crystallization temperature and 973K. [57]

The effect of annealing on Ni-rich thin film is very similar to that on bulk materials. [44, 56] Lenticular Ti<sub>3</sub>Ni<sub>4</sub> precipitates are formed during annealing. Ti<sub>3</sub>Ni<sub>4</sub> has a rhombohedral structure, which belongs to the space group R3. The orientation relationship between Ti<sub>3</sub>Ni<sub>4</sub> and the matrix is:

## (0001) Ti<sub>3</sub>Ni<sub>4</sub>|| (111) matrix

### $[010] Ti_3Ni_4 || [\overline{2} \overline{1}3] matrix$

The mabit plane of the Ti<sub>3</sub>Ni<sub>4</sub> precipitates is (111) of the matrix. [5] The precipitation of  $Ti_3Ni_4$  decreases the nickel content in the matrix and causes an increase in the mastensite

start temperature. [7] In addition, precipitation hardening by  $Ti_3Ni_4$  increases the yield stress of the film, which can improve strain recoverability in the film.

Crystalline Ti-rich thin films contrast the Ti-rich bulk NiTi alloy in that the former is more ductile than the latter. The improved ductility in thin films arises from the suppression of the coarse grain boundary precipitates, which has been observed in Ti-rich bulk material. [47] In Ti-rich films, evolution of microstructure during annealing follows the following sequence: GP-zones  $\rightarrow$  GP zones and Ti<sub>2</sub>Ni precipitates within the grain  $\rightarrow$  spherical Ti<sub>2</sub>Ni precipitates uniformly distributed within the grain  $\rightarrow$  Ti<sub>2</sub>Ni precipitates along the grain boundaries. [44, 58, 59] The Ti<sub>2</sub>Ni precipitates within grains are not in an equilibrium state. When annealed for longer times or at higher temperatures, equilibrium Ti<sub>2</sub>Ni precipitates form along grain boundaries. [7] The precipitates within in the grain can increase the resistance to plastic deformation, which improves the shape memory effect and superelasticity. [60]

It has been reported that the elongation of  $Ni_{50}Ti_{50}$ ,  $Ni_{48.3}Ti_{51.7}$  and  $Ni_{51.5}Ti_{48.5}$  films are 40%, 20% and 8% respectively. [43] Both Ni-rich and Ti-rich thin films in crystalline form have good ductility and can be used as engineering materials.

# 1.2 TRIBOLOGICAL COATINGS

The surface is arguably the **1**<sup>110</sup>st important part of an engineering material, where many components fail due to wear. The task of tribology and surface engineering is to design surfaces to reduce wear loss, while keeping the desirable properties (usually toughness) of the bulk solid materials. The early 1980's saw the development of technologies in surface engineering, such as ion implantation, physical vapor deposition (PVD) and chemical vapor deposition (CVD). A variety of coatings have been developed to protect substrate materials in specific working environments. In the following sections, properties of hard coating materials, and characterization and design aspects of tribological coatings, are discussed.

#### **1.2.1 Hard Coating Materials**

Hard coatings can be produced by a number of techniques, which can be divided into two broad categories – film deposition and surface modification. Among the deposition methods, PVD and CVD are the most widely used techniques for producing hard coatings. Depending on the chemical bonding character, hard coatings can be divided into three groups, i.e.,

(i) Metallic hard materials (transition metal borides, carbides, and nitrides),

(ii) Covalent hard materials (borides, carbides and nitrides of Al, Si, and B as well as diamond)

(iii) Ionic hard materials (oxides of Al, Zr, Ti and Be).

Tables 1.2.1-1.2.3 list the typical properties of these three groups of materials. [61] All show high hardness, high Young's modulus and high melting point. Important parameters in designing tribological coatings include: [62]

- (i) Young's modulus and Poisson's ratio of the coating and substrate
- (ii) Strength of the coating and coating-substrate interface
- (iii) Thickness of the coating
- (iv) Roughness of the mating surfaces
- (v) Surface adsorbtion and reaction

All these parameters influence the mechanical performance of the materials, such as residual stress, fracture, adhesion, friction and wear. These will be discussed in detail in the section followed.

#### **1.2.2 Characterization of Tribological Coatings**

### 1.2.2.1 Residual Stresses

Residual stresses in the coating are critical to coating performance and reliability. Residual stresses of thin films on substrates are produced by processes which would cause the dimension of the film to change if it were not attached to the substrate. Residual stresses include thermal stresses and intrinsic stresses. Thermal stresses are generated by the difference in the thermal expansion coefficient between the film and substrate. The dependence of thermal stress in a planar film,  $\sigma$ , on temperature change, dT, is given by: [63]

$$\frac{d\sigma}{dT} = \Delta \alpha \frac{E_f}{1 - v_f}, \qquad (1.2.1)$$

where  $\Delta \alpha$  is the difference between the thermal expansion coefficient;  $E_f$  and  $v_f$  are the Young's modulus and Poisson's ratio of the film, respectively. Thermal stresses are often dominant when high temperature deposition is adopted or when high temperature annealing occurs during subsequent processing.

Intrinsic stresses are developed during the growth of the film. The magnitude of intrinsic stress is dependent on the relative kinetics of various processes that contribute to stress generation. Factors that influence intrinsic stress include grain growth, excess vacancy annihilation, phase transformation, and epitaxy. The presence of a biaxial stress in thin film on a substrate will cause elastic bending of the substrate. Tensile stresses in the coating cause the specimen bend toward the coating, while compressive stresses in the coating causes the specimen bend toward the substrate, as shown in Figure 1.2.1. [64] If the film thickness is less than one percent of the substrate thickness, the average stress,  $\sigma$ , in thin film can be calculated from the radius of curvature of the substrate using: [63]

$$\sigma = \left[\frac{E_s}{1 - \upsilon_s}\right] \frac{t_s^2}{6Rt_f},$$
 (1.2.2)

where R is the curvature of the substrate;  $E_s$ ,  $v_s$  and  $t_s$  are Young's Modulus, Poisson's ratio and thickness of the substrate, respectively;  $t_f$  is the thickness of the film.

### 1.2.2.2 Adhesion Strength

Interfacial adhesion strength is a measure of the resistance of coatings to debonding or spalling. Interfacial adhesion can be measured by indentation tests, scratch tests, bending tests, or bulge and blister tests. [65-68] The scratch test has been widely accepted as a comparative measurement of the adhesion strength of hard coatings on
metal substrates because it is reliable, simple to use, and requires no special specimen preparation. In the scratch adhesion test, a diamond indenter is drawn over the coated surface under constant or increasing normal load until a critical load is reached at which coating failure occurs. Adhesion is generally quantified using this critical load to failure in a scratch test. [69, 70] Acoustic emission and change in the slope of the timedependent tangential force curve in the progressive-loading scratch test, as well as microscopic observation of the scratch scars, can all be used to determine the critical load. [71-73] During the scratch adhesion test, a compressive stress field is induced ahead of the indenter. When the mean compressive stress exceeds a critical value, the coating detaches from the substrate to lower the elastic energy stored in the coating. The material behind the indenter is subject to a tensile stress, and the material under contact is bent to form the scratch track. The scratch ridge, which is the edge of a scratch along scratching direction, is also subject to bending deformation. [74, 75] A range of non-adhesive failure modes may occur before or along with adhesive failure during scratch test. Two types of major failure produced by scratch tests are: cracking in the through-thickness direction and adhesive failure, as shown in Figure 1.2.2. [76] Sometimes, there are two distinct transition points in the output of the friction force, indicating two "critical loads". The lower value corresponds to the onset of through-thickness cracking around the indenter, while the higher value is associated with coating penetration and detachment. [77-79]

## **1.2.2.3** Hardness

Hardness has long been regarded as a primary parameter defining wear resistance. According to the Archard's wear equation for abrasive wear test, the volume loss,  $\Delta V$ , is linearly proportional to the applied normal load, L, and inversely proportional to hardness, H, [80] i.e.,

$$\Delta V \propto \frac{L}{H}.$$
 (1.2.3)

Therefore, many scientific researches have focused on the development of super-hard (H>40GPa) wear resistant materials. [81]

One of the most effective methods to increase hardness is to decrease the grain size. In metal and alloy films, small grain size causes hardening of materials in agreement with the Hall-Petch relation

$$H = H_0 + kd^{-1/2}, \qquad (1.2.4)$$

where *H* is the hardness;  $H_0$  is an intrinsic material parameter; *d* is the grain diameter and *k* is a constant related to both shear modulus and the critical shear stress for dislocation movement. The Hall-Petch relation has been found to be valid for grain sizes larger than 10nm. For grain sizes smaller than 10nm, grain boundary sliding plays an important role in determining the mechanical properties. [81] The deposited thin films usually have grain sizes smaller than 1 $\mu$ m. The density of the film and defects also influence the hardness. Usually, voids and vacancies decrease the coating hardness.

### 1.2.2.4 Friction and Wear

Friction and wear properties of tribological coatings are often evaluated by sliding wear tests. The normal load and tangential force are measured during sliding wear test. The friction coefficient,  $\mu$ , is defined as the ratio of the tangential force,  $F_{i}$ , to the normal force,  $F_{n}$ :

$$\boldsymbol{\mu} = \frac{F_{\prime}}{F_{n}} \tag{1.2.5}$$

where the tangential force,  $F_l$ , arises from two sources: an adhesion force,  $F_a$ , developed at the contact area between the two contact surfaces, and a deformation force,  $F_d$ , needed to plough into the material, i.e., [80, 82]

$$F_t = F_a + F_d \tag{1.2.6}$$

The adhesion is given by

$$F_a = A\tau \tag{1.2.7}$$

where A is the true contact area between the two surfaces, and  $\tau$  is the shear stress of the junction formed at the contact area. A low friction coefficient is usually desirable for most tribological coatings.

Wear of tribological coatings can be categorized into two types: wear dominated by coating detachment, i.e. fracture in the coating/substrate interface, and wear caused by gradual removal of the coating material.[73, 83] Wear of the first type can be decreased by improving interfacial adhesion; while wear of the second type can usually be reduced by increasing hardness or decreasing the friction coefficient of the coating material.

As discussed in section 1.2.2.3, hardness is the major factor determining the wear resistance of materials. However, recent studies showed that there exists cases where the Archard's equation does not apply, i.e. materials with lower hardness could have better wear resistance. [24, 84] It was suggested that the ratio of elasticity plays an important role in determining wear resistance as well. [26, 27, 84] For instance, some polymers, particularly elastomers, have low hardness and Young's modus and they can provides excellent wear resistance. The elasticity can be easily characterized by the instrumented

indentation experiments using the ratio of hardness to modulus,  $\frac{H}{E}$ , or the ratio of final

indentation depth to maximum indentation depth,  $\frac{h_f}{h_{\text{max}}}$ . Note that  $\frac{H}{E}$  is dimensionless

and it is termed as "elastic strain to failure". [84] H/E can be used to characterize the elastic strain under contact. An almost linear relationship between the ratio of hardness to

reduced modulus,  $\frac{H}{E^*}$ , and  $\frac{h_f}{h_{\text{max}}}$  has been reported. [85, 86] It needs to be pointed out

that no experiments existed that unambiguously demonstrated the effect of H/E without altering other attributes, such as the chemical composition at the surface that could also affect wear, because in most previous studies different materials systems were used to test the effect of H/E. To clearly demonstrate the effect of H/E on wear resistance, the surface chemistry and surface hardness have to be the same.

### **1.2.3** Tribological Coating with Interlayers

Hard ceramic coatings are often deposited on the soft metallic substrates to protect the soft metal from wear loss. Typically, the Young's modulus of ceramic coatings is 3~4 times higher than that of metal substrates. The coefficient of thermal expansion for ceramics is often much smaller that that of metals. Ceramic coatings on metal substrates sometimes have a strong tendency to fail by cracking or delamination due to the large mismatch of mechanical and thermal properties. In addition, if the substrate is not hard enough to carry the load, plastic deformation will take place in the substrate under contact. For a softer substrate, cracks occur in the coating both within the contact area and outside at the substrate material piling-up area. [76] One way to increase the load supporting ability is to deposit thicker coatings. However, the performance of a coating may not improve with increasing coating thickness because the deposited coatings typically have columnar structure. Any crack normal to the surface will be large in thick coating, and may exceed the critical crack length for fracture, whereas in the thin coating this may not be the case. Furthermore, the interfacial thermal stress is proportional to the coating thickness. A large interfacial shear stress often leads to large thermal strain and premature failure of the coatings.

To improve the load supporting ability, adhesion, and wear resistance, composite coatings with various interlayer materials, such as Ni, Ti, Cr and Mo, have been developed. [71, 72, 87-89] With proper choice of interlayer materials and thickness, improved friction, wear and adhesion behavior have been achieved. It has been claimed that interlayers can provide benefits by arresting crack propagation, a problem which can otherwise increase with thickness. [90] It is desirable to produce tribological coatings where the interlayer provides good adhesion to the substrate and the outer layer provides high harness, low friction and good stability.

# 1.3 INSTRUMENTED INDENTATION EXPERIMENTS

Traditional Vickers hardness measurement requires imaging of the indents to calculate the contact area and hardness. Large errors are introduced in the measurement of indentation size. In addition, it is very difficult to image indents of sub-micron scale. With the instrumented indentation technique, hardness can be calculated directly from the load-displacement curves. Instrumented indentation experiments, also termed nanoindentation or depth-sensing indentation experiments, have been widely used in probing mechanical properties at sub-micrometer scale. During an instrumented indentation test, both the applied load and indenter displacement are recorded, and mechanical properties, such as hardness and reduced modulus, are measured. A schematic load-displacement curve from a loading-unloading cycle of the instrumented indentation test is shown in Figure 1.3.1. [91] A variety type of indenters, such as Vickers, Berkovich, Knoop and spherical indenter, were used in indentation tests. [92] Recently, Berkovich indentation and spherical indenters have been widely used for indentation measurement. [91][119] In the following sections, issues related to instrumented Berkovich and spherical indentation experiments will be discussed.

### **1.3.1** Instrumented Berkovich Indentation Experiments

### 1.3.1.1 Oliver-Pharr's Method for Hardness and Modulus Measurement

A Berkovich diamond indenter, which has a triangular pyramid shape, can be easily manufactured since three facets always intersect at one point. It has the same areato-depth ratio as the traditional Vickers indenter. Berkovich indentation experiments have found wide application in measuring hardness and Young's modulus of bulk materials



and thin films. [93-95] A detailed description of Berkovich indentation experiment the analysis method for measuring hardness and modulus is presented in this section.

The hardness, H, is equal to the average pressure under the indenter, calculated as the applied load,  $F_{max}$ , divided by the contact area,  $A_c$ , between the indenter and the sample:

$$H = \frac{F_{\max}}{A_c}.$$
 (1.3.1)

For a prefect Berkovich indenter, the relationship bet ween contact area,  $A_c$ , and contact depth,  $h_c$ , is given by the area function: [91]

$$A_c = 24.5h_c^2.$$

Accurate determination of contact area and contact depth are critical in nanoindentation measurement.

Doemer and Nix [96] to first proposed that the contact depth can be calculated from load-displacement curves by assuming that the initial unloading stiffness is linear. This method was later modified by Oliver and Pharr, [91] and who's method is now widely accepted to determine contact depth, contact area, hardness, and Young's

The Oliver and pharr's method [91], first proposed in 1992, assumes that a conical indentation process can be used to simulate the Berkovich indentation process because the conical indenter, like the Berkovich indenter, has the same depth-area relationship and geometric singularity at the tip. The Berkovich indenter is equivalent to a conical indenter with a half-angle of 70.3°, as shown in Figure 1.3.2. [97] For a conical in  $\mathcal{A}$  enter, the contact depth,  $h_c$  is given by:

24



$$h_{c} = h_{max} - 0.72 \frac{F_{max}}{S},$$
 (1.3.3)

where  $h_{max}$  is the displacement at the maximum load;  $F_{max}$ , and S is the initial unloading stiffness, respectively. [91] Based On a large number of experimental observations, Oliver and Pharr suggested that the contact depth for Berkovich indentation is slightly different from equation (1.3.3) and is given by: [91, 98]

$$h_c = h_{\max} - 0.75 \frac{F_{\max}}{S}.$$
 (1.3.4)

A comparison of the contact depth for Berkovich indentation experiment and conical indentation experiment is shown in Figure 1.3.1.

Accurate determination of the initial un loading stiffness is crucial in nanoindentation analysis. It was observed that the un loading curve obeys a power-law relationship: [91]

$$F_{u} = K(h - h_{f})^{m}, \qquad (1.3.5)$$

where  $F_u$  is the force during unloading; h is the indenter displacement during unloading, and  $h_f$  is the residual indentation depth after unloading. The constants K and m can be determined by a least square fitting of the relationship between  $F_u$  and  $(h - K_f)$ . Initial unloading stiffness, S, is then found by analytically differentiating equation 1.3.5 and evaluating the derivative at the peak load:

$$S = \frac{dF_u}{dh}\Big|_{F_u = F_{max}}$$
(1.3.6)

The relation ship between the initial unloading stiffness and reduced modulus,  $E^*$ , is  $g = v \in \mathbb{R}$  by: [99]



$$S = \frac{dF}{dh}\Big|_{F=F_{max}} = 2E^* \sqrt{\frac{A_c}{\pi}}, \qquad (1.3.7)$$

The reduced modulus,  $E^*$ , is given by:

$$\frac{1}{E^*} = \frac{(1 - \upsilon_s^2)}{E_s} + \frac{(1 - \upsilon_i^2)}{E_i}, \qquad (1.3.8)$$

where  $E_s$  and  $v_s$  are Young's modulus and Poisson's ratio for the specimen, respectively;  $E_i$  and  $v_i$  are Young's modulus and Poisson's ratio for the indenter, respectively. Diamond is the most popular indenter material becaus c of its high stiffness and hardness. The Young's modulus and Poisson's ratio of the di amond indenter are 1141GPa and 0.07, respectively. For a rigid indenter with infinite modulus, the reduced modulus is expressed as:

$$\frac{1}{E^{*}} = \frac{(1 - v_{s}^{2})}{E_{s}}$$
(1.3.9)

Equation (1.3.7) was first derived by Sneddon for elastic contact between a rigid, axisymmetric punch of an arbitrary smooth profile and an elastic half-space. It applies to both cornical and spherical indenters. Recently, Cheng and Cheng [86, 100] proved that this equation holds true for elastic-plastic solids with or without work hardening and residual stress. The measured initial unloading stiffness can thus be used to calculate the reduced modulus if the contact area can be accurately determined.

Practically, no Berkovich tip is perfectly sharp at the end. The tip rounding effect is taken into account by the indenter shape function calibration. For a rounded Berkovich  $t \neq p$ , as a good approximation, the shape function is given by: [91]

$$A_c = 24.5h_c^2 + C_1h_c + C_2h_c^{1/2}$$
(1.3.10)







The constants  $C_1$ ,  $C_2$  can be **obtained** by a least square fitting of the relationship between the contact area and contact **depth**. By indenting a material with a known Young's modulus, the contact area can be calculated using equation 1.3.7. The contact depth can be determined using equation 1.3.4. Most often, fused silica is used as the calibration material. The Young's modulus and Poisson's ratio of fused silica are 72GPa and 0.17, respectively. [101]

# 1.3. 1.2 Piling-up and Sinking-in

Extensive finite element modeling of conic al indentation in elastic-perfectly plastic [102-104] and elastic-plastic [85, 86, 97, 98, 105, 106] solids has been conducted. It was found that, the contact depth  $(h_c)$  can be larger than the indentation depth at the maximum load  $(h_{max})$ , i.e. piling-up occurs; or the contact depth can be smaller than the indentation depth at the maximum load, i.e. sinking-in occurs.

For a conical indenter with some specific angle, the degree of piling-up and sinking-in is dependent on the ratio of yield stress to Young's modulus, Y'E, and the work hardening exponent, n, as shown in Figure 1.3.3. [97, 107, 108] For highly elastic materials (large Y/E and n) sinking-in occurs and the Oliver-Pharr method can be used to determine the contact depth. However, for materials with low Y'E and n, material piling. up occurs. It is claimed that, as a simple practical rule, when the ratio of residual indentation depth to maximum indentation depth,  $\frac{h_f}{h_{max}}$ , is less than 0.7, the Oliver-Pharr

rethod provides a reasonable estimate of the contact area. However, when  $\frac{h_f}{h_{\text{max}}} > 0.7$ ,

the Oliver-Pharr method underestimates the contact area due to material piling-up. As is



obvious in equation (1.3.4), the contact depth  $(h_c)$  is always smaller than the indentation depth at maximum load  $(h_{max})$  when Oliver-pharr's method is used. [107] Material pilingup has been observed in Berkovich indents on aluminum. The projected contact areas measured by AFM were up to 50% greater than those calculated using the Oliver-Pharr method. [109] To accurately determine the contact area in the case of piling-up, we need to rneasure the profile of the residual indents after unloading using surface profilometer. The "top point" shown in Figure 1.3.4 can be used to **d** efine the contact perimeter. [110]

# 1.3.1.3 Scaling Relationships

Some interesting scaling relationships have been reported in conical indentation experiment using dimensional analysis and finite element modeling. The scaling relationships between the ratio of irreversible work to total work,  $\frac{W_p}{W_{tot}}$ , ratio of residual depth to maximum indentation depth,  $\frac{h_f}{h_m}$ , ratio of hardness to reduced modulus,  $\frac{H}{E^*}$ , have been reported. For a conical indenter with an arbitrary angle, a single One-to-one relationship exits between  $\frac{W_p}{W_{tot}}$  and  $\frac{h_f}{h_m}$ , as shown in Figure 1.3.5. [105, 106, 111] This

relationship is approximately linear for  $\frac{h_f}{h_m} > 0.4$  and the expression is given by:

$$\frac{W_p}{W_{tot}} = (1+\gamma)\frac{h_f}{h_m} - \gamma \quad \text{for} \quad \frac{h_f}{h_m} > 0.4, \qquad (1.3.11)$$

where  $\gamma = 0.27$ . This general relationship is independent of material properties and investmenter angle. For a conical indenter of given half-included angle,  $\theta$ , an approximately



linear relationship exists between  $\frac{h_f}{h_m}$  and  $\frac{H}{E^*}$ , as shown in Figure 1.3.6. [85, 106, 112]

The relationship is given by:

$$\frac{h_f}{h_m} = 1 - \mathcal{A} \frac{H}{E^*}, \qquad (1.3.12)$$

wh ere

$$\lambda = 1.5 \tan(\theta) + 0.327$$
 for  $60^{\circ} \le \theta \le 80^{\circ}$ . (1.3.13)

For a conical indenter with sharp angle, e.g. 45°, the **1** inear relationship between  $\frac{h_f}{h_m}$  and

 $H/E^*$  remains valid although the angular dependence  $\frown f \lambda$  no longer applies.

# 1.3.1.4 Correlation between Indentation and Uniaxia I Tensile Experiments It is suggested the representative strain, $\varepsilon_r$ , for conical indentation is given by [92,

113]:

$$\varepsilon_r = 0.2 \tan \theta , \qquad (1.3.14)$$

where,  $\theta$ , is the half included angle of the conical indenter. Berkovich and Vickers indenters are equivalent to a conical indenter with 70.3° half-included angle. The representative strain for Berkovich and Vickers indentation is approximately equal to 0.08. Tabor claimed that the significance of representative strain is that hardness (H) equals 2.8 times the true stress ( $\sigma_r$ ) at the representative strain, i.e. [92]

$$H = 2.8\sigma_r$$
. (1.3.15)

where  $\sigma_r$  is the true stress at 0.08 true strain in an uniaxial tensile test.



It has been reported that equation (1.3.15) applies only to highly plastic materials. For highly-elastic the ratio of hardness to flow stress (termed as the constraint factor) is smaller than 2.8. The constraint factors decrease from 2.8 to 1.7 for highly plastic materials to highly-elastic materials, respectively. [86, 112]

Recently, there have been arguments about the value of the representative strain. By mapping the strain distribution of the subsurface under the indents, Chaudhri [114] suggested that the representative strain ranges from  $\bigcirc$ .25 to 0.36. However, using finite element calculation, Mata et. al. [115] suggested that the representative strain should be close to  $\bigcirc$ . 1.

Efforts have been made to explore the possibil ity of deriving the true stress-strain relationships using instrumented conical or pyramidal indentation experiments. [105, 116, 117] It has been found that different combinations of yield stress and work hardening exponent can lead to the same load-displacement curve in a sharp indentation test, as shown in Figure 1.3.7. Therefore, the stress-strain relationship may not be uniquely determined from load-displacement curve of conical or experiments. [105]

# 1.3.2 Instrumented Spherical Indentation Experiments

# 1.3.2.1 Analyzing Methods

Since its inception by Brinell about 100 hundred years ago, spherical indentation techniques have been widely used to measure hardness of materials. [92, 118-121] In the spherical indentation test, a hard spherical indenter is pressed into a flat surface under a

30



normal load making impression. Hardness and reduced modulus can also be measured in instrumented spherical indentation test using equations 1.3.1 and 1.3.7.

In spherical indentation experiments, as in Berkovich indentation experiments, accurate determination of the contact area is crucial to the measurement of hardness and reduced modulus. In spherical indentation, the circle delimiting contact between the indenter and the indentation is usually not in the plane of the original surface but may be above or below it. The piling-up or sinking-in makes it difficult to determine the contact depth and area under indenters. Two types of methods, i.e., Norbury-Samuel's method and Oliver-Pharr's method, have been used to determine the contact area in spherical indentation experiments.

By imaging the indent profile after unloading using a microscope, Norbury and Samuel [122] found that the relationship between the contact radius, a, and the radius at the original surface, a' satisfies  $c^2 = a^2/a'^2$ , where  $c^2$  is a constant dependent only on the work hardening exponent, n,

$$c^{2} = \frac{a^{2}}{a^{2}} = \frac{5(2-n)}{2(4+n)}.$$
(1.3.16)

Hill et. al. [123] analyzed the Brinell indentation and claimed that Nobury and Samuels, observation are valid. Equation 1.3.16 has been widely used in spherical indentation test to determine contact area and material properties. [124-128] Evidently, according to equation 1.3.16, the piling-up and sinking-in depends on the work hardening exponent only, and it is independent of indentation depth and other material properties. However, recent finite element analysis shows that the extent of piling-up/sinking-in is a function of the applied load and material properties, such as yield stress, in addition to the work hardening exponent. [129, 130]

31



Oliver-Pharr's method [91] is another method that has been used to determine contact area in spherical indentation tests. For spherical indentation experiments, the contact area,  $A_c$ , is given by a simple geometry consideration: [131]

$$A_{c} = \pi (2Rh_{c} - h_{c}^{2}), \qquad (1.3.17)$$

where R is the indenter radius. The contact depth,  $h_c$ , is given by equation 1.3.3. Obviously, in the Oliver-Pharr method, contact depth,  $h_c$ , is assumed to be less than the maximum indention depth,  $h_{max}$ . Therefore, the Oliver-Pharr method applies only when sinking-in occurs. It underestimates the contact area when piling-up occurs.

# 1.3.2.2 Representative Strain for Spherical Indentation Experiments

Spherical indentation differs from Berkovich indentation in that the angle between the indenter and specimen surface changes during indenter penetration, as does the extent of the strain under the indenter. Tabor [132, 133] demonstrated that there was a depthsensitive representative strain,  $\varepsilon_r$ , that could be associated with spherical indentation experiment, expressed as:

$$\varepsilon_r = 0.2 \frac{d}{D} = 0.2 \frac{a}{R},$$
 (1.3.18)

where  $\alpha$  and d are the contact radius and diameter, respectively; R and D are the radius and diameter of the indenter, respectively. Tabor [92, 132, 133] also showed that, for some metals, the hardness, H, is about 2.8 times the true stress,  $\sigma_r$ , for a strain equal to the represent ative strain, i.e., the constraint factor, CF, is:

$$CF = \frac{H}{\sigma_r} = 2.8 \text{ when } \varepsilon_r = \varepsilon.$$
 (1.3.19)

where  $\mathcal{E}$  is the true strain and  $\mathcal{E}_r$  is the representative strain given by equation 1.3.18. Figure 1.3.8 shows the relationship between the representative strain ~ hardness and true stress~ true strain for spherical indentation in metals. [132] The correlation between spherical indentation experiments and uniaxial tensile data indicates that, using the concept of representative strain and constraint factor, spherical indentation experiments may possibly be used to measure the true stress-strain relationship. Compared with the tensile test, the spherical indentation experiment has the advantages in that it is nondestructive and can be conducted at small scale.

Francis [134] argued that spherical indentation in elastic/plastic materials evolves in three distinct stages — elastic, elastic-plastic, and fully-plastic, as shown in Figure 1.3.9. [125] The deformation is purely elastic when H/Y < 1.1, where H is the hardness and Y is the yield stress of the undeformed material. In the purely-elastic indentation range, the material around and underneath the indenter deforms elastically. The analytical solution to elastic indentation is given by the Hertzian equation: [113]

$$a = \left(\frac{3F_{\max}R}{4E^*}\right)^{1/3}$$
, when a << R, (1.3.20)

where a is the contact radius,  $F_{max}$  is the applied indentation load, R is the indenter radius, and  $E^*$  is the reduced modulus. When H/Y reaches 1.1, plastic deformation starts at a point below the center of the contact region. This occurs at a depth dependent on the strain hardening of the material, but is always close to 0.5a below the bottom of the indentation impression. In the elastic-plastic range, the plastic zone is surrounded by elastic ally strained material. When  $H/\sigma_r \approx 2.8$ , fully plastic deformation is established and  $H/\sigma_r$  remain approximately constant with increasing indentation depth. In the fully-plastic indentation range, the plastic zone reaches out to the surface and all the material around the indenter deforms plastically.

It has been found that the constraint factor increases when the indentation evolves from the elastic to the fully-plastic stage. Constraint factors from 1.1 to 3 have been used in deriving true stress-strain relationship using spherical indentation experiments, depending on the stages of the indentation experiments. [135-140] However, so far, there has been no systematic study of the limitation of using the constraint factor to derive the stress-strain relationship.

### **CHAPTER 2**

# ON THE STUDY OF MICROSCOPIC SHAPE MEMORY EFFECT, SUPERELASTIC EFFECT AND WEAR BEHAVIOR OF NITI ALLOY

### **2.1 INTRODUCTION**

NiTi alloys are well-known for the shape memory and superelastic effect. Since the first discovery of shape memory effect in NiTi in 1960's, [1-3] there have been extensive research efforts on both the fundamental understanding and industrial applications of NiTi alloys. Recent years have seen an increasing interest in using NiTi alloys for small-scale applications, including shape memory thin films for MEMs devices and, in this study, wear resistant surfaces. For example, shape memory alloys exhibit desirable wear properties under cavitation erosion [141-143] and dry sliding wear conditions. [20, 22, 23, 26-28] However, there exist few studies on the indentation behavior of NiTi alloys. [26, 29, 32] The indentation behavior of NiTi is interesting because (i) the indentation experiments may be used to characterize the shape memory **arrd** superelastic effect at small scale, which will be especially useful for characterization of NiTi films on substrates, and (ii) the loading condition in wear tests is very similar to that in indentation experiments. The indentation study of NiTi alloys can help us **unders**tand the wear behavior of NiTi alloys.

This chapter first presents a systematic study of shape memory and superelastic effect using instrumented indentation experiments to answer the following questions: (i) how does the indenter geometry influences the shape memory and superelastic effect (ii) what are the effects of indenter radius and indentation depth on the mechanical response of shape memory materials? In addressing these questions, a set of quantitative characterization methods using micro and nanoindentation techniques have been developed. Specifically, spherical and Berkovich and Vickers pyramidal indenters were used to determine the mechanical response of NiTi alloys over a wide range of indentation depths. The magnitude of the shape memory effect was quantitatively characterized by the thermal-induced depth recovery ratio of the residual indentation depth. The magnitude of the superelasticity was quantitatively characterized by the depth and work recovery ratios obtained from the load-displacement curves. It is found that (i) the magnitude of the shape memory and superelastic effects can be rationalized using the concept of the representative strain and maximum plastic strain, and (ii) instrumented indentation techniques, especially the spherical indentation experiments, are useful in quantifying shape memory and superelastic effects at micrometer and nanometer length scales.

In order to look into the possibility of using NiTi as a novel tribological material, dry sliding wear behavior of martensitic, austenitic and amorphous NiTi was studied under different loads using pin-on-disk wear test. It was found that the wear resistance of NiTi alloys increases in the order of martensitic, austenitic, and amorphous. The austenitic NiTi is less wear resistant than amorphous material although the former has a higher elastic recovery ratio. To make superelastic NiTi wear resistant, the surface ploughing needs to be prevented.

36

### 2.2 INSTRUMENTED INDENTATION EXPERIMENTS

#### 2.2.1 Sample Preparation and Experimental Methods

Melt-solidified NiTi shape memory (specimen BH) and superelastic (specimera BS) alloys were obtained from Shape Memory Application, Inc. (San Jose, California) in the form of 0.75mm and 0.43mm thick flat annealed sheets, respectively. The nominal composition of sample BH and BS is 50.8 at.% Ni, balance Ti, with oxygen and carbon levels below 0.17 at.% and 0.22 at.%, respectively. Characteristic phase transformation temperatures were measured using a TA Instrument 2929 Modulated Differential Scanning Calirometry at a heating and cooling rate of 5 K/min. Regular X-ray diffraction (XRD) measurements were carried out on a Siemens D500 diffractometer using Cu-K<sub> $\alpha$ </sub> radiation at 40 kV voltage and 30mA current. Microfocus XRD was carried out on a Simens D5000 diffractometer using a spot radius of 50 µm and Cu-K<sub> $\alpha$ </sub> radiation at 40 kV voltage and 30 mA current.

Samples were mechanically polished, finishing with a 0.25 µm diameter diamond paste, to give an average surface roughness of less than 50nm. Berkovich indentation experiments were conducted using a Nano Indenter XP from MTS System Inc.. A Berkovich diamond indenter was used to make indentation with residual depths ranging from 500 to 1000 nm. The tip radius of the rounded Berkovich indenter is less than 150 nm. Instrumented Vickers and spherical indentation experiments were conducted using a CSEM Hardness Tester from CSEM Instruments. A Vickers diamond indenter was used for residual depths ranging from 1000 to 6000 nm. Spherical diamond indenters with radii 213.4 and 106.7 µm, measured by scanning electron microscope (SEM) imaging, were used for instrumented spherical indentation experiments on the CSEM indenter. Both the applied load and indenter displacement were recorded during the entire loading and unloading cycle of instrumented indentation experiments. The indentation experiments were conducted at room temperature (25 °C).

To characterize the shape memory effect of specimen BH, 3-D profile of the spherical and Vickers indents were measured using a WYKO RST-Plus optical profilometer, while the profiles of Berkovich indents were measured by a tapping mode atomic force microscope (AFM) from Digital Instruments. After topographical characterization of indents, the samples were heated in air to 150 °C for 10 minutes to transform martensite phase into austenite phase and cooled back to ambient temperature. Profiles of the same indents were measured by the methods described above after thermal-induced recovery.

Tensile tests of specimen BH and BS were conducted using a United Testing System tensile tester. The gauge length was set at 20 mm and the displacement rate was 1 mm/min. Displacement of specimens during tensile test was monitored by a laser optical extensometer. The tensile experiments were conducted at room temperature (25 °C).

### 2.2.2 Results and Discussion

### 2.2.2.1 Transformation Temperatures and Structures

Transformation temperatures of specimen BH and BS were measured by differential scanning calirometry (DSC) tests, as shown in Figure 2.1. From DSC measurements, the rhombohedral "R-phase," martensite, and austenite start and finish temperatures ( $R_s$ ,  $R_f$ ,  $M_s$ ,  $M_f$ ,  $A_s$  and  $A_f$ , respectively) were determined and are summarized in Table 2.1. The martensite finish temperature of specimen BH is slightly

above room temperature (RT), which indicates that it is martensitic at room temperature. In specimen BH, the transformation enthalpies for austenite  $\rightarrow$ R-phase, R-phase  $\rightarrow$ martensite, and martensite  $\rightarrow$ austenite transition are 3.9, 11.3 and 23.1 J/g, respectively. In specimen BS,  $A_s < RT < A_f$  and  $R_f < RT < R_s$ , which indicates that BS sample is a mixture of B2 and R-phase at room temperature. The transformation enthalpies for austenite  $\rightarrow$ R-phase, and R-phase  $\rightarrow$ austenite transition are 3.4 and 4.4 J/g, respectively. X-ray diffraction patterns, Figure 2.2, shows that sample BH consists of B19' monoclinic martensite and BS consists a mainly of B2 austenite and a small amount of R-phase.

#### 2.2.2.2 Shape Memory Effect of Indents

The shape memory effect arises from the recovery of strain during transformation of a deformed martensite to austenite upon heating. In this study, recovery effect of indents was determined from surface profile measurements by defining a thermal-induced recovery ratio,  $\delta$ , as

$$\delta = \frac{h_f - h_f}{h_f},\tag{2.1}$$

where  $h_f$  is the residual indentation depth recorded immediately after unloading and  $h_f$ is the final indentation depth after the completion of thermal-induced recovery. A schematic illustration of the thermal-induced recovery of the indent is shown in Figure 2.3.

#### 2.2.2.2.1 Berkovich and Vickers Indents

Figures 2.4(a-b) show the profile of the Berkovich and Vickers' indents or specimen BH (shape memory NiTi) before and after heating. The thermal-induced recovery ratio of Berkovich and Vickers indents is plotted in Figure 2.5. The recovery ratio of both Berkovich and Vickers indents on specimen BH is about 0.34 and is depth independent from 500 to 6000 nm.

### 2.2.2.2.2 Spherical Indents

The geometries of the spherical indenters with radius of 213.4 and 106.7 µm are shown in Figure 2.6(a) and (b), respectively. The tip radius was measured by SEM imaging. For specimen BH, a spherical indenter with 213.4µm radius (Figure 2.6(a)) was used. Optical micrographs of spherical indents on specimen BH before and after heating, Figure 2.7(a) and (b), show the recovery of indents. To quantitatively characterize the recovery effect, 3D profiles of indents were measured using a WYKO optical **profilometer**. Figure 2.7 (c) and (d) shows the 3D profile of an indent made at 8 N before **and** after heating, respectively. Residual indentation depths of the indent before and after **heating** were obtained from 3D profile of the indents, and the thermal-induced recovery **ratio** was calculated using equation (2.1). The relationship between the thermal-induced **recovery** ratio and the residual indentation depth is presented in Figure 2.7 (e). It is **evident** that shallow indents disappeared completely after heating, while deep indents **recove**red almost completely. The magnitude of recovery is a function of indentation **depth** for a given spherical indenter radius. The concept of representative strain is invoked to present the depth-dependence of recovery ratio for spherical indentation in shape memory alloys. For a spherical indenter of radius R, the representative strain,  $\varepsilon_r$ , associated with the indentation experiment is given by: [92]

$$\varepsilon_r = 0.2a/R, \qquad (2.2)$$

where *a* and *R* are the contact radius and indenter radius, respectively. The representative strain is dimensionless. Cross-section profiles of the spherical indents produced at 10 N and 25 N load are illustrated in Figure 2.8, which shows that no material piling-up occurs even at the maximum applied load of 25 N. A schematic illustration of the indentation sinking-in and meaning of the symbols are shown in Figure 2.9. The contact depth,  $h_c$ , can be calculated from load-displacement curves using the Oliver-Pharr method, [91] since no material piling-up occurs in this study. Specifically, the contact depth is obtained from:

$$h_c = h_{\max} - 0.75(F_{\max}/S),$$
 (2.3)

where  $h_{max}$  is the penetration depth at the maximum load,  $F_{max}$ , and S is the initial unloading stiffness calculated from the unloading curve. The contact radius is determined from the geometry and is given by:

$$a = \sqrt{2h_c R - h_c^2} , \qquad (2.4)$$

The relationship between the representative strain and thermo-activated recovery ratio is plotted in Fig. 2.10. It is evident that the recovery ratio is constant and close to 1 when the representative strain is lower than a maximum recoverable representative strain of

about 0.047. The thermally induced recovery ratio starts to decreases with increasing representative strain when the representative strain exceeds a critical value.

The true stress-strain curve from tensile test for the same NiTi shape memory alloy is also shown in Fig. 2.10. It exhibits the well-known behavior that includes, with increasing strain, initial elastic deformation, twinning deformation, and, finally, additional elastic deformation plus plastic deformation due to dislocation activitiy.[5] The twinning deformation corresponds to the plateau region in the stress-strain curve, while dislocation slip starts at the end of the stress plateau. The strain at the end of the stress plateau is regarded as the critical strain for complete recovery. For specimen BH, a critical strain of about 0.047 corresponds to the maximum recoverable strain upon heating in the uniaxial tensile experiment. Fig. 2.10 also shows that the *maximum recoverable representative strain* from spherical indentation coincides with the critical strain in a tensile experiment. This observation suggests that spherical indentation can be used to probe the maximum recoverable strain for the shape memory effect, especially for sample configurations where tensile measurements become impractical.

### 2.2.2.3 Superelasticity under Indentation

In this study, the indentation-induced superelastic effect was characterized by the depth- and work-recovery ratio measured directly from indentation load-displacement curves. A schematic representation of the elastic recovery due to removal of the load is shown in Figure 2.11. The depth recovery ratio is defined as:

$$\eta_h = \frac{h_{\max} - h_f}{h_{\max}}, \qquad (2.5)$$

where  $h_{\max}$  is the indenter displacement at maximum indentation load,  $h_f$ , is the residual indentation depth at which the load becomes zero during unloading. The work recovery ratio,  $\eta_w$ , is defined as:

$$\eta_{w} = \frac{W_{u}}{W_{t}} = \frac{\int_{h_{f}}^{h_{max}} Pdh}{\int_{0}^{h_{max}} Pdh}$$
(2.6)

where  $W_i$  is the total work done during loading and  $W_u$  is the reversible work during unloading.

### 2.2.2.3.1 Berkovich Indentation

Figure 2.12(a) shows the load-displacement curves of Berkovich indentations in specimen BS (superelastic NiTi) and annealed copper. Copper was chosen as the comparison material because it represents metals having elastic-plastic behavior. Figure 2.12(b) shows the depth and work recovery ratio of Berkovich indentation at various depths. Evidently,  $\eta_w$  and  $\eta_h$  for specimen BS are about 0.45, which is significantly larger than the value of 0.08 measured for copper. Both the depth and work recovery ratios are depth independent.

### 2.2.2.3.2 Spherical Indentation

Load-displacement curves for spherical indentation (R=213.4 $\mu$ m) on specimen **BS** and copper are shown in Figure 2.13(a). It is evident that the specimen BS displays a **much** greater recovery ratio than that of copper. The depth recovery ratio and
representative strain, together with the true stress-strain curve of specimen BS, are shown in Figure 2.13(b). By comparing the recovery ratios from two radii of 106.7 and 213.4µm in Figure 2.13, it is evident that the depth recovery ratio indeed scales with the representative strain and is independent of the tip radius. Contrasting with Berkovich indentations, the magnitude of both the depth and work recovery ratios is significantly greater under spherical indentation conditions compared to the Berkovich indents. The recovery is nearly complete when the representative strain is less than a maximum recoverable representative strain of about 0.05.

To explore the mechanism of the high recovery ratio, a microfocus XRD experiment on a Rockwell C indent made in specimen BS was carried out to study indentation-induced phase transformation behavior. Figure 2.14 (a) and (b) shows the XRD spectra of the non-indented area, and the area inside the indent, respectively. The (002) diffraction peak of martensite phase appears in the indented area, which indicates that the austenite  $\rightarrow$  martensite phase transformation was induced by the applied indentation load. Superelasticiy can therefore occur under the indentation loading conditions. As we know from the uniaxial tensile test that this transformation is associated with a large reversible strain. The appearance of martensite in the indented area and can't transform back to the austenite phase when the load is removed, which corresponds to the irreversible part in the load-displacement curves.

The plateau in the true stress-strain curve of the superelastic NiTi alloy (specimen BS) results from a stress-induced-martensite phase transformation. For specimen BS, a **Cri**tical strain of about 0.05 corresponds to the maximum recoverable strain below which

a completely reversible phase transformation from martensite to austenite can occur upon unloading in the tensile experiment. Figure 2.13(b) shows that the maximum recoverable representative strain from spherical indentation coincides with the critical strain in the tensile experiment. Dislocation slip is initiated when the strain is greater than the critical strain. Accordingly, the depth recovery ratio decreases with increasing representative strain once the representative strain exceeds the critical strain of 0.05. This observation suggests that spherical indentation can be used to probe the maximum recoverable strain by the superelastic effect.

#### 2.3.3 Representative Strain and Strain Distribution under Indenters

For ideally sharp pyramidal or conical indenters, the representative strain is determined by the face angles. Since no length scale is involved in describing the indenter geometry, the representative strain is independent of indentation depth. For Berkovich and Vickers indentations in elastic-plastic solids the representative strain is approximately 0.08 for all indentation depths. [113] Hence, it is reasonable to expect that, for ideal Vickers and Berkovich indenter, both the shape memory and superelastic recovery ratios should be independent of indentation depth, provided that there is no other length scale involved in describing the indenter geometry. However, for real Berkovich and Vickers indenters, which will have some degree of tip blunting, recovery ratio is expected to be close to that of spherical indentations when the indenters). Tip blunting needs to be taken into account when doing shallow indentation measurement **Using Berkovich or Vickers indenter**. The constant recovery ratio observed in this study

indicates that the effect of tip blunting is insignificant when the indentation depth is greater than 500nm, which is consistent with the fact that the tip radius of the Berkovich indenter is about 150nm.

For spherical indentation in elastic-plastic solids, the representative strain produced is not constant but varies with contact radius according to 0.2a/R. [91, 92, 133] Since the contact radius increases with increasing indentation load, so does the representative strain. For specimens BH and BS, shape memory and superelastic effects under uniaxial tension or compression exist only up to a maximum recoverable strain of 0.05. We can therefore expect that, in spherical indentation experiments, the recovery ratio decreases with indentation depth when the representative strain exceeds the recoverable strain limit.

In is instructive to note that the recovery ratios are much larger for spherical indentation than that for pyramidal indentation at the same representative strain of 0.08. This difference may be related to the magnitude and the spatial distribution of the maximum stress and strain for the two indenter geometries. Indeed, using finite element analysis, Mata *et al.* [115] showed that the plastic strain level attained directly underneath sharp indenter tips can be as high as 2.5 for elastic-plastic solids. The maximum plastic strain for sharp indenters in annealed copper is less than 0.1 under spherical indentation [144] when the a/R value is less than 0.3, which is about the maximum a/R in this study.

In this work, finite element modeling was used to study the strain distribution under sharp and spherical indenters at a representative strain of 0.08. A detailed description of the mesh and boundary condition for the finite element modeling will be

presented in Chapter 4. The stress-strain response of specimen BH obtained from tensile tests was used to determine the relevant constitutive parameters for finite element modeling. Figure 2.15(a) shows the strain distribution under a conical indenter with 70.3° half-angle, in which the representative strain is 0.08. Figure. 2.15(b) shows the strain distribution under a spherical indenter with representative strain of 0.08. It is found that the maximum plastic strain under conical indenter (half angle = 70.3°) is 0.79; while it is 0.18 for spherical indentation at the representative strain of 0.08. The blank region under the conical indenter indicates the region with a strain larger than 0.18. Thus, a sufficiently large volume of material directly under the pyramidal indenter is so highly strained that significant deformation occurs by dislocation motion, which deteriorates the shape memory and superelastic effect. It appears that the strain under the spherical indenter is largely accommodated by martensite twinning in the shape memory NiTi alloy or by stress-induced martensite transformation in the superelastic NiTi alloy, leading to large shape memory and superelastic effects, respectively.

#### **2.3 DRY SLIDING WEAR BEHAVIOR OF NITI ALLOYS**

#### **2.3.1 Sample Preparation and Experimental Methods**

Dry sliding wear behavior of NiTi alloys with different structures, i.e., martensite (specimen BH), austenite (BS) and amorphous NiTi thin film, was studied. The surface finish of specimen BH and BS for the wear test was the same as in the indentation test (see section 2.3.1). An amorphous TiNi thin film was deposited on a surface-oxidized (100) silicon substrate by DC magnetron sputtering. The target material was Ni<sub>51</sub>Ti<sub>49</sub> **augmented** with pure Ti inserts, as shown in Figure 2.16. The base pressure achieved was

better than  $6 \times 10^{-6}$ Pa. Argon with purity of 99.99% was used as the working gas and the working pressure is 0.533Pa. The working distance between the target and the substrate was 64mm. The substrate temperature was measure by a K-type thermocouple placed in contact with the backside of the substrate. The substrate temperature was maintained at 300°C by a built-in substrate heater in the chamber. The target was pre-sputtered for 30 minutes before deposition to obtain stable output flux. The thickness of the amorphous film, measured by scanning electron microscope, was 4 $\mu$ m.

The Berkovich indentation test was carried out at a maximum load of 36mN and the testing method was the same as described in section 2.3.1. Pin-on-disk dry sliding wear tests were performed using an Implant Science ISC-200 Tribometer. Wear tests were conducted in air at room temperature with a sliding velocity of 0.045m/s. The applied load ranged from 0.245N to 4.9N. The pins were made of 52100 steel and were 3.175 mm in diameter. Young's modulus and Poisson's ratio of the pin were 210GPa and 0.3, respectively. The cross-section area of the wear track after 200 revolutions was measured using a Wyko RST Plus optical surface profilometer and wear rate was calculated accordingly.

#### 2.3.2 Results and Discussion

A XRD  $\theta$ -2 $\theta$  scan of the as-deposited NiTi thin film is shown in Figure 2.17. A broad diffuse peak around 42° indicates the short-range ordered structure of amorphous NiTi. Differential scanning calirometry (DCS) test shows a crystallization temperature of 453°C for the amorphous film.

Figure 2.18 shows the load-displacement curves of specimenw BH, BS and amorphous thin film from nanoindentation test with a Berkovich tip. Mechanical properties, such as hardness, Young's modulus and depth recovery ratio, were obtained from the nanoindentation test and listed in Table 2.2. Sample BS, which consists mainly of austenite, shows a higher hardness, Young's modulus, and ratio of reversible work to total work than martensitic NiTi (specimen BH). The hardnesses of specimens BH and BS were 2.5 and 4.4GPa, respectively. The amorphous NiTi thin film has the highest hardness at 7.9GPa, although its work recovery ratio is lower than that of specimen BS.

Wear loss v.s load of specimens BH, BS, and amorphous NiTi thin film are plotted in Figure 2.19. It is not surprising that specimen BS has a better wear resistance than specimen BH because specimen BS has a higher hardness and a larger ratio of reversible work to total work than that of specimen BH. The amorphous NiTi thin film displayed the best wear resistance due to its high hardness.

Figure 2.20 (a) and (b) show microfocus XRD collected outside the and inside the wear track, respectively, of specimen BS. As in the indentation test, the martensite (002) peak appears after the wear test, which indicates that martensite was stress-induced during the test. Specimen BS, despite its superelasticity and high elastic recovery ratio, does not provide better wear resistance than an amorphous thin film. It is believed that ploughing of materials during sliding wear deteriorates the recoverability of superelastic NiTi.

#### **2.5 CONCLUSIONS**

Microscopic shape memory and superelastic effects exist under indentation loading conditions (e.g., spherical and pyramidal indentations). The magnitude of indentation recovery for martensitic and austenitic NiTi alloys has been studied. It can be conclude that:

(1) Both the shape memory and superelastic recovery ratios are independent of depth under Berkovich and Vickers indenters,

(2) The recovery ratio of spherical indents depends on the representative strain. It remains constant when the representative strain is below the critical strain for maximum recovery. The recovery ratio decreases with increasing representative strain when it exceeds the critical strain for maximum recovery.

(3) At the representative strain of 0.08, the recovery ratios are lower for sharp indenters than that for spherical indenters, which is attributed to the different strain level under the indenter. The maximum plastic strain under Berkovich indenter is much higher than that under the spherical indenter.

(4) Instrumented indentation, especially instrumented spherical indentation, offers a new method for studying shape memory and superelasticity at micrometer and nanometer length scales.

(5) Indentation-induced and wear-induced martensite is formed during indentation and wear test, respectively.

(6) Dry sliding wear resistance of martensitic, austenitic and amorphous NiTi are compared. The wear resistance of the austenitic NiTi is not as good as the amorphous

NiTi although the former has a higher recovery ratio. To use  $\leq uperelastic$  NiTi as a tribological material, the surface ploughing needs to be prevented.

(7) The austenitic NiTi sample  $\mathbb{B}S$  used in this study is not perfected for superelasticity because the sample consists of both austenite and R-phase at the test temperature. A higher recoverability and better wear resistance would be expected in an austenitic NiTi with martensite start temperature slightly higher than test temperature.

#### CHAPTER 3

# IMPROVE THE ADHESION AND WEAR RESISTANCE OF CHROMIUM NITRIDE COATING ON ALU MINUM SUBSTRATE USING A SUPERELASTIC INTERLAYER

#### **3.1 INTRODUCTION**

Various hard coatings have been developed to protect soft substrates from wear loss. [61, 145] Both high hardness and good adhesion are critical in making good wear resistant coatings. One approach to increase the load-carrying ability is to grow a thicker coating so that the applied load will be distributed mostly in the hard phase. However, it is usually the case that the hard coating and soft substrate exhibits charmatic mismatch of Young's modulus and coefficient of thermal expansion. This can lead to large residual stresses, especially when high temperature processing is involved. The interfacial shear stresses increase with increasing coating thickness and cause the failure in the at the interface. Therefore, an interlayer, which has a good mechanical and the match with both the hard coating and the substrate, is often grown to improve the adhesion. [72, 146]

Hardness has traditionally been regarded as a primary parameter controlling wear resistance. However, recent studies suggested that the ratio of hardness to modulus,  $\frac{H}{E}$ , also plays an important role in determining wear resistance. It was found that high  $\frac{H}{E}$  is beneficial to wear resistance. [84] In addition, finite element modeling of the indentation experiments shows that  $\frac{H}{E}$  is proportional to the work or depth recovery ratio. [106] Therefore, it will be desirable to make tribological coatings having high hardness and depth recovery ratio.

This chapter focuses on the novel tribological application of superelastic NiTi films as interlayer materials between hard coating and soft substrates. The purpose of this study is to develop a novel wear resistant material by taking advantage of the high hardness of the surface coating and high depth recovery ratio of the superelastic NiTi interlayer. Indentation, scratch, and pin-on-disk wear test were conducted to study the hardness, adhesion, and wear behaviors of this novel layered composite material. Tribological behavior of samples with other interlayer materials and different coating thickness was compared. It was found that the superelastic NiTi interlayer can dramatically improve adhesion and wear resistance of hard coatings on soft substrates.

# 3.2 SAMPLE PREPARATION AND EXPERIMENTAL METHODS

MPLE PREPARATION Austenitic NIII, marcant materials between a CrN hard coating and an aluminum substrate. Descriptions of the specimens are shown in Table 3.1. Substrate material was 6061-T6 aluminum plate, 20mm×20mm×3mm in size. The aluminum plate was polished through 0.25 µm diameter diamond paste and subsequently ultrasonically cleaned in acetone and methanol. NiTi thin films were deposited on both aluminum and silicon (100) substrate by DC magnetron sputtering, the latter for use in DSC and XRD experiments. A schematic structure of the DC magnetron sputtering equipment for NiTi thin film deposition is shown in Figure 3.1. The base pressure achieved was better than 2.7×10<sup>-5</sup> Pa. An austenitic NiTi thin film was

deposited from Ni49.8Ti target; while martensitic NiTi thin films was deposited from Ni<sub>48</sub>Ti target. The target was pre-sputtered for 30 minutes before sputter deposition to obtain stable plasma. Working **pr**essure was set at 0.33Pa and working distance between the target and substrate was 64rm. Substrate temperature was controlled by a built-in substrate heater in the chamber. Argon of 99.99% purity was used for the generation of plasma. NiTi film was deposited at a substrate temperature of 300°C for 60 minutes at a deposition rate of 1.1nm/s. The films were annealed at 550°C for 60 minutes right after deposition to crystallize the films. Thickness of the film was determined by measuring the step of the masked area using a WYKO surface profilometer. The NiTi coated 6061-T6 aluminum was then transferred to a TEER unbalanced magnetion sputtering system. The specimens were sputter-cleaned in argon atmosphere for 60 seconds. A CrN coating was made by depositing from two pure chromium targets of 99.99 % purity in a nitrogencontaining argon environment. The base pressure of the system  $\sim as 8 \times 10^{-4}$  Pa and the pressure during the deposition was 0.13Pa. The working gas was a proprietary mixture of 99.99% pure argon and 99.99% pure nitrogen. The nitrogen gas flow rate 150V bias applied to the substrate.

CrN films were upped Composition of the NiTi film was measured by wet chemical analysis. Specifically, samples were dissolved with nitric and hydrofluoric acid and measurements were made by inductively coupled plasma optical emission microscopy (ICP/AES). Characteristic phase transformation temperatures of NiTi thin film were determined using a TA Instrument DSC 2929 Modulated differential scanning calorimeter (DSC). The temperature ranged from -50°C to 200°C under a controlled heating/cooling rate of

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5K/min. X-ray diffraction (XRD) measurements were carried out t on a Siemens D500 diffractometer using Cu-Ka radiation at 40 kV voltage and 30mA current.

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Indentation properties (e.  $\mathscr{B}$ ., hardness, Young's modulus and the recovery ratio) of were measured using the Nano XP instrument from MTS with a Berkovich diamond indenter and a spherical diamond indenter with nominal radius of  $10\mu m$ . The applied indentation loads ranged from 5mN to 200mN to test the mechanical properties at various indentation depths.

Adhesion strength of the coatings was evaluated by scratch tests using a CSEM micro-scratch tester. A progressive load from 0 to 6N was applied to scratch all the samples. The spherical scratch indenter had a tip raclius of 213.4 µm. The scratch scars were observed using a Hitachi S4000 scanning electron microscope (SEM) to evaluate the adhesion.

Pin-on-disk dry sliding wear tests were carried out on an Implant Science tribometer (Model ISC-200), using a tungsten carbide ball of 3.17 Smm in diameter under an unlubricated condition. The applied load was 1N and the sliding speed was 0.08m/s in tests varied between 3000 and 101,000 cycles, depending on the wear 3000m/s in specimens. The friction coefficient was recorded during the wear test. The wear rate was measured with a Wyko optical surface profilometer. Indentation, scratch, and wear tests were all conducted at room temperature (25°C).

p B pr Pe S2

## 3.3 RESULTS AND DISCUSSION

#### 3.3.1 Structure Characterization

The NiTi film deposited from the Ni<sub>49.8</sub>Ti<sub>50.2</sub> target was found to be Ni-rich with a composition near Ni<sub>51.8</sub>Ti<sub>48.2</sub> (specimen S1). The film deposited from the Ni<sub>48</sub>Ti<sub>52</sub> target was found to be slightly Ti-rich with a composition near Ni <sub>49.5</sub>Ti<sub>50.5</sub> (specimen S2). It is apparent that about 1.5 ~ 2 at.% of titanium was lost during the sputtering process.

The as-deposited NiTi thin film was amorphous and it was subsequently annealed to crystallize it. From DSC measurements, the rhombohedral "R-phase", martensite, and austenite start and finish temperatures  $(R_s, R_f, M_s, M_f, A_s \text{ and } A_f, \text{ respectively})$  were determined. DSC curves of specimen S1 and S2 are shown in Figure 3.2(a) and (b), respectively. The composition and phase transformation temperature of the two types of NiTi films are listed in Table 3.2. For specimen S1,  $A_s$  is  $1^{\circ}$ C and  $A_f$  is  $15^{\circ}$ C in the heating cycle;  $R_s$  is  $8^{\circ}$ C and  $R_f$  is  $-4^{\circ}$ C in the cooling cycle. Therefore, specimen S1 should be austenitic at room temperature. Specimen S2 has a much higher transformation temperature than that of specimen S1. The martensite finish temperature of indicates that it should be martensitic at room temperature.

indicates that it should be matched XRD of specimen S1 and S2, shown in Figure 3.3, confirms the above predictions. Specimen S1 shows a (110) diffraction peak from the austenite phase with a B2 structure. The (122) diffraction peak of Ni<sub>4</sub>Ti<sub>3</sub> also appears, which was formed by precipitation process during annealing. The (020), (111), (002), and (021) diffraction peaks from NiTi martensite phase, which has a monoclinic structure, appear in specimen S2. CrN coating was deposited on the top of specimen S1, SZ = the Cr interlayer andbase aluminum substrate, in each case after sputter cleaning for 60 seconds. An XRD pattern of the specimen with 5µrn thick CrN coating on aluminum substrate (specimen CrN5-Al) is shown in Figure 3.4. The weak peaks at  $2\theta=37.1^{\circ}$ , 43.5° and 75.5° are indexed as (111), (200) and (311) diffraction of CrN, respectively.

#### **3.3.2 Mechanical Properties**

#### 3.3.2.1 Indentation Test

Indentation properties of the coatings and substrate, such as hardness, Young's modulus and recovery ratio, were obtained by instrumented indentation experiment. Hardness, H, and reduced Young's modulus,  $E^*$ , were determined from the maximum load and initial unloading slope of the unloading curve using Oliver-Pharr's method. [91] The depth recovery ratio,  $\eta_h$  is defined as the ratio of recoverable indentation depth to indenter displacement at maximum load:

$$\eta_h = \frac{h_{\max} - h_f}{h_{\max}}$$

where  $h_{max}$  is the indenter displacement at maximum load while  $h_f$  is the (3.1) indentation depth after unloading. Hardness,  $H/E^*$  and  $\eta_h$  represent the strength and elasticity of the materials.

Load-displacement curves of Berkovich indentation tests on an  $606_{1-T6}$ aluminum substrate, 4 µm thick auetenitic NiTi film on a Si substrate (specimen S1), 4 µm thick martensitec NiTi film on a Si substrate (specimen S2), 4 µm thick Cr on a Si substrate, and 5µm thick CrN coating on a 6061-T6 aluminum substrate are shown in Figure 3.5(a). The indentation depths were less than 10 percent race f the film thickness to minimize the influence of substrates on coating property measurements. From the loaddisplacement curve of a Berkovich indentation test both hardness and Young's modulus can be calculated using Oliver-Pharr's method, [91] as discussed in section 1.3.1.1. Mechanical properties obtained from the nanoindentation test are listed in Table 3.3. The hardness and Young's modulus of the CrN coating (23GPa, 257GPa) are much larger than those of the aluminum substrate (0.94GPa, 77.6GPa). There exists a large mechanical mismatch between the CrN hard coating and aluminum substrate. However, the Young's modulus of specimen S1 (95GPa) and specimen S2 (89.3GPa) are not very different from that of the aluminum substrate (77.6GPa).

For the interlayer and substrate materials, the hardness decreases in the order of Cr, S1, S2 and Al, while the depth recovery ratio decreases in the order of specimen S1, Cr, specimen S2, and aluminum. The depth recovery ratio of superelastic NiTi film (specimen S1) is higher than that of martensitic NiTi film (specimen S2), which is consistent with the observation of bulk NiTi alloys in section 2.1.4. Figure 3. that there exists an approximately linear relationship between the depth recovery ratio,  $\eta_h$ , and the ratio of hardness to reduced modulus,  $\frac{H}{E^*}$ . Clearly, Figure 3.5(b) shows that the depth recovery ratio depends on both hardness and Young's modulus of the tested materials. A material with low hardness may have high depth recovery ratio if it has a small Young's modulus. As is observed that the austenitic film (specimen S1, H=4.7 GPa, E=318.4GPa) although the former has a lower hardness. A similar relationship between the depth recovery ratio and  $\frac{H}{E^*}$  has been reported by Cheng and Cheng based on the finite element calculation. [147]

For all the CrN coated Composite coatings, the composite hardness and depth recovery ratio were also calculated from the indentation load-displacement curves and the results are shown in Figure 3.6. It was found that the composite hardness and work recovery ratio are strongly dependent on interlayer materials, coating thickness and indentation depth. The 5µm CrN coated aluminum (specimen CrN5-Al) shows much higher composite hardness and, accordingly, better load-carrying ability than the 1µm CrN coated aluminum (specimen CrN1-Al). The specimen with austenite NiTi interlayer (specimen CrN-S1-Al) has a larger work recovery ratio than the specimen with martensitic NiTi interlayer (specimens CrN-S2-Al) and Cr interlayer (specimen CrN-Cr-Al), although specimen CrN-Cr-Al has larger composite hardness.

The large recovery ratio of specimen CrN-S1-Al arises from the superclastic NiTi interlayer. A large recovery ratio of sharp and spherical indents on austenitic NiTi alloy and indentation-induced martensite transformation were noted in section 2.3. The reversible strain can be up to as large as several percent in uniaxial tensile  $t_{est}$ .  $S_{trees}$  induced phase transformation under indenter has also been observed  $u_{sing}$   $T_{EM}$  and superclasticity occurs under the indentation loading condition. [29]

### 3.3.2.2 Adhesion Test

The interfacial adhesion strength of the CrN coated specimens was compared qualitatively by observing the scratches using SEM imaging. SEM images of the end of the scratches are shown in Figure 3.7. Flakes of delaminated CrN coating at the scratch end are observed on specimen CrN1-Al, CrN5-Al and CrN-S2-Al. The coating delamination occurs as a result of the compressive stress field ahead of the indenter. Cracks caused by bending are a lso observed inside the scratch scar on specimen CrN-S2-Al. As shown in Figure 3.7 (a) and (b), increasing the thickness of the CrN hard coating has little beneficial effect on improving interfacial adhesion. Nevertheless, no delamination occurs at the end of the scratches on specimens with Cr interlayer and superelastic NiTi interlayer, as shown in Figure 3.7(d) and (e). Specimens with austenitic NiTi and Cr interlayers, i.e., specimens CrN-S1-Al and CrN-Cr-Al, show better adhesion despite the fact that they have lower composite hardness than that of CrN5-Al.

Specimen with austenitic interlayer (CrN-S 1-Al) shows much better adhesion than specimen with martensitic NiTi interlayer (CrN-S2-Al) does, although there is little chemistry difference between the interlayer materials. The different interfacial adhesion strength must be due to the different mechanical properties of the austenitic and martensitic NiTi. As is known that martensitic NiTi is highly plastic and a residual strain is left when the applied stress exceeds its elastic limit of less than one percent. Nevertheless, the austenitic NiTi is superelastic and its deformation is reversible. No residual deformation is left when the load is removed, and the reversible strain can be as large as several percent. The improved adhesion may be attributed to the large reversible strain of the superelastic NiTi.

The stress-strain curve of the superelastic NiTi alloy bears some similarities to that of elastomeric polymer adhesives, as shown in Figure 3.8. [5, 148] A detailed comparison of the mechanical properties of superelastic NiTi and a typical elastomeric polymer (e.g., polyisoprene) is listed in Table 3.4. Obviously, both of them have large

elastic strain without permanent deformation, and a hysteresis associated with the loading-unloading cycle. [5, 1 48] However, the elastic modulus and strength of the superelastic NiTi alloy are several orders of magnitude greater than that of the polymeric adhesives, which indicates that the superelastic NiTi material may act as a high strength rnetallic adhesive for bonding ceramic coatings to ductile substrates. This study demonstrates that the superelastic NiTi indeed functions as good bonding material. Furthermore, it is speculated that other materials with large reversible strain can potentially be good bonding materials.

A chromium interlayer can provide good ad hesion between CrN and aluminum substrate as well. However, as will bee seen in the next section, the wear resistance of the composite coating with Cr interlayer is not as good as the composite coating with superelastic NiTi interlayer.

#### 3.3.2.3 Dry Sliding Wear test

The durability, friction coefficient and wear rate of the suite of wear specimens were measured by pin-on-disk wear tests. Figures 3.9 (a) and (b) shows the change of friction coefficient during pin-on-disk test. Figures 3.9(a) shows that specimen CrN-S2. Al and CrN1-Al fail after 1100 and 3000 cycles, respectively, which is indicated by a sudden increase in the friction coefficient. The worn surface was observed using WYKO surface profilometer and SEM microscopy. It was found that the CrN hard coating has been cort through, exposing aluminum substrate. The poor adhesion of the single CrN coating with aluminum substrate and martensitic NiTi interlayer leads to premature failure of the coating. The 5µm CrN coated aluminum (specimen CrN5-Al) shows much longer lifetime (the test was halted before failure) than the  $1\mu$ m CrN coated aluminum (specimen CrN1-Al). By increasing the thickness of the CrN hard coating, the durability can be increased dramatically due to the increased hardness and load-carrying ability. Durability of the coating can also be improved using Cr or superelastic interlayer, as shown in Figure 3.9(b).

Interestingly, the composite coating with superelastic interlayer (specimen CrN-S1-Al) shows a lower friction coefficient than that with the Cr interlayer (specimen CrN-Cr-Al) in both sliding wear test (Figure 3.9) and scratch test (Figure 3.10), although they have the same surface chemistry and specimen CrN-Cr-Al has a higher hardness. The friction coefficient,  $\mu$ , is defined as the ratio of the tangential force,  $F_i$ , to the normal force,  $F_n$ :

$$\mu = \frac{F_{\prime}}{F_{\pi}} \tag{3.2}$$

If no elastic recovery occurs inside the wear track formed by the sliding indenter, Figure 3.11(a), the tangential force should balance with two types of forces: In adhesion force,  $F_a$ , developed at the contact area between the two contact surfaces, and a deformation force,  $F_d$ , needed to plough into the material, i.e., [80, 82]

$$F_t = F_a + F_d \tag{3.3}$$

The adhesion force is given by

$$F_a = A\tau \tag{3.4}$$

where  $\checkmark$  is the true contact area between the two surfaces and  $\tau$  is the shear stress of the junction formed at the contact area. In this study, the junction shear stress should be the same since they have the same surface coating. The contact area increases with

decreasing hardness. Therefore, specimen with superelastic interlayer (CrN-S1-A1) should have a larger contact area and adhesion force than specimen with Cr interlayer (CrN-S1-Al) since the former has a lower hardness. For the configuration shown in Figure 3.11(a), the deformation force,  $F_d$ , was found to be dependent on the true contact area. [149] The larger the true contact area, the more material needs to be ploughed into, and the larger the deformation force. A low hardness will lead to high deformation force. Therefore, materials with low hardness should show larger tangential force and friction coefficient if elastic recovery effect is not considered. This is contradictory to what was observed in this study.

If the elastic recovery inside the wear track is taken into account, Figure 3.11(b), the tangential force should balance with an extra pushing force,  $F_p$ , which acts in the same direction as the tangential force,

$$F_t = F_a + F_d - F_p \tag{3.5}$$

The change of the tangential force due to the elastic recovery will depend on the relative contribution from the pushing force and adhesion force. The friction coefficient will decrease if the contribution from pushing force is dominant. The extent of the elastic recovery is directly proportional to the depth recovery ratio measured by indentation tests.

In addition, materials in front of the indenter either pile up (Figure 3.12(a)) or sink in (Figure 3.12(b)) when the indenter is forced into materials. A larger deformation force is required when piling-up occurs, while a smaller deformation force is needed when sinking-in happens. Finite element simulation of the indentation experiments shows that, for highly elastic material (high  $\frac{H}{E^*}$  or large depth recovery ratio), material around the indenter tends to sink-in. However, for highly plastic material (low  $\frac{H}{E^*}$  or small depth recovery ratio), material around the indenter tends to pile-up. [97] Therefore, it is expected that, compared to specimen with superelastic interlayer (CrN-S1-Al), specimen with Cr interlayer (CrN-Cr-A1) tends to pile up since the latter has a smaller depth recovery ratio. To study the extent of piling-up/sinking-in during sliding test, WYKO surface profilometer was used to measure the profiles of the scratches on specimen CrN-S1-Al and CrN-Cr-Al, as shown in Figure 3.13. As expected, less material piles up along the edge and at the end of the scratch in specimen CrN-S1-Al than that in specimen CrN-Cr-Al.

Therefore, friction coefficient is a function of hardness, elastic recovery, and material piling-up/sinking-in. However, there exists no theory linking the friction coefficient with these parameters. A better understanding of the friction coefficient requires extensive numeric modeling of the sliding process. This study demonstrates that, friction coefficient of tribological coatings can be reduced using an interlayer with high H/E (or large depth recovery ratio).

The wear loss of all the composite coatings was shown in Figure 3.14. For specimen CrN1-Al and CrN-S2-Al, the wear loss was measured after failure of the coating. For specimen CrN-S1-Al, CrN-Cr-Al, and CrN5-Al, the wear loss was measured when the wear tracks were about 0.5 micrometer deep. Note that the aluminum substrates of specimen CrN1-Al and CrN-S2-Al were exposed and the wear loss does not truly represent the abrasive loss of the CrN coating itself. Specimen CrN-S1-Al shows a lower wear loss, 540 nm<sup>2</sup>/N, than that of CrN-Cr-Al, 2200 nm<sup>2</sup>/N. The superelastic NiTi interlayer can effectively improve the wear resistance of the composite coating. Specimen CrN5-Al has the lowest wear rate of  $340 \text{ nm}^2/\text{N}$ . The wear resistance of  $\text{CrNS}_{Al \text{ is only}}$  slightly better than that of CrN-S1-Al at the applied load of 1N despite the fact that specimen CrN5-Al has a much higher hardness. At higher testing load, the composite coating with superelastic interlayer (specimen CrN-S1-Al) may have better performance than that of CrN5-Al due to its improved adhesion.

It is instructive to note that specimen CrN-S1-Al is more wear-resistant than specimen CrN-Cr-Al although the former has a lower hardness. This observation is contradictory to the classical Archard's law for abrasive wear, [80] which states that the wear loss is inversely proportional to the hardness. Leyland and Matthews [84] suggested that, in addition to hardness, H/E may play an important role in determining the wear resistance. It has been found that H/E is proportional to the depth recovery ratio. [106] A large fraction of the deformation under indenter is elastic for materials with high H/E (or large depth recovery ratio), which will not contribute to the wear loss. This is the first unambiguous experiment demonstrating the effect of H/E (or depth recovery ratio) on wear loss, which rules out the surface chemistry effect since the surface coating was kept the same. This study demonstrates that both high hardness and large H/E (or depth recovery ratio) are desirable in making wear resistant coatings.

### 3.4 CONCLUSIONS

It was found that the composite hardness and elastic recovery ratio are strongly dependent on coating thickness and indentation depth. The hardness of composites increases with increasing hard coating thickness. However, increasing hard coating thickness has little beneficial effect on interfacial adhesion strength. By using proper interlayer material, such as Cr or superelastic NiTi, the interfacial adhesion can be improved. As compared to Cr interlayer, the superelastic NiTi interlayer can effectively decrease the friction coefficient and wear loss of the composite coating. The ratio of hardness to Young's modulus Or depth recovery ratio, in addition to hardness, needs to be taken into account in the design of tribological coatings. Ŀ

#### **CHAPTER 4**

# INSTRUMENTED S PHERICAL INDENTATION EXPERIMENTS

#### **4.1 INTRODUCTION**

Since the inception by Brine11 about 100 hundred years ago, spherical indentation experiments have become one of the standard methods for measuring hardness of materials. [92, 118, 119] Recent years have seen an increasing interest in instrumented spherical indentation techniques for measuring the mechanical properties of materials across multiple length scales. By analyzing the load-displacement curves, several researchers have suggested methods of obtaining hardness, elastic modulus, stress-strain relationships, and residual stresses from instrumented spherical indentation measurements. [91, 120, 122, 127, 131, 138, 150, 151] However, most of the previously proposed methods depend on the estimation of the contact area under the spherical indenter, which is difficult, especially when the surface around the indenter exhibits

In this work, by extending a recently developed scaling approach [86, 106] to spherical indentation in elastic-plastic solids with work-hardening, two previously unknown relationships between hardness, reduced modulus, indentation depth, indenter radius, and work of indentation were revealed. Together with a well-known relationship [91, 100] between reduced modulus, initial unloading slope, and contact area, an energybased nethod was proposed to determine the contact area, reduced modulus, and hardness of materials in instrumented spherical indentation experiments. The proposed

method also provides a new way of calibrating the effective radius of imperfect spherical indenters. The validity of the energy-based method is tested by instrumented spherical indentation experiments on copper, aluminum, tungsten, and fused silica. These newly found relationships also provide fresh insights into contact problems that are ubiquitous in many science and engineering areas, including friction, wear, as well as macro- and mano-scale mechanical forming processes.

Tabor [92] showed that, for some metals, hardness is about 2.8 times the true stress, for a strain equal to the representative strain associated with spherical indentation. Thereafter, ratio of hardness to true stress ranging from 1.1 to 2.8, when indentation process evolves from elastic to fully-plastic, has been used to derive true stress-strain relationships using spherical indentation experiments. [135-139] In this study, finite element calculation was used to study the constraint factors for spherical indentation on elastic-plastic materials at various depths.

#### 4.2 DIMENSIONAL ANALYSIS

A three dimensional, rigid, spherical indenter of radius R indenting into  $e_{lastic}$ plastic materials with strain-hardening is considered in this study. The stress-strain ( $\sigma_{\epsilon}$ ) curves  $\circ$ f the solid under uniaxial tension are taken as: [153]

$$\sigma = E\varepsilon , \text{ for } \varepsilon \leq Y/E$$

$$\sigma = K\varepsilon^{n}, \text{ for } \varepsilon \geq Y/E$$
(4.1)

where E is the Young's modulus, Y is the initial yield stress, K is the strength coefficient, and n is the strain-hardening exponent. To ensure continuity of stress and strain at the initial Yield stress, we note  $K = Y(E/Y)^n$ . Consequently, either the set of (E, Y, K) or set of (E, Y, n) is sufficient to describe the stress-strain relationship. We use the set of (E, Y, n) in the latter analysis. The friction coefficient at the contact surface between the indenter and the solid is assumed to be zero.

Sections 4.2.1 to 4.2.3 focus on the dimensional analysis of spherical indentation in elastic-plastic materials with work hardening. The purpose of the dimensional analysis is to find the essential relationships between dimensionless parameters. For those who are not familiar with the dimensional analysis, please see the appendix "Fundamentals of Dimensional Analysis and  $\Pi$  Theorem" for details.

### 4.2.1 Dimensional Analysis of Loading

Both the applied load and indenter displacement were recorded during a loading and unloading cycle in an instrumented indentation test. Elastic recovery occurs when the load is removed. A representative load-displacement curve and associated depth and work recovery are shown in Figure 4.1. In the spherical indentation process, for an isotropic elastic-plastic solid following a power-law strain-hardening rule, the two dependent variables, force (F), and contact depth  $(h_c)$ , must be functions of all of the

$$F = f_L(E, v, Y, n, h, R)$$
  
$$h_c = g(E, v, Y, n, h, R). \qquad (4.2)$$

(4.3) where v is the Poisson's ratio and h is the indentation depth. Among the six governing parameters, E, v, Y, n, h and R, E and R have independent dimensions. Dimensions of the remaining governing and governed parameters are given by:

$$[Y] = [E]$$
  

$$[v] = [E]^{0} [R]^{0}$$
  

$$[n] = [E]^{0} [R]^{0}$$
  

$$[h] = [R]$$
  

$$[F] = [E] [R]^{2}$$
  

$$[h_{c}] = [R]$$
  
(4.4)

By applying the II theorem in dimensional analysis [154], equation 4.2 and 4.3 become:

$$F = ER^2 \prod_{\alpha} \left( \frac{Y}{E}, \nu, n, \frac{h}{R} \right) = ER^2 \prod_{\alpha} \left( \prod_{1}, \nu, n, \frac{h}{R} \right)$$
(4.5)

$$h_{c} = R \prod_{\beta} \left( \frac{Y}{E}, \nu, n, \frac{h}{R} \right) = R \prod_{\beta} \left( \prod_{1}, \nu, n, \frac{h}{R} \right)$$
(4.6)

where  $\Pi_1 = \frac{Y}{E}$  is a dimensionless function. The total work during loading is given by:

$$W_{t} = \int_{0}^{h_{\text{max}}} Fdh = ER^{2} \int_{0}^{h_{\text{max}}} \prod_{\alpha} \left( \prod_{1}, \nu, n, \frac{h}{R} \right) dh = ER^{3} \prod_{r} \left( \prod_{1}, \nu, n, \frac{h_{\text{max}}}{R} \right)$$

where

 $\prod_r$  is a dimensionless

function such

(4.7) that

$$R\frac{\partial}{\partial h}\prod r\left(\frac{Y}{E}, v, n, \frac{h}{R}\right) = \prod_{\alpha}\left(Y/E, v, n, \frac{h}{R}\right)$$

### 4.2.2 Dimensional Analysis of Unloading

Unloading occurs after the indenter reaches the maximum i indentation depth,  $h_{max}$ . Therefore, during unloading, the force  $(F_u)$  and residual indentation depth  $(h_f)$  are also dependent on  $h_{max}$ , and they are given by:

$$F_{u} = f_{u}(E, v, Y, n, h, R, h_{\max})$$
(4.8)

$$h_f = \mathcal{S}_u(E, \nu, Y, n, \boldsymbol{R}, h_{\max})$$
(4.9)

By applying the II theorem in dimensional analysis [154], equation 4.8 and 4.9 become:

$$F_{u} = ER^{2} \prod_{r} \left( \prod_{1}, \nu, n, \frac{h}{R}, \frac{h_{\max}}{R} \right)$$
(4.10)

$$h_f = R \prod_{\chi} \left( \prod_{1}, \nu, n, \underbrace{\mathcal{I}_{n_{\max}}}_{R} \right)$$
(4.11)

The reversible work during unloading is given by:

$$W_{u} = \int_{h_{f}}^{h_{\max}} F_{u} dh == ER^{2} \int_{h_{f}}^{h_{\max}} \prod_{\gamma} \left( \prod_{1}, \nu, n, \frac{h}{R}, \frac{h_{\max}}{R} \right) dh$$
$$= ER^{3} \prod_{\mu} \left( \prod_{1}, \nu, n, \frac{h_{\max}}{R} \right)$$
(4.12)

where  $\Pi_{\mu}$  is a dimensionless function  $R \frac{\partial}{\partial h} \Pi_{\mu} \left( \frac{Y}{E}, v, n, \frac{h}{R} \right) = \Pi_{\gamma} \left( Y/E, v, n, \frac{h}{R}, \frac{h_{\text{max}}}{R} \right).$  that

# 4.2.3 Scaling Relationships from Dimensional Analysis

The ratio of irreversible work to the total work for a complete loading-unloading cycle is written as:

$$\frac{W_{r}-W_{u}}{W_{r}} = \frac{ER^{2}\prod_{r}\left(\prod_{1},\nu,n,\frac{h_{\max}}{R}\right) - ER^{2}\prod_{\mu}\left(\prod_{1},\nu,n,\frac{h_{\max}}{R}\right)}{ER^{2}\prod_{r}\left(\prod_{1},\nu,n,\frac{h_{\max}}{R}\right)} = \prod_{\mu}\left(\prod_{1},\nu,n,\frac{h_{\max}}{R}\right)$$
(4.13)

The ratio of residual depth to total depth can be obtained by dividing both sides of equation (4.11) by  $h_{max}$ ,

$$\frac{h_f}{h_{\max}} = \frac{R}{h_{\max}} \prod_{\chi} \left( \prod_{1}, \nu, n, \frac{h_{\max}}{R} \right) = \prod_{\delta} \left( \prod_{1}, \nu, n, \frac{h_{\max}}{R} \right)$$
(4.14)

At the maximum indentation load, hardness, H, is given by:

$$H = \frac{F_{\text{max}}}{A_c} = \frac{F_{\text{max}}}{\pi a^2} = \frac{F_{\text{max}}}{\pi (2Rh_c - h_c^2)}$$
(4.15)

where  $A_c$  is the contact area, a is the contact radius. The force and contact depth at the maximum indentation depth,  $h=h_{max}$ , are given by:

$$F_{\max} = ER^{2} \prod_{\alpha} \left( \frac{Y}{E}, \nu, n, \frac{h_{\max}}{R} \right) = ER^{2} \prod_{\alpha} \left( \prod_{1}, \nu, n, \frac{h_{\max}}{R} \right)$$
(4.16)  
$$h_{c} \Big|_{h=h\max} = R \prod_{\beta} \left( \frac{Y}{E}, \nu, n, \frac{h_{\max}}{R} \right) = R \prod_{\beta} \left( \prod_{1}, \nu, n, \frac{h_{\max}}{R} \right)$$
(4.17)

By combining equation (4.15) (4.16) and (4.17), the hardness can be expressed as:

$$H = \frac{ER^2 \prod_{\alpha} \left( \prod_{1}, \nu, n, \frac{h_{\max}}{R} \right)}{\pi \left\{ 2R^2 \prod_{\beta} \left( \prod_{1}, \nu, n, \frac{h_{\max}}{R} \right) - R^2 \prod_{\beta}^2 \left( \prod_{1}, \nu, n, \frac{h_{\max}}{R} \right) \right\}} = \frac{E}{\pi} \prod_{o} \left( \prod_{1}, \nu, n, \frac{h_{\max}}{R} \right)$$
(4.18)

Consequently,

$$\frac{H}{E'} = \frac{H(1-\nu^2)}{E} = \frac{(1-\nu^2)}{\pi} \prod_o \left(\prod_{1}, \nu, n, \frac{h_{\max}}{R}\right) = \prod_{\sigma} \left(\prod_{1}, \nu, n, \frac{h_{\max}}{R}\right) \quad (4.19)$$

According to equation (4.13) (4.14) and (4.19), it is evident that  $\frac{W_{i} - W_{i}}{W_{i}}$ ,  $\frac{h_{i}}{h_{max}}$ 

and  $\frac{H}{E^*}$  are all dependent on the dimensionless parameters, Y/E, v, n, and  $h_{max}/R$ . It is therefore interesting to study the relationship between the dimensionless parameter  $\frac{W_r - W_u}{W_r}$ ,  $\frac{h_f}{h_{max}}$ , and  $\frac{H}{E^*}$ . By applying the dimensional analysis to the spherical indentation experiments, the number of independent variables has been reduced from six (i.e., E, v, Y, n, h and R) to four (Y/E, v, n, and  $h_{max}/R$ ).

#### 4.3 FINITE ELE MENT ANALYSIS

Since there is no analytical solution for spherical indertation in elastic-plastic materials, a finite element analysis was used to study the problem. In this work, an extensive finite element computation was carried out using AB AQUS [155] to explore the relationship between  $\frac{h_f}{h_{max}}$ ,  $\frac{W_t - W_u}{W_t}$ , and  $\frac{H}{E^*}$ . The radius of the rigid indenter was lum. Young's modulus was 200GPa and Poisson's ratio was 0.2. The strain-hardening exponent, *n*, was chosen to be 0.1, 0.3, and 0.5, respectively, which represents materials from heavily worked to fully annealed state. For each strain-hardening exponent, five different Y/E values were used, namely, 0.002, 0.005, 0.01, 0.025, and 0.1, which represent materials from soft metals to hard ceramics. For each combination of *n* and Y/E, computations were carried out for several values of  $h_{max}$ , allowing the evaluation of the scaling functions for a range of  $\frac{h_{max}}{R}$  values from 0.05 to 0.5. The rate-independent, incremental theory of plasticity in ABAQUS was used in the finite element calculations. In particular, the plasticity theory uses the von Mises' yield surface model with associated plastic flow rule. Because of the axisymmetry of the problem, a two-dimensional mesh was used, as shown in Figures 4.2(a) and (b). Note that Figure 4.2(b) shows the magnified region of the top-left corner in Figure 4.2(a), which will be in contact with the indenter. The smallest element in the contact region is 25nm. As for the boundary conditions, the bottom edge was fixed in directions 1 and 2, and the axis of symmetry (left edge in Figure 4.2(a)) was fixed in direction 1. The true contact area,  $A_r$ , along the curved contact surface was calculated by the ABAQUS program. The contact depth,  $h_c$ , was calculated using equation:

$$h_{\rm c} = A_{\rm c}/2\pi R \tag{4.20}$$

(1 20)

Load-displacement curves were obtained from the finite element calculations. Residual indentation depth,  $h_f$ , and maximum load,  $F_{max}$ , were obtained from the load-displacement curves for each given  $h_{max}$ . The total work,  $W_i$ , and reversible work,  $W_{\mu}$ , are obtained by integrating the loading and unloading curves, respectively.

# 4.3.1 **Piling-up/Sinking-in in Spherical Indentation**

3.1 **Prime** ... During the spherical indentation process, materials around the indenter may pileup (Figure 4.3) or sink-in (Figure 2.9). In this study, the ratio of contact depth to maximum indentation depth,  $h_c/h_{max}$ , is used to evaluate the extent of piling-up  $(h_c/h_{max}>1)$  and sinking-in  $(h_c/h_{max}<1)$ . The calculated values of  $h_c/h_{max}$  for various materials at different indentation depths are shown in Figure 4.4 (a)-(e). It is clear that, in general,  $h_c/h_{max}$  depends on  $h_{max}/R$ , n, and Y/E for spherical indentation in elasticplastic solids with strain-hardening. For materials with small values of Y/E and n or indentation with large  $h_{max}/R$ , piling-up  $(h_c/h_{max}>1)$  tends to occur, while sinking-in  $(h_c/h_{max}<1)$  tends to occur for materials with large Y/E and n or at small indentation depth. These observations can be understood by the fact that sinking-in always occurs for Hertzian elastic contacts while piling-up occurs for rigid-plastic contacts. [92] Thus, the ratio of "elastic component" to "plastic component" of deformation decreases with increasing  $\frac{h_{max}}{R}$  and decreasing values of Y/E and r for spherical indentation in elasticplastic solids with work-hardening.

It is instructive to note that the extent of **pilin** *g-up* and sinking-in is independent of depth for conical and pyramidal indentation in the same class of solids. This depth independence is the consequence of the absence of a length parameter associated with ideally sharp conical and pyramidal indenters. It is also instructive to compare the present numerical results with some early experimental work by Norbury and Samuels [122] who believed that piling-up and sinking-in depended on work-hardening exponent only. Their observation was based primarily on indentation in metals (i.e., small values of Y/E with n values from 0.0 to 0.5) where the effect of *n* is dominant. In general, however, the degree of piling-up and sinking-in depends on Y/E, *n*, and  $h_{max}/R$  which makes the determination of contact area under load difficult using conventional methods. In the following analysis, we show that it is possible to circumvent this difficulty of estimating contact area using an energy-based method derived from a scaling relationship between  $H/E^*$  and  $(W_r - W_u)/W_r$ .

### 4.3.2 Relationship between hor max and (Wr-Ww)/W,

The representative load-displacement curves, obtained by finite element calculations, of a material with Y/E = 0.025, v = 0.2, and n = 0.5 at various depths are shown in Figure 4.5. By analyzing the load-displacement curves of all materials simulated, we observed a relationship between  $\frac{W_i - W_u}{W_i}$  and  $\frac{h_f}{h_{\text{max}}}$ , which is shown in

Figure 4.6. This relationship can, from a least-square fit, be written as

$$\frac{h_f}{h_{\max}} = \frac{W_t - W_u}{W_t} \quad . \tag{4.21}$$

Equation (4.21) shows that the degree of permanent deformation, measured by the ratio of residual depth to maximum indenter displacement,  $\frac{h_f}{h_{max}}$ , is simply related to the ratio

of irreversible work to total work,  $\frac{W_{i} - W_{u}}{W_{i}}$ . The measurement of one leads to the

measurement of the other. In practice, however, the determination of the work can be made more accurately than the measurement of residual indentation depth,  $h_f$ , since the former is from the integration of loading-displacement curves while the latter is from the estimation of a single point on the unloading curve. Furthermore, this relationship is "universal," because it does not depend on the details of the mechanical behavior of solids, such as E, Y, and n. Nor does the relationship depend on the indenter radius, R, or indentation depth, h. This new relationship is analogous to a relationship previously established for conical and pyramidal indentation in elastic-plastic solids with strainhardening. [105, 106] Together, they demonstrate that a simple linkage exists between the work of indentation and deformation that is independent of the details of materials properties and indenter geometry.

# 4.3.3 Relationship between H/E \* and (W-W)/W,

An approximately linear relationship between  $\frac{H}{E^*}$  and  $\frac{W_t - W_u}{W_t}$  for spherical

indentation in elastic-plastic solids is revealed in Figure 4.7. For each fixed  $h_{max} / R$ , this relationship can be expressed as

$$\frac{(W_{t} - W_{u})}{W_{t}} = B \frac{H}{E^{*}} + 1 , \qquad (4.22)$$

where **B** is found to depend on  $\frac{h_{\text{max}}}{R}$  only (see, Figure 4.8), i.e.,

$$B = -1.687 \left(\frac{h_{\text{max}}}{R}\right)^{-0.62}.$$
 (4.23)

Combining equations (4.22) and (4.23), it is obtained that

$$\frac{H}{E^*} = 0.5928 \left(\frac{h_{\text{max}}}{R}\right)^{0.62} \left(\frac{W_u}{W_t}\right).$$
(4.24)

Thus, the ratio of hardness to reduced modulus,  $\frac{H}{E^*}$ , can be obtained by determining

$$\frac{h_{\max}}{R}$$
 and  $\frac{W_u}{W_t}$ . Recently, an approximately linear relationship between  $\frac{H}{E^*}$  and  $\frac{W_u}{W_t}$  was

obtained for conical and pyramidal indentation in elastic-plastic solids with strianhardening. [85, 106, 116] The two quantities were found to be proportional to each other with the proportionality factor a function of the indenter angle in conical indentation
modeling and experiments. Equation (4.24) shows that, for the first time, a similar relationship exists for spherical indentation in elastic-plastic solids.

By combining equation (4.24) with the definition of hardness  $H = \frac{F_{\text{max}}}{A_c}$  and a

well known relationship between reduced modulus,  $E^*$ , initial unloading stiffness, S, and contact area,  $A_c$ : [91, 100]

$$E^* = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A_c}}, \qquad (4.25)$$

it was obtained that:

$$A_{c} = \left[\frac{1.903F_{\max}}{\left(\frac{h_{\max}}{R}\right)^{0.62}\left(\frac{W_{u}}{W_{t}}\right)S}\right]^{2}, \qquad (4.26)$$
$$E^{*} = \frac{0.4657S^{2}\left(\frac{h_{\max}}{R}\right)^{0.62}\left(\frac{W_{u}}{W_{t}}\right)}{F_{\max}}, \qquad (4.27)$$

$$H = 0.276 \left(\frac{h_{\text{max}}}{R}\right)^{1.24} \left(\frac{W_u}{W_t}\right)^2 \frac{S^2}{F_{\text{max}}},$$
(4.28)

Since  $F_{\max}$ ,  $\frac{h_{\max}}{R}$ ,  $\frac{W_{\mu}}{W_{\ell}}$ , and S can all be measured directly from load-displacement

curves, contact area, reduced modulus, and hardness can in principle be obtained from equations 4.26, 4.27, and 4.28, respectively. This new method is called the "energy based method" for spherical indentation analysis since the elastic energy  $(W_u)$  and total energy  $(W_l)$ , are used to determine the mechanical properties. The main advantage of the energybased rmethod is that it applies to both piling-up and sinking-in while the commonly used methods cannot be used when piling-up occurs. While this method is based on the analysis of rigid spherical indentation in elastic-plastic solids with strain-hardening, it is necessary to test its robustness through experiments under realistic and often imperfect conditions, such as non-sphericity and non-rigidity of spherical indenters.

# 4.4 EXPERIMENTAL APPLICATION OF THE ENERGY-BASED METHOD

## 4.4.1 Sample Preparation and Experimental Methods

Spherical indentation experiments were conducted using a Nano Indenter XP from MTS with a rounded conical diamond indenter. The included cone angle was 90° and the nominal tip radius was  $10\mu$ m. The load range was between 10 and 300mN. At least five indentations were made at each load to generate average values and standard deviations reported in this work. The indentation experiments were conducted using load control with a constant loading rate. Unloading was initiated immediately after the load reached the prescribed maximum load at the end of each loading cycle without a holding period. All indentations were conducted at room temperature. The mechanical properties of all the tested materials, i.e., pure copper, 6061-T6 aluminum, pure tungsten, and fused silica, are shown in Table I. [101, 156, 157] The composite reduced modulus,  $E^*$ , is given by

$$\frac{1}{E^*} = \frac{1 - \upsilon_s^2}{E_s} + \frac{1 - \upsilon_i^2}{E_i},$$
(4.29)

where  $E_s$  and  $v_s$  are the Young's modulus and Poisson's ratio of the sample, respectively.  $E_i$  and  $v_i$  are the Young's modulus and Poisson's ratio of the indenter, respectively. Specifically,  $E_i = 1141$ GPa and  $v_i = 0.07$  for the diamond indenter. The fused silica sample was obtained from MTS as the standard calibration material. Copper, aluminum, and tungsten samples were mechanically polished, finishing with 0.25µm diameter diamond paste. The average surface roughness, measured using a Wyco optical profilometer, was 20, 49, and 23 nm for the polished copper, aluminum, and tungsten samples, respectively.

# 4.4.2 An Experimental Proof of the Relationship between $h_f / h_{max}$ and $(W_r W_w)/W_t$

The relationship between  $\frac{h_f}{h_{\text{max}}}$  and  $\frac{(W_i - W_u)}{W_i}$  for copper, aluminum, tungsten,

and fused silica is shown in Figure 4.9, together with finite element results. It is evident

that 
$$\frac{h_f}{h_{max}}$$
 is approximately proportional to  $\frac{(W_i - W_u)}{W_i}$ , which is consistent with the finite

element analysis. The agreement suggests that this relationship is insensitive to the finite elasticity of the diamond indenter and imperfections in the diamond indenter geometry. However, the imperfection in the spherical shape of the diamond indenter can be shown, in section 4.5.4, to cause problems for direct applications of equations 4.26 - 4.28. In section 4.5.3, a novel method for obtaining an effective radius for imperfect spherical indenters will be established to circumvent these problems.

# 4.4.3 A Novel Method for Indenter Shape Function Calibration

For indenter shape calibration, instrumented spherical indentation experiments were conducted on copper for depth ranging between 150nm and 1850nm. The values for S,  $F_{\text{max}}$ ,  $h_{\text{max}}$ , and  $W_{\mu}/W_{\mu}$  were obtained from load-displacement curves shown in Figure 4.10. Equation 4.27 was then used to calculate the effective tip radius,  $R_{eff}$ , at various depths, assuming a constant composite reduced modulus for copper,  $E_{Cu}^{*} = 127.2$  GPa. The relationship between  $R_{eff}$  and  $h_{max}$  is shown in Figure 4.11. Ideally, for a perfect spherical indenter, the effective tip radius should be independent of the indentation depth. However, in this work, the effective tip radius was found to be a function of indentation depth due to its imperfect geometry. An increase of more than 50% in effective tip radius over the depth was observed. A power-law fit was used to interpolate the effective indenter radius. This indenter "shape function" is given by (see, Figure 4.11)

$$R_{eff} = 1915.6 h_{max}^{0.2755}$$
 for 150nm  $< h_{max} < 1850$ nm. (4.30)

The manufacturing of a perfect spherical diamond indenter becomes challenging as the tip radius becomes smaller. In addition, the worn surface of a used indenter can cause the non-sphericity. Therefore, a regular calibration of the indenter shape is critical for accurate measurement. The method described above can be used to calibrate the shape function of any non-perfect spherical indenter. The proposed method is efficient and it requires no extra investment in capital equipment.

### 4.4.4 Hardness and Young's Modulus Measurement by the Energy-based Method

Using the same diamond indenter, spherical indentation experiments were then conducted on 6061-T6 aluminum, tungsten, and fused silica with indentation depth from 180nm to 1650nm. The load-displacement curves are shown in Figure 4.12(a)-(c). The composite reduced modulus ( $E^*$ ) for aluminum, tungsten, and fused silica, calculated using equation 4.27, together with the shape function equation 4.30, at various depths is

plotted in Figure 4.13(a). As expected, the measured composite reduced modulus values are approximately depth independent. The measured composite reduced modulus of aluminum ranges from 74.3 to 78.6 GPa. The composite reduced modulus of tungsten ranges from 296 to 316.8GPa. Compared with the calculated composite reduced modulus of aluminum and tungsten in Table I, the difference is within 8%, which suggests that the proposed energy-based method together with indenter shape calibration is applicable to materials with a wide range of elastic modulus values. The measured composite reduced modulus of fused silica is between 58.2 and 60.4GPa. The difference between the calculated and measured value for fused silica is within 16%. It should be noted that the fused silica data also exhibit the largest deviation in the correlation between  $h_f / h_{max}$  and  $(W_{t}, W_{u})/W_{t}$  (see, Figure 4.9). These differences may be caused by indentation-induced microcracking for brittle materials such as fused silica. It also suggests that the relationship between  $h_{f}/h_{max}$  and  $(W_{f}-W_{u})/W_{f}$  may be used to help screen materials for which the new method is applicable. Specifically, the energy-based method consists of the following steps:

(1) Using equations 4.27 and 4.29 to determine the effective indenter radius,  $R_{eff}$ , as a function of indentation displacement,  $h_{max}$ , by indenting a material with a known, depth independent Young's modulus and Poisson's ratio. This shape function is an interpolation function over the indentation depth of interest and is not necessary of the form given by equation 4.30.

(2) Checking the applicability of the energy-based method by plotting  $h_f / h_{max}$ and  $(W_t - W_u) / W_t$ . A necessary condition is that the correlation exists for materials of interest. (3) Evaluating the reduced modulus for materials of interest using equations 4.27
 and 4.29 together with the shape function determined in step (1).

The robustness of this method is seen from the evaluation of the reduced modulus values for several materials using an imperfect spherical indenter with a varying effective radius of about 50%. The method does not depend on assumptions about piling-up and sinkingin of materials around the spherical indenters.

Finally, hardness values for fused silica, W, Al, and Cu are obtained using equation 4.28 together with the indenter shape function equation 4.30. The results are shown in Figure 4.13(b). While these values are within the range of reported hardness for the Cu, Al, and W, detailed comparison is complicated because of several factors. Specifically, (i) most of the literature data were obtained using Berkovich indenters where a pronounced indentation size effect was reported for these materials. [158-160] Strain-gradient plasticity is believed to be one of the primary mechanisms responsible for the increase in hardness with decreasing indentation depth.[161] (ii) The indentation size effect is different under spherical indenters, where the hardness is not expected to show depth dependence but is expected to depend on the radius of spherical indenters. [162] (iii) Hardness increases with indentation depth for spherical indentation in elastic-plastic solids with work hardening. [92] With an imperfect spherical indenter, such as the one used in this work, it is possible that the two effects, work hardening and strain-gradient plasticity, cancel each other because of increasing  $R_{eff}$  with depth, resulting in a slightly decreasing hardness for Cu, Al, and W with depth (see, Figure 4.13 (b)). While the imperfection in sphericity can be remedied for modulus measurements using a shape function (e.g., Equation 4.30), hardness is indenter shape dependent. It is therefore

desirable to use as perfect a spherical shape as possible for hardness measurements using spherical indenters.

## 4.5 CONSTRAINT FACTORS FOR SPHERICAL INDENTATION EXPERIMEENTS

For spherical indentation, the constraint factor, CF, is defined as the ratio of hardness,  $\mathbb{F}_{1}$ , to true stress,  $\sigma$ , when the representative strain equals the true strain, i.e.,

$$CF = \frac{H}{\sigma}, \quad \text{when } \varepsilon_r = \varepsilon.$$
 (4.31)

where  $\varepsilon$  is the true strain in uniaxial tensile test, and  $\varepsilon_r$  is the representative strain given by

$$\varepsilon_r = 0.2 \frac{a}{R}.$$
(4.32)

where a is the contact radius. Given the constraint factor, the true stress-strain relationship can be determined by the hardness-representative strain relationship. In this work, the constraint factors for elastic indentation, elastic-plastic indentation and fully-plastic indentation were studied using finite element calculations.

The relationship between true stress-strain and hardness-representative strain curves for spherical indentation on elastic, soft elastic-plastic and hard elastic-plastic materials are shown in Figure 4.14(a) (b) and (c), respectively. The horizontal axis represents true strain or representative strain of the same value. Figure 4.14 (a) shows that, for the contact between a rigid indenter and an elastic material with E=200K,  $\nu=0.2$ , the constraint factor is close to 2.21. The analytical solution for the contact between a rigid indenter and an elastic flat surface has been solved by Hertz. Specifically, for elastic contact, the contact radius, a, is given by [113]

$$a = \left(\frac{3F_{\max}R}{4E^*}\right)^{1/3}, \qquad \text{when a} << R.$$
(4.33)

Note that we also have  $H = \frac{F_{\text{max}}}{\pi a^2}$ ,  $E^* = \frac{E}{1 - v^2}$  and  $\sigma = E\varepsilon = 0.2 \frac{aE}{R}$ . By combining

these three equations and equations 4.31, 4.32, and 4.33 together, the constraint factor for elastic contact with a **ri**gid indenter is obtained, i.e.,

$$CF = \frac{H}{\sigma} = \frac{20}{3\pi(1-\nu^2)}.$$
 (4.34)

For elastic contract with a rigid indenter, the constraint factor is dependent on Poisson's ratio ratio only. Specifically, constraint factors increase from 2.12 to 2.83 when Poisson's ratio increases from 0 to 0.5, as shown in Table 4.2. For v=0.2, equation 4.34 gives a constraint factor of 2.21, which is consistent with the finite element result. Figure 4.14(b) shows relationships between hardness and true stress for spherical indentation on a soft material with Y/E=0.002 and n=0.3, which represents typical metallic materials. It shows that the constraint factor is close to 2.8 for all the indentation tests from  $h_{max}/R=0.02$  to  $h_{max}/R=0.5$ . The finite element results are consistent with Tabor's observation of spherical indentation on metals. [129] Figure 4.14(c) shows the relationship between hardness and true stress for spherical indentation on hard materials with Y/E=0.025 and n=0.3. The constraint factor is less than 2.8 for all the indentation tests from  $h_{max}/R = 0.02$  to  $h_{max}/R$ 

Figure 4.15 shows the constraint factors for all materials tested at different indention depth. The horizontal axis,  $E^*a/\sigma R$ , includes information of both material properties  $(E^*/\sigma)$  and the indentation test (a/R). It shows that the constraint factor reaches

2.8 when  $\frac{E^{*}a}{\sigma R} \approx 40$ , which indicates the beginning of full-plasticity in indentation experiments. The constraint factor remains about 2.8 with increasing indentation depth once full-plasticity is reached. For soft materials (low Y/E and n), full-plasticity can be easily achieved. For example, for materials with Y/E=0.002, n=0.3,  $\frac{E^{*}a}{\sigma R} = 41$  when  $h_{max}/R = 0.02$ . For hard materials (high Y/E and n), there is a large elastic-plastic transition range, and constraint factor increases from  $\frac{20}{3\pi(1-\nu^{-2})}$  to 2.8 with increasing indentation depth. Full-plasticity and the constraint factor of 2.8 can't be reached even at large indentation depth. For example, for materials with Y/E=0.025 and n=0.3,  $\frac{E^{*}a}{\sigma R} = 19$  when  $h_{max}/R = 0.5$ .

In conclusion, the constraint factor for spherical indentation processes is dependent on material properties and indentation depth. It changes from  $\frac{20}{3\pi(1-\nu^2)}$  to

2.8 when indentation evolves from elastic to fully-plastic. Caution must be taken when using spherical indentation to derive stress-strain relationship of hard materials, such as ceramics or materials with large work hardening exponent, because there exists a large elastic-plastic transition range for those materials. For soft materials, a constraint factor of 2.8 may be used to derive true stress-strain relationship approximately. However, as ment is need in section 2.3.5, indenter radius plays an important role in the hardness measurement due to the indentation size effect.

#### **4.6 CONCLUSIONS**

The extent of piling-up/sinking-in and the relationships between  $\frac{H}{E^*}$ ,  $\frac{W_i - W_u}{W_i}$ ,

and  $\frac{h_f}{h_{\max}}$  have been investigated using dimensional analysis and finite element calculations. For spherical indentation in elastic-plastic materials, there is an equivalence between  $\frac{h_f}{h_{\max}}$  and  $\frac{W_e - W_u}{W_i}$ . For a fixed  $\frac{h_{\max}}{R}$ , a linear relationship exists between  $\frac{H}{E^*}$ and  $\frac{W_e - W_u}{W_i}$  and the proportionality depends on  $\frac{h_{\max}}{R}$  only. Using the above relationships, together with the initial unloading stiffness, an energy-based method has been proposed to derive the contact area, reduced modulus and hardness of materials from instrumented spherical indentation experiments. This new method can also be used to calibrate the effective tip radius of an imperfect spherical indenter. The validity of the new method was studied by instrumented indentation experiments on copper, aluminum, tungsten, and fused silica. Constraint factor for spherical indentation experiment has been

studied using finite element calculations as well. The constraint factor changes from  $\frac{20}{3\pi(1-v^2)}$  to 2.8 when indentation evolves from elastic to fully-plastic. For soft material, the fully-plastic indentation can be easily reached; however, for hard material there exists a large elastic-plastic transition region. Caution must be taken when using const raint factor to derive stress-strain relationships.

#### **CHAPTER 5**

### SUMIMARY AND FUTURE WORK

This study, for the first time, presented a systematic study of the shape memory and superelastic effect of NiTi alloys at the micrometer scale using instrumented indentation experiments. It was found that the shape memory and superelastic effects exists under indentation loading conditions and the recoverability depends on both the indenter geometry and indentation depth. For Berkovich and Vickers indentation experiments, the recovery ratio is a constant at all indentation depths. For spherical indentation experiments, the recovery ratio decreases with increasing indentation depth and scales with the representative strain. For both shape memory and superelastic NiTi alloys, the maximum strain for complete recovery can be measured by the instrumented spherical indentation experiments. Instrumented indentation techniques can be used to quantitatively characterize the shape memory and superelastic effect at small size scale, such as thin films on substrates and welded joints.

The thermally-induced recovery of the indents on the shape memory alloy indicates that the shape memory thin films may be used as a self-healing coating, in which the damage caused at low temperature can be healed at high temperature. It also indicates that a shape memory alloy can be used as a material that can change surface rougheess according to the environmental temperature.

 $M^{otivated}$  by the high elasticity of the superelastic NiTi and its potential applice as a novel tribological material, the wear behavior of the superelastic NiTi

88

was studied. It was found that the wear rate of superelastic NiTi is larger than that of the amorphous NiTi. Ploughing during sliding test deteriorates the recoverability of the superelastic NiTi, which can be prevented by deploying a hard layer on the top of superelastic NiTi.

Based on the above indentation and wear experiments on superelastic NiTi, a novel layered composite coating was produced. This composite coating is made of a superelastic NiTi interlayer deposited between a metallic substrate and a hard ceramic coating. The superelastic interlayer provides high elasticity while the hard coating prevents ploughing. It was found that the composite coating with superelastic interlayer has good interfacial adhesion, low friction coefficient, and good wear resistance. This experimental observation suggests that (i) superelastic NiTi can be used a high strength "metallic adhesive", and (ii) increasing the interlayer elasticity can decrease the friction coefficient and improve wear resistance. Thus, elasticity, in addition to hardness, plays an important role in determining the friction and wear behavior of the tribological materials. This observation will be useful in the design of better tribological coatings. Future study of this novel composite coating should include the quantitative measurement of the adhesion strength and optimization of the interlayer thickness.

To further explore the spherical indentation experiments, a general study of the spherical indentation in elastic-plastic materials was conducted. Using dimensional analysis and finite element modeling, new scaling relationships between the

$$\dim_{\mathcal{R}_{i}} h_{i}$$
 were revealed for the first time.

Basec these relationships and a well-known relationship between reduced modulus, initial initi spherical indentation experiment was proposed. The robustness of the new energy-based method was verified by spherical indentation experiments in materials with a wide range of Young's moduli and Poisson's ratios. The proposed energy-based analysis method also provides an efficient and low-cost approach for indenter shape function calibration.

The constraint factor for spherical indentation process was studied using finite element calculation. It was found that the constraint factor changes from  $\frac{20}{3\pi(1-v^2)}$  to

2.8 when indentation evolves from elastic to fully-plastic. For highly-plastic materials, a constraint factor of 2.8 may be used to derive the true stress-strain relationship approximately. However, for highly-elastic materials, there exists a large elastic-plastic transition range within which the constraint factor is a function of indentation depth and material properties. The constraint factor of 2.8 can not be used to derive stress-strain relationship of highly-elastic materials. Future study will focus on how to obtain the stress-strain relationship using the information from the whole indentation load-displacement curve.

APPENDIX

#### **APPENDIX**

### FUNDAMENTALS OF DIMENSIONAL ANALYSIS AND IT THEOREM

Physical properties are expressed as a number associate with some unit. The choice of unit for the measured properties is arbitrary. For example, we can choose either meter (m) or millimeter (mm) as the unit when we measure the length. Whatever the unit is chosen, the length should be the same. Therefore, for physical property x, the measured number should increase by a factor of X when the unit decreases by a factor of X. We say that the dirmension of physical property x, denoted by [x], equals the factor X.

The physical units can be divided into to types: the fundamental units and the derived units. For instance, once the units for length and time are chosen as the fundamental units, the unit for velocity becomes a derived one. The dimension of velocity can be expressed in the form of the dimension of length and time

$$[v] = [l][t]^{-1}.$$
 (A1)

It has been proved that the dimension of any physical property is always a power-law monomial. For the length-mass-time unit system, the dimension of any physical property z can be expressed as

$$\begin{bmatrix} z \end{bmatrix} = \begin{bmatrix} l \end{bmatrix}^{\alpha} \begin{bmatrix} t \end{bmatrix}^{\beta} \begin{bmatrix} m \end{bmatrix}^{\gamma}$$
(A2)

where [1], [t] and [m] are the dimensions of length, time and mass, respectively.  $\alpha, \beta$ and  $\sum_{are real number}$  associated with z. A group of physical properties  $z_1, z_2, ..., z_i$  is dimensionally independent if the relationship

$$\left[z_{1}\right]^{a_{1}}\left[z_{2}\right]^{a_{2}}\dots\left[z_{n}\right]^{a_{n}}=1$$
(A3)

exists only when  $a_1 = a_2 = \dots = a_n = 0$ .

A physical law specifies the relationship between a governed variable, z, and a group of governing variables,  $z_1, z_2, ..., z_n$ , in the mathematical form of

$$z = f(z_1, z_2, ..., z_n)$$
 (A4)

Among the *n* governing variables, let  $z_1...z_i$  be dimensionally independent. Therefore, the dimension relationship can be express as

$$[z] = [z_1]^{\alpha_1} [z_2]^{\alpha_2} \dots [z_i]^{\alpha_i}$$
(A5)

$$\left[z_{i+j}\right] = \left[z_{1}\right]^{\alpha_{j1}} \left[z_{2}\right]^{\alpha_{j2}} \dots \left[z_{i}\right]^{\alpha_{ji}}, \quad j = 1, 2, \dots, n-i$$
 (A6)

According to equation (A5) and (A6), the following physical quantities should be dimensionless

$$\Pi = \frac{z}{z_1^{\alpha_1} z_2^{\alpha_2} \dots z_i^{\alpha_i}}$$
(A7)

$$\Pi_{j} = \frac{Z_{i+j}}{Z_{1}^{\alpha_{j1}} Z_{2}^{\alpha_{j2}} \dots Z_{i}^{\alpha_{ji}}}, \quad j = 1, 2, \dots, n-j$$
(A8)

Then, the equation A4 can be transformed into new form

$$\Pi = f(z_1, ..., z_i, \Pi_1, ..., \Pi_{n-i})$$
(A9)

Not when the unit system for the physical property  $z_1, ..., z_i$  changes from one to another the number of physical properties  $z_1, ..., z_i$  changes accordingly. Nevertheless, the number for  $\Pi$  should remain unchanged since it is dimensionless. Therefore,  $z_1, ..., z_i$ should not appear in equation A9 and the equation for  $\Pi$  should be

$$\Pi = f\left(\Pi_1, \dots, \Pi_{n-i}\right) \tag{A10}$$

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It is obvious that, by transforming equation A4 into A10, the governing variables change from *n* dimensional variable to *n*-*i* dimensionless variables. This is known as the  $\Pi$ theorem. The foundation of the  $\Pi$  theorem is that the physical law should not be dependent on the arbitrarily chosen unit system. The dimensional analysis can help us find the essential relationships between physical properties.

A detailed description the dimensional analysis and  $\Pi$  theorem can be found in the work by Barenblatt [154] and Cheng. [163] In addition, Cheng and Cheng [85, 86, 103, 106, 147] pioneered the study of instrumented indentation using the dimensional analysis.

Phases	Crystal system	Lattice Parameters	;	Space	group
martensite	nm,	P21/m	n [9]		
		c=0.4646nm,β=97.78	[8]		
R-phase	trigonal	a=0.3012nm, α=89.53°	[7]	P3	[9]
austenite	cubic	a=0.3012nm	[8]	Pm 3 r	n [9]

**Table 1.1.1** Crystal Structure and lattice parameters of NiTi alloys.

Materials	Density	Melting	Hardness	Young's	Resistivity	СТЕ
	(g/cm <sup>3</sup> )	Point	(HV)	modulus	(μΩ.cm)	(10 <sup>-6</sup> K <sup>-1</sup> )
		(°C)		(GPa)		
TiB <sub>2</sub>	4.5	3225	3000	560	7	7.8
TiC	4.93	3067	2800	470	52	8.0-8.6
TiN	5.4	2950	2100	590	25	9.4
ZrB <sub>2</sub>	6.11	3245	2300	540	6	5.9
ZrC	6.63	3445	2560	400	42	7.0-7.4
ZrN	7.32	2982	1600	510	21	7.2
VB <sub>2</sub>	5.05	2747	2150	510	13	7.6
VC	5.41	2648	2900	430	59	7.3
VN	6.11	2177	1560	460	85	9.2
NbB <sub>2</sub>	6.98	3036	2600	630	12	8.0
NbC	7.78	3613	1800	580	19	7.2
NbN	8.43	2204	1400	480	58	10.1
TaB <sub>2</sub>	12.58	3037	2100	680	14	8.2
TaC	14.48	3985	1550	560	15	7.1
CrB <sub>2</sub>	5.58	2188	2250	540	18	10.5
Cr <sub>3</sub> C <sub>2</sub>	6.68	1810	2150	400	75	11.7
CrN	6.12	1050	1100	400	640	2.3
Mo <sub>2</sub> B <sub>5</sub>	7.45	2140	2350	670	18	8.6
Mo <sub>2</sub> C	9.18	2517	1660	540	57	7.8-9.3
W <sub>2</sub> B <sub>5</sub>	13.03	2365	2700	770	19	7.8
WC	15.72	2776	2350	720	17	3.8-3.9
LaB <sub>6</sub>	4.73	2770	2530	400	15	6.4

 Table 1.2.1 Properties of metallic hard materials. [61]

Materials	Density	Melting	Hardness	Young's	Resistivity	СТЕ
	(g/cm <sup>3</sup> )	Point	(HV)	modulus	(μ <b>Ω.cm</b> )	(10 <sup>-6</sup> K <sup>-1</sup> )
		(°C)		(GPa)		
B <sub>4</sub> C	2.52	2450	3000~4000	441	0.5×10 <sup>6</sup>	4.5(5.6)
BN(cubic)	3.48	2730	~5000	660	10 <sup>18</sup>	/
C(diamond)	3.52	3800	~8000	910	10 <sup>20</sup>	1.0
В	2.34	2100	2700	490	10 <sup>12</sup>	8.3
AlB <sub>12</sub>	2.58	2150	2600	430	2×10 <sup>12</sup>	/
SiC	3.22	2760	2600	480	10 <sup>5</sup>	5.3
SiB <sub>6</sub>	2.43	1900	2300	330	107	5.4
Si <sub>3</sub> N <sub>4</sub>	3.19	1900	1720	210	10 <sup>18</sup>	2.5
AlN	3.26	2250	1230	350	10 <sup>15</sup>	5.7

 Table 1.2.2 Properties of covalent hard materials. [61]

Materials	Density (g/cm <sup>3</sup> )	Melting Point (°C)	Hardness (HV)	Young's modulus (GPa)	Resistivity (μΩ.cm)	СТЕ (10 <sup>-6</sup> К <sup>-1</sup> )
Al <sub>2</sub> O <sub>3</sub>	3.98	2047	2100	400	10 <sup>20</sup>	8.4
AlTiO <sub>5</sub>	3.68	1894	/	13	10 <sup>16</sup>	0.8
TiO <sub>2</sub>	4.25	1867	1100	205	1	9.0
ZrO <sub>2</sub>	5.76	2677	1200	190	10 <sup>16</sup>	11(7.6)
HfO <sub>2</sub>	10.2	2900	780	/	1	6.5
ThO <sub>2</sub>	10.0	3300	950	240	1016	9.3
BeO	3.03	2550	1500	390	10 <sup>23</sup>	9.0
MgO	3.77	2827	750	320	10 <sup>12</sup>	13.0

 Table 1.2.3 Properties of ionic hard materials. [61]

Table 2.1 Phase transformation temperatures and structures of specimen BH and BS.

Specimen	A <sub>s</sub> (°C)	A <sub>f</sub> (°C)	R <sub>s</sub> (°C)	R <sub>f</sub> (°C)	M <sub>s</sub> (°C)	M <sub>f</sub> (°C)	Structure
BH	72	94	63	56	47	27	B19'
BS	3	46	44	4.0	/	/	B2 + R-phase

**Table 2.2** Mechanical Properties of martensitic (specimen BH), austenitic (specimen BS), and amorphous NiTi thin film obtained from nanoindentation test.

Specimen	Hardness (GPa)	E (GPa)	E <sup>*</sup> (GPa)	H/E <sup>*</sup>	ղհ
BH	2.5	43.6	46.9	0.0553	0.33
BS	4.4	64.3	67.9	0.0648	0.47
Amorphous TiNi	7.9	158.0	153.6	0.0514	0.32

Specimen	CrN1-Al	CrN5-Al	CrN-S1-Al	CrN-S2-Al	CrN-Cr-Al
CrN thickness (µm)	1	5	1	1	1
Interlayer material	No	No	Ni51.8at%- Ti	Ni49.5at%-Ti	Cr
Interlayer thickness (µm)	/	/	4	4	4

**Table 3.1** Description of specimens

 Table 3.2 Composition and phase transformation temperatures of NiTi thin films.

Specimen	Film	Target	A <sub>s</sub>	A <sub>f</sub>	R <sub>s</sub>	R <sub>f</sub>	Ms	M <sub>f</sub>
	compositio <b>n</b>	composition	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)
<b>S</b> 1	Ni51.8at%- Ti	Ni49.8at%-Ti	1	15	8	-4	1	1
S2	Ni49.5at% -Ti	Ni48.0at%-Ti	67	96	1	/	62	28

Material	Al	S1 (Ni51.8at%- Ti)	S2 (Ni49.5at%-Ti)	Cr	CrN
H (GPa)	0.94	4.7	2.4	6.7	22.6
E (GPa)	77.6	95.0	89.3	318.4	252.6
$\eta_h$	0.067	0.33	0.23	0.16	0.64

**Table 3.3** Nanoindentation properties of aluminum substrate, interlayer materials (S1, S2 and Cr) and CrN hard coating.

**Table 3.4** A comparison of the mechanical properties of between superelastic NiTi and polyisoprene.

Materials	Young's modulus (GPa)	Tensile strength (GPa)	Elongation	Recoverable strain
Superelastic NiTi	75	754-960	15.5%	5~8%
Polyisoprene	0.002~0.1	0.01	100~800%	100~800%

Note: Polyisoprene is a thermoset elastomeric polymer.

Materials	Young's modulus E (GPa)	Poisson's ratio v	Composite Reduced modulus E* (GPa)	Reference
Copper	126	0.345	127.2	[156]
6061-T6 Aluminum	70.4	0.347	74.8	[157]
Tungsten	409.8	0.28	320.4	[157]
Fused silica	72	0.17	69.6	[101]

**Table 4.1** Mechanical properties of the tested materials.

**Table 4.2** Relationship between Poisson's ratio and constraint factor for elastic contact with a rigid spherical indenter.

Poisson's ratio	0	0.1	0.2	0.3	0.4	0.5
Constraint factor	2.12	2.14	2.21	2.33	2.53	2.83



Figure 1.1.1 DSC test shows characteristic phase transformation temperatures of NiTi shape memory alloy.

$\overbrace{(T < M_{f})}{}$ heating $(T > A_{f})$		deform $(T \leq A_1)$	$\xrightarrow{\text{perform}}_{\text{perform}}$	
(2)	(h)	(c)	40000 (1)	(e)
(a)	(0)	(c)	(a)	(0)

Figure 1.1.2 A schematic representation of the shape memory effect of NiTi alloy. [5]



Figure 1.1.3 A schematic representation of superelasticity of NiTi alloy.



Figure 1.1.4 Representative stress-strain curves of shape memory and superelastic NiTi alloys. [4]

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Figure 1.1.5 Phase diagram of binary NiTi alloy.



Figure 1.1.6 NiTi shape memory alloy: dependence of martensite strart temperature on composition. [4]



Figure 1.1.7 A comparison of wear rates between Ti50Ni47Fe3 and SAE 52100 steel. [20]



Figure 1.1.8 A schematic representation of sputtering process.



Figure 1.2.1 Residual stresses in thin films cause bending of the specimen. [64]

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**Figure 1.2.2** Schematic representation of coating failure modes in the scratch test in profile and plan view: spalling failure (a); buckling failure (b); chipping failure (c); conformal cracking (d), and tensile cracking (e). [76]



Figure 1.3.1 A schematic illustration of the load-displacement curve of instrumented indentation test and the graphical interpretation of contact depth. [91]



Figure 1.3.2 Illustration of conical indentation experiment. [97]



Figure 1.3.3 Degree of piling-up and sinking-in,  $h_c/h$ , as a function of the ratio of yield stress to Young's modulus, Y/E, and work hardening exponent, n, in conical indentation experiments. [97]



**Figure 1.3.4** The top-point, instead of the cross point, defines the contact perimeter when piling-up occurs. [110]

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Figure 1.3.5 A relationship between the ratio of irreversible work to total work,  $W_p/W_t$ , and ratio of residual depth to maximum indentation depth,  $h_f/h_m$ , in conical indentation experiments. [106]

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Figure 1.3.6 A relationship between the ratio of residual indentation depth to maximum indentation depth,  $h_f/h_m$ , and ratio of harness to reduced modulus,  $H/E^*$ , in conical indentation experiments. [106]



Figure 1.3.7 Different combination of Y/E and n can lead to the same load-displacement curve in conical indentation experiments: Highly elastic materials (a), and high plastic materials (b). [105]



Figure 1.3.8 Relationship between representative strain ~ hardness and true strain ~ true stress. Curve A, mild steel. Curve B, annealed copper. O × hardness measurement. — stress-strain curve. ( $P_m$  stands for the hardness in this figure.) [132]



Figure 1.3.9 A schematic illustration of the evolution of plastic zone during spherical indentation process: elastic (a), elastic-plastic (b), and fully-plastic (c). [125]



Figure 2.1 DSC curves of specimen BH (a) and BS (b).



Figure 2.2 XRD patterns of specimen BH and BS.



Figure 2.3 A schematic illustration of thermally activated recovery of indent on shape memory alloy (specimen BH).



Figure 2.4 Change of residual indentation depth was observed for Berkovich indent (a) and Vickers indent (b) on a NiTi shape memory alloy (specimen BH) after heating to above austenite finish temperature.



**Figure 2.5** Relationship between recovery ratio and residual indentation depth for Berkovich and Vickers indents on a NiTi shape memory alloy (sample BH).



Figure 2.6 Geometry of the spherical indenters measured by SEM: R=213.4  $\mu m$  (a) and R=106.7  $\mu m$  (b).



Figure 2.7 Spherical indents on a NiTi shape memory alloy (specimen BH): before heating (a), after heating (b), 3D profile of indent before heating (c), 3D profile of indent after heating (d), and recovery ratio as a function of residual indentation depth (e). Figures (c) and (d) are in color.



Figure 2.8 Cross-section profile of the spherical indents on specimen BH shows that no piling-up occurs.



Figure 2.9 A schematic illustration of indentation sinking-in for spherical indentation experiments.

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**Figure 2.10** Relationship between thermally activated recovery ratio and representative strain, and the relationship between the true stress and true strain of a NiTi shape memory alloy (specimen BH). The recovery ratio starts to decrease when the representative strain exceeds the critical strain in the stress-strain curve.



Figure 2.11 A schematic representation of the elastic recovery of indents after removal of the load.

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**Figure 2.12** Berkovich indentation of a superelastic NiTi alloy (specimen BS) and copper: load-displacement curves (a), and depth (squares) and work (triangles) recovery ratios upon unloading at various depths (b). Filled symbols for NiTi and unfilled symbols for copper.



Figure 2.13 Load-displacement curves of spherical indentation on a superelastic NiTi alloy (specimen BS) and copper (R=213.4 $\mu$ m) (a), and relationship between the depth recovery ratio and representative strain, and the relationship between the true stress and true strain of the superelastic NiTi alloy determined in a tensile test (b). The recovery ratio starts to decrease when the representative strain exceeds the critical strain in the stress-strain curve.



Figure 2.14 XRD shows indentation induced austenite  $\rightarrow$  martensite transformation in specimen BS: non-indented area (a) and inside the indent (b).

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Figure 2.15 Finite element modeling of strain distribution under sharp indenter (a) and spherical indenter (b). The white region right under the conical indenter has a minimum strain larger than the maximum strain under the spherical indenter. Regions with the same color have a plastic strain of the same value in (a) and (b). Images in this figure are in color.



Figure 2.16 A schematic figure of the target for the deposition of amorphous NiTi film.



Figure 2.17 XRD of amorphous NiTi thin film.



Figure 2.18 Load-displacement curves of martensitic (specimen BH), austenitic (specimen BS) and amorphous NiTi.



Figure 2.19 Dry sliding wear rate of martensitic (specimen BH), austenitic (specimen BS) and amorphous NiTi.



Figure 2.20 XRD spectra show wear-induced austenite  $\rightarrow$  martensite transformation in specimen BS: outside the wear track (a) and inside the wear track (b).



**Figure 3.1** A schematic illustration of the structure of sputtering equipment for deposition NiTi thin films.



Figure 3.2 DSC curves of post-annealed NiTi thin films show that, at room temperature, specimen S1 is austenitic (a), while specimen S2 is martensitic (b).



Figure 3.3 XRD patterns of post-annealed NiTi thin films: S1 (a), and S2 (b).



Figure 3.4 XRD pattern of 5µm thick CrN coating on aluminum substrate (specimen CrN5-Al).



**Figure 3.5** Berkovich indentation test on various materials: load-displacement curves (a) and the relationship between  $H/E^*$  and depth recovery ratio (b).



Figure 3.6 Berkovich indentation tests at various depths: composite hardness (a), and depth recovery ratio (b).













Figure 3.7 SEM images of the end of scratches on CrN1-Al (a), CrN5-Al (b), CrN-S1-Al (c), CrN-S2-Al (d), and CrN-Cr-Al (e). The arrow indicates the scratch direction.



Figure. 3.8 A schematic illustration of the stress-strain curves of superelastic NiTi (a) and elastomeric polymer (b).



Figure 3.9 Friction coefficient and durability of coatings obtained by pin-on-disk test: specimen CrN1-A land CrN-S2-Al (a), and specimen CrN-Cr-Al, CrN5-Al and CrN-S1-Al.



**Figure 3. 10** Friction coefficient of specimen CrN-S1-Al and CrN-Cr-Al measured by scratch test using progressive load up to 2N.







Fig. 3.12 Illustration of a spherical indenter sliding on a material: piling-up (a) and sinking-in (b).



Figure 3.13 Extent of material piling-up around a scratch made by a progressive load up to 6N: 3D profile of CrN-SI-AI (b), cross-section profile of CrN-Cr-AI (c), and cross section profile of CrN-SI-AI (d). Note that dash lines in (a) an (b) indicate the locations for cross section profile. Figures (a) and (b) are in color.



Figure 3.14 Wear rate of the specimens. Note that the Y-axis is in logarithm scale.


Figure 4.1 Schematic illustration of indentation load-displacement curve and definition of the irreversible work,  $W_r$ - $W_u$ , and reversible work,  $W_u$ .

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Figure 4.2 Finite element modeling: overall mesh and contact counterparts (a), and magnified image of the top-left part of the overall mesh (b).



Figure 4.3 A schematic illustration of indentation piling-up for spherical indentation experiment.





**Figure 4.4** Extent of piling-up  $(h_c/h_{max}>1)$  and sinking-in  $(h_c/h_{max}<1)$  as a function of  $h_{max}/R$  (a-c), Y/E (d), and strain-hardening exponent n (e), in spherical indentation simulations. Note that (a), (b) and (c) represent materials with strain-hardening exponent n=0.1, 0.3 and 0.5, respectively, (d) represents material with n=0.1,  $h_{max}/R=0.05$ , 0.2 and 0.4, (e) represents materials with Y/E=0.05,  $h_{max}/R=0.05$ , 0.2 and 0.4. PU stands for piling-up and SI stands for sinking-in.



Figure 4.5 Calculated load-displacement curves of a material with Y/E=0.025, v=0.2, and n=0.5 at various indentation depths.



Figure 4.6 Finite element result shows that, for all the materials studied, a linear relationship exists between  $h_f / h_{max}$  and  $(W_l - W_u)/W_l$ .



Figure 4.7 For each fixed  $h_{max}/R$ , a linear relationship exists between  $H/E^*$  and  $(W_r - W_u)/W_t$  for spherical indentation in elastic-plastic solids with work-hardening.



Figure 4.8 A linear relationship between  $ln(h_{max}/R)$  and ln(-B).



Figure 4.9 Spherical indentation experiments show that a linear relationship exists between  $h_f / h_{max}$  and  $(W_t - W_u)/W_t$ . The finite element results are also shown in this figure.



Figure 4.10 Experimental load-displacement curves for spherical indentation in a copper sample.



Figure 4.11 Effective indenter radius,  $R_{eff}$ , as a function of indentation depth,  $h_{max}$  for an imperfect spherical diamond indenter.



Figure 4.12 Experimental load-displacement curves obtained from instrumented spherical indentation experiments in aluminum (a), tungsten (b), and fused silica (c).



Figure 4.13 Measured composite reduced modulus (a) and hardness (b) using the energybased method together with indenter shape calibration. The error bar indicates the standard deviation of the measured values.



Figure 4.14 Relationship between hardness and true stress for spherical indentation in elastic material (a), material with Y/E=0.002, n=0.3, and (c) material with Y/E=0.025, n=0.3. The horizontal axis represents true strain or representative strain of the same value.



Figure 4.15 Constraint factors for various materials at different indentation depths: n=0.1 (a), n=0.3 (b) and n=0.5 (c). Note that the scale for x-axis is different in (a), (b) and (c).

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