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Nanoindentation under Dynamic Conditions

Jeffrey M. Wheeler
Clare College, University of Cambridge

A dissertation submitted for the degree of Doctor of Philosophy
at the University of Cambridge.

Preface

This dissertation is submitted for the degree of Doctor of Philosophy at the University of Cambridge. The work described in this document was carried out in between October 2005 and October 2008 under the supervision of Prof. T. W. Clyne in the Department of Materials Science & Metallurgy at the University of Cambridge.

To the best of my knowledge the work described in this dissertation is original, except where reference has been made to the work of others, and has not been submitted, in part or entirety, for any degree or qualification at any other university.

Jeffrey M. Wheeler
Clare College
University of Cambridge
February 2009

Abstract

Nanoindentation has emerged as a leading technique for the investigation of mechanical properties on small volumes of material. Extensive progress has been made in the last 20 years in refining the instrumentation of nanoindentation systems and in analysis of the resulting data. Recent development has enabled investigation of materials under several dynamic conditions.

The palladium-hydrogen system has a large miscibility gap, where the palladium lattice rapidly expands to form a hydrogen-rich β phase upon hydrogenation. Nanoindentation was used to investigate the mechanical effects of these transformations on foils of palladium. Study of palladium foils, which had been cycled through hydrogenation and dehydrogenation, allowed the extent of the transformed region to be determined. Unstable palladium foils, which had been hydrogenated and were subject to dynamic hydrogen loss, displayed significant hardening in the regions which were not expected to have transformed. The reason for this remains unclear.

Impact indentation, where the indenter encounters the sample at relatively high speeds, can be used to probe the strain rate dependence of materials. By combining impact indentation and elevated temperature indentation, the strain rate dependence of the superelasticity of nickel-titanium was probed over a range of temperatures. Similar trends in elastic energy ratios with temperature were observed with the largest elastic proportions occurring at the austenite finish transformation temperature.

Multiple impact and scratch indentation are two modes of indentation which are thought to approximate erosive and abrasive wear mechanisms, respectively. These were utilised to investigate the wear resistance of several novel coatings formed by plasma electrolytic oxidation (PEO) of Ti-6Al4-V. Multiple impact indentation results appear to subjectively rank the erosive wear performance of both ductile and brittle materials. Comparison of normalised performance of coating systems on aluminium in abrasive wear to scratch hardness showed similar degrees of resistance.

Jeffrey M. Wheeler, 2009

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I am grateful to many members of the department for their help with various pieces of equipment. Thanks go to members of the Gordon Laboratory for day-to-day support, advice and mutual time-wasting. Special thanks are due to Sonya Pemberton and Andy Collier. The results of their Part III projects, conducted partly under my supervision, make up significant portions of chapters 6 and 7, respectively. I am also grateful to Sandra Korte for commiseration on indenter difficulties and putting up with my various rants.

A few lines are insufficient to thank my parents for all their efforts which made this possible. It is a greater testament to their efforts that I was able to accomplish this than to my efforts in accomplishing it.

Nomenclature

Roman Symbols

a	nm	Radius of contact impression on conical/spherical indents
A	nm^2	Contact area
A_F	$^{\circ}C$	Austenite transformation finish temperature
A_{LB}	nm^2	Contact area normal to the indenter which is load bearing during scratch indentation
A_{PT}	nm^2	Projected tangential contact area which is subjected to tangential loading during scratch indentation
A_S	$^{\circ}C$	Austenite transformation start temperature
B	-	Correction factor for polygonal indenters
c	-	Mole fraction of hydrogen to palladium
C_c	-	Critical mole fraction of hydrogen to palladium
C_0	$nm\ mN^{-1}$	System compliance, inverse of Stiffness, S , on data uncorrected for frame compliance, C_F
C_F	$nm\ mN^{-1}$	Compliance of the indenter frame
C_S	$nm\ mN^{-1}$	Compliance of the tip and sample, inverse of Stiffness, S , on data corrected for frame compliance, C_F
D	m^2s^{-1}	Diffusion coefficient
D_0	m^2s^{-1}	Pre-exponential factor for diffusion
DHV	-	Dynamic Vickers Hardness
d	μm	Diagonal length of residual impression after Vickers indentation
E	GPa	Young's modulus
E_i	GPa	Young's modulus of indenter tip
E_r	GPa	Reduced modulus
f_{int}	-	Intercept correction factor for surface displacement extrapolation
h	nm	Displacement
h_c	nm	Displacement during contact
h_e	nm	Displacement during spherical indentation which is elastic
h_f	nm	Displacement of final impression after unloading
h_m	nm	Displacement measured during oblique incidence indentation
h_{max}	nm	Displacement at peak load
h_s	nm	Displacement of the surface at the contact perimeter
h_{tan}	nm	Maximum depth to which a conospheroidal indenter approximates a sphere
h_{total}	nm	Total displacement during spherical indentation
H	GPa	Hardness – mean pressure supported by sample
H_{Dyn}	GPa	Dynamic Hardness – mean pressure supported by sample under impact indentation

H_S	GPa	Scratch Hardness – mean pressure supported by sample
HV	-	Vickers Hardness
K	J	Impact kinetic energy
k_B	$J K^{-1}$	Boltzmann constant - $1.380658e-23 \pm 1.2e-28$
L	m	Length
l	-	Dimensionless fitting parameter
m	-	Dimensionless fitting parameter
n	-	Number of atoms
p	atm	Pressure of H_2 atmosphere
P	mN	Load
Q	$kJ mol^{-1}$	Activation energy
R	$J mol^{-1} K^{-1}$	Molar gas constant - $8.31451 \pm 7.0e-05$
S	$mN nm^{-1}$	Stiffness – dp/dh at peak load and depth
T	$^{\circ}C$	Temperature
T_c	$^{\circ}C$	Critical temperature above which hydrogen has no miscibility gap in palladium
t	sec	Time
v	m^3	Atomic volume
v_0	m^3	Atomic volume of pure palladium
V	m^3	Volume
W_P	J	Work of indentation which is plastic
W_{total}	J	Total work of indentation
W_u	J	Work of indentation which is elastically recovered during unloading

Greek Symbols

α	-	Hydrogen-poor phase of palladium
α'	-	Designation for hydrogen-poor phase of palladium used by some authors
α_{max}	-	Maximum H-Pd mole fraction for α palladium
β	-	Hydrogen-rich phase of palladium
β_{min}	-	Minimum H-Pd mole fraction for β palladium
ΔH	$kJ mol^{-1}$	Enthalpy of formation
ΔS^0	$J K^{-1} mol^{-1}$	Entropy of formation
ε	-	Strain
η	Pa	Linear work hardening parameter
φ	$^{\circ}$	Angle between indenter face and central axis
ν	-	Poisson's ratio
ν_i	-	Poisson's ratio of indenter
σ	MPa	Stress
σ_y	MPa	Yield stress

Table of Contents

Preface.....	i
Abstract.....	ii
Acknowledgements.....	iii
Nomenclature.....	iv
Table of Contents.....	vi
1 Introduction	1
1.1 Hardness Measurement.....	1
1.2 Nanoindentation.....	2
1.3 Structure of Thesis	2
2 Nanoindentation	4
2.1 Nano-Indentation Procedures.....	4
2.1.1 Oliver and Pharr's Analysis	5
2.1.2 Indenter Compliance and Shape Function	8
2.1.3 Thermal Drift and Creep.....	8
2.2 Spherical Indentation	9
2.3 Secondary Concepts.....	13
2.3.1 Indenter Geometry	13
2.3.2 Pile-up and Sink-in Behaviour.....	14
2.3.3 Contact Area-Independent Functions	15
2.3.4 Work of Indentation.....	15
2.3.5 Indentation Strain Rate	16
2.3.6 Indentation Strain Fields	17
2.4 Calibration Materials	18
3 Elevated Temperature, Impact and Scratch Indentation.....	21
3.1 Elevated Temperature Indentation.....	21
3.1.1 Elevated Temperature Systems.....	21
3.1.1.1 Axial-Loading Systems.....	22
3.1.1.2 Pendulum-based Systems.....	24
3.1.2 Reactivity at Elevated Temperatures	25
3.1.2.1 Oxidative Diamond Loss	26
3.1.2.2 Tip-Sample Interaction	27
3.2 Impact Indentation	27
3.2.1 Projectile-based Dynamic Hardness Apparatus.....	28
3.2.2 Pendulum-based Dynamic Hardness Apparatus.....	31
3.3 Scratch Testing.....	34
4 Experimental Methods.....	38
4.1 Materials and Specimen Preparation	38
4.1.1 Palladium Foils	38
4.1.2 Superelastic NiTi	40
4.1.3 PEO Coatings.....	41
4.1.4 Metallographic Preparation.....	42
4.2 Characterisation	43
4.2.1 Optical Microscopy.....	43
4.2.2 Scanning Electron Microscopy	43
	vi

4.2.3	Atomic Force Microscopy	43
4.2.4	X-ray Diffraction	43
4.2.5	X-ray Energy Dispersive Spectroscopy (EDS).....	44
4.3	Quasi-Static Indentation.....	44
4.3.1	Tip Shape Characterisation	45
4.4	Impact Indentation	45
4.5	Scratch Indentation	47
4.6	Elevated Temperature Indentation	48
4.6.1	Diamond Indenter Oxidation	49
4.6.2	Diamond Indenters Used <400°C	55
4.6.3	Step Discussion	56
4.7	Tribological Testing.....	57
5	Indentation of the Pd-H System	59
5.1	Aims of Research	59
5.2	Review of the Palladium-Hydrogen System.....	59
5.2.1	Pressure-Composition-Temperature Relations	59
5.2.2	Crystallography	61
5.2.3	Hydrogen Adsorption/Diffusion	63
5.2.4	Phase Transformation Mechanism.....	65
5.2.5	Volume Expansion	67
5.2.6	Mechanical Behaviour	68
5.3	Characterising Sample Dynamics	73
5.3.1	Gravimetric Analysis	73
5.3.2	Crystallography.....	75
5.3.3	Microstructure.....	77
5.4	Nanoindentation Results	78
5.4.1	Single Phase Compositions.....	79
5.4.2	Two Phase Compositions.....	83
5.5	Hardening and Hydrogen Egress	88
5.6	Summary	91
6	Impact Indentation of Superelastic NiTi	93
6.1	Aims of Research	93
6.2	Review of Superelasticity	93
6.2.1	General Superelasticity	94
6.2.1.1	Strain Rate Dependency of Superelastic Behaviour	96
6.2.1.2	Temperature Effect on Superelastic Behaviour	97
6.3	Impact Loading	98
6.3.1	Data Analysis	99
6.3.2	Dynamic Compliance.....	103
6.3.3	Strain Rates during Impact.....	105
6.4	Quasi-static and Impact Indentation of NiTi	108
6.5	Summary	113
7	Multiple Impact and Scratch Indentation of PEO Coatings	114
7.1	Aims of Research	114
7.2	Review of PEO Coating Systems	115
7.2.1	Erosive Wear.....	116
7.2.2	Abrasive Wear	118
7.3	Characterisation Results.....	119
		vii

7.3.1	Coating Thickness and Morphology	119
7.3.2	Coating Composition	122
7.3.3	Mechanical Properties.....	124
7.4	Multiple Impact Indentation	127
7.4.1	Low Sampling Rate Data Analysis	128
7.4.2	Impact Hardness Analysis.....	130
7.4.3	Multiple Impact Fatigue.....	133
7.4.4	Impact Indentation at Oblique Incidence	138
7.4.4.1	Adaptation for Oblique Testing	138
7.4.4.2	Measurement Corrections	138
7.4.4.3	Maximum Depths.....	139
7.5	Erosive Wear Behaviour	143
7.5.1	Sandblasting of Ti-6Al-4V Coating.....	143
7.6	Comparison of Wear to Multiple Impact Testing.....	145
7.7	Scratch Indentation	146
7.7.1	Displacement Rate Sensitivity	147
7.7.2	Elastic Scratch Deformation	147
7.7.3	Scratch Indentation of PEO Coating Systems	149
7.7.3.1	Substrate Alloys	149
7.7.3.2	Coatings on Aluminium Alloys	150
7.7.3.3	Coatings on Ti-6Al-4V	151
7.7.3.4	Mean Depths and Roughness.....	153
7.7.4	Scratch Hardness.....	155
7.8	Abrasive Wear Behaviour.....	157
7.9	Summary	158
7.9.1	Novel Ti Coatings	158
7.9.2	Multiple Impact Testing.....	158
7.9.2.1	Oblique Multiple Impacts	160
7.9.3	Scratch Testing.....	160
7.9.4	Wear Comparison	162
8	Conclusions & Future Work.....	163
8.1	Indentation of Pd-H System.....	163
8.2	Impact Indentation of Superelastic NiTi.....	164
8.3	Multiple Impact and Scratch Indentation of PEO Coatings.....	164
8.3.1	Novel Ti Coatings	164
8.3.2	Multiple Impact Testing.....	165
8.3.2.1	Oblique Multiple Impacts	166
8.3.3	Scratch Testing.....	166
8.3.4	Wear Comparison	167
9	References	168

1

Introduction

Nanoindentation as a tool for investigation of mechanical properties on small length scales is introduced, with a view toward high temperature characterisation. An outline for the remainder of this dissertation is provided.

1.1 Hardness Measurement

It has been nearly two centuries since the first hardness test was developed by Mohs¹ in 1822. In that time, the state of the art has progressed from using reference materials to rank scratch relative resistance to the application of contact mechanics principles using instrumented, automated systems to probe mechanical properties on the nanometre scale.

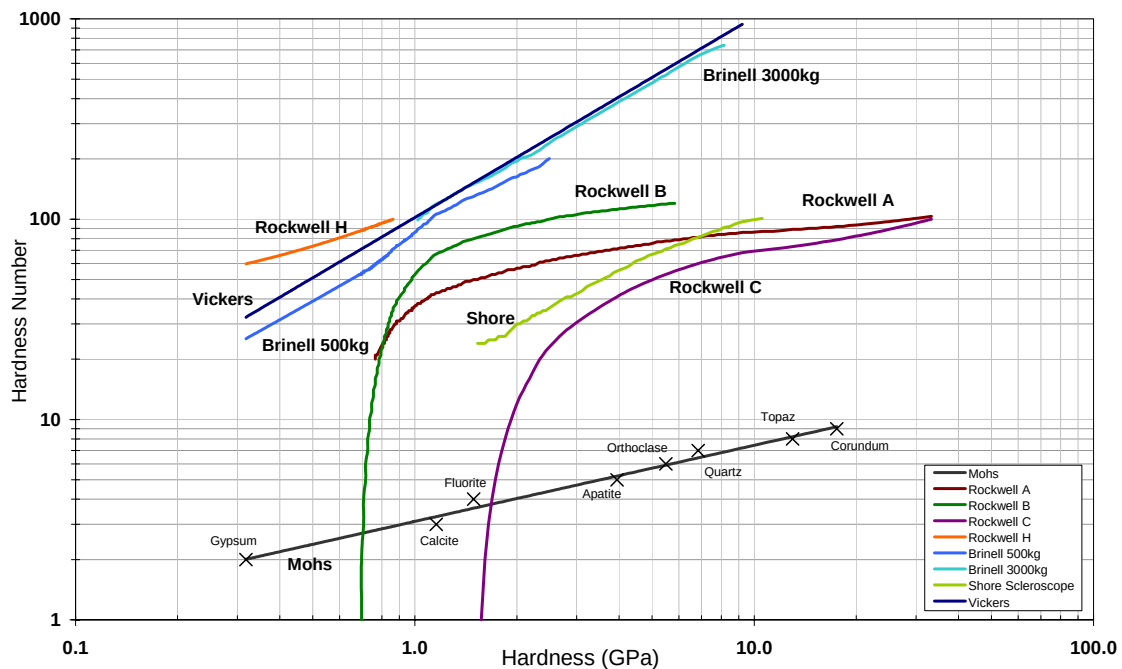


Fig. 1.1. Rough equivalent hardness conversion chart for various standard hardness tests to Berkovich hardness^{2, 3}.

Many different standard tests (Fig. 1.1) have been developed in the intermediate period, and these have been extensively used by science industry for research,

development, and quality control purposes. This is a testament to the significance of hardness testing as one of the most powerful and straightforward mechanical tests.

1.2 Nanoindentation

In the last two decades, instrumented indentation capable of probing the nanometre scale, i.e. nanoindentation, has emerged as an important technique for characterising mechanical behaviour on small length scales. Initial application of this technique was applied to thin film investigation^{4, 5} and investigation of small length scale effects^{6, 7}. Recent studies have involved indentation in a variety of environments, including immersion in liquids⁸, high and low temperatures^{9,10,11}, and high strain rate testing¹². This allows for measurement of mechanical behaviour in simulated *in vivo* or in industrial conditions.

Nanoindentation systems have thus enjoyed enormous popularity as they represent the current state of the art of a long tradition of hardness testing machines and they are effectively non-destructive and can be applied to very small specimens. There is now considerable interest in the further development to extend their capabilities. Thus this dissertation examines the further application of instrumented-indentation techniques, or Nanoindentation, to the investigation of materials under dynamic conditions and establishes some of the possibilities and limitations for obtaining new and unique information from a range of challenging materials systems where such approaches could be beneficially applied.

1.3 Structure of Thesis

Chapter 2 discusses the general application of instrumented indentation analysis. The current state of analyses for both pyramidal/conical and spherical indenter geometries is provided. Secondary concepts, such as work of indentation, indentation strain rate, and the strain field under indentations, are also presented.

Chapter 3 details the progress on developing indentation techniques under dynamic conditions. The conditions of elevated temperature, impact and scratch are focussed upon. The design considerations for indentation systems for elevated temperature operation and impact are discussed.

Chapter 4 describes the experimental methods used in this investigation. The metallurgical preparations conducted prior to indentation testing and characterisation are presented. The procedures utilised during quasi-static, impact and scratch indentation are also delineated.

Chapter 5 contains the research conducted on the palladium-hydrogen system, which is of interest due to its instability under ambient conditions, and its relevance to hydrogen storage technology. The initial aims of the work are introduced in the first section. A brief background on the properties of the system is then provided, and the various techniques used to generate and characterise the palladium hydrides are described. The results of investigating the mechanical variation due to hydrogenation/dehydrogenation via nanoindentation are finally discussed.

Chapter 6 presents the research conducted on the impact indentation of a superelastic nickel-titanium alloy. The initial aims of the work are introduced. A brief background on superelasticity is provided in the following section, and the analysis of the impact indentation data is described. The variation in superelastic behaviour, as observed with elevated temperature, quasi-static and impact indentation, is discussed.

Chapter 7 describes the work performed using multiple impact and scratch indentation on novel coatings generated using plasma electrolytic oxidation (PEO) on Ti-6Al-4V alloys. The initial aims of the work are introduced in the first section. A brief background on PEO coatings is given in the next section, and the characterisation of their microstructural properties and composition are described. The analysis used on multiple impact indentation data, and the results, is delineated. Multiple impact results are compared to erosive wear performance of the coatings. Scratch indentation results are also discussed and compared to abrasive wear performance.

Chapter 8 summarises the conclusions of this investigation, as well as recommendations concerning future work to be carried out in the area.

2

Nanoindentation

The applications of nanoindentation techniques to various materials are described. Basic analyses for extraction of mechanical properties, such as hardness and elastic modulus, are discussed. Both pyramidal and spherical indenter tip geometries and their analyses are discussed. A brief discussion on extraction of stress-strain relationships using spherical indenters is provided. The characteristics of materials suitable for use as calibration standards are also described.

2.1 Nano-Indentation Procedures

Nanoindentation is the application of controlled load (μN - mN range), with concurrent measurement of depth (nm - μm range) through use of a hard indenter tip. A typical load-displacement curve for a ductile metal is shown in Figure 2.1.

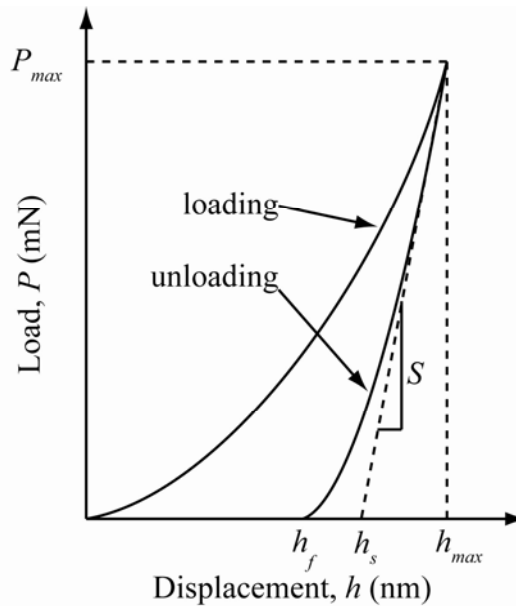


Fig. 2.1. Typical load-depth curve from an indentation, showing $f_{\text{int}} = 1$.

Unlike a stress-strain curve from a tension test, extraction of mechanical properties from such plots is not straightforward. The loading portion of the curve incorporates convoluted response of the material to strain including elastic, plastic and even phase transformation deformation mechanisms. However, the unloading portion of the curve, for most materials, consists mainly of elastic recovery. Deviations from smooth

behaviour such as pop-in and pop-out displacements are commonly observed^{13, 14} in some materials, such as alumina and silicon. It is by analysis of this portion that hardness and elastic modulus can be determined.

2.1.1 Oliver and Pharr's Analysis

Though many analyses¹⁴⁻²⁰ exist for the interpretation of load-displacement data from nanoindentation, the most popular was proposed by Oliver and Pharr¹⁴. This is utilised throughout this work to determine hardness and modulus from indentation data. Oliver and Pharr determined that the unloading curve follows a power law relation

$$P = l(h - h_f)^m \quad (2.1)$$

and proposed the following analysis. The stiffness of the elastic contact, S , is the derivative of Equation 2.1, dP/dh , evaluated at the peak load, P_{max} , and peak depth, h_{max} . Displacement of the surface surrounding the contact region is expected and differs from sink-in, which will be discussed later, in that it does not affect the contact area. If the indenter tip used is a flat punch, S could be used directly to extrapolate the surface displacement, h_s , as shown in Figure 2.1. However, for conical indenters or paraboloids of revolution, S must be adjusted with an intercept correction factor, f_{int} , to account for the effects of indenter geometry, yielding the relation

$$h_{max} - h_s = f_{int} \frac{P_{max}}{S} \quad (2.2).$$

Values for f_{int} , for commonly used indenter shapes, are provided in Table 2.1 in §2.2.1. Assuming sink-in/pile-up is negligible; subtracting the surface displacement from the maximum displacement yields the depth of the contact impression

$$h_c = h_{max} - h_s \quad (2.3).$$

This is illustrated schematically for conical indentations (axisymmetric) in Figure 2.2, with various dimensions labelled.

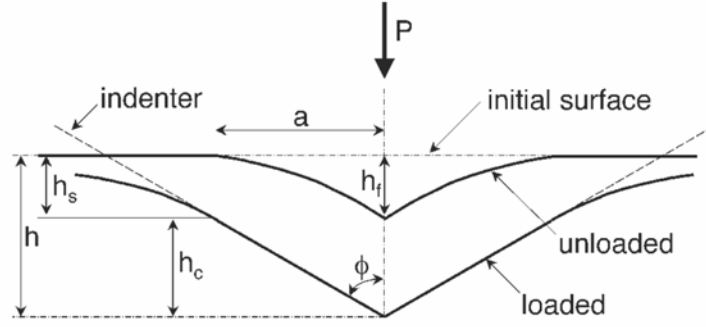


Fig. 2.2. Schematic representation of a section through the peak of a conical indent with relevant quantities labelled¹⁴.

The contact area is dictated by the indenter geometry,

$$A = F(h_c) \quad (2.4),$$

where F is a function relating penetration depth to projected contact area for the indenter. This projected contact area is the cross sectional area of the indenter at the depth of interest. This is used, instead of the surface area in contact with the material, because it has a physical relationship to the stress applied to the sample.

The various common indenter shapes have well-defined functions relating their ideal depth-contact area relationship. It is not uncommon for these ideal functions (listed in Table 2.1) to be used, especially for larger indentations, to arrive at approximate values. However, inevitable variation occurs in the manufacture of indenters, so the experimental determination of the shape function for each indenter is recommended. A method for this is described in the §2.1.2.

Hardness is defined as the load supported by the area of material in contact with the indenter

$$H = \frac{P}{A} \quad (2.5).$$

This is essentially an empirical ranking exercise, although the hardness value will depend on constitutive properties such as the yield strength and work hardening parameters of the material.

Determining the elastic modulus of the sample requires another extra consideration. The indenter tip, while preferably made of diamond, is not perfectly rigid. It

elastically deforms simultaneously with the sample, so account must be taken of this. It can be shown that the apparent “reduced” modulus is given by

$$E_r = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i} \quad (2.6).$$

This reduced modulus can be determined from the sample stiffness and the contact area, using

$$E_r = \frac{\sqrt{\pi}}{2B} \frac{S}{\sqrt{A}} \quad (2.7).$$

Here another correction factor, B , is introduced. This factor addresses the axial variation in stress introduced by non-axisymmetric, polygonal, indenter shapes. There has been intense debate over the values of $B^{21, 22}$. Values for f_{int} and B can be found in Table 2.1 in §2.2.1.

The intercept factor, f_{int} , was described by Oliver and Pharr²¹ in terms of an effective indenter shape, as illustrated in Figure 2.3. This shows schematically how the pressure distribution under the indenter causes different amounts of recovery under the indenter during unloading/reloading, causing a deviation from flat punch behaviour.

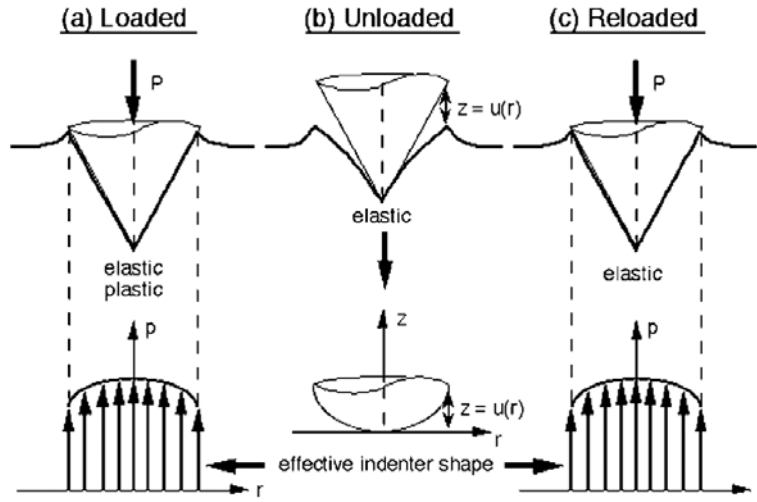


Fig. 2.3. Schematic illustrating the concept of effective indenter shape resulting from the pressure distribution under the indenter²¹.

A method used for determination of the values of f_{int} is described by Pharr and Bolshakov²³. Values of f_{int} were found to be dependent on the indenter shape and the material constants which describe the unloading behaviour of the material. However,

values of f_{int} were only found to vary between 0.74-0.79 over the range of materials, according to the results of Finite Element modelling studies.

2.1.2 Indenter Compliance and Shape Function

Considering that the sample and the indenter tip are not the only elastic components in the loading system, it is apparent that the frame compliance should be determined, in order to subtract its effect

$$C_0 = C_S + C_F \quad (2.8),$$

where C_0 is the observed, uncorrected compliance, C_S is the compliance of the sample and C_F is the frame compliance. Since the compliance of the sample and indenter are measured experimentally as the inverse of the stiffness, this can be expressed as

$$C_0 = C_F + \frac{\sqrt{\pi}}{2BE_r} \frac{1}{\sqrt{A}} \quad (2.9).$$

This demonstrates the necessity of a priori knowledge of the indenter shape function for determining the frame compliance. However, it is sometimes the case that both the shape function and the frame compliance are initially unknown. In this case, an iterative procedure achieving increasingly accurate approximations can be used. First, it can be assumed that the shape function of the indenter is ideal for its geometry and a (soft) sample can be indented at high loads, to create very large contact impressions. This minimises the deviation from ideal geometry, and, by using a reference sample of known reduced modulus, an approximate value for the frame compliance can be determined. Using that frame compliance value in Equation 2.9 allows the shape function to be estimated. By iterating this procedure, the values for the compliance and shape function can be refined for smaller indentations. Alternatively, the shape function can be determined directly by careful measurement of the shape of the tip using a traceably calibrated, precision metrology device such as an AFM.

2.1.3 Thermal Drift and Creep

Creep and thermal drift are very different phenomena, but corrections are made for their occurrence using similar procedures. Thermal drift occurs when the indenter system as a whole is not in thermal equilibrium. It results in displacements from thermal expansion/contraction being measured, instead of or in addition to,

indentation displacements. This can be minimised by placing the system in a thermally controlled chamber, but experimental measurement of the drift rate during each indentation should be made for accurate work. This is done by holding at a fixed load, e.g. ~20% of maximum applied load, for a fixed period during the lower part of the unloading curve and measuring the displacement over time.

Creep deformation may also occur during indentation. This is most easily observed during a hold period at maximum load. The influence of creep behaviour on instrumented indentation measurements, hardness and modulus, was systematically studied by Chudoba and Richter²⁴. It was found that the effect of creep on measurements are minimised by holding for a fixed period of experimentally determined duration at maximum load to allow creep displacement to become negligible. The period varies with material, but is commonly between 15-60 seconds for ambient temperature testing of soft metals.

2.2 Spherical Indentation

Pyramidal indentation can be thought of as a specific case of spherical nanoindentation. In spherical indentation, the relatively uniform, radially symmetric strain field applied to the sample is proportional to the indentation depth divided by the radius of curvature of the indenter²⁵, whereas in pyramidal/conical indentation an ideally sharp tip will cause a region of infinite strain directly below the tip, even at very low depths. This is equivalent to saying that the initial stage of indentation using a sharp cone or pyramid corresponds to spherical indentation using an infinitely small tip radius, such that the flow strain commensurate with that cone angle is instantly achieved²⁶. Figure 2.4 illustrates how the contact areas of blunted indenters of various tip radii, with a Berkovich equivalent cone angle, compare to the contact area of an ideal Berkovich indenter.

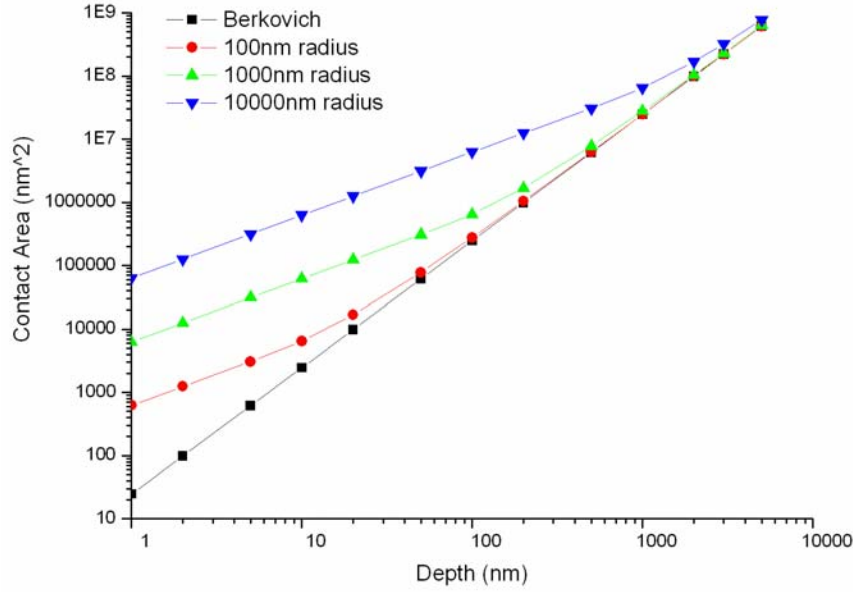


Fig. 2.4. Contact areas as a function of penetration depth calculated by the author for an ideal Berkovich indenter and conospheroidal indenters of different tip radii with an equivalent cone angle.

In reality, this is not the case for pyramidal/conical indenters at small depths, since they do not possess tips of ideal sharpness. Conical indenters whose tips are carefully blunted such that they approximate spheres of a desired radius are term conospheroids or conospheroidal indenters. Once indentation strain with a spherical tip surpasses the yield point, hardness and modulus results should be similar to those attained using a pyramidal indenter. Below the yield point, spherical indentation can provide more information on the elastic-plastic transition.

Historically, spherical indentation was more heavily researched, since it is more amenable to analysis; however, during the advent of micro/nano-scale indenters the pyramidal indenter tip became more popular, due to its effectiveness over a range of length scales and relative ease of manufacture. With the recent availability of conospheroidal indenters, with tip radii as small as 100 nm, several authors have proposed methods and analyses for their use in depth-sensing nanoindenters. The great majority of these are based on the Hertzian equation,

$$P = \frac{3}{4} E_r R^{\frac{1}{2}} h_e^{\frac{3}{2}} \quad (2.10),$$

where R is the radius of the spherical indenter and h_e is the elastic displacement.

There are several reviews^{22, 27-30} of these methods and their merits. Here the analysis proposed by Basu et al²⁷ is briefly described, since it effectively combines several of the merits of previous methods.

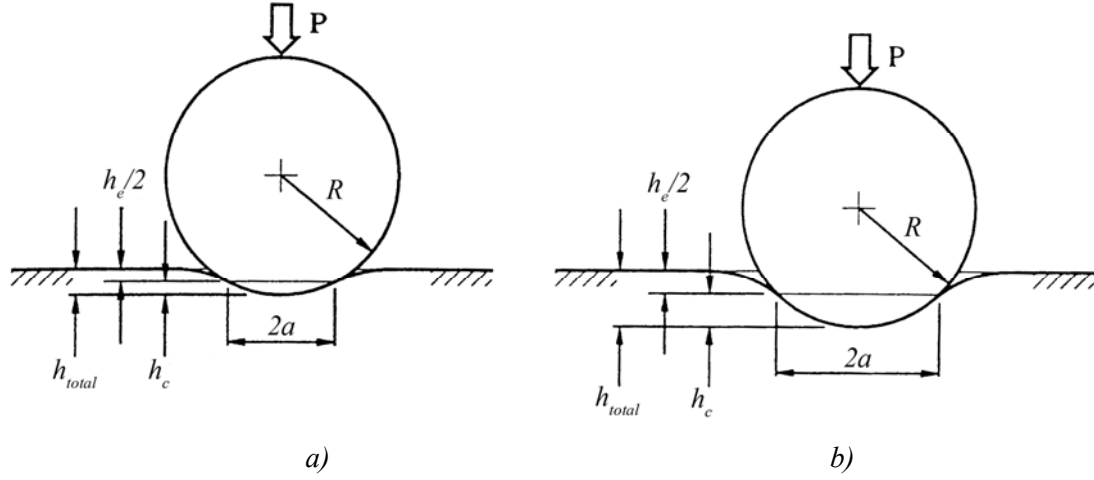


Fig. 2.5. Schematic representation of a) an elastic and b) an elastic-plastic spherical indentation³¹.

For the elastic regime, where the indenter does not leave a remnant impression ($h_f = 0$), Sneddon³² demonstrated that

$$h_e = h_{total} = \frac{a^2}{R} \quad (2.11),$$

where a is the radius of the circle of contact - see Figure 2.5. Differentiating the Hertz equation with respect to depth, h , and then substituting the differential into Equation 2.10 yields

$$P = \frac{2}{3} \frac{dP}{dh} h_e \quad (2.12).$$

As was mentioned earlier, dP/dh is equivalent to the stiffness, S , so

$$h_e = \frac{2}{3} \frac{P}{S} \quad (2.13).$$

Once h_e has been determined, it can be used, with Equation 2.11, to determine the contact radius, a , for an isotropic elastic solid

$$a = \frac{S}{2E_r} \quad (2.14).$$

In the elasto-plastic regime, where h_f is greater than zero, many aspects of spherical analysis are the same as for using a Berkovich indenter, such as the determination of the stiffness and contact depth from the unloading curve, using Equations 2.2 and 2.3,

and use of a ‘reduced’ modulus in Equation 2.6. This can be shown to be valid by assuming the contact depth, h_c , to be given by

$$h_c \approx h_{total} - \frac{h_e}{2} \quad (2.15).$$

Combining this with Equation 2.13 yields

$$h_c = h_{total} - \frac{3}{4} \frac{P}{S} \quad (2.16),$$

which is equivalent to Equation 2.3 combined with Equation 2.2, using the prescribed value of 0.75 for f_{int} .

For small spheres, where manufacturing limitations make perfect sphericity impossible to achieve, Equation 2.10 can be used on reference samples of known modulus, to determine an area function. For spheres greater than 2 μm in diameter, the contact area is generally determined by assuming perfect spherical geometry, rather than an experimentally-determined area function. The contact area is thus a function of the indenter radius, R , and the contact depth h_c :

$$A = \pi(2h_c R - h_c^2) \quad (2.17).$$

This area can then be used to determine the hardness with Equation 2.5 and the ‘reduced’ modulus with Equation 2.7.

Spherical indentation can be used to gain information about the yielding behaviour of materials, by plotting indentation ‘stress-strain’ curves. Tabor²⁵ determined that the flow stress is a simple function of the contact pressure for most metals:

$$\sigma \approx 0.36 \frac{P}{A} \quad (2.18).$$

Strain can be estimated by using Tabor’s²⁵ representative strain equation:

$$\varepsilon = 0.2 \left(\frac{a}{R} \right) \quad (2.19).$$

These representative strain values are equivalent to those achieved with a conical indenter whose cone angle approximates to the contact angle of the sphere with the sample surface²⁶.

2.3 Secondary Concepts

In §2.1, the main features of standard (pyramidal) nanoindentation were outlined. However, there are many secondary concepts of potential significance. These include indenter geometry and parameters which do not require knowledge of the contact area. A special case of this is the work of indentation, and its relationship to the plasticity index H/E_r . Finally, the issue of local and average strain rate is addressed.

2.3.1 Indenter Geometry

There are several different indenter geometries in common usage. Some of these, such as the Brinell sphere, Rockwell conospheroids, and Vickers and Knoop pyramids, are mostly used for macro-micro scale indentation. For the pyramids, this is due to the inevitable line of conjunction (chisel edge) formed across the tip of a four-sided pyramid whenever one side deviates from ideal geometry. Berkovich and cube corner indenters, however, are uniquely suited to nano-scale testing, since they can be manufactured with very small tip radii by virtue of their three-sided pyramidal geometry. Parameters for common indenter shapes are provided in Table 2.1.

Indenter Shape	Projected Area	Centerline-to-face Angle, ϕ	Equivalent Cone Angle	Intercept Factor, f_{int}	Correction Factor, B
<i>Sphere</i>	$\pi(2Rh_c - h_c^2)$	-	-	0.75	1
<i>Cone</i>	$\pi(h_c \tan(\phi))^2$	ϕ	ϕ	0.72	1
<i>Berkovich</i>	$24.562h_c^2$	65.3°	70.32°	0.75	1.05
<i>Cube Corner</i>	$2.598h_c^2$	35.26°	42.28°	0.75	1.034
<i>Vickers</i>	$24.504h_c^2$	68°	70.2996°	0.75	1.012
<i>Knoop</i>	$65.438h_c^2$	86.25° & 65°	-	0.75	1.012

Table 2.1. Geometric factors for commonly used indenter profiles^{21, 33, 34}.

For computational simplicity, pyramidal indenters are frequently modelled as cones with an angle which gives them equivalent depth-area functions as the pyramid. Spherical indenter tips manufactured for nano-scale indentation are generally conospheroids, a cone with a rounded tip which has a uniform radius of curvature until it becomes tangent with the cone. This tangent depth, h_{tan} , is the maximum depth at which the indenter can be accurately analysed as a sphere, and, for a blunted pyramidal indenter, it is the absolute minimum depth at which the indenter can be analysed as a pyramid.

2.3.2 Pile-up and Sink-in Behaviour

The Oliver and Pharr analysis assumes that the material around the contact impression deforms elastically during indentation. However, plastic deformation can occur in the surrounding material. Bolshakov and Pharr³⁵ used finite element modelling to study the influence of basic mechanical properties on this behaviour. They modelled the indenter as a rigid cone with the same area-to-depth ratio as a Berkovich indenter and assumed a frictionless interface between the indenter and the sample. In materials with a high modulus to yield stress ratio, E_r/σ_y , the material surrounding the indent was found to pile up around the indentation and increase the effective contact area. In materials with low values of E_r/σ_y , the material surrounding the indent was found to sink in and reduce the effective contact area from that expected in Figure 2.2. Work hardening favoured sink-in behaviour. Both of these behaviours cause significant error in measured contact area and thus modulus and hardness measurement. These behaviours and their associated plastic zones are illustrated in Figure 2.6.

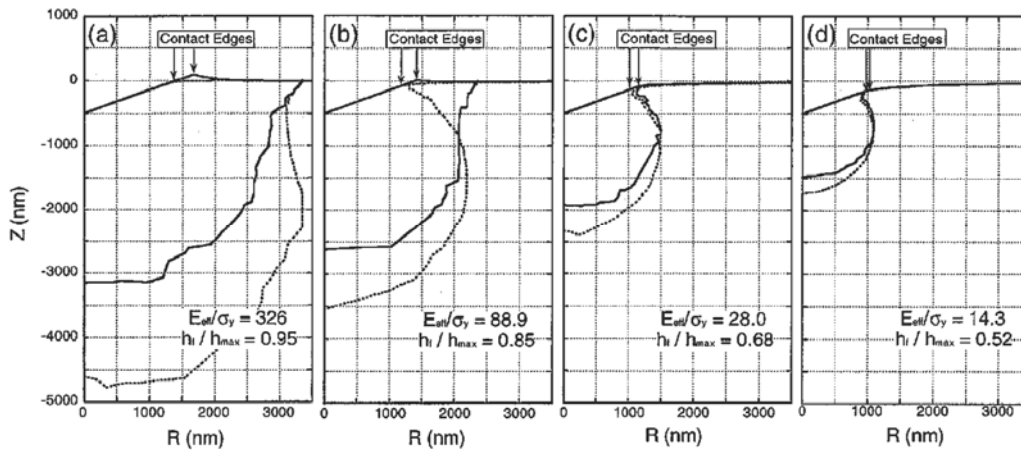


Fig. 2.6. Surface contours and plastic zones predicted by FEM for materials with different values of E_r/σ_y ³⁵. Non-work hardening materials ($\eta = 0$) are represented by solid lines and work-hardening materials ($\eta = 10 \sigma_y$) by broken lines.

The elastic recovery ratio after complete unloading, h_f/h_{max} , was found to be a good indicator for pile-up behaviour with $h_f/h_{max} > 0.7$ indicating some degree of pile-up behaviour³⁵.

Correcting for pile-up induced error is difficult without a priori knowledge of the mechanical properties and work hardening behaviour of the material. An effective solution for most materials is to image the residual contact impression to determine the actual area.

2.3.3 Contact Area-Independent Functions

There is an alternative method of determining the frame compliance that does not require the area function to be known beforehand³⁶. This method was derived from the realization that H/E^2 is independent of the contact area³⁷

$$\frac{P}{S^2} = \frac{\pi}{(2B)^2} \frac{H}{E_r^2} = PC_s^2 \quad (2.20).$$

Solving Equation 2.20 for C_s , and substituting that into Equation 2.8, yields

$$\sqrt{P}C_0 = \frac{\sqrt{\pi}}{2B} \frac{\sqrt{H}}{E_r} + \sqrt{P}C_F \quad (2.21).$$

Interpretation of this equation requires the realization that, for raw data, uncorrected for frame compliance, the stiffness, S , is the inverse of C_0 , not the sample compliance, C_s . With this in mind, Equation 2.21 reveals that, for samples with no indentation size effect, a plot of $P^{1/2}C_0$ vs. $P^{1/2}$ yields a linear relationship, with slope C_F and a y-intercept equal to the second term in Equation 2.21. Using this technique, instead of that previously outlined, removes the need for iteration. Another solution, for samples with well known H or E_r , is to apply Equation 2.20 to directly determine the other value.

2.3.4 Work of Indentation

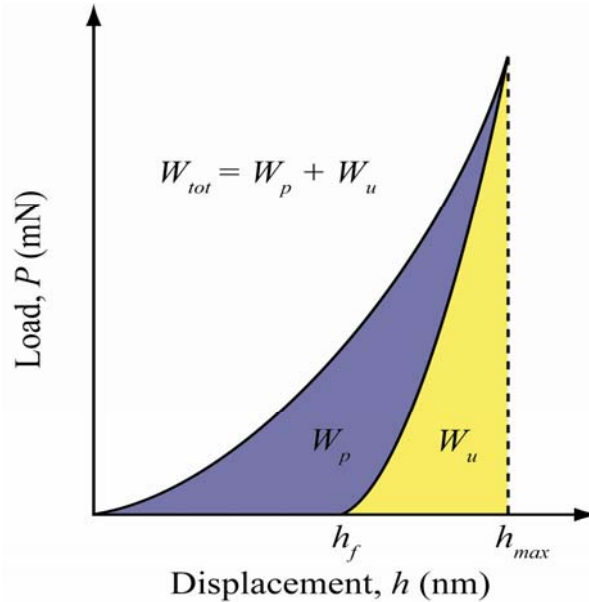


Fig. 2.6. Schematic showing the definition of plastic, elastic and total work of indentation.

Cheng and Cheng³⁸ also demonstrated a relationship of H/E_r to the work of indentation, independent of pile-up behaviour, using dimensional analysis and finite

element modelling studies. The relationship, while rigorous, was mathematically complex and dependent on numerous factors. Oliver and Pharr²¹ approximated this relationship as

$$\frac{W_{tot} - W_u}{W_{tot}} \cong 1 - 5 \frac{H}{E_r} \quad (2.22),$$

where W_{tot} is the total work of indentation, the integral of the loading curve, and W_u is the elastically recovered work, the integral of the unloading curve. This method has been found to give better estimates of hardness and modulus for samples with high elastic recovery³⁹.

2.3.5 Indentation Strain Rate

For materials displaying power-law creep behaviour, Cheng and Cheng⁴⁰ used dimensional analysis techniques to propose that the ‘indentation strain rate’ for self-symmetric indenters can be expressed as

$$\dot{\varepsilon} = \frac{\dot{h}}{h} \quad (2.23),$$

or the ratio of the rate of penetration to the depth already achieved. However, for a spherical indenter, which is not self-symmetric, the size and shape of the stress and strain fields are affected also by the ratio of indenter diameter to indent size. Tabor’s equation for the representative strain under spherical indenter, Equation 2.19, allows the strain to be determined as a function of contact radius. The relationship between the penetration depth, h_f , and the contact radius, a , is

$$a = \sqrt{2Rh_f - h_f^2} \quad (2.24).$$

With R being the radius of the indenter. Substituting Equation 2.24 into Equation 2.19 yields Tabor’s representative strain as a function of depth:

$$\varepsilon = 0.2 \left(\frac{\sqrt{2Rh_f - h_f^2}}{R} \right) \quad (2.25).$$

Discretely differentiating the strain values obtained using Equation 2.25 against time on a displacement-time curve can then be used to determine the spherical indentation strain rates.

This result is relevant to a wide range of materials, since, under plastic loading, many ‘soft’ materials display creep, particularly at elevated temperatures. This effect

explains errors observed in constant loading rate testing of power law creep and work hardening materials. It was probably largely due to the relatively high strain rate loading being imposed at shallow depth levels. By using a computer-controlled feedback system, proportional loading can be achieved, which maintains the rate of penetration as being proportional to the current depth. This produces constant strain rate indentation, which yields uniform hardness data over a wide range of depths. Another benefit of loading at a constant strain rate is that it evenly spaces datapoints, if they are taken at regular time intervals, over the entire range of depths tested.

2.3.6 Indentation Strain Fields

Both Tabor's representative strain, Equation 2.19, and the indentation strain rate described by Equation 2.23, take average values for strain over a complex strain field which extends to a significant depth below the indentation. This strain varies in magnitude depending on its distance from the indenter, and the field develops in size and morphology with increasing indenter penetration depth, until plastic flow is fully developed. Tip shape has a significant effect on the strain field, as illustrated in Fig. 2.7.

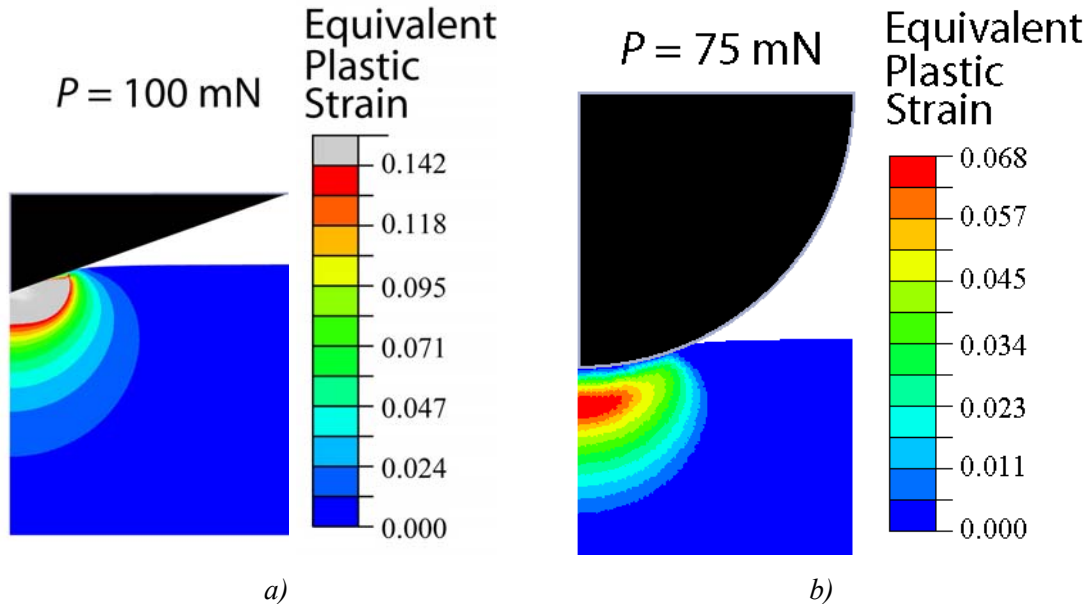


Fig. 2.7. Finite element analysis predictions of equivalent plastic strain fields from a) Berkovich and b) a $10 \mu\text{m}$ radius spherical indenter on a NiTi alloy⁴¹.

Some efforts^{42, 43} have been made to experimentally quantify the strain fields of large indentations by using micro-Vickers hardness measurements on cross sections of the indents. Other investigators^{44, 45} have utilized speckle markings or fiducial indentations on cross sections to track the strain fields under indentations. These

studies have broadly agreed with theoretical predictions and finite element models. However it has been demonstrated that friction between the indenter and sample can significantly change the strain field⁴⁶. Friction between the sample and the indenter can constrain the plastic flow of material in contact with and directly below the indenter. This creates a region of ‘dead’ material which increases the effective size of the indenter⁴⁴. This effect is expected to be especially relevant for flat punch, spherical and high cone angle indenters. Even ‘sharp’ indenters have a finite tip radius, so a similar, though smaller, effect is expected. Best practices for determining the strain fields under indentations would utilise finite element models informed and confirmed by experimental measurements including force-displacement curves from indentation and indentation topology measurements.

2.4 Calibration Materials

As with all high precision instruments, nanoindentation systems require calibration and calibration standards. Three calibration measurements are required for all nanoindentation systems, relating to frame compliance, indenter area function, and cross-hair or targeting alignment. The analyses for the former two of these are described in §2.1. These two calibrations also share some desired material properties for their calibration standards.

<i>Material</i>	<i>Elastic Modulus, E</i>	<i>Poisson's Ratio, ν</i>	<i>Hardness</i>	<i>Reduced Modulus, E_r</i>
<i>Diamond</i> ⁴⁷	<i>1141 GPa</i>	<i>0.07</i>	<i>> 100 GPa</i>	<i>n/a</i>
<i>Fused Silica</i> ⁴⁷	<i>72 GPa</i>	<i>0.17</i>	<i>8.8 GPa</i>	<i>69.6 GPa</i>
<i>Sapphire</i> ⁴⁸	<i>370 GPa</i>	<i>0.25</i>	<i>30 GPa</i>	<i>292 GPa</i>
<i>Tungsten</i> ⁴⁹	<i>412 GPa</i>	<i>0.28</i>	<i>~6.6 GPa</i>	<i>322 GPa</i>
<i>Tool steel</i> ⁴⁷	<i>220 GPa</i>	<i>0.28</i>	<i>8.8 GPa</i>	<i>200 GPa</i>
<i>Aluminium</i> ⁵⁰	<i>70.8 GPa</i>	<i>0.36</i>	<i>0.25 GPa</i>	<i>76 GPa</i>

Table 2.2. Materials properties of commonly used calibration standard materials when coupled with a diamond indenter.

It is preferable that standards show no significant pile-up or sink-in behaviour and very little creep. Pile-up is reduced by using a material with a high H/E_r ratio. Indentation creep can also cause errors in measurement. It is desirable for accuracy and expediency that hold times for primary creep to become negligible are short (<15 seconds). Standard materials should also be elastically isotropic and give consistent modulus results over any range of indentation depths. Standards should be economical and easily obtainable in an optically flat or highly polished condition. For testing over

a range of temperatures, it is desirable that samples show a high degree of thermal stability. Finally, it is desirable that the standard materials show little or no Indentation Size Effect. This effect, which is currently a very active area of research in nanoindentation^{6, 7, 47, 48, 50-52}, is characterised by an increase in hardness for indentations of decreasing depth/size. Several theories have been advanced to explain this phenomenon including characteristic size plastic band deformation⁵³, strain gradient plasticity and geometrically necessary dislocations⁵⁴⁻⁵⁷, a critical thickness layer⁵⁸⁻⁶⁰, dislocation starvation and mechanical annealing^{61, 62}. In some materials, such as aluminium, this effect could also be a simple effect of a thin layer of surface oxide, if the sample is not carefully prepared. Figure 2.8 illustrates the relationship of hardness with indentation depth for several materials. The bimodal behaviour observed for the nickel Superalloy corresponds to the (harder) precipitates becoming distinguishable from the matrix.

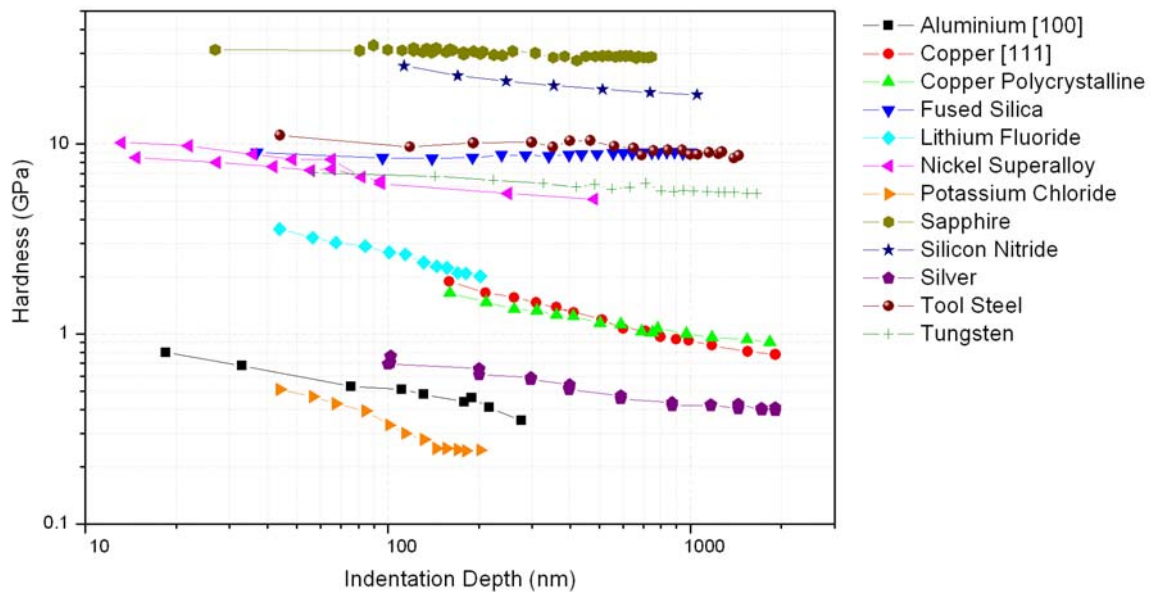


Fig. 2.8. Hardness as a function of indentation depth for several materials showing Indentation Size Effects^{6, 7, 47, 48, 50-52}.

For the indenter area function determination, it is desirable that the materials be relatively hard and stiff. This ensures that loads applied at very low penetration depths are still large enough to be well within the force resolution of the indentation system. Thus both sapphire and fused silica are appropriate for this calibration; however, fused silica is superior on elastic isotropy, economy and creep criteria.

Frame compliance determination is typically the primary calibration, since the area function determination requires a priori knowledge of the compliance. For this calibration, it is desirable that the standard materials have a low H/E_r ratio. This ensures that a large and stiff contact can easily be achieved, so that the indenter area function can be assumed as ideal, with a minimum of error, for the first approximation. For this reason, high purity aluminium and tungsten are highly suitable for this calibration. Both materials are also effectively elastically isotropic under indentation⁶³.

For the cross hair or targeting alignment calibration, a very soft material, that can easily be prepared to a high polish or level of flatness, is desired. Since this test needs to be performed any time that indenter tips are exchanged in the system, economy plays a larger role. A generic piece of an aluminium alloy is ordinarily suitable. This calibration determines the offset between the location of the indenter tip and the location of the centre of the focus of the microscope in the positioning stage of the nanoindentation system. Therefore, the only requirement of the material is that it readily holds a clear indentation impression.

3

Elevated Temperature, Impact and Scratch Indentation

Techniques for nanoindentation under dynamic conditions are described. Dynamic conditions are divided into three categories: elevated temperature, impact and scratch. The additional complications encountered in elevated temperature indentation testing are described, along with the capabilities of the two basic types of nanoindentation equipment that are used to generate impact loading. Methods of determining dynamic indentation hardness and mechanical behaviour under impact loading are discussed.

3.1 Elevated Temperature Indentation

The environment in which micro-mechanical testing is performed can generally be broken down into two major components: temperature and atmosphere. Since all mechanical properties are temperature-dependent, the temperature of the environment is of great significance. Atmosphere also plays a significant role, since many materials rapidly form oxide or nitride layers in ambient air or may be sensitive to humidity. At elevated temperatures, atmospheric reactions generally become more pronounced. Much insight into these issues and on creep, yield, and elastic behaviour of materials has been achieved using elevated temperature micro-indentation systems⁶⁴⁻⁷⁹. However, the desire to probe materials properties at ever decreasing length scales and test materials of smaller volumes with increasing levels of instrumentation have made the capability to perform elevated temperature nanoindentation in a controlled environment of great interest. This also presents several unique technical challenges. In this section, these challenges, along with several environment-dependent properties, are discussed.

3.1.1 Elevated Temperature Systems

There are several basic requirements for the design of an indentation system. There must be a mechanism for applying a controlled load, a sensor to precisely monitor depth, a hard tip of known geometry to contact the sample and a platform to position

the sample. Even with these constraints, significant variations in design are possible. Typically, nanoindenter designs in global use fit into one of two categories: axial-loading nanoindenters or pendulum-based nanoindenters. Each has different complications with performing at elevated temperature. Another important consideration is the effect the surrounding atmosphere has on the tip and sample at elevated temperature.

3.1.1.1 Axial-Loading Systems

Axial-loading nanoindenters are manufactured by several companies. The popularity of these machines is partly due to the force and displacement resolutions, which are on the order of 0.5 μN and 0.3 nm. Two of these machines (Hysitron's Triboindenter and MTS's Nanoindenter II) have been modified for elevated temperature capability^{10, 80}. The Hysitron Triboindenter operates via a piezoelectric force transducer and capacitance depth-sensing indenter head⁸¹. The chief difficulty with achieving accurate and repeatable results at elevated temperature with piezoelectric devices is in insulating the piezoelectric transducer, since the piezoelectric response of the transducer varies with temperature. Care must also be taken to protect the depth-sensing capacitors. The various steps taken by one author¹¹ are shown in Figure 3.1.

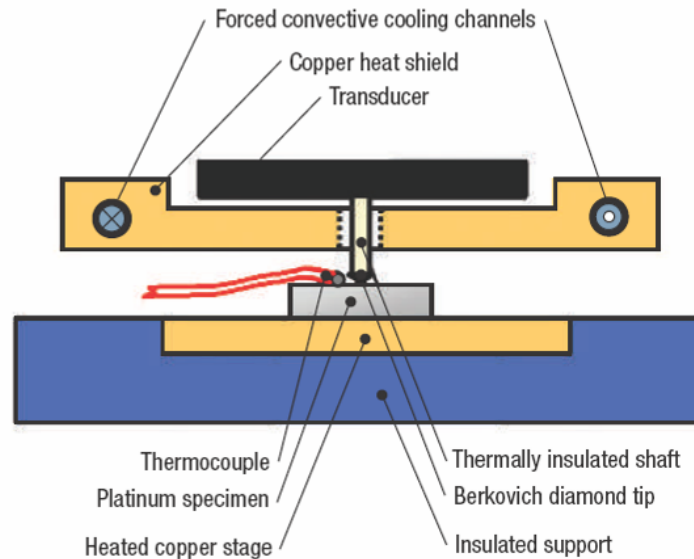


Fig. 3.1. Schematic representation of a piezoelectric indenter modified for elevated temperature¹¹.

The positioning of the indenter head vertically above the heated sample exacerbates the situation, since the transducer lies in the direct path of convective heat flow from the heated sample. A high thermal conductivity, cooled copper heat shield was

introduced to counter this. Thermal drift is a problem which becomes increasingly important at increasing temperatures. A key question is whether thermal equilibrium between the indenter tip and the sample is achieved prior to, and maintained during, indentation. In this system, the tip is allowed to hover just above the surface of the sample or held in contact with the sample to equilibrate for an hour or more before indentation. However, during indentation the thermally-insulated shaft is relied upon to prevent heat flow. Hysitron's standard temperature control module has a temperature range of -25°C to 125°C ⁸². The maximum achieved temperature that has been reported¹¹ with this type of setup is 410°C .

The other axial-loading nanoindentation system to be modified for controlled temperature operation was purpose built from MTS's NanoIndenter II¹⁰. This system operates with a vertical solenoid made of (low coefficient of thermal expansion) "Invar" nickel-iron alloy to apply the load and actuate the capacitance-based displacement sensor (Figure 3.2). Again, both of these devices are prone to conductive and convective heating. The solenoid load cell has no major difficulty with elevated temperature operation, but the capacitance depth sensor is vulnerable. To account for this, Lucas¹⁰ replaced the capacitance depth sensor with a laser-based displacement measurement system (Axiom 2/20™). This involved fixed mirrors mounted on both sample and indenter shaft. The entire system was also enclosed in an ultra high vacuum (UHV) chamber, with a sapphire window for the laser system.

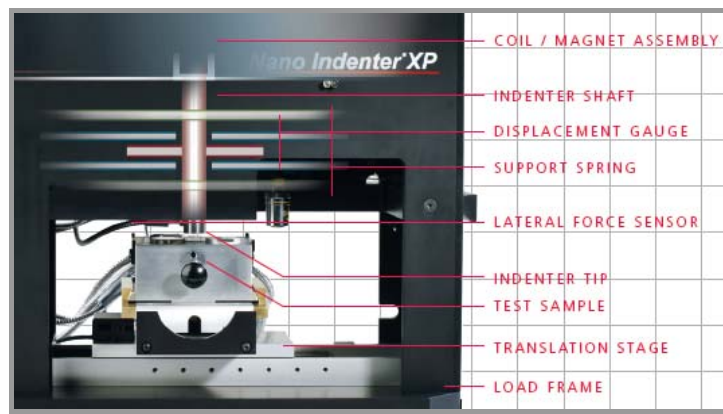


Fig. 3.2. Schematic representation of a solenoid indenter⁸³.

Thermal equilibrium is accomplished at elevated temperature in this system with digitally controlled resistance heaters in the indenter shaft near the tip and the copper sample stage, but at low temperatures cooling is accomplished by flowing liquid

nitrogen through the copper shroud containing the indenter shaft and through the sample stage. This system has a temperature range of -100°C to 300°C ¹⁰.

Equipment of this type has been used to study surface-constrained plasticity⁸⁴, mechanical behaviour at elevated temperatures in metallic thin films⁸⁵, indentation creep of indium¹⁰, deformation mechanisms in metallic glasses⁸⁶, and the elastic-plastic transition^{11, 80}.

3.1.1.2 Pendulum-based Systems

Pendulum-based nanoindenters are manufactured and distributed principally by MicroMaterials Ltd. These machines sometimes include two separate pendulums for different load ranges. High load experiments (500 mN-20 N) are performed using the MicroTest pendulum, while low load (0.05 mN-500 mN) experiments make use of the NanoTest pendulum.

The loading system is shown schematically in Figure 3.3. By passing a current through the coil at the top of the pendulum, it is deflected towards the magnet. This pushes the indenting tip towards the sample, the displacement being measured by the capacitor plates fitted level with the indenting tip.

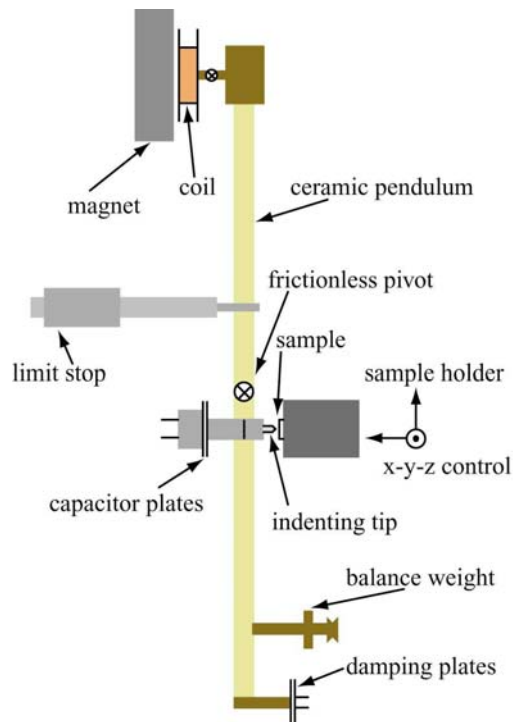


Fig. 3.3. Schematic representation of the MicroMaterials loading and displacement sensing system.

Since pendulum-based indenters do not utilise piezoelectric transducers, and the horizontal orientation minimises convective heating, the chief concern with operating them at elevated temperature is thermal drift. To minimise this, both the sample and indenter tip are heated and maintained at thermal equilibrium using resistance heaters and control thermocouples with closed loop electronics (Figure 3.4). In order to ensure thermal stability, both sample and tip are heated and left in close proximity to equilibrate prior to indentation. One objective of doing this is to ensure that the electronic circuitry close to the pendulum is fully stabilised prior to experimentation. It also helps to ensure that any thermal expansion in the pendulum or elsewhere was complete prior to acquisition of data. Radiative heating of the capacitor depth-sensing electronics is prevented by the use of the static aluminium heat shield. This system has been utilised in air at temperatures of up to 400°C⁹, but the heating system is inherently capable of higher (~1000°C) temperatures.

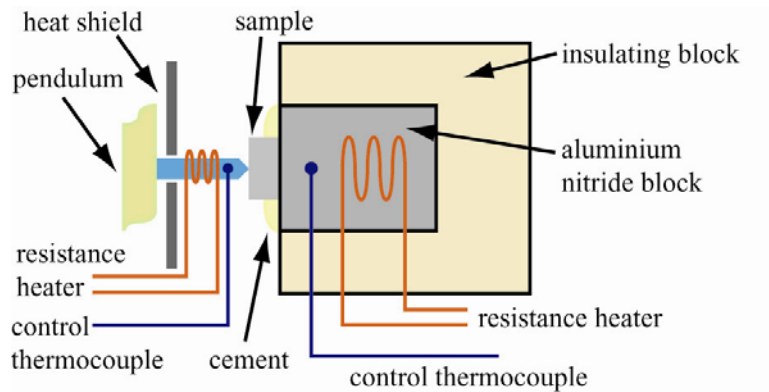


Fig. 3.4. Schematic of the hot stage and heated tip set-up for pendulum indenters.

Equipment of this type has been used to study the shape memory effect⁴¹, mechanical behaviour at elevated temperature of reference standard materials^{9, 87, 88}, and iron aluminides⁸⁹.

3.1.2 Reactivity at Elevated Temperatures

In §3.1.1, attention was focused on how elevated temperature can affect the operation of the nanoindenter, especially the load cell and displacement sensors. However, high temperature also makes reactions with and/or between the sample, indenter tip and the surrounding atmosphere more likely.

3.1.2.1 Oxidative Diamond Loss

At elevated temperature, oxidation rates rise sharply for many materials. Direct oxidation of diamond produces CO or CO₂ gas⁹⁰, which, for flowing oxygen, produces a constant etch rate. Formation of a carbon layer on the surface of the diamond also occurs, presumably due to reactions with chemisorbed oxygen, and this layer is then converted to CO and/or CO₂ gas. These three processes compete at different pressures and temperatures, such that some conditions favour the formation of a thick amorphous carbon layer and others the direct oxidation of a clean diamond surface⁹⁰. This carbon layer formation differs from graphitisation of diamond, which occurs at much higher temperatures (e.g. >1200°C) via phase transformation⁹¹. All of these processes act to reduce the surface area to volume ratio, blunting conical and pyramidal indenter tips. The obvious method for decreasing the blunting behaviour is to limit the amount of oxygen present, by lowering the oxygen partial pressure in a sealed chamber.

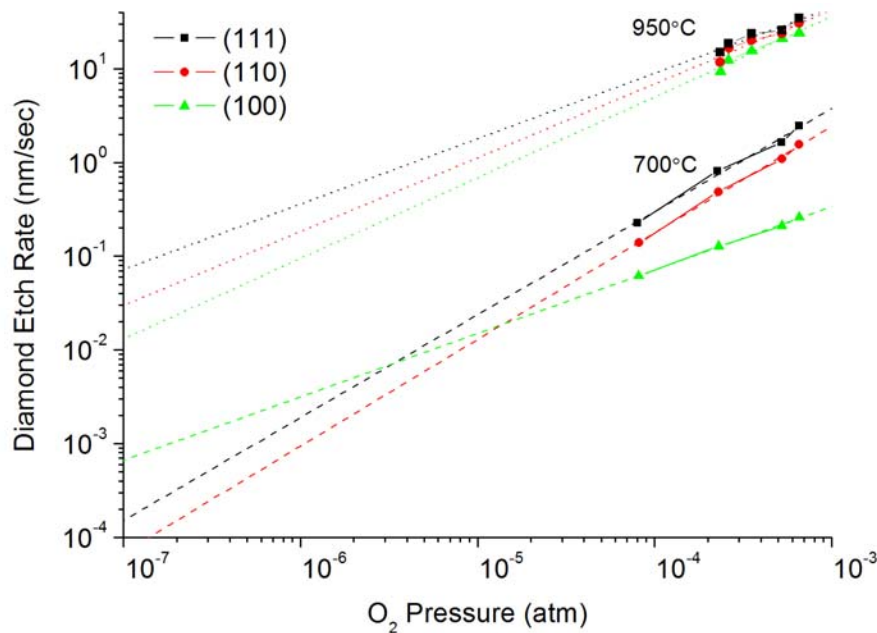


Fig. 3.5. Extrapolated diamond etch rate projected as a function of oxygen pressure from known etch rates for two temperatures⁹².

The etch rates of the low angle crystal faces of diamond have been determined as a function of temperature and pressure⁹² over a limited range (Fig. 3.5). However, this can only be used to estimate the amount of face wear experienced by a diamond tip, and it cannot be used to predict the amount of facet edge wear, which is more relevant to indenter 'sharpness'. Direct observation of tip shape changes after indentation at elevated temperature is required.

3.1.2.2 Tip-Sample Interaction

Interactions with the atmosphere within the indentation system are expected to become less problematic when operating under vacuum or in inert atmospheres. However, interactions between the indenter tip and the sample can be a serious concern. Diamond, the hardest natural material and standard indenter tip material, is obviously of interest. The danger of tip-sample reaction is in converting the diamond tip into a 'carbon donor' to the sample material in order to form a carbide and resulting in the loss of the diamond. This danger is illustrated in a scanning electron micrograph taken by the author (Fig. 3.6) of an indenter after it was used to indent a steel sample at 500°C. Little trace of the diamond can be observed.

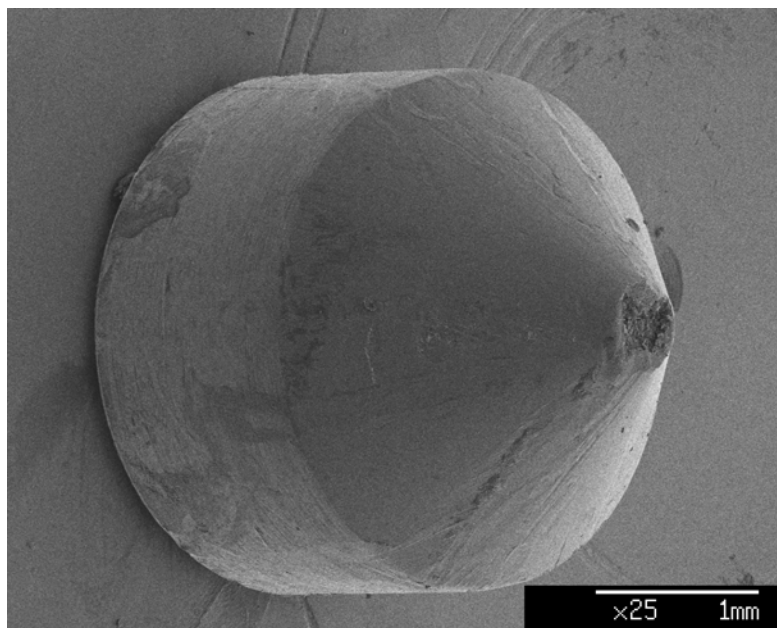


Fig. 3.6. Diamond indenter tip after indenting steel at 500°C.

Thus, indenter tip materials must be selected which are thermodynamically stable with the sample material to be tested over the desired temperature range.

3.2 Impact Indentation

Standard nanoindentation testing can be referred to as quasi-static, meaning that the effects of loading rates (and deformation rates) are assumed to be negligible. As mentioned in §2.2.4, this is not always the case, even for constant loading rate indentation testing, and some materials display behaviour which is dependent on which test parameters are used in proportional loading or constant strain rate testing as well. Impact indentation techniques, however, can introduce testing parameters which

signal a significant departure from the quasi-static loading and into the realm of dynamic loading.

Initial dynamic hardness tests using impact indentation were based on the rebound height of a projectile indenter (coefficient of restitution)^{25, 93-95}. These analyses were limited by the instrumentation available at the time, such that much effort was expended on determining parameters (e.g. maximum depth, time of contact, et cetera) which are directly measured using modern apparatus.

More recent efforts to measure dynamic hardness have been centred on instrumented apparatus with load and/or displacement sensors. The apparatus utilised has varied with each investigator. This review will be broken down to a summary of the research performed using each separate apparatus. The capabilities of the apparatus are varied, and the research performed on them is significant shaped by the capabilities of the apparatus. These can be broken down into two rough categories: projectile impacters and pendulum impacters.

3.2.1 Projectile-based Dynamic Hardness Apparatus

Projectile-based dynamic hardness measurement can be performed over a wide range of impact velocities/energies. Low speed impacts can be achieved using controlled drop towers and utilising gravitational acceleration of the impacter, while high speed impacts can be achieved utilising a gas gun to either directly fire the impacter projectile at the specimen or to fire a projectile at a secondary impacter which is accelerated into the specimen by the impact.

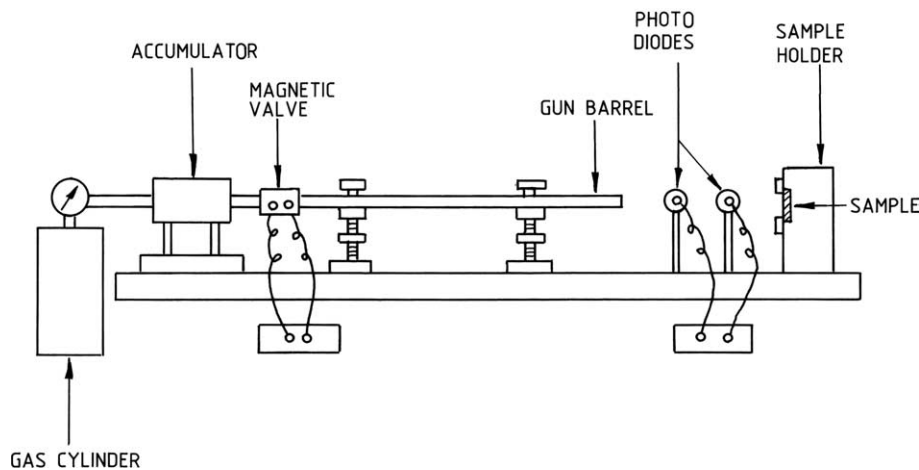


Fig. 3.8. Schematic of a dynamic indentation system⁹⁶.

Tirupataiah and Sundararajan⁹⁶⁻⁹⁸ used a 4.76 mm tungsten carbide sphere as a dropweight projectile and as the projectile from a gas gun (Fig. 3.8). Photogates were used to measure the incident and rebound velocity of the indenter. The dynamic hardness was defined as the energy expended during impact over the volume of the residual impression. The kinetic energy loss was assumed to be entirely due to plastic deformation; all of which was also assumed to be converted adiabatically into heat. This led to a critical strain value for each material, which corresponded to the temperature rise being significant enough to cause localised softening/melting of the material under the indenter. The analysis was found only to be valid for materials with a strain hardening exponent greater than 0.2, otherwise localised softening occurred. Yield pressures determined using this technique were found to correlate well with those from conventional high strain rate testing methods: high speed compression testing and split Hopkinson pressure bar.

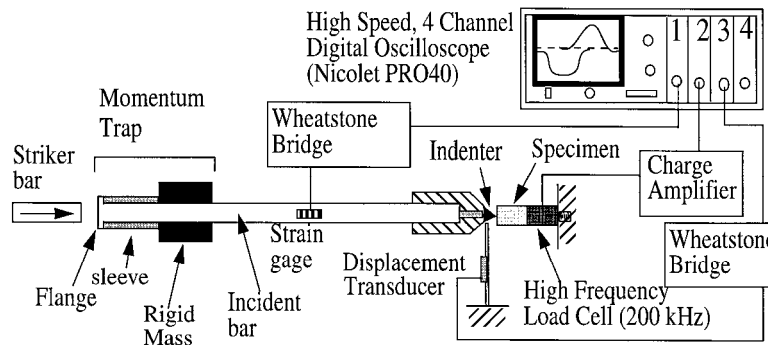


Fig. 3.9. Schematic of a dynamic indentation system.

Koeppel et al⁹⁹⁻¹⁰¹ also used a gas gun to generate high strain rate indents. However, unlike Tirupataiah and Sundararajan, Koeppel used the gas gun to accelerate a modified split Hopkinson bar with a Vickers indenter on its end. The load was dynamically monitored during impact, as well as the incident velocity of the impactor. Dynamic hardness was initially defined as the same as the Vickers hardness,

$$DHV = HV = 1.8544 \frac{P}{d^2} \quad (3.1)$$

with the load taken to be the peak load during impact and d as the diagonal length of the residual impression. This value of dynamic hardness was found to correlate to increases in dynamic yield stress, with the strain rate defined as the indenter velocity over the indent size. This was achieved by comparing measured quasi-static and dynamic yield stress values to the DHV and HV values using Tabor's representative strain.

Koeppel and Subhash¹⁰⁰ then refined their definition of dynamic hardness as

$$H_{\text{Dynamic}} = \frac{K}{V} \quad (3.2)$$

or the impact energy over the maximum volume, which largely resembles the definition of Martel from over a century previous⁹³. This was part of an effort to measure the difference in plastic zone between dynamic and static indentations. This was achieved using metallographic analysis and microhardness measurements of indentation cross sections. It was found that the plastic zone size had an inverse relationship to the yield stress, and, since yield stress generally increases with strain rate, the plastic zone was found to be reduced at higher strain rates.

Brittle materials were also examined using this technique¹⁰¹. It was observed that for all brittle materials tested, dynamic hardness values were much greater than quasi-static values. Glasses were found to be increasingly damage-prone at high strain rates, while zirconia was less. Other materials investigated showed no difference in damage/crack behaviour.

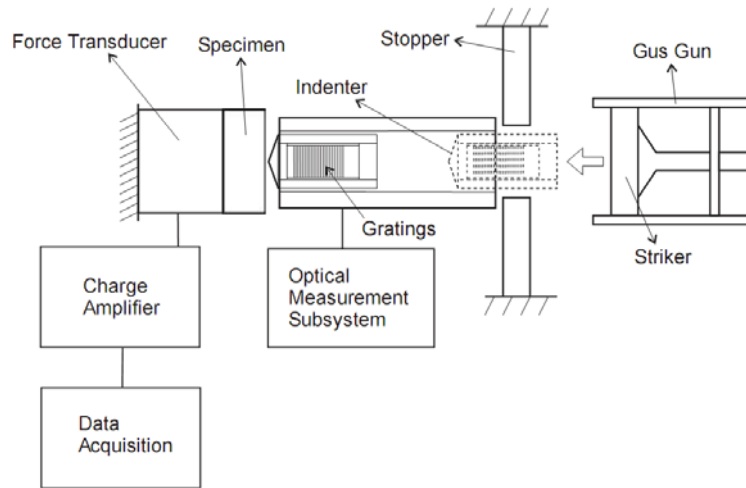


Fig. 3.10. Schematic of a dynamic indentation system¹⁰².

Lu et al¹⁰² expanded on Koeppel et al's work by implementing a similar gas gun-based system, but with the addition of a moiré fringe-based laser displacement sensor. This allowed the contact time to be directly measured, leading to a definition of strain rate based on Tabor's representative strain over the impact duration. The indenter used was a tungsten carbide cone with an angle providing an equivalent depth-area relationship to a Berkovich indenter. This allowed direct pairing with an axi-

symmetric modelling approach. This was designed using a Newtonian mechanics centred theory developed by Andrews et al¹⁰³ and Giannakopoulos¹⁰⁴, and allowed analytical predictions of maximum and residual depths, contact time, and rebound velocity. These were all found to correlate well with FEA results, and Lu et al expanded this to include correlation to experimental results.

3.2.2 Pendulum-based Dynamic Hardness Apparatus

Pendulum-based apparatus for dynamic indentation covers a different range of impact velocities than projectile-based systems. With a pendulum-based system, very low to medium velocities can be achieved with a single instrument, in contrast with projectile systems, which require different setups: dropweight towers for low speeds and gas-guns for high speeds. Pendulum-based systems also have the advantage of scalability, which allows them to be used for nano-scale dynamic hardness measurement.

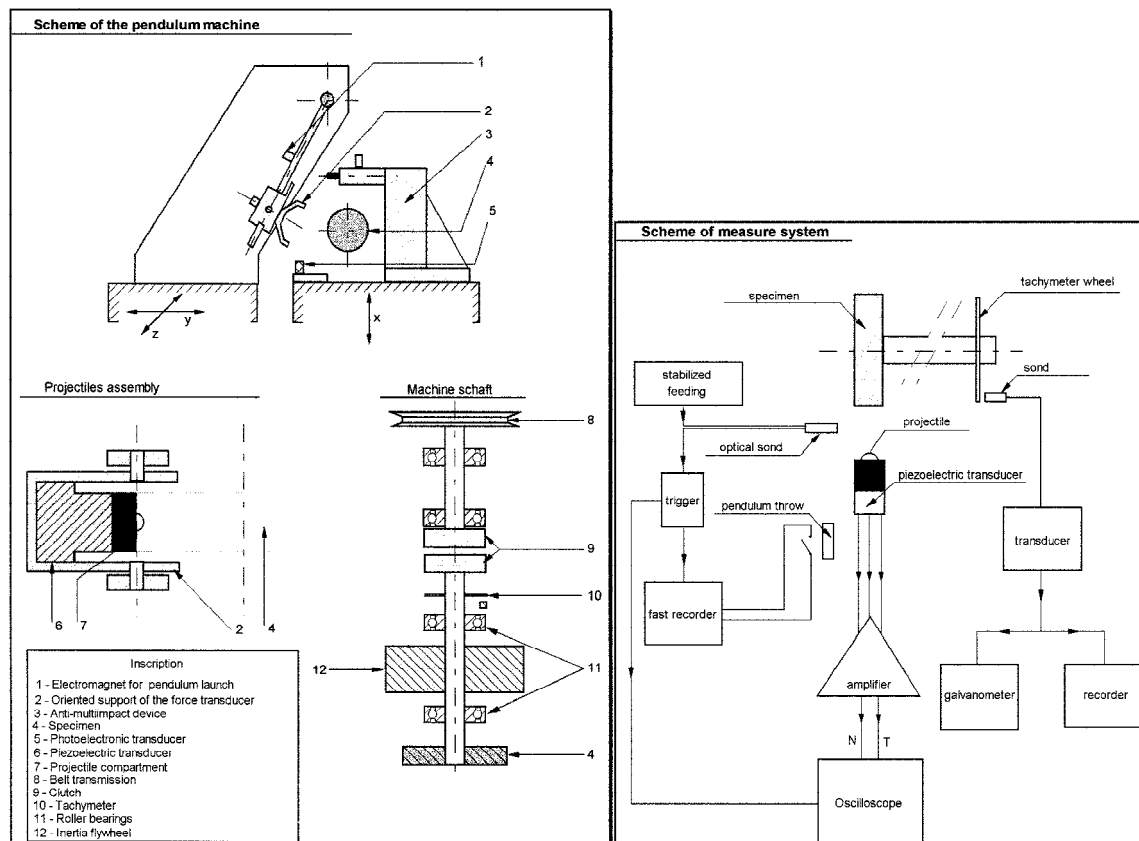


Fig. 3.11. Schematic of a dynamic indentation system¹⁰⁵.

Nobre et al^{105, 106} utilised a macro-scale pendulum device, shown in Figure 3.11, for conducting dynamic hardness measurement. The indenters used were 10.7 mm diameter sintered alumina spheres, although the system allows for flat, cylindrical and spherical indenters to be used. This system features a piezoelectric force sensor

capable of resolving normal and tangential loads and photogate sensors for measuring the incident and rebound velocities. Results obtained from normal impacts were validated against Tirupataiah and Sundararajan's method⁹⁶. This system also allows for rotation and translation of the sample during impacts, which allows effectively oblique impacts to occur by varying the velocity of the sample. This allowed for the simulation of single particle impacts, and it was demonstrated that a critical tangential force is required for chip generation and removal during impacts.

Another design of pendulum-based dynamic indenter is the commercially available MicroMaterials NanoTest platform. This system can consist of two balanced pendulums, one for micro-scale testing and one for nano-scale testing (Fig. 3.12).

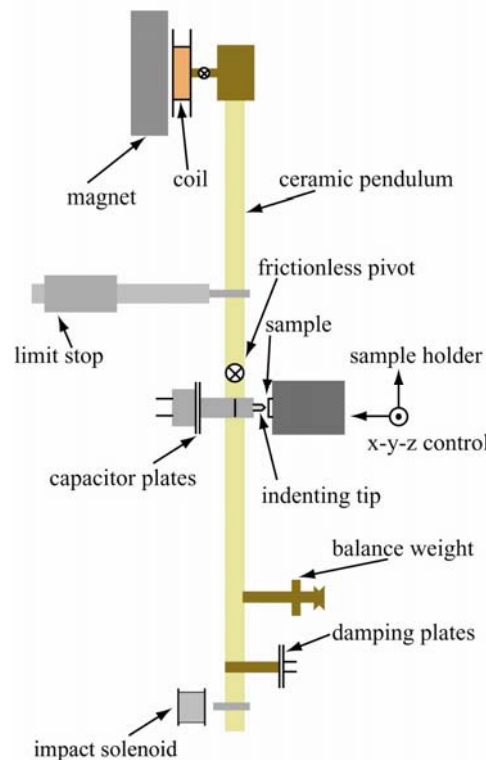


Fig. 3.12. Schematic representation of the MicroMaterials pendulum fitted with a solenoid for impact testing.

The MicroMaterials Ltd. NanoTest NTX series controller features high speed datalogging capability in the 1-5 MHz range, so that displacement can be measured dynamically using capacitor plates positioned directly behind the indenter tip during impact events. The system consists of a stiff, ceramic pendulum which is balanced on a frictionless leaf spring pivot. Force is applied using a permanent magnet and electromagnetic coil. During impact loading, the base of the pendulum is restrained

using the impact solenoid while the accelerating load is applied at the force coil. When the impact solenoid current is released, the pendulum swings forward under the applied accelerating load. Various velocities can be achieved by varying the acceleration load and spacing between the solenoid and pendulum. A current limitation of this technique is that the indenter is allowed to continue to rebound under the applied load until it comes to rest, thus the residual impression is the result of a succession of impacts and is not useful for determining true dynamic hardness.

Beake et al¹⁰⁷⁻¹⁰⁹ initially developed this system for simulating repetitive impact loading, such as interrupted cutting for thin hard coatings. These investigations lacked the temporal resolution to observe the displacement-time relationship of impact penetration, so that only the depth after the indenter had come to rest on the sample could be measured. Initially, fused silica, silicon and DLC coatings were tested to compare their failure after multiple impacts. In the impacts prior to failure, an increase in rest depth was observed, which was attributed to blister development and microcrack swelling. Failure was observed in the data as a rapid increase in rest depth, corresponding to the material yielding under the indenter instead of elastically accommodating the impact energy. Continued development¹¹⁰⁻¹¹² of this testing on more hard coatings, such as amorphous carbon and CrAlTiN, lead to the probability of failure after a certain number of impacts being characterised using Weibull statistics:

$$P(f) = \frac{n}{N+1} \quad (3.3)$$

where n is the ranking out of N impacts where failure occurred.

As mentioned in §3.1.1.2, this system is also capable of elevated temperature testing. This was used^{113, 114} to compare multiple impact testing failure to flank wear generated during end milling at the service temperatures. Good correlation between the two tests was found for TiCN, TiAlN and AlCrN tool bit coatings. The ratio of hardness to elastic modulus, H/E , was also found to correlate to wear performance, with lower H/E value corresponding to longer impact/milling life.

Constantinides et al¹² explored the mechanical response of polymers with this system. Their system featured the NTX controller with sufficient temporal resolution to

dynamically follow the displacement during impact, so they were able to develop a numerical model for the pendulum motion and impact forces. However, this is described in a reference work yet to be published. Only polypropylene and Lucite were observed to show strain rate dependent behaviour within the rates examined. For the other polymers investigated, polyethylene, polystyrene, polycarbonate, and polymethylmethacrylate (PMMA), the ratio of rest depth to maximum depth was found to be directly related to the ratio of impact energy dissipated by plastic deformation, W_p/W_t . Capacity for energy dissipation was found to greatly increase for temperatures above the glass transition temperature for the polymers.

3.3 Scratch Testing

Scratch testing is probably the oldest form of hardness testing. The first comparative ranking scale of scratch hardness was developed by Mohs¹ in 1822. This scale makes use of reference minerals with assigned rankings. These minerals are fairly evenly spaced over a wide range of hardness (Fig. 1.1). However, a more quantitative and well-defined method was necessary for precision research. The next stage of logical development featured a diamond stylus, using a defined load, and then measuring the width of the remaining scratch^{115, 116}. This is the basic principle on which many modern scratch tests are performed, but available technology at the time of development did not allow reliable measurements.

One of the earlier automated, instrumented micro-scratch test machines was developed at IBM by Wu et al¹¹⁷. This machine was capable of high resolution monitoring of penetration depth, normal and tangential load, and acoustic emission along the entire length of a scratch. The precision sample positioning ability, combined with the ultra-low loads achievable, allowed this system to perform pre- and post-scratch profile scans of the sample surface. This feature allowed the depth profile of the scratch to be directly determined by the scratch tester, rather than characterising the residual impression using a secondary technique such as microscopy, metrology, or profilometry. These capabilities are now standard features on most commercially available scratch testing systems, and more advanced systems¹¹⁸ featuring *in situ* observation in a scanning electron microscope now exist.

Two modern definitions of indentation scratch hardness are commonly found in the literature¹¹⁹. The first of these is traditionally termed the scratch hardness,

$$H_s = \frac{P}{A_{LB}} \quad (3.4)$$

or the normal load, P , over the cross sectional area of the ‘front’ half of the indenter.

The second definition is termed the ploughing hardness,

$$H_p = \frac{P_T}{A_{PT}} \quad (3.5)$$

Or the tangential force, P_T , over the vertical cross-section of the indenter normal to the orientation of the scratch direction or projected tangential contact area, A_{PT} .

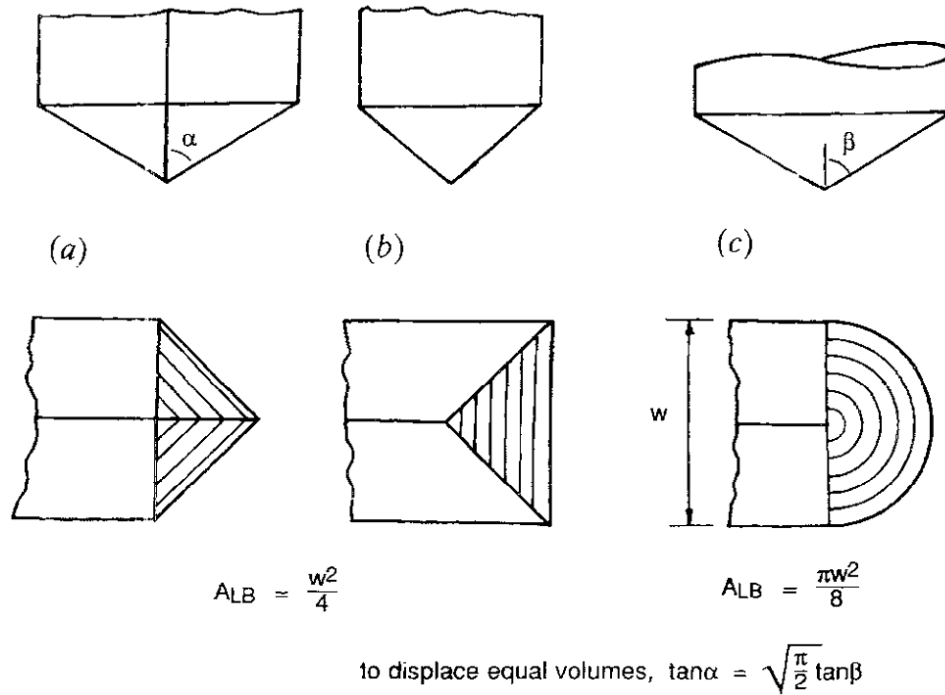


Fig. 3.13. Schematic of A_{LB} for pyramidal indenters aligned (a) edge first and (b) face first as well as for (c) conical indenters¹¹⁹.

It can be seen in Figure 3.13 that for axi-symmetric indenters A_{LB} is equal to one half the standard indentation contact areas, whereas for pyramidal indenters the orientation of the indenter respective to the scratch translation direction must be known to calculate the projected contact area. To calculate a cone angle which displaces equivalent volumes to a known pyramidal geometry, the equation included in Figure 3.13 can be utilised.

The cone angle, or effective cone angle in the case of pyramidal indenters, was shown by Brookes et al¹²⁰ to have a significant effect on scratch hardness. This work in many

ways parallels that of Atkins and Tabor²⁶ on the dependence of indentation hardness on cone angle. Brookes et al showed that the scratch hardness typically increased in relation to indentation hardness as a linear function of the cone angle. The ratio of H_s/H was seen to vary over the range of 0.75-2 with typical values for 140° apical cone angles being ~1.2-1.5 for non-work hardened metals. Cone angles greater than 120° were recommended for reproducible testing, since sharper cones tended to cut into the material. Difficulties encountered in early work on relating scratch hardness to indentation hardness by O'Neill¹¹⁶ using spherical indenters was possibly due to the variation in effective cone angle caused by different depths of scratch penetration. This relationship was expanded by Williams¹¹⁹ to create a map of elastic, elastic-plastic, and fully plastic regimes of scratch behaviour as a function of cone angle and E/σ_Y with increasing E/σ_Y ratio leading to greater plasticity (Fig. 3.14).

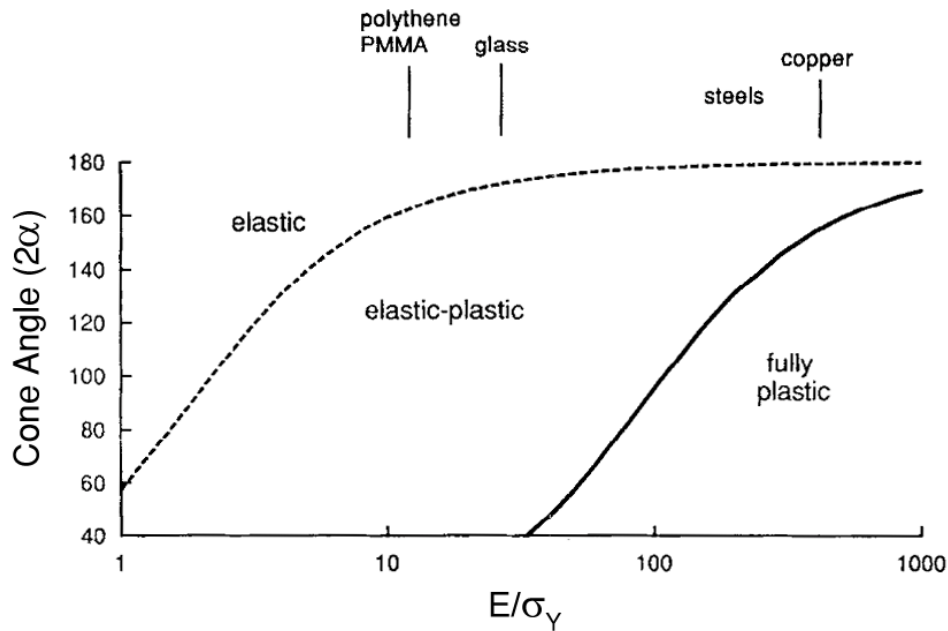


Fig. 3.14. Map of material response plotted as a function of indenter cone angle reproduce from Williams¹¹⁹.

More detailed maps of material response in scratch loading as a function of representative strain, load, and strain rate, have been constructed for polymers by Briscoe et al¹²¹. Elastic scratches observed in hard coatings under ultra-low load indentations on hard coatings¹²² are attributed to an effectively blunt indenter tip at very low relative depths (a/R) producing a high effective cone angle.

Determination of the properties of thin film coatings was one of the driving motivations for the development of high resolution scratch testers. A key property on

which many studies focus is coating adhesion to the substrate. Scratch testing has been used extensively to measure coating adhesion since the method¹²³ was outlined in 1950. The basic method utilises a spherical indenter tip which is scanned along the coating surface at increasing load until coating failure occurs. This critical load provides a qualitative measure of the adhesion strength. Various analyses¹²⁴⁻¹²⁸ have been proposed to relate the critical load to adhesion force. For hard, thin coatings on comparatively soft substrates, this relationship is generally well understood with established failure modes¹²⁹. A current review of the literature in this area has been made by Bull and Berasetegui¹³⁰.

Some efforts¹³¹⁻¹³³ have been made towards correlating multi-pass scratch testing of hard coatings, ceramics, and cermets to abrasive wear testing. These highlight the ability of scratch testing to identify the failure modes occurring during different wear modes when coupled with a secondary monitoring technique, such as microscopy. Since modes of wear often change dynamically as coatings are abraded, direct comparison between scratch testing and actual wear behaviour as a whole is generally not recommended.

4

Experimental Methods

This section details the preparation and testing methods carried out in this work. The pedigree, condition, and treatment of the samples utilised are detailed. Metallographic preparations prior to characterisation and nanoindentation testing are described. Procedures used for hydrogenation and dehydrogenation of palladium samples are illustrated. Sample morphology and structure were characterised using optical microscopy, scanning electron microscopy, x-ray diffraction, and x-ray energy dispersive spectroscopy. Indenter tips were examined using atomic force microscopy to characterise their area functions and determine their feasibility for elevated temperature indentation. Mechanical testing was conducted using nanoindentation, impact indentation, scratch indentation, and sandblast wear testing.

4.1 Materials and Specimen Preparation

The materials investigated during the course of this dissertation are described here. The list provided does not include the samples which were utilised to calibrate the nanoindentation system. Those samples, which included fused silica and tool steel, were provided by the instrument's manufacturer, MicroMaterials Ltd. Soda-lime glass samples used were taken from standard microscope glass slides. Samples of single crystal [100] tungsten and polycrystalline 304L steel were acquired from Goodfellow Ltd. TiN samples were prepared from tool bits acquired from Teer Coatings Ltd, which consisted of a TiN coating on a TiC substrate.

4.1.1 Palladium Foils

Foils of 99.95% pure palladium of two thicknesses, 125 μm and 500 μm ; measuring 25 mm by 25 mm, were acquired from Goodfellow Limited. The foils were supplied in as-rolled condition. The foils were annealed in a Carbolite tube furnace, STF 15/75/450, which had been fitted with a vacuum pump and backfilled with argon. The foils were annealed in an argon atmosphere at 600°C ($T_{\text{Homologous}} = 0.48$, $T_{\text{Melting}} = 1825^\circ\text{K}$)¹³⁴ for 2 hours and allowed to furnace cool overnight. This was

followed by ultrasonic cleaning in acetone for 30 minutes and drying with blotting paper.

The mass of the annealed foils was determined using a Sartorius BP110S microbalance with a nominal precision of ± 0.1 mg. A simple electrolytic cell was used to hydrogenate and dehydrogenate the samples. The cell consisted of a Thandar TS3021S precision DC power supply with a 30 V-2 A capacity, a water bath to maintain thermal equilibrium, an electrolyte solution of 0.1 Mol aqueous sulphuric acid, and a Perspex crosspiece to support the electrodes at a separation distance of 40 mm (Fig. 4.1). A thin foil of platinum, also measuring 25 mm by 25 mm, was used as the anode in the cell. The platinum and palladium foils were suspended by their corners using crocodile clips and only partially submerged, so as to not contaminate the electrolyte solution by submerging the crocodile clip leads. The current density was maintained at 0.8 mA mm^{-2} using the constant current function of the power supply.



Fig. 4.1. Simple electrolytic cell used to charge samples with hydrogen.

The samples were removed from the cell at fixed time intervals, to determine the mass change caused by absorbed hydrogen. The measured mass change was used to calculate the palladium to hydrogen atomic ratio. Error caused by the portion of the palladium foils which had not been submerged in the electrolyte solution was

corrected for by shearing off that portion of the foil, measuring its mass and subtracting that from the initial mass.

After hydrogenation, the foil samples were transversely sectioned normal to the rolling direction. One half of each sample was immediately prepared for indentation testing. This group is referred to as the hydrided samples. The remaining portion of the sample was replaced into the electrolytic cell and dehydrogenated by reversing the polarity of the cell. These samples are referred to as the dehydrided samples.

4.1.2 Superelastic NiTi

Nitinol wire (diameter 0.75 mm) of approximately equiatomic nickel and titanium composition was purchased from Educational Innovations, Inc., Connecticut, USA. In order to determine the appropriate temperatures for elevated temperature indentation and impact testing, differential scanning calorimetry (DSC) was performed by S.R. Pemberton¹³⁵ to determine the forward (A_s) and backward (M_s) transformation temperatures (using a 7.872 mg wire sample).

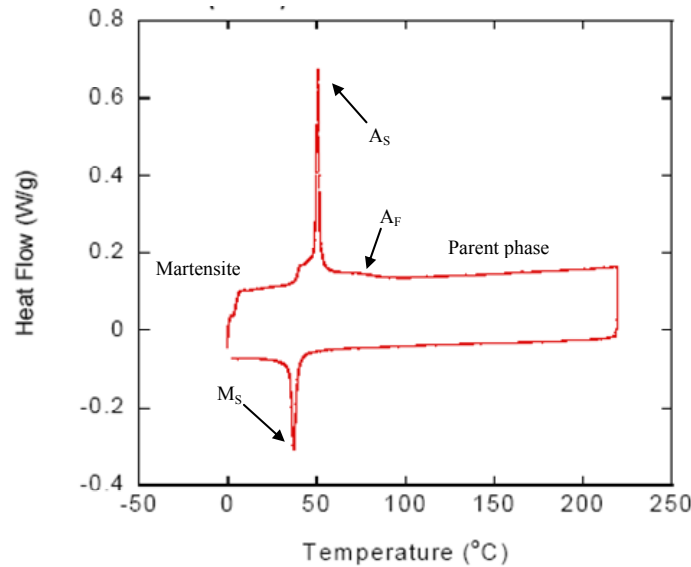


Fig. 4.2. NiTi wire DSC with the upper curve corresponding to the heating and the lower curve to the cooling of the wire reproduced with permission from Pemberton¹³⁵.

From the DSC trace (Fig. 4.2), the transformation temperatures were obtained for the transition from martensite to parent phase on heating and the reverse transformation on cooling.

<i>Transformation Temperature</i>	<i>DSC Values</i>	<i>Nominal Values</i>
A_s	55 °C	54 °C
A_F	70 °C	73 to 74 °C
M_s	45 °C	41 °C
M_F	n/a	27 to 28 °C

Table 4.1. Transformation temperatures for NiTi wire¹³⁵.

These values (Table 4.1) agree well with the manufacturer's nominal temperatures values, considering that it is difficult to predict finish temperatures for transformations from DSC. Transformation start temperatures are defined as occurring at the peaks, since they are the only well defined points available. The martensite transformation finish temperature was not observed.

4.1.3 PEO Coatings

Coatings were produced by A. Collier¹³⁶ on Ti-6Al-4V alloy substrates, using a 10 kW 2nd generation KeroniteTM commercial PEO processing unit. Prior to coating, substrates of dimensions 50 × 30 × 1 mm were ground with 180 grit SiC paper and ultrasonically cleaned in acetone, followed by water. Four aqueous electrolytes were used, referred to here as “aluminate”, “phosphate”, “silicate” and “mixed”. Compositions are given in Table 4.2. Substrates were PEO-processed for a period of 60 minutes, with a constant power output and an initial current density of 20 A dm⁻². During the process, the anodic RMS voltage was in the range 270-300 V and the cathodic RMS voltage varied between -30 V and -90 V, depending on electrolyte composition. Once coated, specimens were ultrasonically cleaned in water and ethanol.

<i>Electrolyte</i>	<i>NaAlO₂ (g l⁻¹)</i>	<i>Na₃PO₄ (g l⁻¹)</i>	<i>SiO₂ (g l⁻¹)</i>	<i>NaOH (g l⁻¹)</i>
<i>Aluminate</i>	12.5	1.5	0	0
<i>Phosphate</i>	1.5	4.5	0	0
<i>Silicate</i>	0	0	5.0	2.0
<i>Mixed</i>	0	2.3	3.0	0

Table 4.2. Electrolyte compositions for PEO coatings generated on Ti-6Al-4V alloy substrates reproduced with permission from Collier¹³⁶.

Samples of uncoated Ti-6Al-4V were also tested, together with uncoated aluminium alloy 5083, aluminium alloy 6060 with 40 µm of sulphuric acid hard anodised coating

(provided by Keronite Ltd.), and Al alloy 5083 with 40 μm of PEO coating (provided by Keronite Ltd.), with the processing conditions broadly described in Table 4.3.

<i>Coating process</i>	<i>Electrolyte</i>	<i>Total salt content (%)</i>	<i>Typical pH</i>	<i>Nominal thickness (μm)</i>	<i>Coating rate ($\mu\text{m}/\text{min}$)</i>	<i>Voltage (V)</i>	<i>Process temp ($^{\circ}\text{C}$)</i>	<i>Coating formation method</i>
<i>Keronite™ PEO</i>	<i>Proprietary alkaline</i>	<i>< 4</i>	<i>7-12</i>	<i>15-60</i>	<i>1 - 4</i>	<i>200 - 900 (pulsed AC)</i>	<i>12 to 30</i>	<i>Plasma oxidation</i>
<i>Hard Anodising</i>	<i>Sulphuric acid H_2SO_4</i>	<i>10 - 20</i>	<i><3</i>	<i>< 60</i>	<i>0.8 - 1</i>	<i>45 - 50 (DC)</i>	<i>-10 to 0</i>	<i>Anodic oxidation</i>

Table 4.3. Typical process parameters during Keronite PEO and hard anodising of aluminium¹³⁷.

4.1.4 Metallographic Preparation

Samples prepared for elevated temperature testing in the NanoTest system were polished using a South Bay Technology (SBT) lapping fixture, Model 150, with successively finer alumina lapping films from 15 μm to 0.03 μm . The sample was fixed to the lapping fixture via SBT Quikstik polymeric adhesive. After polishing, the adhesive was dissolved with acetone, freeing the samples for bonding to the nanoindenter's heated sample stage.

Cross sectional samples of palladium foils, were mounted in transparent epoxy (Streuers EpoFix and Metafix) for metallurgical preparation, with the edge normal to the rolling direction presented for polishing. The mounted samples were ground with successively finer grits of SiC paper, up to 1200 FEPA, and then polished using a diamond abrasive suspension on a polishing wheel down to 1 μm .

Etching of the palladium foil surfaces and cross sections was performed using a solution of 30 ml H_2O , 25 ml HCl , and 5 ml HNO_3 at 75 $^{\circ}\text{C}$ for 1-5 min.

Cross sectional samples of PEO coatings on Ti-6Al-4V were prepared by A. Collier¹³⁶ for SEM characterisation and nanoindentation. Samples were sectioned using an abrasive SiC high speed saw with water as a lubricant. After ultrasonic cleaning in alcohol and water, the sections were mounted in a conductive polymer and then ground with successively finer SiC grit paper up to 4000 grade. Final polishing was performed using a 1 μm diamond abrasive suspension on a polishing wheel.

Surface samples of PEO coatings were cut to size and ultrasonically cleaned by A. Collier¹³⁶ in an identical manner to cross sectional samples. Both cross sectional and surface samples of PEO were sputter coated with ~40 nm of gold using an Emtech K550 sputter coater for 90 seconds at a current of 20 mA prior to SEM characterisation.

4.2 Characterisation

Quantitative and qualitative characterisation of the microstructural and crystallographic characteristics of the samples examined was conducted over a wide range of instruments. These are delineated in this section.

4.2.1 Optical Microscopy

All optical microscopy of specimens was conducted using a calibrated Zeiss Axiolab optical microscope in reflected light mode fitted with a Motic Moticam 1000 digital camera.

4.2.2 Scanning Electron Microscopy

Secondary Electron Imaging (SEI) was used by A. Collier¹³⁶ using a JEOL 5800LV SEM to characterise the surfaces and cross sections of the PEO coatings. The cross sections of the palladium foils were characterised using backscatter electron imaging (BSE) using a JEOL 6340F FEGSEM.

4.2.3 Atomic Force Microscopy

AFM characterisation was performed, with the assistance of R.A. Oliver, using a Veeco Dimension 3100 AFM system with an XY closed-loop scanner using TappingMode™ with RTESPs (Rotated Tapping Etched Silicon Probes). Analysis of the data was accomplished using WsXM software from Nanotec.

4.2.4 X-ray Diffraction

X-ray diffraction was performed in air, using a Philips PW3719 vertical diffractometer with a conventional Bragg goniometer on the palladium foil samples, using Philips X'Pert software. The x-rays were generated with a Philips PW2273 X-ray Tube, using 40 keV accelerating voltage and 40 mA current, with a copper target. The data were collected with X'Pert Data Collector and analyzed with Highscore Plus software, both

written by PANalytical BV. The Palladium foils were orientated with the rolling direction aligned parallel to the plane of the beam scanning. The scan was run from 35° to 130° 2θ , with a step size of 0.05° 2θ and a step time of 2 seconds. The mass of the foils was measured prior to and after diffraction, to ensure that the hydrogen content during the test was known.

X-ray diffraction performed by A. Collier¹³⁶ on PEO coatings on Ti-6Al-4V alloys was carried out using the same instrument with the same accelerating voltage and current values. Scans were run from 10° to 90° 2θ , with a step size of 0.03° 2θ and a step time of 2 seconds.

4.2.5 X-ray Energy Dispersive Spectroscopy (EDS)

EDS was used by A. Collier¹³⁶ in the SEM to collect elemental composition data on the Ti-6Al-4V PEO coating systems. The relative proportions of the elements present in the sample were determined from the relative signal intensities detected. However, it should be noted that there is an inherent inaccuracy with using EDS for quantitative analysis of samples containing oxygen. Atomic percent values are generally only accurate to within 10%. Additionally, the use of point analysis techniques can be misleading, as they may not be entirely representative of the bulk composition. The size of the electron probe volume was roughly calculated using a Monte Carlo simulation. The electron penetration depth determined for the 15kV accelerating voltage used was found to be 1 μm . EDS was conducted on the coatings in section, which gave information of the phase composition of the bulk of the coating without interference of the substrate alloy. Areas in the middle of the sample were selected at random, well away from the outer or inner edges of the coating. Multiple locations on the surface of the coating were also investigated to determine the relation of the surface composition to the bulk composition of the coatings.

4.3 Quasi-Static Indentation

All indentation testing was performed using a Micro Materials Ltd. (MML) NanoTest nanoindentation system.

On palladium foil samples, a regular grid of indents was made on the cross section of each sample. The indenter tip consisted of a pyramidal Berkovich diamond. The

applied force was 15 mN, and the inter-indent spacing was 20 μm . Indentation of hydrided samples was conducted immediately as metallurgical preparations were completed.

On PEO coating cross-sections, nanoindentation testing was performed using a Berkovich diamond indenter tip. Multiple impact and scratch indentation were performed using a 10 μm cono-spheroidal diamond indenter tip. Grids of 10 by 10 indentations were produced on the cross-section, to a depth of 500 nm, using a proportional loading constant of 0.1 and an unloading rate of 2 mN s^{-1} . Intra-indent spacing was adjusted to cover the local thickness of the coating at indentation, but remained $> 10\mu\text{m}$. The position of each indentation row, relative to the position of the substrate interface, was determined using a calibrated optical microscope

4.3.1 Tip Shape Characterisation

Standard methods of monitoring indenter tip condition via indirect inference from indentations of a reference material using the Oliver and Pharr method²¹ or qualitative SEM observation lack direct traceability and are subject to error. The Oliver and Pharr method was used for tip shape determination for the Berkovich indenter used throughout this work. Direct observation of tips via AFM is necessary for reliable observation of changes in tip morphology and dimensions, which significantly affect indentation measurements. AFM characterisation was used to characterise tip shape of the spherical indenter used in impact testing and indentation of NiTi.

After locating the surface and apex of the indenter tip, 512x512 pixel scans of 10 μm by 10 μm and 2.5 μm by 2.5 μm were performed. Indenters were cleaned prior to AFM characterisation via manual indentations into polystyrene. This cleaning treatment removes most bulk contamination to the samples, but maintains the tips in a similar condition to normal service.

4.4 Impact Indentation

Impact indentation tests were typically conducted with 7 different acceleration loads: 1, 2, 5, 10, 20, 50, and 100 mN. This is the force experienced behind the indenter tip throughout the impact. All tests were performed with an initial standoff distance of $\sim 15\mu\text{m}$. A solenoid, positioned at the base of the pendulum, was used to restrain the

pendulum motion during load build-up. Once the desired acceleration load had been reached, the solenoid was released, allowing the pendulum to swing forward and impact the sample. The raw depth data were processed using customised LabView analysis programs.

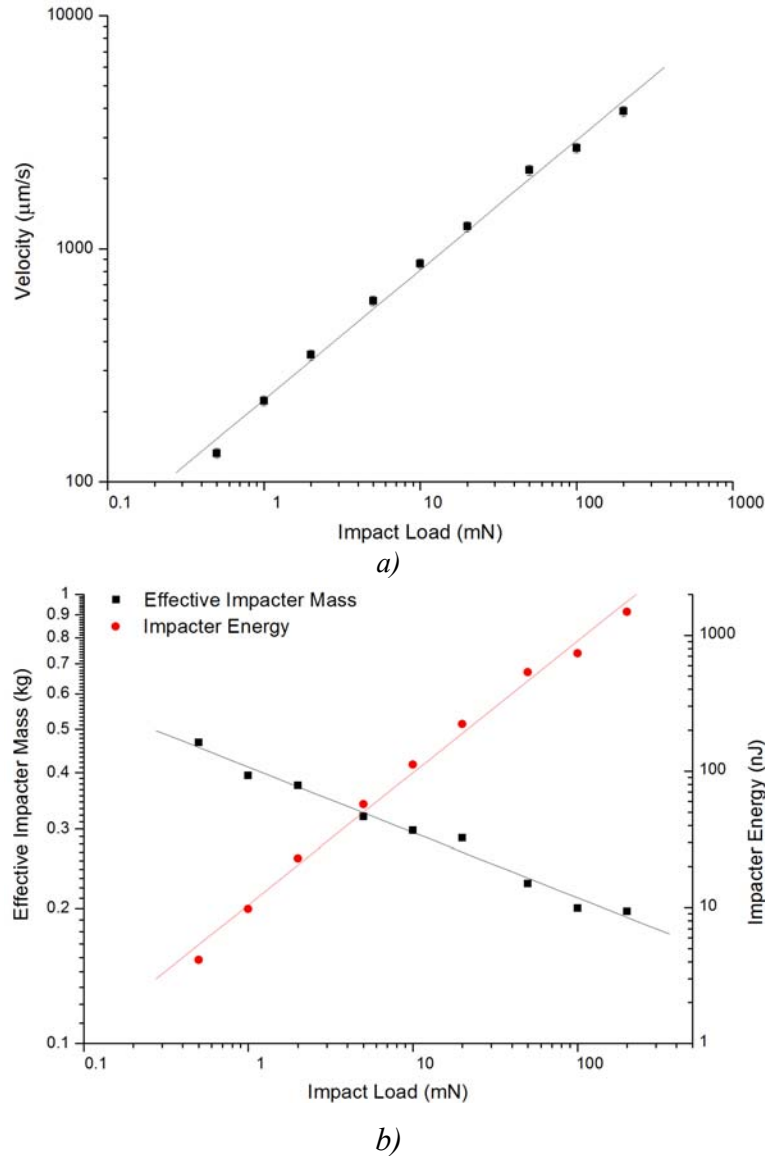


Fig. 4.3. Nanoindent indenter velocity immediately prior to impact a) and effective impactor mass and energy b) as a function of applied impact load at a standoff distance of $15\ \mu\text{m}$.

Calibration tests on a commercial soda-lime glass slide were also conducted using the dynamic hardness mode of the NanoTest system over a wider range of loads, 0.5-200mN, at a sampling rate of 8kHz. At this rate, the displacement of the indenter is highly resolved during the approach, rebound, and coming to rest on the sample under the applied load. The velocity and acceleration of the indenter was measured via polynomial fits of the discrete differential of the approach portion of the displacement

data as a function of the impact load (Fig. 4.3a), i.e. before the indenter contacts the sample at displacement ≥ 0 nm. Using simple kinematics relations ($F=MA$ and $K=0.5MV^2$), the effective mass of the indenter as a function of impact load was determined using the acceleration values, and from this the impact energy values were estimated (Fig. 4.3b).

Impact indentation of NiTi wire samples were performed using the high sampling rate Dynamic Hardness module of the NanoTest platform at a range of temperatures: 25°C, 37.5°C, 45°C, 55°C, 70°C, 100°C, and 120°C. All impacts were repeated three times at various accelerating loads from 1 to 100 mN, with impacts at 5, 10 and 20 mN carried out at all temperatures. Impact acceleration load was varied until the desired penetration depth was achieved.

Impact indentation of the coated material systems was performed using the low sampling rate Multiple Impulse module of the NanoTest platform with a sampling rate of 5 Hz at a impact frequency of ~ 0.25 Hz, for 400 s, generating 100 impacts at each location. Impact locations were spaced 50 μ m apart, with each acceleration load applied in a minimum of 3 different locations.

4.5 Scratch Indentation

Scratches 250 μ m in length were performed, with the load being linearly increased to maximum load during the first 25 μ m and then held constant at the maximum loads (10, 20, 50, and 100 mN) for the remainder of the distance. These are depicted in Figure 4.5, along with a constantly increasing load ramp along the length of the scratch, which was used in some specimens for comparison with the results at individual load plateaux.

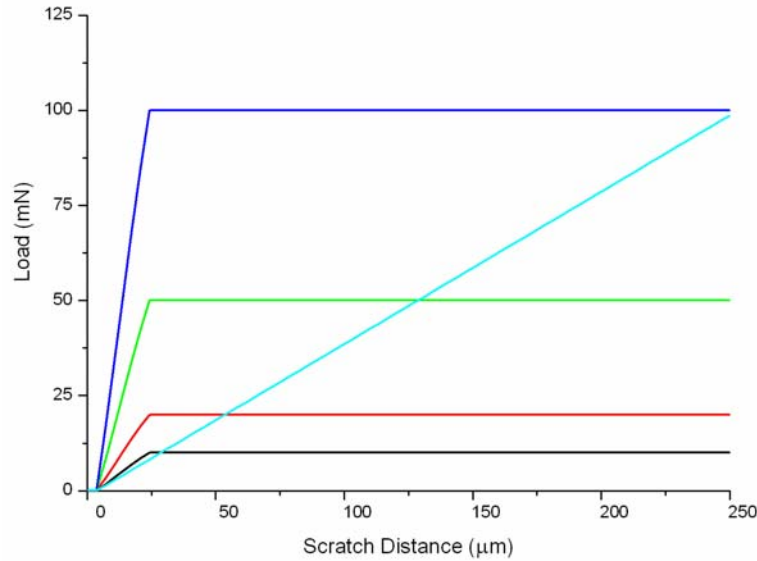


Fig. 4.5. Specified normal loading profiles over the length of the scratches.

All scratches were performed parallel to each other, at 50 μm spacing. Surface profiles were taken using a very low load (0.05 mN), along the length of each scratch, before and after scratching using the technique described by Wu¹¹⁷. The difference between these topology scans was taken as the plastic scratch depth. Loads indicated are the normal applied loads. Lateral forces were not monitored, and lateral displacement rates were held constant at 10 $\mu\text{m/s}$.

4.6 Elevated Temperature Indentation

Nanoindentation testing of materials at elevated temperatures is an increasingly active field of research^{9, 11, 41, 80, 87, 88}. Several approaches have been taken by nanoindentation system manufacturers towards enabling elevated temperature testing. These generally utilise Berkovich geometry diamond indenters for testing non-ferrous materials at temperatures $<400^\circ\text{C}$ and sapphire indenters for ferrous materials and all other materials at temperatures up to $\sim 750^\circ\text{C}$. Diamond indenters are not normally used for temperatures greater than 400°C due to the oxidation behaviour of diamond in air. Sapphire tips remain chemically stable in air at higher temperatures, but sapphire cannot be used for indentation of materials of comparable or greater hardness to itself. This is a significant limitation as many materials in high temperature applications, such as hardmetals for tool bits and DLC coatings for wear, are harder than sapphire.

Atmosphere also plays a significant role, since many materials rapidly form oxide or nitride layers in ambient air. At elevated temperatures, this behaviour generally becomes more pronounced. Therefore, the ability to perform nanoindentation testing where the dynamics of the environment can be controlled is of great interest and also presents several technical challenges.

All samples which were prepared for high temperature indentation were first metallographically prepared in the freestanding condition as detailed in §4.1.3 and then mounted to one the NanoTest's hot stages using FortaFix FC6 high temperature adhesive. Both the indenter tip and the hot stage were then heated to the desired temperature, using nichrome heating elements and Eurotherm 2216e temperature controllers. The indenter chamber was allowed to thermally equilibrate overnight, and then the indentation schedule performed.

Elevated temperature indentation of NiTi wire samples was performed using a 10 μm radius cono-spheroidal diamond indenter tip. Indentations were undertaken at room temperature, 37.5°C, 55°C, 70°C, 100°C, 120°C and 200°C. In this manner, the response of superelastic NiTi to indentation loading could be probed over a large range of temperatures from below A_S , through to A_F and up to 200°C. All indentations were repeated three times at locations 50 μm apart at constant loading rates of 2.5 mN s^{-1} , 10 mN s^{-1} and 20 mN s^{-1} and a constant unloading rate of 5 mN s^{-1} . A dwell time at the end of loading was included, allowing indentation creep to occur sufficiently during holding, for creep deformation to become insignificant during unloading.

4.6.1 Diamond Indenter Oxidation

Following the discussion in §3.1.2.1, a brief investigation into the effects of high temperature oxidation on the geometry of diamond indenter tips was conducted to determine the stability and validity of their usage. After initial AFM characterisation, a commercially obtained natural type IIa diamond Berkovich indenter was exposed to three high temperature treatments in succession with AFM characterisation following each treatment. The first of which consisted of heating the tip to 450°C in air for 30 minutes, and the following treatments exposed the tip to 750°C and 900°C in 1 atmosphere of static, commercial purity Argon (30-45ppm O_2) for 90 minutes each. Additionally, a Berkovich and a 10 μm radius conospheroidal tip which had been

utilised for at least 5 years of intermittent use at various temperatures $\leq 400^{\circ}\text{C}$ for elevated temperature indentation testing in air have been characterised using the AFM to examine the effects of long term exposure to oxidation and mechanical wear from indentation.

The initial scan of the Berkovich indenter exposed to high temperature oxidation includes a limited amount of sample mount drift, however improvements to the sample mount corrected this for all subsequent scans. Results for the initial state of the Berkovich indenter (Fig. 4.6a) show fairly sharp facet edges as illustrated by the triangular profiles of the contour lines, however several irregular bumps are also observable. This is partially due to contamination and partially due to surface roughness. In the derivative projection (Fig. 4.6b), contamination can be distinguished from the roughness by two features: steep side slopes, shown as bright and dark edges, and in the lower two facets it overlays the step features (which are further discussed in §4.6.3). The steps frame or continue around rough surface irregularities but are covered by contamination. The sample drift which occurred during scanning laterally translated the data towards the right of the image and caused the Berkovich to appear skewed. This also changed the apparent slopes of the facets and directions of the steps on the facets. The lowest facet edge may appear flatter due to it drifting with the direction of scan as well.

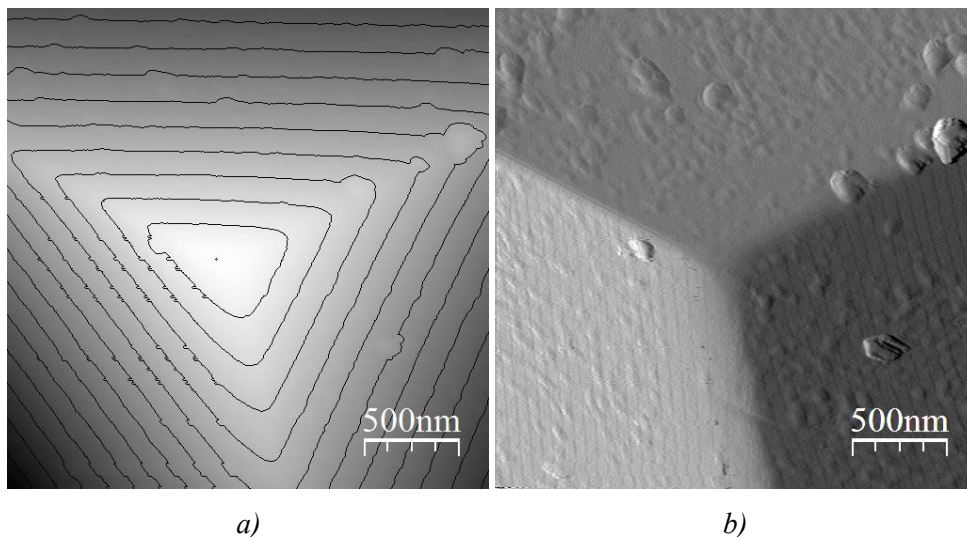


Fig. 4.6. AFM data showing the initial state of the berkovich indenter in a) plain projection with contour lines at 50 nm intervals and b) a derivative projection.

The sample drift was eliminated prior to acquisition after the diamond had been heated to 450°C in air for 30 minutes. However, some noise is observable in a few scanlines. This exposure condition was selected as it is near the maximum allowable temperature for diamond Berkovich indentation in air. The absence of sample drift induced skew in the data can be observed in the roughly equiangular triangles of the contour lines in Figure 4.7a. Facet edge blunting is also observable in the rounded corners of the contour lines. The step features (Fig. 4.7b) now appear to be approximately normal to the facet slopes but remain absent in the upper facet. The surface roughness is reduced in this condition, but the surface features which are observable are larger bodies which continue over several steps.

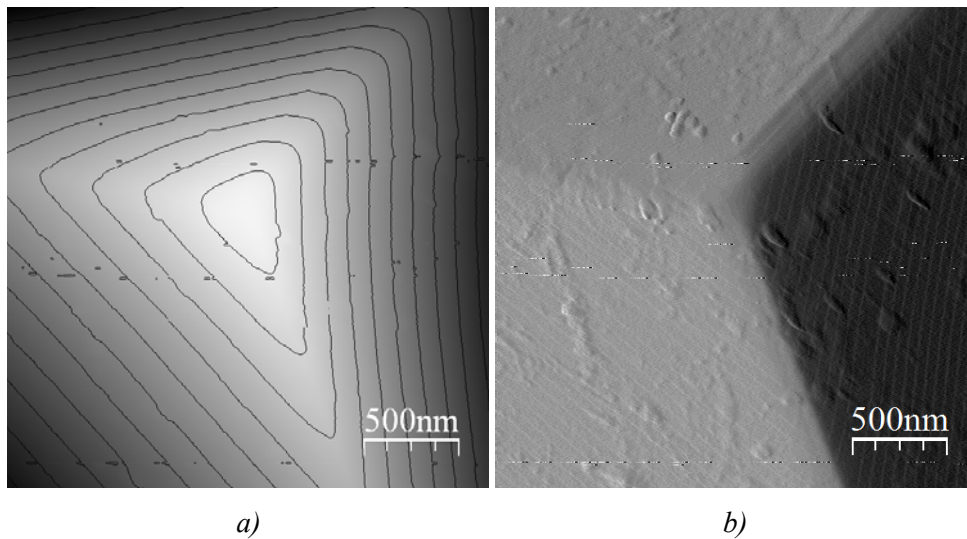


Fig. 4.7. AFM data showing the berkovich indenter after 30 minutes at 450°C in air in a) plain projection with contour lines at 50 nm intervals and b) a derivative projection.

After a 90 minute exposure at 750°C in commercially pure argon (Fig. 4.8), extensive edge ridging is observable as well as an approximately flat area at the apex. The effect of the ridging on the contour lines (Fig. 4.8a) is to significantly reduce the projected area in the region of the corners affected. The ridge of bumps alongside the upper right and lower facet edges is contamination. Interestingly, the lowest facet edge which occurs at the junction of the two facets with step features appears to be sharper than in the previous condition. Surface roughness on all facets also appears to be lower.

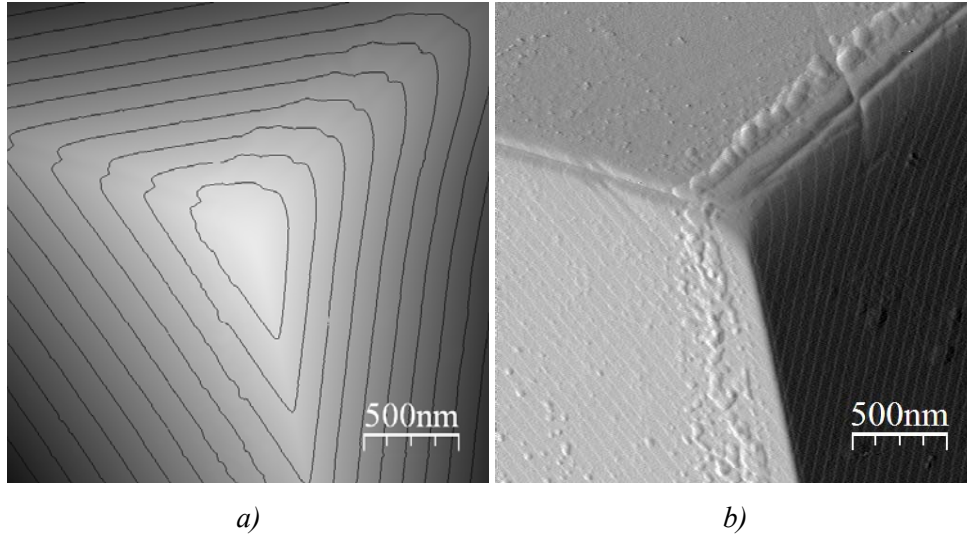


Fig. 4.8. AFM data showing the berkovich indenter after 90 minutes at 750°C in argon in a) plain projection with contour lines at 50nm intervals and b) a derivative projection.

The final exposure condition, to which the Berkovich diamond was exposed, 90 minutes at 900°C in argon, had a significantly different effect on the diamond than the previous conditions. Rather than smooth blunting or attack at the apex and facet edges, etch pits are observed on the entire surface of the diamond (Fig. 4.9b). Oxidative attack also appears to have occurred uniformly on all facets edges as well, which can be observed in the uniform rounding of the corners on the contour lines in Figure 4.9a. This apparent change in oxidative etching/erosion behaviour could be due to a different regime of oxidative attack due to the elevated temperature or could be representative of a much more advanced stage of the same oxidation modes that were accelerated by the elevated temperature.

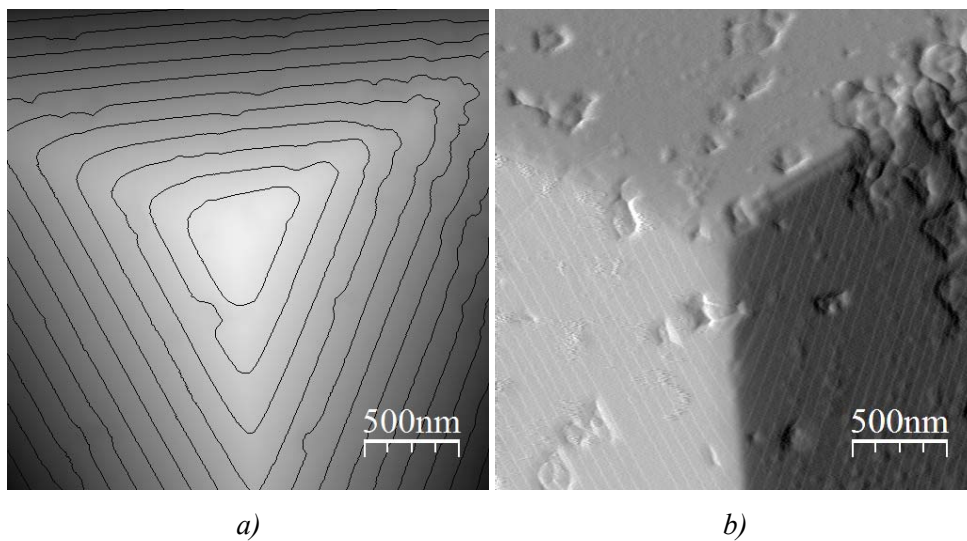


Fig. 4.9. AFM data showing the berkovich indenter after 90 minutes at 900°C in argon in a) plain projection with contour lines at 50nm intervals and b) a derivative projection.

A convenient way to illustrate these results is by using orthogonal 3D renderings. Figure 4.10 shows the progression of the 4 exposure conditions of this Berkovich diamond as view from a 45 degree downward angle aligned to one of the facet edges. This type of representation allows rapid apprehension of the data and qualitative information about the observable features.

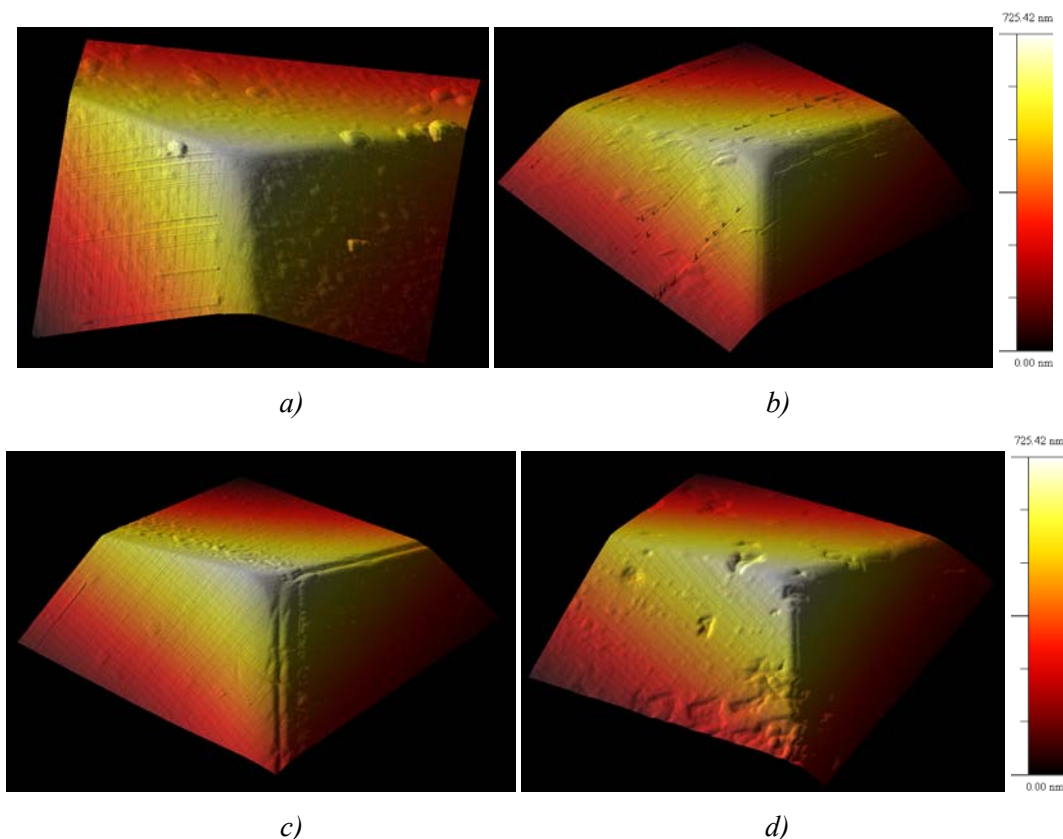


Fig. 4.10. Orthogonal 3D projections of AFM data shown at 45 inclination aligned to reference edge in a) initial, b) 450°C in air, c) 750°C in Argon and d) 900°C in Argon.

For quantitative analysis, cross sectional or projected area functions were extracted from the data using height histograms. From the apex to a depth of 150 nm, areas functions were extracted from the 2.5 μm by 2.5 μm scans and areas from depths of 150 nm to 1500 nm were extracted from the 10 μm by 10 μm scans. This was done to ensure that the entire projected area for each depth was contained within the bounds of the scan. A small discontinuity can be observed in the plots at the point where the data the two scans meet.

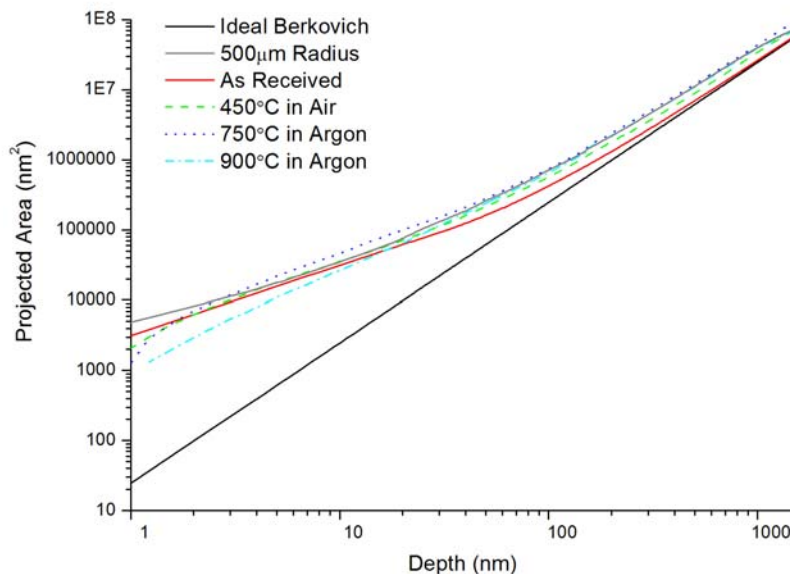


Fig. 4.11. The projected area as a function of depth from the apex as compared to an ideal Berkovich tip and an equivalent area conospheroid with a 500 μm radius tip.

It is unfortunate that the data of the initial condition was affected by sample drift, as this could quantitatively affect the data. The lateral drift would make the tip appear elongated and increase its apparent area, while the areas at greater depths from the apex would be less affected. This is potentially observed in Figure 4.11, as the initial condition remains near ideal berkovich areas at higher depths and then rapidly blunts near the tip. In all conditions, the area functions approximate more closely a conospheroidal tip with a 500 μm radius tip on a 70.3° cone, which is a cone that has the same area-depth relationship as an ideal berkovich pyramid.

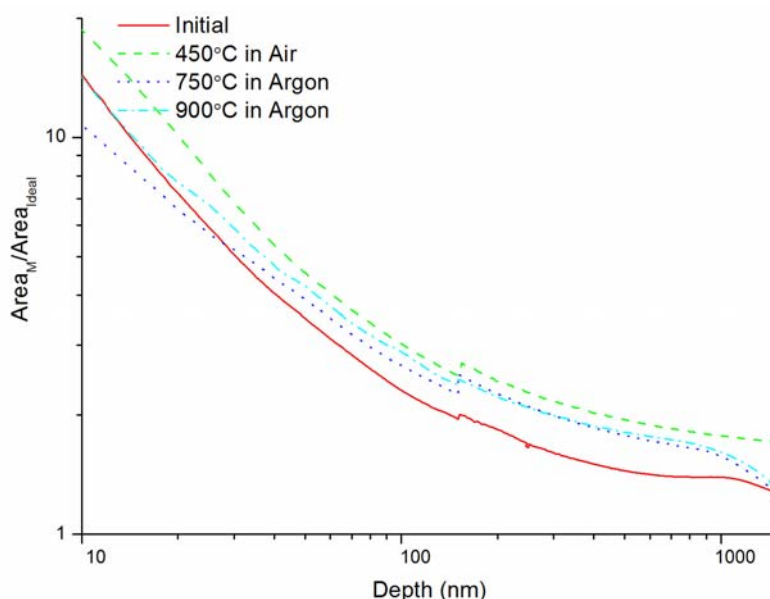


Fig. 4.12. The ratio of the measured area to the ideal Berkovich area as a function of depth.

A plot comparing the ratio of the measured area to ideal area for each condition (Fig. 4.12) is a direct method to quantitatively compare the change in area functions between successive exposures. It is observed that for depths greater than 30 nm, the initial condition is significant closer to an ideal berkovich pyramid, i.e. a ‘sharper’ indenter. The next condition, 30 minutes at 450°C in air, is surprisingly the most ‘blunt’ of all the conditions with the greatest deviation from idea over all depths. The indenter apparently ‘sharpens’ after the next exposure for 90 minutes at 750°C in argon, however morphological examination of the data (Fig. 4.8) shows that the reason for this is the attack on the facet edges reducing the cross sectional area. This does effectively ‘sharpen’ the indenter; however it causes a deviation from the ideal three-sided pyramidal shape which is analytically undesirable for analysis of indentation data. The final condition of the indenter after 900°C in argon for 90 minutes shows a fairly uniform ‘blunting’ of the indenter from previous condition after exposure at 750°C in argon. However, the effect of the etch pitting observed in Figure 4.9 on the friction and deformation during indentation may cause a significant difference between the indenters performance and that of a smooth faced indenter of similar ‘bluntness’.

4.6.2 Diamond Indenters Used <400°C

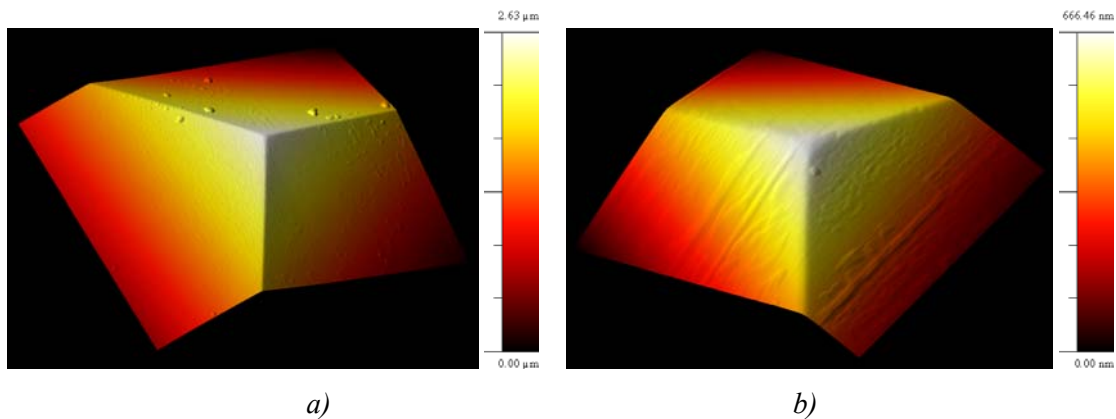


Fig. 4.13. Orthogonal 3D projections of AFM data taken from a Berkovich indenter used at temperatures <400°C shown at 45 inclination aligned to reference edge in a) 10 μm by 10 μm scan and b) 2.5 μm by 2.5 μm scan.

Two diamond indenters which had been in extended elevated temperature service over several years on a variety of materials and range of temperatures <400°C were examined to ascertain the effects of long term service. The results of this are shown in Figures 4.13 and 4.14. The berkovich indenter (Fig. 4.13) displays a somewhat stable,

uniformly 'blunted' appearance without the 'blunted' facet edges observed in Figure 4.7. Interestingly, no step features were observed on any of the facets.

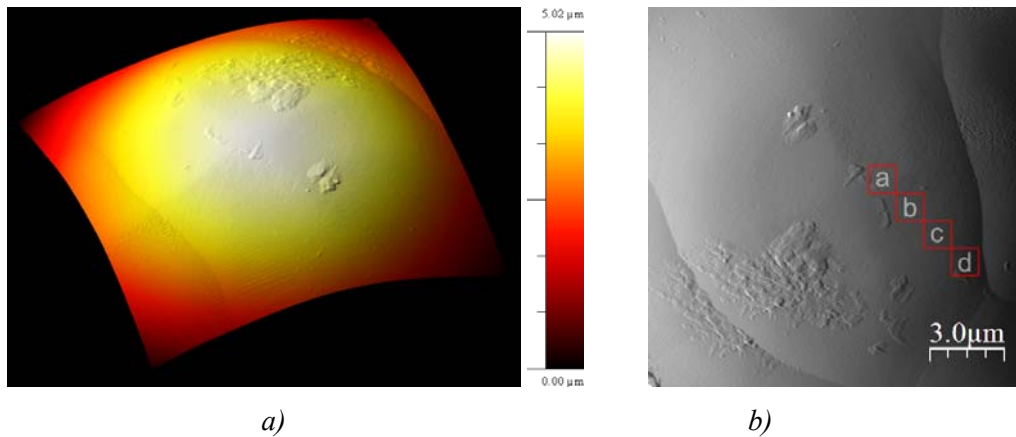


Fig. 4.14. Orthogonal 3D projection of AFM data taken from a 15 μm by 15 μm scan of a 10 μm radius conospheroidal indenter used at temperatures $<400^\circ\text{C}$ shown at 45 inclination a) and b) the derivative image with high resolution scan regions shown.

The sphericity of the conospheroidal indenter (Fig. 4.14) remains apparently unaffected after the prolonged service without any faceting or severe blunting. A crack-like ridge is observed around at a depth of 1.5 μm from the apex, and a faint cross-shape centred on the apex is barely distinguishable. This cross shape is possibly a remnant of the indenter's original shape prior to mechanical grinding into the conospheroidal geometry. Without data on the initial states of these indenters, it is impossible to speculate on the exact degree of oxidation or blunting which might have taken place, however, it appears that they have remained nominally stable.

4.6.3 Step Discussion

One of the most intriguing features discovered during the course of this investigation is the steps which were observed on the surfaces of two of the indenters. The absence of the steps on the historical Berkovich indenter and on the upper face of the successively oxidised Berkovich indenter is also curious. These steps are possibly a result of the orientation of the surface relative to the low energy planes of the diamond single crystal. This was tested via examination of the spherical indenter (Fig. 4.14 & 4.15). By taking high resolution scans at successively greater distances from the apex, the angle of the tangent surface relative to the internal structure was effectively varied. It is observable that the spacing of the step features is dependent upon the slope of the surface. At the bottom right corner of Figure 4.15d the steps are spaced

~30 nm apart, while at the top left corner of Figure 4.15a the steps are spaced ~110 nm.

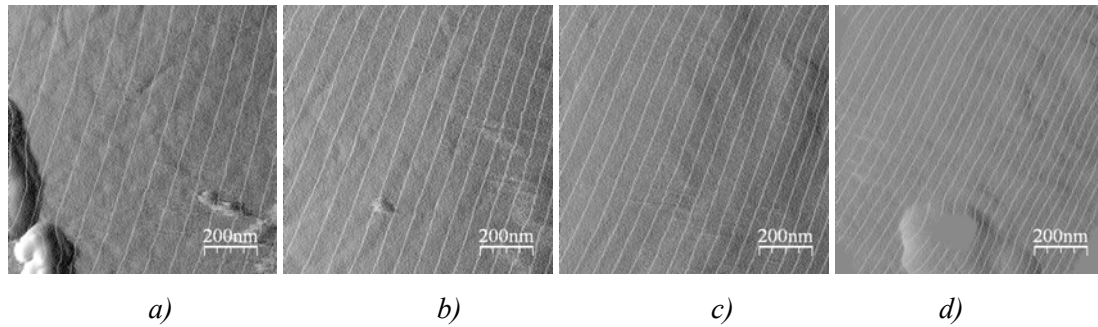


Fig. 4.15. 1 μm by 1 μm derivative images of AFM data taken from regions highlighted in Figure 4.14b.

This suggests that the surfaces which do not demonstrate step features may be sufficiently aligned to the low energy planes of the diamond to be at a spacing either too great or too small to be resolved. It is worth noting that during oxidation these steps will likely translate along the surface, as the vertically displaced portion of the steps is likely to have a different surface energy to the flat portion. If a step encountered a surface asperity during oxidation induced translation, the irregular shape of the asperity would likely have a high surface energy causing it to be preferentially consumed and reduced to a planar surface. This might effectively 'polish' planar surfaces as was observed in Figures 4.10a-4.10c. If neighbouring facets are appropriately aligned to each other, this same action might sharpen the edges of the pyramid, as was observed in the lower edge in Figure 4.7a. Considering both of these effects, it is possible to imagine an indenter geometry sufficiently well aligned to the diamond internal structure that it would 'sharpen' during oxidation. This might produce diamond indenters etched to near theoretical sharpness in a similar manner to the method by which AFM probes are prepared. Considering the cubic structure of diamond, it is possible that the most effective indenter geometry may be a cube corner. Further work is necessary to determine the reason for the apparent absence of steps on some faces, the relationship of the steps to existing surface science models, and the optimum orientation to produce sharpening.

4.7 Tribological Testing

Sandblast-type erosion testing was conducted by A. Collier¹³⁶ using a Guyson Euro 2SF blast cleaning cabinet, with an inlet pressure of 3.2 bar and a gun-to-sample

distance of 30 cm at 90° incidence. A shutter was used to ensure the samples were only exposed to a steady particle stream.

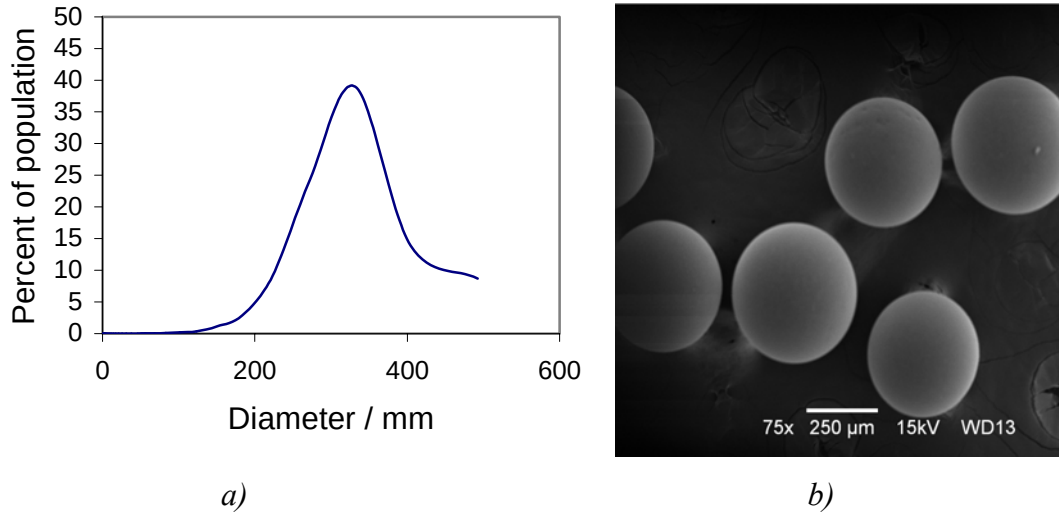


Fig. 4.16. Erodent a) particle size distribution and b) shape as characterised by electron microscopy reproduced with permission from A. Collier¹³⁶.

The particles used were spherical silica beads, with a diameter of $300 \pm 23 \mu\text{m}$. A particle size distribution (Fig. 4.16a) of the silica beads used was obtained using a Malvern Mastersizer 2000 particle size analyser. Particle velocity was estimated to be 13 m s^{-1} using a very crude approximation by assuming that the particles travel at the same speed as the air flow. The velocity of the air flow was calculated very approximately from force exerted against a fixed plate, which was measured using a load cell.

5

Indentation of the Pd-H System

The palladium-hydrogen system shows complex mechanical behaviour at ambient atmospheric conditions, since its composition and microstructure can dynamically change as hydrogen escapes. Nanoindentation has been used to study the effect of redistribution of hydrogen within palladium.

5.1 Aims of Research

The selection of the palladium-hydrogen system for investigation was suggested by one of the author's funding agencies. It was envisioned that nanoindentation might be used to probe the differences in mechanical behaviour between pure palladium and palladium saturated with hydrogen, particularly how the hydrogen might be reorganised by the high stresses induced by sharp indentation.

5.2 Review of the Palladium-Hydrogen System

A review of the properties of the palladium-hydrogen system is required in order to discuss indentation results, which are discussed in §5.3 and onward.

The palladium-hydrogen system is non-stoichiometric and does not form a stable compound under ambient conditions¹³⁸. The solubility of hydrogen in palladium depends on temperature and the pressure of the surrounding hydrogen atmosphere. Under ambient conditions, the hydrogen partial pressure in the atmosphere is 0.55ppm by volume¹³⁹, so assuming favourable surface activation it is very likely that outgassing will occur in any specimen of palladium which contains a significant amount of hydrogen. This work examines the effects of hydrogen storage and outgassing on palladium using nanoindentation. The available literature on the known effects and behaviour of hydrogen in palladium relevant to this work is briefly reviewed here.

5.2.1 Pressure-Composition-Temperature Relations

The pressure-composition-temperature (p-c-T) relationships for H-Pd were systematically characterised by Wicke, Nernst, and Frieske¹⁴⁰ (Figure 5.1).

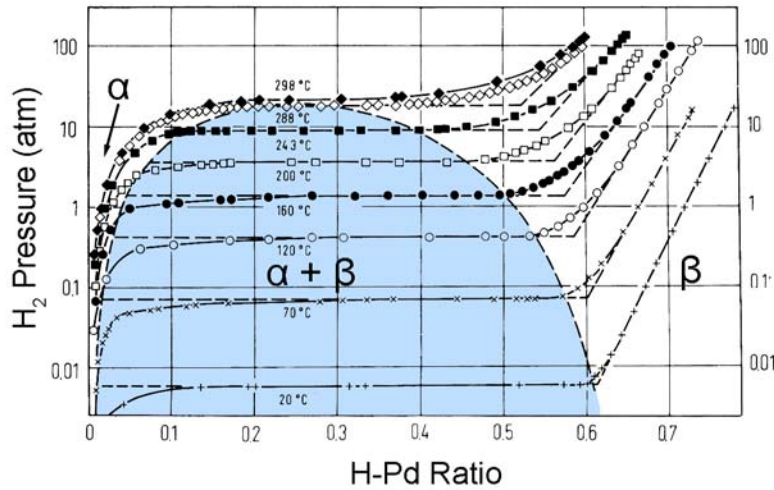


Fig. 5.1. Pressure-composition isotherms and phase fields for the palladium-hydrogen system. The pressure is shown against H-Pd atomic ratio in the resultant structures¹⁴⁰.

The hydrogen content in Figure 5.1 was determined gravimetrically using bulk palladium, and the magnetic susceptibility was concurrently measured at each point. Isothermal absorption/desorption curves display hysteresis. Nernst showed that the desorption branches of the isotherms can be taken as the equilibrium curves within the miscibility gap and the β , or α' , phase region. However, if the two isotherm branches diverge in the α phase region, the absorption branch is nearer to equilibrium than the desorption branch¹⁴⁰. The limits of the phase fields (the shaded region) can be determined by extrapolating the linear regions of each pressure plateau to the absorption/desorption envelopes. This is shown on Figure 5.1 as dashed lines. This technique was also applied to magnetic susceptibility isotherms to more reliably determine the minimum compositions for the β phase. The solubility limits of the α and β phases are presented in Table 5.1.

Temp (°C)	α_{max} (mole fraction H)	β_{min} (mole fraction H)
-78.5		0.635 ± 0.003
-30		0.629 ± 0.003
0	0.0055 ± 0.001	0.615 ± 0.003
20	0.008 ± 0.002	0.607 ± 0.002
70	0.017 ± 0.002	0.575 ± 0.002
120	0.030 ± 0.002	0.540 ± 0.003
160	0.046 ± 0.002	0.504 ± 0.003
200	0.075 ± 0.002	0.459 ± 0.004
243	0.117 ± 0.002	0.399 ± 0.005
288	0.21 ± 0.01	0.29 ± 0.01

Critical points: $T_c = 292 \pm 2^\circ\text{C}$; $c_c = 0.250 \pm 0.005$

Table 5.1. Phase field limits of hydrogen-palladium system¹⁴⁰.

The plateau pressures in Figure 5.1 can be calculated as a function of temperature using the relation

$$\ln p = -\frac{\Delta H}{RT} + \frac{\Delta S^0}{R} \quad (5.1)$$

where $\Delta H = 4.1 \pm 0.42 \text{ kJ/mol}$ of H_2 and $\Delta S^0 = 97.5 \pm 1.25 \text{ J K}^{-1} \text{ mol}^{-1}$ of H_2 within the temperature range of 20-300°C. Further discussions of the thermodynamics of hydrogen, $\text{Pd}_\alpha\text{-H}$, and $\text{Pd}_\beta\text{-H}$ interactions are available elsewhere¹⁴⁰.

5.2.2 Crystallography

At ambient temperature, pure palladium has a face centered cubic (FCC) crystal structure, with a lattice parameter of 0.3890 nm. When charged with hydrogen, the unit cell expands isotropically until the hydrogen content achieves the maximum α phase solubility, α_{max} , corresponding to a lattice parameter of 0.3894 nm. If the hydrogen content is increased past its maximum soluble mole fraction, α_{max} , an expanded isomorphic β phase forms (via mechanisms discussed in §5.2.4), with a lattice parameter of 0.4025 nm, to accommodate the extra hydrogen. This phase continues to grow as more hydrogen is added according to the lever rule, until total conversion to the β phase occurs at the β_{min} mole ratio value (values given in Table 5.1). If more hydrogen is added after full conversion to β phase has taken place, Schirber and Morosin¹⁴¹ found that between hydrogen contents (Pd-H atomic ratios) of 0.8 and 0.98 at 77°K the unit cell of the β phase expands linearly as hydrogen atoms occupy more of the lattice.

The position of the hydrogen atoms in the FCC palladium lattice was determined via neutron diffraction¹⁴². In the hydrogen-rich, β phase the hydrogen atoms were confirmed to occupy only the octahedral interstitial sites. For low hydrogen contents (α phase) octahedral sites were also indicated, but the responses were mostly below the sensitivity of the instrument, due to the small content of hydrogen. The atomic ratio (molar fraction) of H-Pd equals the percentage of octahedral sites occupied. At an H-Pd ratio of 1, PdH, the crystal lattice theoretically has the NaCl structure.

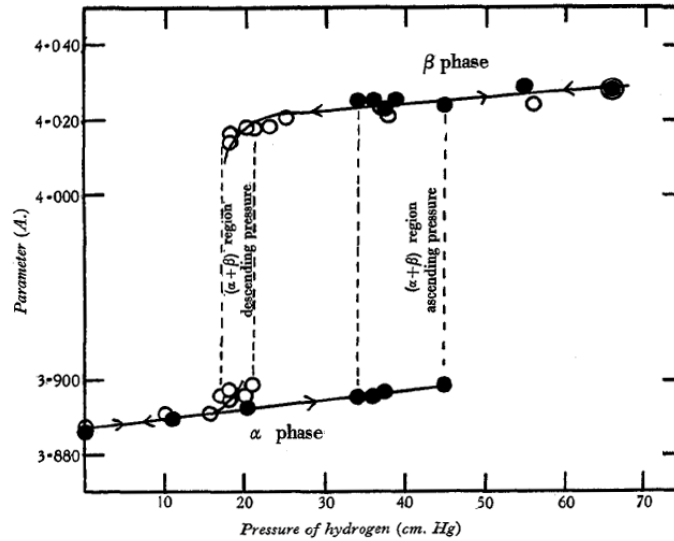


Fig. 5.2. Lattice parameter hysteresis with equilibrium hydrogen pressures at $100^{\circ}\text{C}^{143}$.

When passing through the miscibility gap on the p-c-T diagram, the $\alpha+\beta$ region, there is a pronounced hysteresis in the lattice parameter change (Figure 5.2). This was attributed to the instrument sensitivity being insufficient to detect the presence of small fractions of the minority phase.

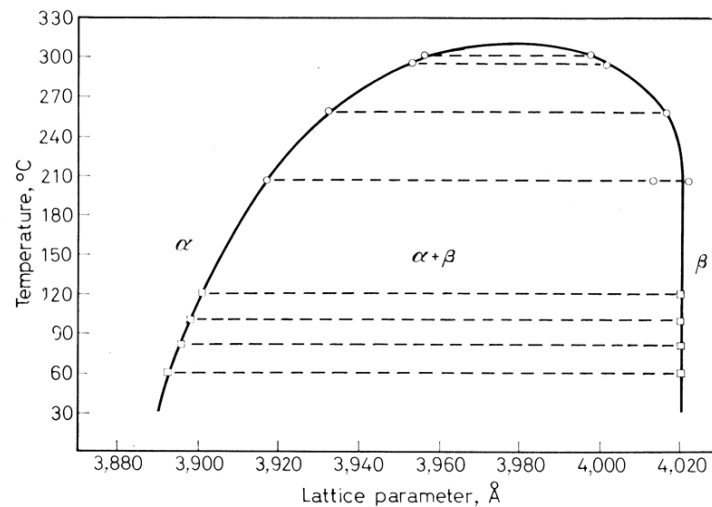


Fig. 5.3. Lattice parameter variation around the miscibility gap with temperature¹⁴⁴.

The solubility of hydrogen in palladium varies with temperature. At higher temperatures, the α phase is stable to higher H-Pd ratios. This is due to thermal expansion of the lattice allowing a larger quantity of hydrogen atoms to be accommodated before saturation of the α phase forces nucleation of the β phase. The increased solubility at higher temperatures also allows the β phase to nucleate with a smaller unit cell than is necessary at ambient temperature. Thus, the lattice parameters of the α and β phases vary with temperature (Figure 5.3). When loaded

supercritically, the lattice parameter is a smooth, continuous function of hydrogen content and temperature.

5.2.3 Hydrogen Adsorption/Diffusion

There are three ways to introduce hydrogen into palladium: gas overpressure, electrolytically, or with a plasma¹⁴⁵. Using palladium as the cathode in an electrolytic cell has been extensively used and researched since the discovery of hydrogen's significant solubility in palladium by Graham¹⁴⁶. The hydrogen content of palladium charged with this technique has been analysed using Coulometry, gravimetry, and by electrical resistance. A thorough summary of the research in this area until 1967 was provided by Lewis¹³⁸.

Electrolytic charging of palladium with hydrogen involves five elements: an electrolyte bath, a palladium cathode, a platinum anode, platinum lead wires (to prevent contamination) and a power supply. The electrolyte is typically sulphuric acid or sodium hydroxide. The reaction at the palladium cathode, when current is passed through the system, produces atomic hydrogen which is absorbed into the palladium cathode.

Until the advent of ultra high vacuum (UHV) techniques, the electrolytic charging technique was the only way to achieve high hydrogen contents in bulk palladium at low temperatures. Earlier studies using gas overpressure in non-UHV conditions required the surface to be activated by grinding the palladium into a fine black powder (palladium black) to achieve high hydrogen contents. The electrolytic method easily achieves the necessary dissociation of the H₂ molecule to allow absorption into bulk palladium. It allows the attainment of hydrogen contents which would, at ambient temperature, otherwise require overpressures of 100-1000 atmospheres. This is due to the two extra steps required for molecular hydrogen gas to penetrate the surface of the metal and enter the bulk lattice. Broadly, the complete process occurs via three steps: the initial chemisorption of the molecular hydrogen gas to the surface, the dissociation of the hydrogen into subsurface sites and the passage of hydrogen from the subsurface sites into the interior.

Introducing hydrogen into palladium using a plasma involves bathing a sample of palladium in hydrogen gas at low pressures heated or otherwise excited into the plasma state. This produces energetic atomic hydrogen which easily penetrate into the palladium where they are absorbed; bypassing chemisorption and dissociation.

Once inside the bulk of the material, diffusion of hydrogen in the α phase of palladium occurs via thermally activated jumps from octahedral site to octahedral site, so that

$$D = D_0 \exp\left(\frac{-Q}{k_B T}\right) \quad (5.2)$$

where D is the diffusion coefficient in $\text{m}^2 \text{s}^{-1}$, Q is the activation energy in kJ mol^{-1} , k_B is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J mol}^{-1} \text{ K}^{-1}$), and T is absolute temperature (K).

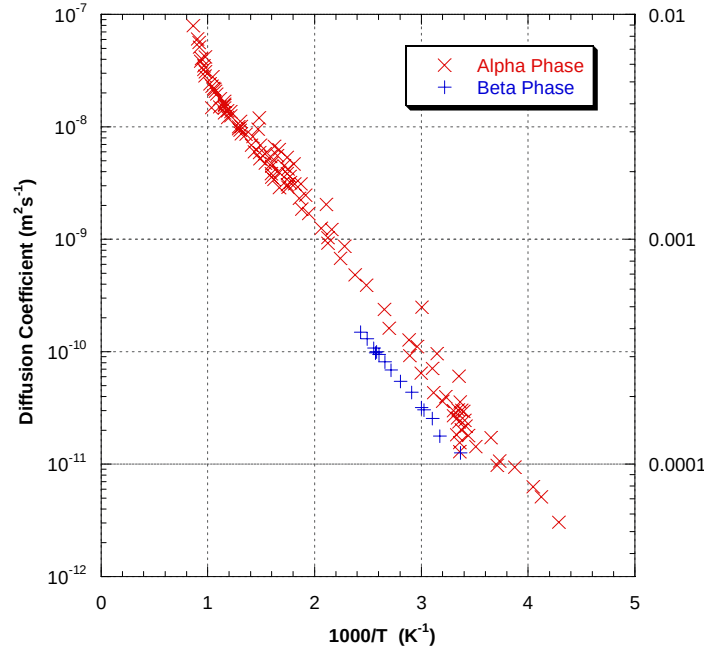


Fig. 5.4. Diffusion coefficient for hydrogen in α^{147} and β^{148} ($\text{PdH}_{0.7}$) phase palladium as a function of temperature.

Volkl and Alefeld¹⁴⁷ collected the work of 25 different authors who used various different methods to determine the diffusion rate of hydrogen in palladium, to produce the alpha phase portion of Figure 5.4. From this plot, Volkl and Alefeld determined the pre-exponential factor and activation energy to be $D_0 = 2.90 \cdot 10^{-7} \text{ m}^2 \text{s}^{-1}$ and $Q = 22.08 \text{ kJ mol}^{-1}$. The self-diffusion of palladium is much slower, with $D_0 = 2.05 \times 10^{-5} \text{ m}^2 \text{s}^{-1}$ and an order of magnitude higher activation energy, $Q = 226 \text{ kJ mol}^{-1}$. The mean diffusion distance, $\sim (Dt)^{1/2}$, for 1000s is shown on the

right hand axis of Figure 5.4. At room temperature, the diffusion distance for α phase palladium is on the order of 200 μm in 1000s.

In cold-worked specimens, diffusion can be assisted in the α phase by dislocation pipe diffusion¹⁴⁹. Since the reformation of the α phase from the β phase creates a high dislocation density¹⁵⁰, this can present a significant assist to outgassing hydrogen.

Seymour¹⁴⁸ used NMR spectroscopy to determine the diffusion coefficient of hydrogen in β phase palladium (Figure 5.4) over the temperature range from 23°C to 140°C. NMR was used to measure the magnetic dipole relaxation times, which yield the interstitial mean jump time. The pulsed-field-gradient spin-echo method was used to measure the model-specific diffusion coefficient. Seymour determined the pre-exponential factor and activation energy to be $D_0=9.0\cdot 10^{-8} \text{ m}^2 \text{ s}^{-1}$ and $Q=21.89\pm 0.576 \text{ kJ mol}^{-1}$. This puts his activation energy figures in agreement, within experimental error, with Volkl and Alefeld's¹⁴⁷ fit for α phase palladium. One might surmise that the activation energy remains constant with hydrogen content, while the pre-exponential factor decreases proportionally to the amount of unoccupied octahedral sites.

5.2.4 Phase Transformation Mechanism

The hydrogen-induced phase transformation in the hydrogen-palladium system must be considered separately for $\alpha\rightarrow\beta$ and $\beta\rightarrow\alpha$ transformations, since they affect the material differently. The hydride transformation occurs by a different mechanism than classic phase transformations¹⁵¹. This is because of the greatly differing mobilities of the two species involved. The hydrogen has an extremely high diffusion rate, allowing long distance transport, but the metal, palladium, is only capable of moving short inter-atomic distances. The two of these combine to produce a diffusive-cooperative phase transformation, in which the hydrogen organises and rearranges via diffusion and the palladium host lattice reorganises only through the non-diffusive shift mechanism, similar to a martensitic transformation.

The β phase nucleates and grows at dislocations and vacancies, coherently as plates or incoherently as dendritic precipitates within the α phase host lattice¹⁵¹. The phase

transformation is accompanied by a significant volume expansion, $\sim 10\%$ at room temperature, due to the abrupt increase in lattice parameter. The phase transformation to β phase does not occur uniformly or continuously (except above the supercritical temperature), so the strain of expansion varies locally in both orientation and intensity. This results in significant deformation of the macrostructure and large internal strains. It is therefore desirable to avoid the $\alpha \rightarrow \beta$ transformation in engineering applications.

Supercritical loading of the palladium lattice with hydrogen avoids the deleterious effects of the $\alpha \rightarrow \beta$ transformation. By loading with hydrogen above the critical temperature or pressure, the hydrogen solubility remains sufficiently high to accommodate hydrogen without a phase change. The crystal lattice expands uniformly to accommodate the hydrogen, which diffusionally flows into the octahedral sites. Changes to the microstructure and orientation of the palladium are completely avoided. If one then lowers the temperature into the miscibility gap on the p-c-T, the hydrogen content and lattice parameter remains stable in a supersaturated state, though presumably with internal strain present.

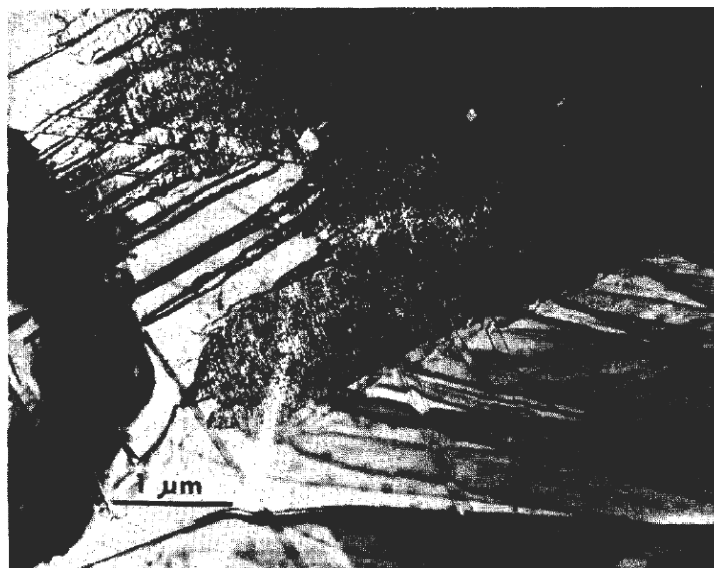


Fig. 5.6. Transmission electron micrograph of the discontinuous front of $\beta \rightarrow \alpha$ transformation, with high dislocation densities appearing in the new (dark) α phase in the upper right¹⁵⁰.

The $\beta \rightarrow \alpha$ transformation is most easily observed after supercritical hydriding. This provides a 'clean' and unstrained microstructure in which to observe the transformation. In the initial stages of the transformation, coherent or semi-coherent

stable precipitates of α phase form near the free surface¹⁵⁰. These possibly act as diffusion outlets for hydrogen to outgas, via dislocation pipe diffusion or by virtue of the higher hydrogen diffusion rate in the α phase.

The rest of the transformation proceeds by a discontinuous reaction, which is often accompanied by microcrack formation and generation of high dislocation densities (Figure 5.6). The microstructure, grain size and orientation of the palladium does not change, but its fine structure does change via dislocation network formation¹⁵².

5.2.5 Volume Expansion

Two ways to study the expansion are via linear expansion (as a function of the hydrogen mole fraction) and via the relative proportions of the phases present and their unit cell parameters. One method lends itself to manual $\Delta L/L$ measurement and the other to x-ray lattice parameter measurement. Peisl¹⁵³ suggested the following analysis for the former. Adding n atoms of hydrogen into a volume V of palladium changes the volume by

$$\Delta V = n\Delta v \quad (5.3)$$

where Δv is the change in volume of palladium per hydrogen atom. Writing the atomic volume of pure palladium as v_0 and the hydrogen-palladium atomic ratio as c gives

$$\frac{\Delta V}{V} = c \left(\frac{\Delta v}{v_0} \right) \quad (5.4).$$

Therefore, measuring the relative volume change (cube of the relative length change) as a function of the hydrogen content yields $\Delta v/v_0$, which is the slope of the line plotted in Figure 5.7.

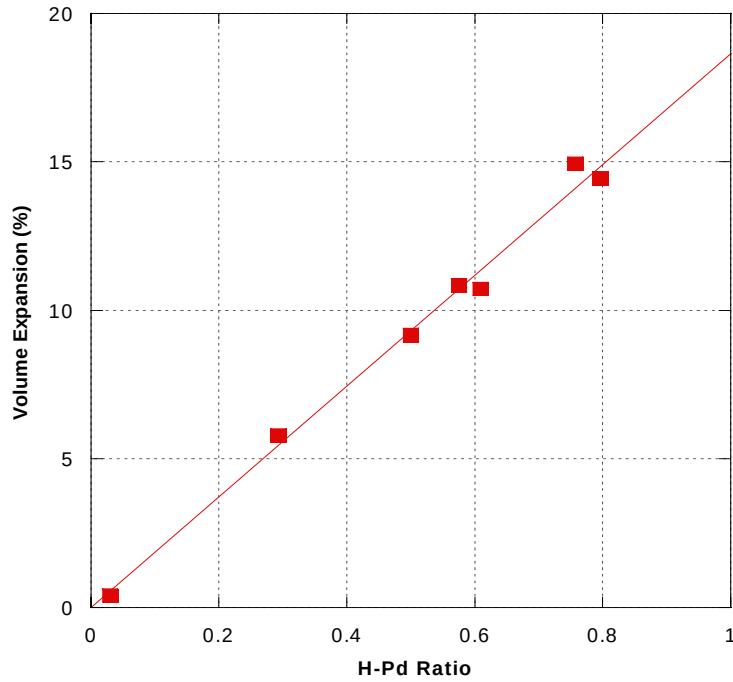


Fig. 5.7. Volume expansion in palladium as a function of hydrogen content¹⁵³.

Peisl¹⁵³ gives a list of values for $\Delta v/v_0$, as determined by various investigators, and deduces that the value of $\Delta v/v_0$ for palladium is 0.19 ± 0.01 (Figure 5.7). This fits a trend for volume change associated with hydrogen content for a range of FCC metal and alloys. The volume expansion value noted for an H:Pd ratio of 0.61 corresponds to the 11% expansion to the β phase, which possesses an H:Pd ratio of 0.61 at room temperature.

5.2.6 Mechanical Behaviour

There are two different regimes of mechanical behaviour in the H-Pd system. If the hydrogen is held stable within the palladium by some technique, such as maintaining gas overpressure, the material effectively behaves as an H-Pd alloy, with properties varying with composition. Instead, if the material is not held under stable conditions and the $\beta \rightarrow \alpha$ transformation is allowed to occur, the material behaves as hydrogen-treated material (similar to a heat treated material).

Due to the difficulty of measuring mechanical properties under conditions for maintaining a stable hydride, there are limited data on its mechanical properties. Unless otherwise noted, it is believed the discussed studies did not utilise supercritical

loading to avoid the $\alpha \rightarrow \beta$ transformation, so that the transformations effects are present in addition to those due to the presence of the interstitial atomic hydrogen.

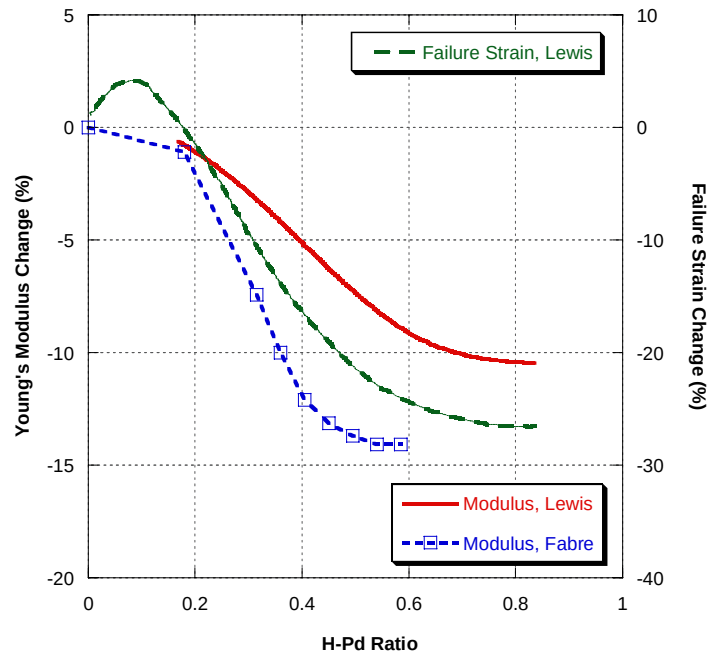


Fig. 5.8. Relative decrease in Young's modulus and failure strain for increasing amounts of 'stable' hydrogen^{138, 154}.

Early studies investigated the mechanical properties of electrolytically loaded samples of Pd wire. Presumably, all mechanical testing was conducted very swiftly after loading to limit outgassing and $\beta \rightarrow \alpha$ transformations. These data are broadly corroborated by a recent study by Fabre et al¹⁵⁴ (Figure 5.8), using microcantilevers to investigate resonance frequencies under a controllable hydrogen atmosphere. Difference between stiffness values obtained by Lewis and Fabre may be due to variation in measurement technique. The observed decrease with increasing hydrogen content is probably due to the increase in lattice parameter. The hydrogen atoms force the palladium atoms farther apart, effectively weakening the palladium interatomic bonding; yielding a lower elastic modulus. This would also tend to reduce the maximum strain tolerable by the material.

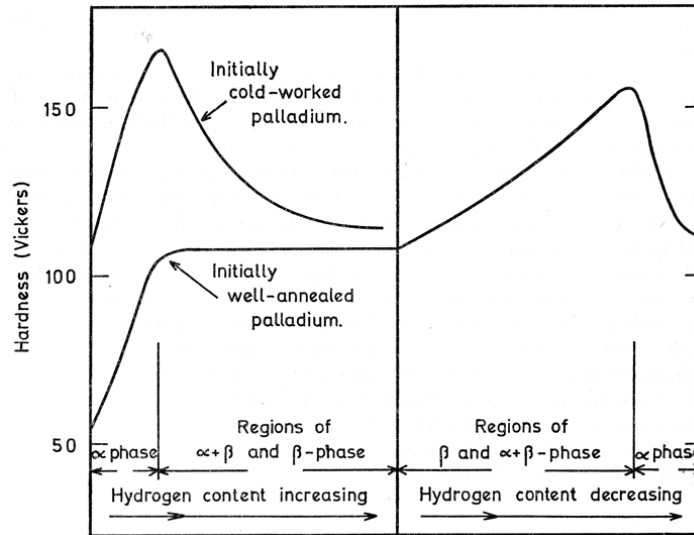


Fig. 5.9. Hardness variation during an electrolytic absorption/desorption cycle¹³⁸.

Changes in hardness over the course of an electrolytic loading cycle have also been investigated¹³⁸. The results of this (Fig. 5.9) are shown as a function of time spent in the electrolytic cell, without details of specimen geometry, surface activation, electrolyte concentration, current density, etc. In the absence of such information, it is impossible to give an accurate figure for the hydrogen content. It was observed¹³⁸ that both the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations produced increases in hardness. The decrease in hardness of the cold-worked specimen is possibly due to the formation of β phase grains relocating dislocations to the edges of the new grains. A cause for the decrease in hardness observed at the end of the desorption cycle is not immediately apparent.

There are two types of hydrogen treatment for palladium: those that allow deformation ($\alpha \rightarrow \beta$ transformations) and those that do not (supercritically loaded). The former of these two was characterised by Anderton et al¹⁵⁵. They loaded samples to various H-Pd ratios, and then completely removed the hydrogen in vacuo at elevated temperature. The results of this (Fig. 5.10) indicate completely different behaviour from that for 'stable' hydride compositions. Changes in modulus were not quantified by Anderton et al, but Figure 5.10 clearly demonstrates a positive correlation between stiffness and increasing levels of achieved H-Pd ratio.

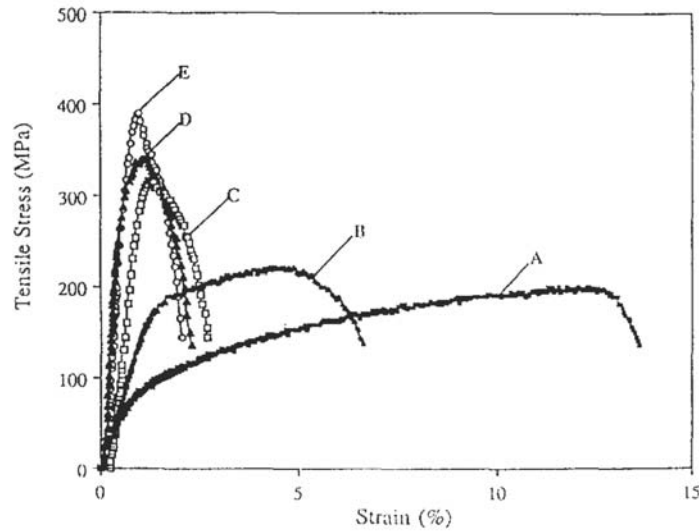


Fig. 5.10. Effect of partial $\alpha \rightarrow \alpha + \beta \rightarrow \alpha$ cycling on mechanical properties: (A) vacuum annealed, (B) cycled to $H\text{-Pd} = 0.20$, (C) cycled to $H\text{-Pd} = 0.35$, (D) cycled $H\text{-Pd} = 0.49$, (E) cycled to $H\text{-Pd} = 0.66$ ¹⁵⁵.

The changes in ultimate strength, yield strength and ductility, however, were quantified by the authors (Figure 5.11). The increases in strength and losses in ductility are most easily explained by the increased dislocation densities left behind by the relative amount of material to undergo the $\beta \rightarrow \alpha$ transformation. All samples would have acquired the same amount of deformation from the $\alpha \rightarrow \beta$ transformation.

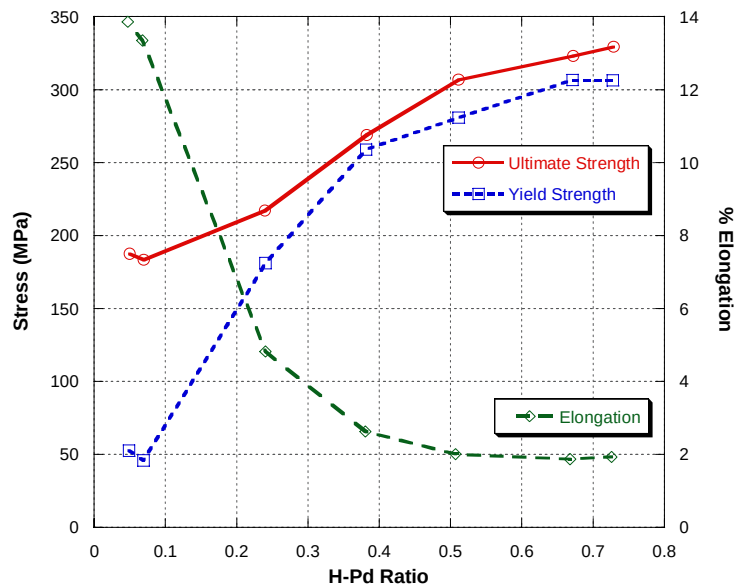


Fig. 5.11. Effect of partial $\alpha \rightarrow \alpha + \beta \rightarrow \alpha$ loading on mechanical properties at 50°C extracted from Figure 5.10 by the authors¹⁵⁵.

Anderton et al¹⁵⁵ also measured the change in hardness with the level of $H\text{-Pd}$ attained (Figure 5.12). This also demonstrates a correlation between the amount of the

miscibility gap traversed, the relative amount of material to undergo the $\beta \rightarrow \alpha$ transformation, and the hardness. The lack of hardness increase for the last point fits with this, since both of the last two points had experienced full conversion to the β phase.

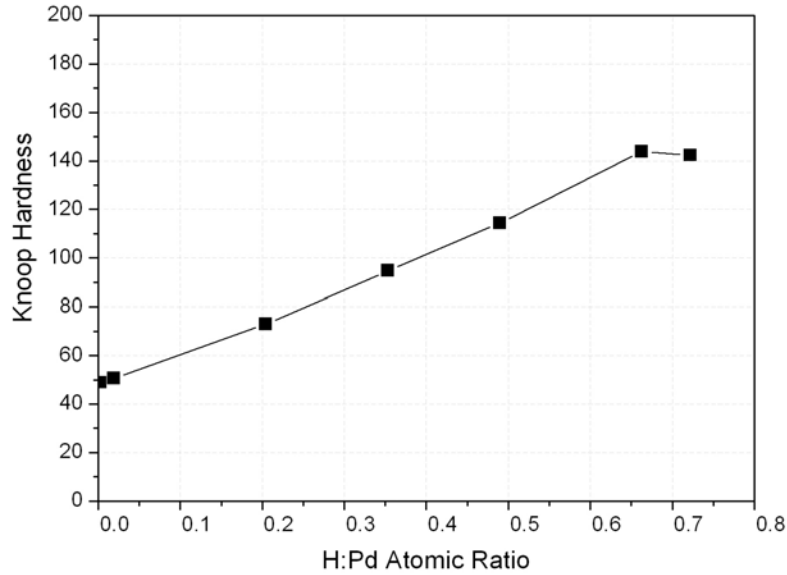


Fig. 5.12. Effect of partial $\alpha \rightarrow \alpha + \beta \rightarrow \alpha$ cycling on Knoop hardness, H-Pd ratio indicated is maximum level reached before unloading¹⁵⁵.

Hydrogen treatments using supercritical loading to the β phase have been extensively characterised¹⁴⁵. These treatments only allow the $\beta \rightarrow \alpha$ transformation, so they create high dislocation densities without producing gross deformation.

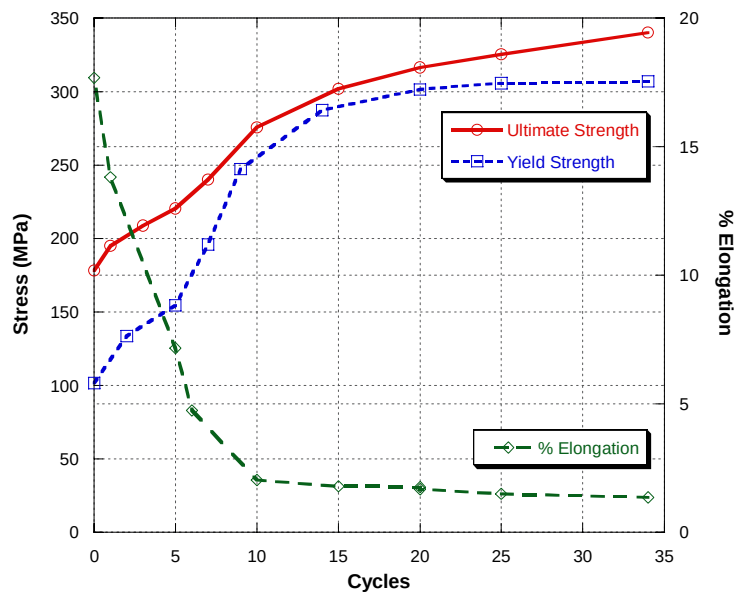


Fig. 5.13. Effect of supercritical $\beta \rightarrow \alpha$ cycling on mechanical properties¹⁴⁵.

The simplest form of this treatment, cycles of supercritical full conversion to β phase followed by complete hydrogen removal, yields results (Figure 5.13) similar to those reported by Anderton et al. However, it takes ~ 30 cycles of this $\alpha \rightarrow \beta$ transformation-free treatment to yield the same behaviour as one full $\alpha \rightarrow \beta \rightarrow \alpha$ cycle. This demonstrates the significant effect of the $\alpha \rightarrow \beta$ transformation on mechanical properties.

5.3 Characterising Sample Dynamics

In samples which are dynamically changing, it is necessary to know both the original and final states between which it is in transit and the period over which the system changes. In the case of palladium-hydrogen, the initial state can be defined as the state of the palladium prior to the introduction of hydrogen, and the final state as that where hydrogen is either at equilibrium concentration with the surrounding atmosphere or when the hydrogen has been entirely removed. The equilibrium concentration of hydrogen in palladium under ambient temperature and pressure is less than 1%. Any hydrogen in the palladium above this level will tend to dynamically escape

5.3.1 Gravimetric Analysis

Gravimetric analysis is one of the simplest and most effective ways of characterising the composition of palladium-hydrogen samples. It is assumed that the hydrogen content change is solely responsible for any observed change in specimen mass. The ratio of hydrogen to palladium in the specimens during the electrolytic introduction of hydrogen was determined by in this way. Changes in mass were used to calculate the molar ratios as a function of electrolytic charging time, producing hydrogenation curves of the type as shown in Figure 5.14.

All the samples were charged using a current density of 0.8 mA mm^{-2} , so the overlapping curves are to be expected. Observed variations are likely to be due to the effect of repeated removal from the electrolytic cell for gravimetric measurements introducing error in treatment time. It is apparent from this curve that hydrogen saturation (Pd:H stoichiometry) was not achieved with this current density and specimen thickness within the time scale employed.

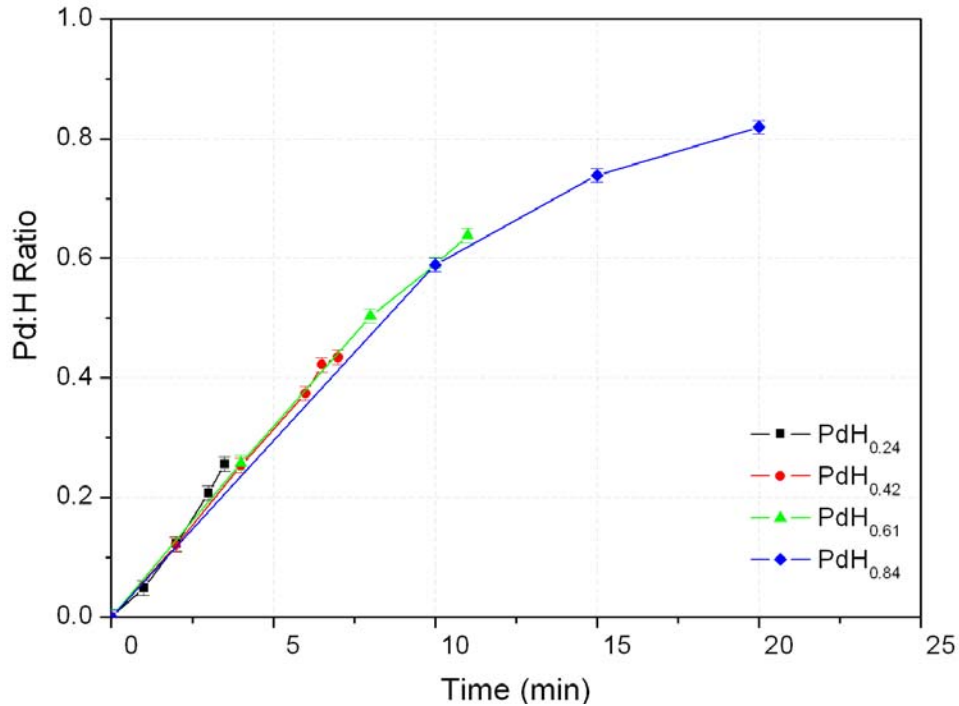


Fig. 5.14. Hydrogenation curve for 125 μ m thick palladium foils during electrolytic charging with legend indicating final H:Pd ratios for each foil.

Longer treatment times are expected to result in an asymptotic approach towards a H:Pd ratio below that of unity. Given the high diffusivity ($Dt^{0.5} \sim 200 \mu\text{m}$ in 1000s) of hydrogen in palladium (see §5.2.3), it might be expected that the hydrogen would readily become uniformly distributed throughout the sample thickness during charging; however the limited solubility of hydrogen within α -Pd (see §5.2.1) suggests that phase transformations to β -Pd may prevent this.

Hydrogen mass loss from the samples was monitored until sectioning and mounting for indentation. During a 4 day period, hydrogen mass loss in the thin (125 μm) foils was on the order of 0-2mol%. Since the hydrogen could diffuse through the entire thickness of the material in a tiny fraction of that time, it is apparent that the rate limiting step for hydrogen loss was release at the surface rather than diffusion from the interior.

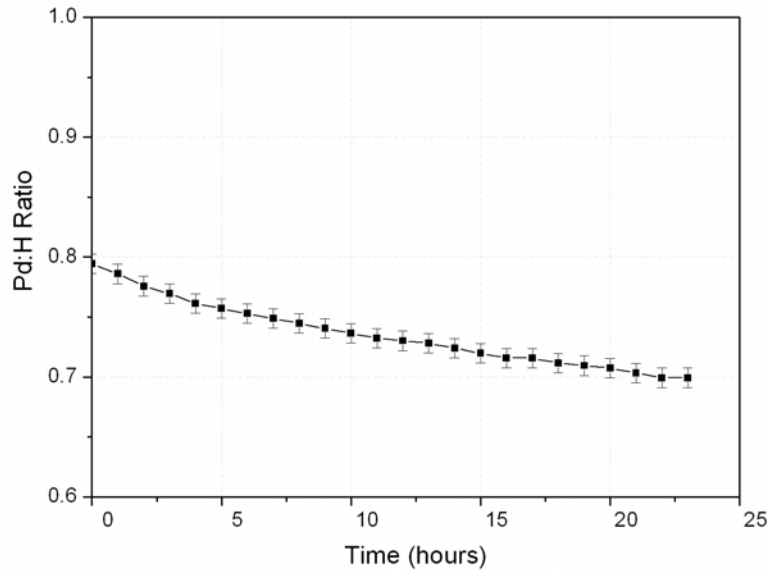


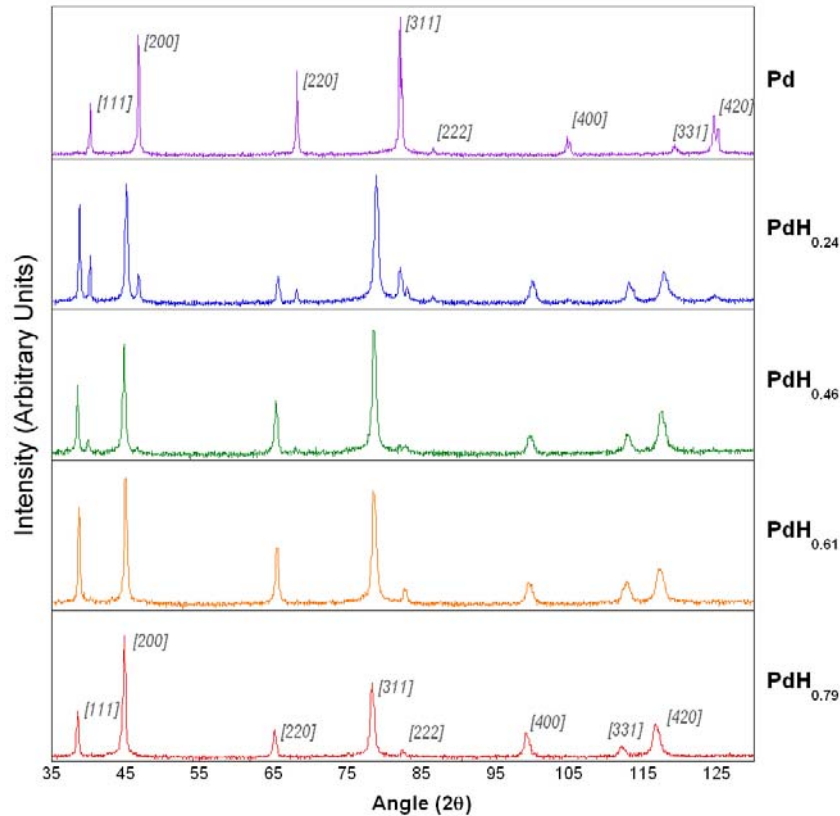
Fig. 5.15. De-hydrogenation curve for a 500 μm thick palladium foil in air.

Experimental data shown in Figure 5.15 illustrate the asymptotically-decreasing trend of (gravimetrically inferred) Pd:H ratio as a function of exposure time, from a 500 μm thick palladium foil initially charged to $\text{PdH}_{0.8}$ and left freestanding in ambient temperature and pressure. This is consistent with observations in previous work¹³⁸, which suggests that hydrogen loss follows a logarithmically decreasing trend, with the loss within the first 24 hours being the most significant. It may be noted that the rate of outgassing is expected to be dependent on the surface area to volume ratio of the specimen, as well as the surface activation.

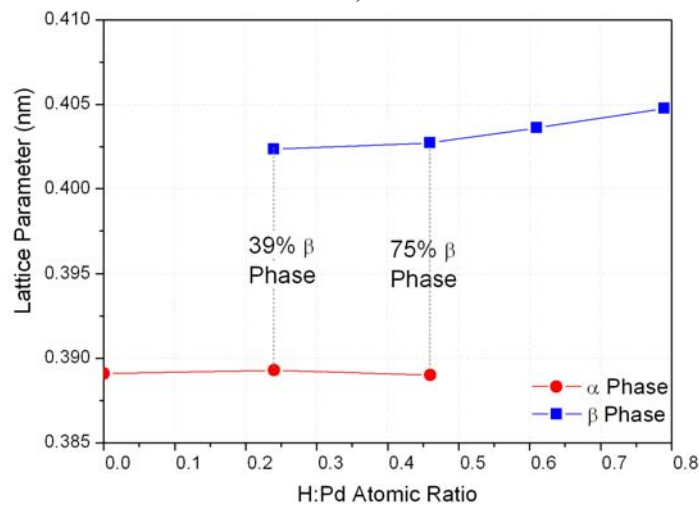
5.3.2 Crystallography

To confirm the extent of beta phase transformation, x-ray diffraction data were collected. These data (Figure 5.16a) confirm formation of beta phase in proportions roughly consistent with gravimetric analysis. By comparing these results to reference standards in the powder diffraction file, peak assignments were made. The pure, annealed palladium sample produced very clear, sharp peaks, allowing accurate determination of the lattice parameter. The data from the sample of $\text{PdH}_{0.24}$ clearly shows peaks from both α and β phases. The α phase peaks are very weak in the data from $\text{PdH}_{0.46}$, with only a miniscule (111) peak easily observable. $\text{PdH}_{0.61}$ and $\text{PdH}_{0.79}$ samples show only β phase peaks. This agrees with gravimetric determination of the Pd:H ratios and predictions from the p-c-T diagram (Fig. 5.1).

The lattice parameters for each phase in each foil were calculated, using peak positions calculated from custom-fitted peak profiles. These were all accurately determined to four significant figures with the exception of the parameter for the α phase for $\text{PdH}_{0.46}$, which was only determined to three significant figures, due to the relatively low intensity of its peaks. The lattice parameter values were found to be consistent with those determined by Owen and Jones¹⁴³ (Figure 5.16b).



a)



b)

Fig. 5.16. a) X-ray diffraction peaks and b) determined lattice parameters for hydrided foil specimens.

Since two of the hydrogenated specimens, $\text{PdH}_{0.24}$ and $\text{PdH}_{0.46}$, were in the two-phase region of the p-c-T diagram, the lever rule was applied to gravimetric calculations of the overall hydrogen contents of the specimens to determine the relative phase contents. An attempt was made to calculate these values from peak intensity ratios in datasets, in which both sets of peaks were observed, for comparison. However, the strong crystallographic texture (possibly from rolling) led to the values differing substantially from those of the available standards from powder samples, making this impossible.

5.3.3 Microstructure

For polycrystalline materials, such as those being studied here, the grain size can affect mechanical behaviour, since grain boundaries, and the need for grains to deform in a cooperative way, constrain dislocation motion. In order to confirm that annealing had removed any grain shape anisotropy from rolling, the grain structure in the materials was determined directly through metallographic examination, after etching as specified in §4.1.4. The grain size was measured by lineal analysis and calculated as specified by ASTM E112.

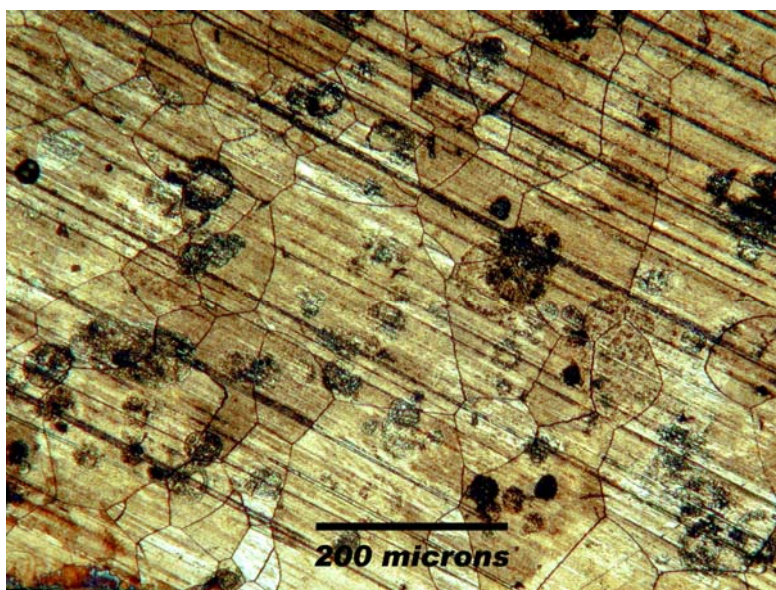


Fig. 5.17. Typical micrograph from the unpolished, rolled surface of the palladium foil samples.

The surface of the rolled foils showed a slight tendency towards a duplex grain structure, with equiaxed grain shapes (Fig. 5.17). This is consistent with some grain boundary pinning or partial recrystallisation from the annealing performed on all foil samples. Linear features observable in Figure 5.17 are artefacts from rolling. All

samples were assumed to possess regular equiaxed grains of uniform size during grain size measurement. All the rolled surfaces of the samples were found to have a mean ASTM grain size of 4.0 ± 0.3 or an average grain size diameter of $82 \pm 10 \mu\text{m}$.

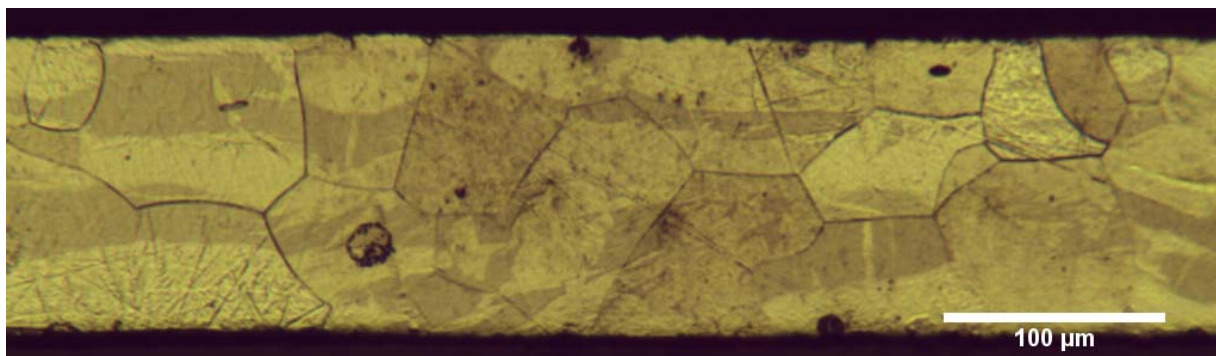


Fig. 5.18. Cross-sectional micrograph from foil of composition PdH_{0.24}, displaying intergranular tint.

The cross section of the foils displayed equiaxed grains, with an intergranular tinting or surface staining present in the samples with hydrogen contents within the miscibility gap: PdH_{0.24} (Fig. 5.18) and PdH_{0.46}. The intergranular tint was not observed in the other samples and may be the result of an unknown interaction between the etchant and subsurface hydrogen. There was no change in grain size with hydrogen content, in agreement with previous observations¹⁵². All cross-sectional samples were found to have a mean ASTM grain size of 4.5 ± 0.2 or an average grain diameter of $67 \pm 9 \mu\text{m}$. This is slightly smaller than that observed for the free surfaces of the samples ($82 \pm 10 \mu\text{m}$), but little evidence of grain shape anisotropy from rolling was seen in either direction. This suggests that the foils underwent recrystallisation from annealing after rolling.

5.4 Nanoindentation Results

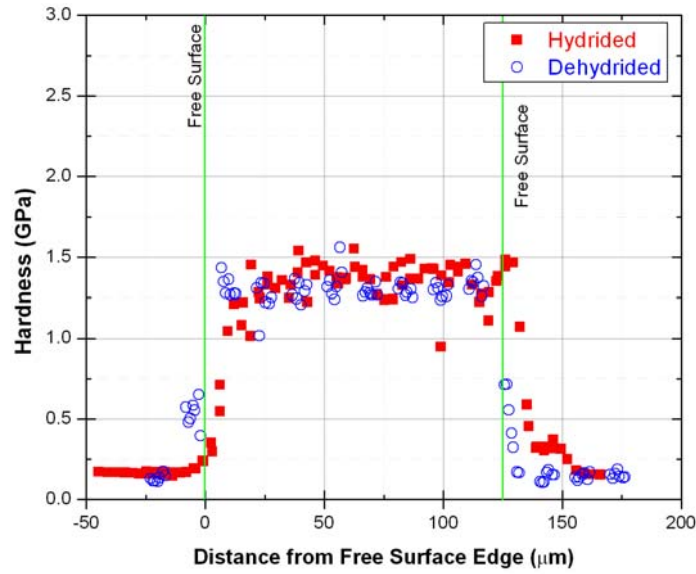
In order to examine the effects of the hydrogenation/dehydrogenation, it is important to determine the precise condition of the specimens during indentation. To facilitate this, it is sensible to examine the results in the order of the complexity of their hydrogenation/dehydrogenation histories. Single phase systems, i.e. annealed non-hydrogenated samples and fully hydrogenated/dehydrogenated samples, are simplest and will be discussed first. Following those, two phase systems will be discussed.

Hardness data from nanoindentation arrays on specimen cross sections are presented as profiles of hardness, as a function of distance from the free surface of the specimen. Indentation was carried out immediately after metallurgical preparation of

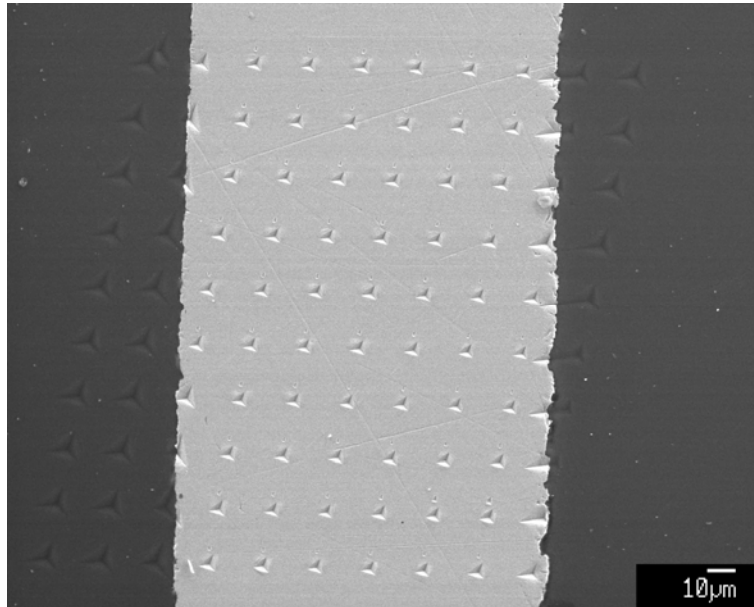
the sample to minimise hydrogen losses. All samples exposed to hydrogen at sufficient levels to form the β phase are expected to undergo some degree of deformation due to the $\alpha \rightarrow \beta$ transformation, which has an associated volume expansion. This increases the hardness. Furthermore, since none of the samples were kept in the hydrogen atmosphere that would be necessary to retain constant hydrogen content, some hydrogen losses from outgassing are expected. For samples in the hydrided condition, an estimate of the reduction in average hydrogen content due to outgassing prior to and during indentation, is 3-5 mol%. For samples within or near the miscibility gap, this means some $\beta \rightarrow \alpha$ transformation is expected to occur as the hydrogen content decreases. This produces a hardness increase, reported to be linearly proportional to the amount of phase transformation¹⁵⁵. However, examination of the p-c-T diagram show the sample of PdH_{0.79} to be sufficiently far into the β phase region that loss of even 18 mol% hydrogen would not be enough to initiate any $\beta \rightarrow \alpha$ transformation. The samples within/near the miscibility gap show the mixed effects of both transformations. A local variation in the intensity of these effects would explain the increased variation in mechanical properties for these samples.

5.4.1 Single Phase Compositions

The results for the annealed baseline specimens (Fig. 5.19), which were not subjected to any hydrogenation/dehydrogenation, though they are labelled as such since they were metallographically prepared alongside those groups, display uniform hardness across the specimen thickness. This reveals that the annealing removed any mechanical anisotropy, which rolling might have produced.



a)



b)

Fig. 5.19. Nanoindentation hardness profiles a) from annealed baseline samples as a function of distance from the left free surface edge and b) a SE Micrograph of one of the indentation grids.

The hardness of each of the baseline specimens from each group is the same (~1.4 GPa). Intermediate values between the minimum (fully within mounting epoxy) and maximum (fully within specimen thickness) plateau are caused by the indent falling on the interface between the two materials. The main conclusion of this test is that neither the metallurgical preparation of the sample nor the internal microstructure produced a discernable variation in the hardness of baseline samples mounted and polished with either the hydrided or dehydrided samples.

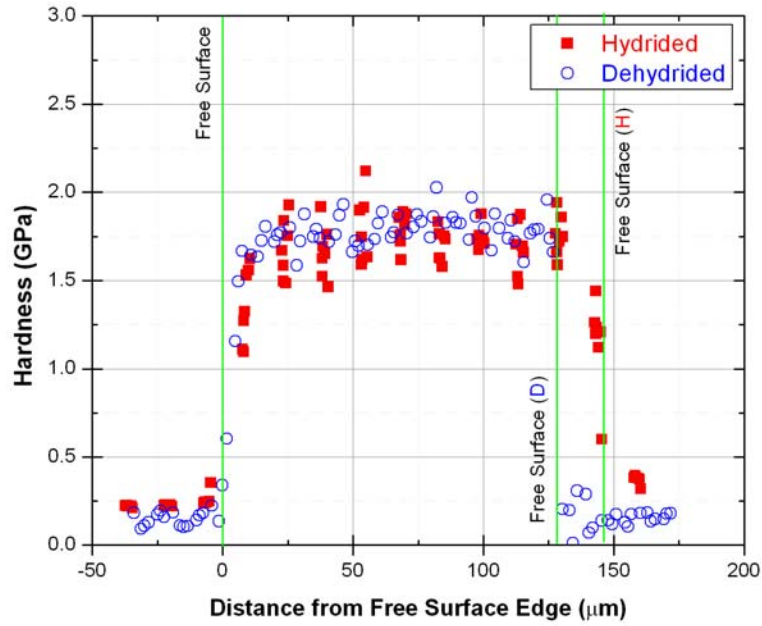


Fig. 5.20. Nanoindentation hardness profiles from a fully hydrided foil, $\text{PdH}_{0.79}$, as a function of distance from the left free surface edge.

The fully hydrided specimens, $\text{PdH}_{0.79}$, displayed uniform hardness values of ~ 1.8 GPa across the specimen thickness in both hydrided and dehydrided conditions (Fig. 5.20). It was observed that the specimen in the hydrided condition was thicker than the dehydrided specimen. This is consistent with the volume expansion expected from the phase transformation¹⁵³ (see §5.2.5). The dehydrided sample is observed to have returned to the nominal thickness of 125 μm after dehydrogenation.

Comparison of representative load-displacement relationships from these samples/conditions (Fig. 5.21) suggests that the fully hydrided/dehydrided condition had undergone the greatest degree of hardening relative to the annealed sample. However, the sample in the fully hydrided condition is also observed to have hardened to a significant degree.

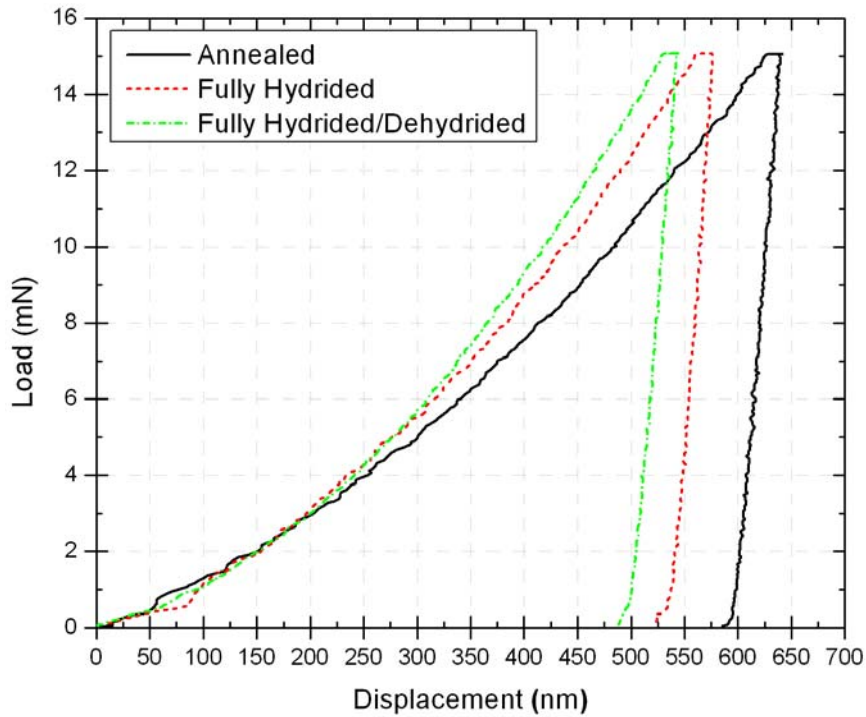


Fig. 5.21. Nanoindentation load-displacement curves from the annealed baseline cross section and from the cross section of foil $\text{PdH}_{0.79}$ in fully hydrided and hydrided/dehydrided conditions. The hardening of the sample in the dehydrided group is due to the full hydrogenation to $\text{PdH}_{0.79}$ and full dehydrogenation, and the accompanying phase transformations. Since the sample in the hydrided group possessed near equivalent hardness, it suggests that a similar amount of phase transformations must have occurred within it immediately prior to indentation. However, since gravimetric analysis data show only a small amount of hydrogen loss, it is suggested that only the region near the polished, sectioned surface of the specimen had experienced reverse transformations due to outgassing. To rephrase, the small volume of material being strained under the indenter had already lost enough hydrogen prior to indentation to nearly reach the fully dehydrided condition and experienced significant hardening from reverse phase transformations. Since all samples experienced similar conditions and had similar outgassing time frames, it is expected that other samples had similarly dehydrided at the sectioned surface.

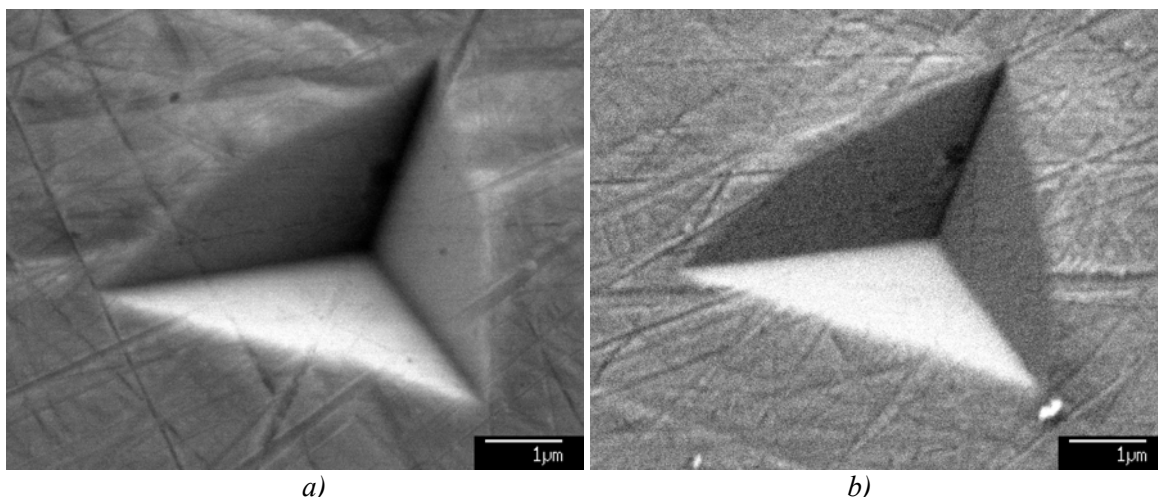


Fig. 5.22. Backscatter electron micrographs of 15 mN indentations in a) annealed palladium and b) fully hydrided, $\text{PdH}_{0.79}$ with both demonstrating pile-up.

Examination of the residual indentations using electron microscopy (Fig. 5.22) suggests that pile-up behaviour may be causing hardness measurements to be slightly exaggerated. The amount of barrelling present in the hydrided sample is also observed to be slightly reduced compared to the annealed sample. This suggests that some work hardening has occurred³⁵, which is consistent with Anderton's¹⁵⁵ results on partial hydrogen cycling.

5.4.2 Two Phase Compositions

By examining the hardness profiles of the partially-hydrided samples (Fig. 5.23-5.25), it appears that discrete regions of the hydrogen-rich, β phase form, instead of a uniform distribution of hydrogen. Dehydrided specimens display significant hardening in the regions near the free surface edges, showing hardness values similar to the peaks observed in the hydrided samples, with the central regions remaining near annealed values. This fits with the discontinuous fronts of β phase propagation described in the literature^{150, 151}

However, if the hydrogen escaped directly from the sectioned surface, as observed in the fully hydrided sample, then it would be expected that the hydrided samples would have a similar hardness profile to the dehydrided samples. Instead, it is observed that the central regions, which were expected to remain in the α phase, displayed significant hardness increases. This suggests that outgassing is not a simply surface egress process in two phase systems.

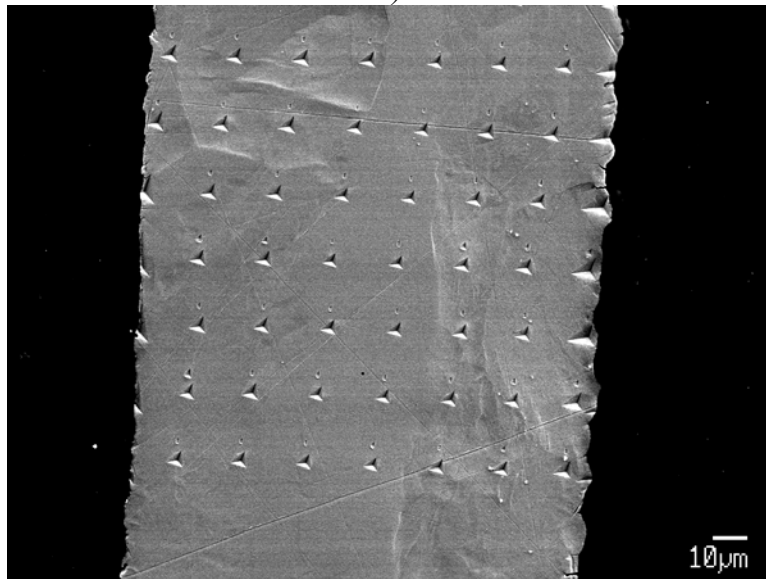
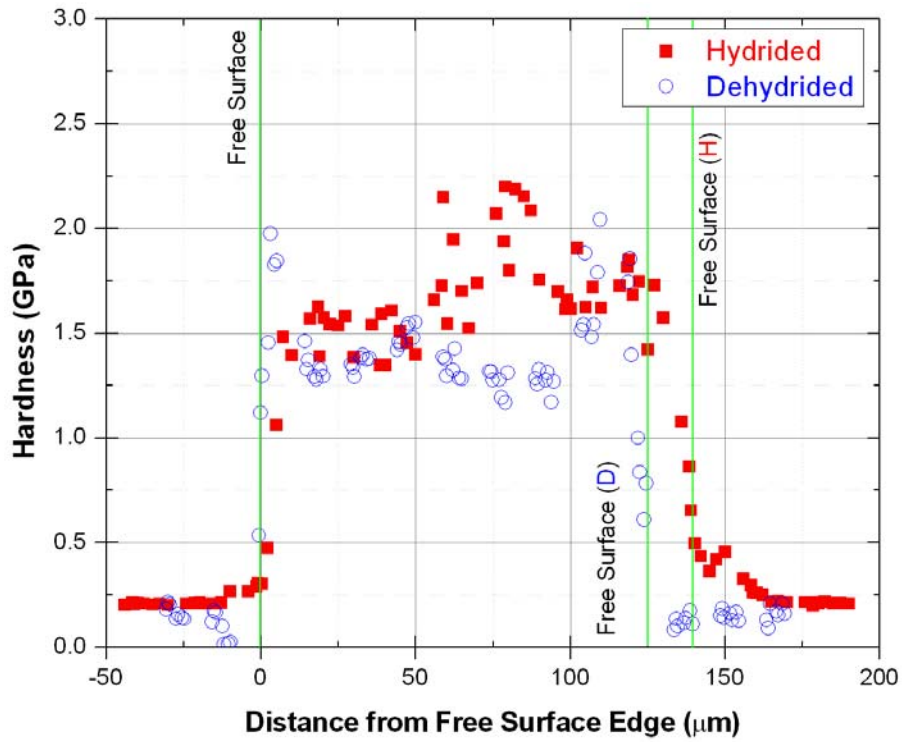


Fig. 5.23. Nanoindentation results a) from partially hydrided/dehydrided palladium foil, $\text{PdH}_{0.24}$, as a function of distance from the left edge and b) an SEM image of the indentation grid on the hydrided sample.

The hardened region penetrates in from the sample walls to a depth proportional to the amount of β phase hydride formed. Hydrided specimens display reciprocal behaviour in the middle of the specimen thickness, while the regions nearer the edges remain relatively close to the annealed values. SEM observation of partially hydrided samples in the weeks following indentation testing, by which time the hydrogen had

significant time to escape, displayed surface deformations in the regions near the specimen edges (Fig. 5.23b).

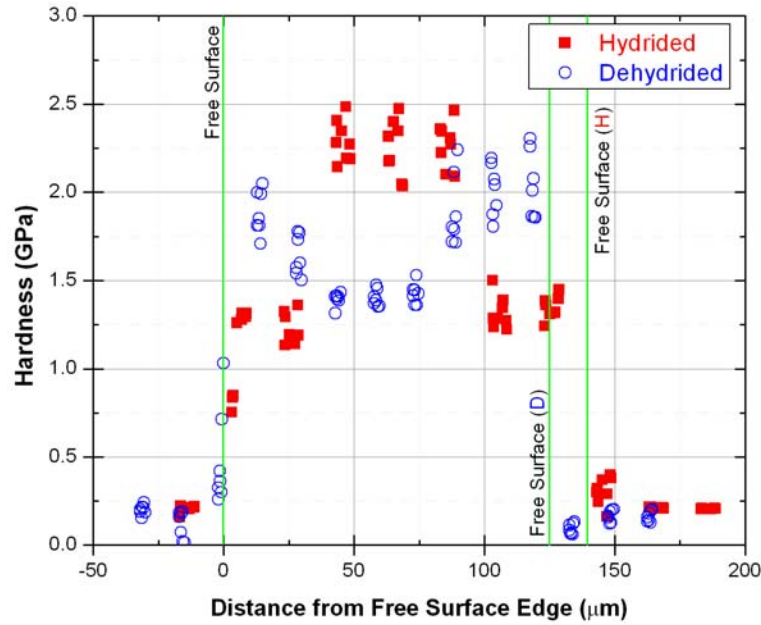


Fig. 5.24. Nanoindentation hardness profile from a partially hydrided foil, $\text{PdH}_{0.42}$, as a function of distance from the left specimen edge.

Similar behaviour was noted in foil specimens of greater thickness (Fig. 5.25). However, the central plateau in the hydrided condition has values much lower than those observed in thinner foils (Fig. 5.23 & 5.24). Dehydrided samples achieve a similar degree of hardening as observed in thinner samples.

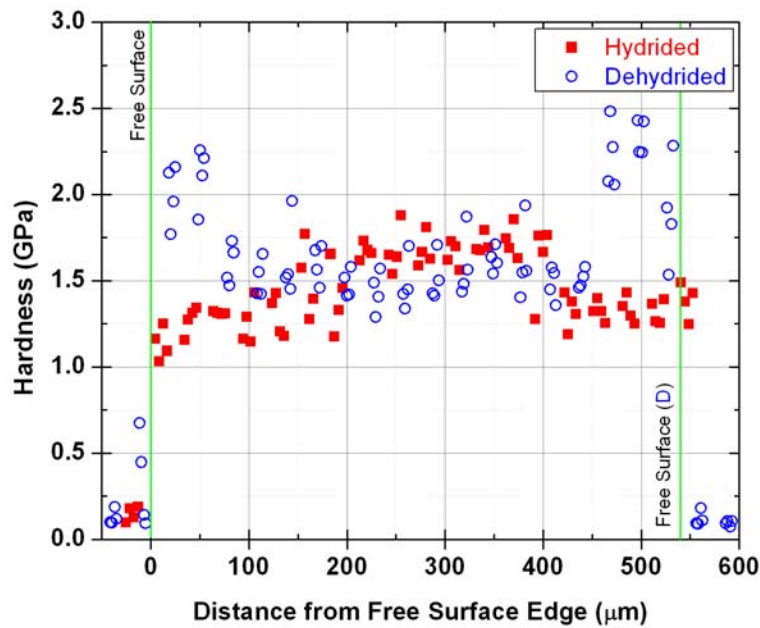


Fig. 5.25. Nanoindentation results from partially hydrided/dehydrided palladium thick foils as a function of distance from the left edge, for hydride level of $\text{PdH}_{0.33}$.

This two phase case is most easily understood for the dehydrided samples. Portions of the dehydrided samples were caused to transform into the β phase and then transformed back into a hydrogen-free condition. These portions experienced both forward and reverse transformations, and are hence expected to have effectively been subjected to cold work from this. Thus, it appears in the partially hydrided samples (Fig. 5.23-5.25) that the transformed regions expanded inward from the outer edges as the hydrogen content of the specimens increased. This can be confirmed by comparing the widths of the transformed/hardened regions to the amount of palladium transformed to the β phase as predicted using gravimetric analysis.

To examine these ‘sample-wide’ trends a bit more closely, representative load-displacement curves from different regions within the partially hydrided/dehydrided sample $\text{PdH}_{0.42}$ are shown in Figure 5.26. The region within the center of the sample is presumed to be in the α phase, while the β phase region is presumed to be the outer regions near the free surfaces.

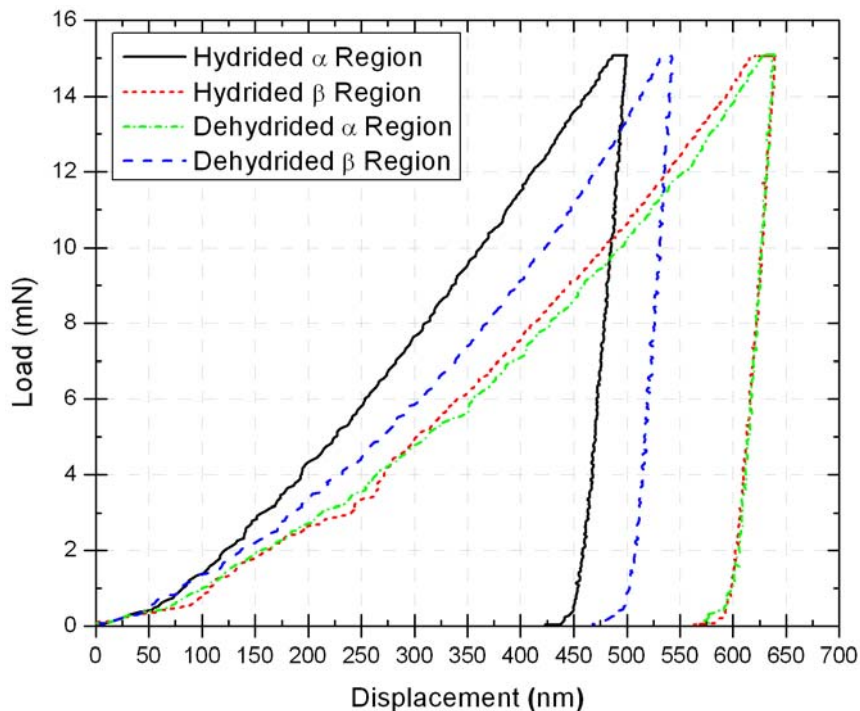


Fig. 5.26. Nanoindentation load-displacement curves from the cross section of a partially hydrided foil, $\text{PdH}_{0.42}$, showing differences between regions thought to have transformed to α or β phase indented in hydrided and hydrided/dehydrided conditions.

This presumption is supported by the close resemblance of the load-displacement curve in the dehydrided sample’s α phase region to the annealed load-displacement

curve (Fig. 5.21). The load-displacement curve from the dehydrated β phase region also agrees with the results from the dehydrated sample, $\text{PdH}_{0.79}$ (Fig. 5.21). Interestingly, the curve from the hydrided β phase region also appears to show identical behaviour to the annealed sample. This seemingly suggests that no phase transformations have occurred in that region, or that, if there is the large amounts of hydrogen present underneath the indentation, the hydrogen has no significant effect on mechanical properties. Even more interestingly, the load-displacement curve from the dehydrated sample's α phase shows the greatest degree of hardening observed in all samples, which suggests that something significant is occurring where very little hydrogen is expected to be.

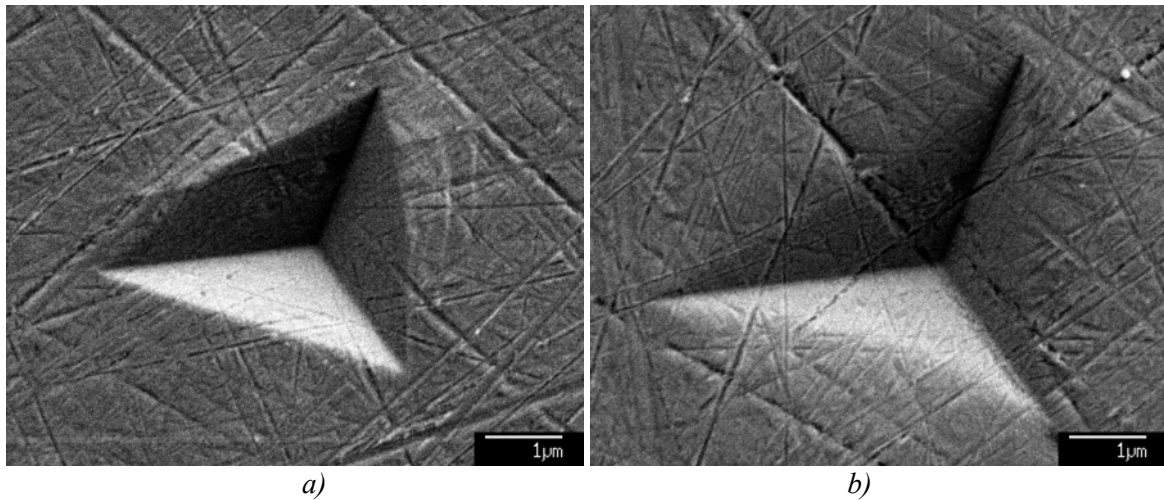


Fig. 5.27. Backscattered electron micrographs of 15 mN indentations in partially hydrided, $\text{PdH}_{0.42}$ in the a) α phase region and b) the β phase region.

Examination of the residual impressions (Fig. 5.27) from within these aberrant regions yields some insight. The indentation within the α phase region shows a similar degree of pile-up to the fully hydrided indentation in $\text{PdH}_{0.79}$ (Fig. 5.22), which suggests that a similar hardening mechanism might be responsible. The indentation within the β phase region, however, shows a significant amount of sinking-in. This would cause the apparent hardness from the Oliver & Pharr analysis to underestimate the actual hardness, and it is also a complete reversal of the pile-up behaviour observed in the annealed sample, which possessed a nearly identical load-displacement curve. This would suggest a drop in E_r/σ_y ratio and an increase in work hardening, which conflicts with the observed similar load-displacement curves.

5.5 Hardening and Hydrogen Egress

Since the strains introduced by the forward and reverse phase transformations are proposed as being responsible for the hardening, it is sensible to examine the regions where these transformations take place. It is also instructive to consider the path of the hydrogen egress, as this can affect the direction of the propagation of the phase transformations.

Indentation of the samples which had been dehydrogenated electrolytically prior to metallographic preparation and indentation suggests that the β phase propagated inward from the free surface with increasing hydrogen contents as schematically illustrated in Figure 5.28a. As a known amount of hydrogenation and dehydrogenation was performed on these samples, the phase transformations experienced can also be projected (Fig. 5.28b).

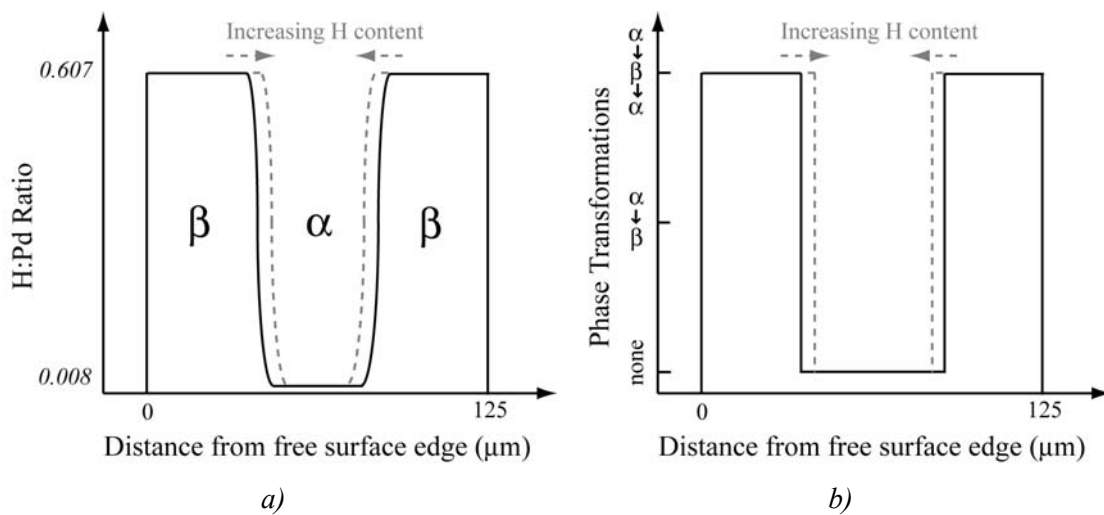


Fig. 5.28. Schematics of a) expected hydrogen content prior to dehydrogenation and b) expected phase transformations as a function of distance from the free surface edge in dehydrided palladium foils.

In the two phase composition, hydrided specimens, significant hardening occurred in the centre of the thickness (Fig. 5.23-5.25). This suggests that phase transformations, which appear to be the dominant mechanism by which hardening occurs, were occurring in regions expected to be α phase, as diagrammed in Figure 5.29b. However, those regions are not expected to contain enough hydrogen to generate the amount of reverse transformation necessary to generate the observed hardening (Fig. 5.29a).

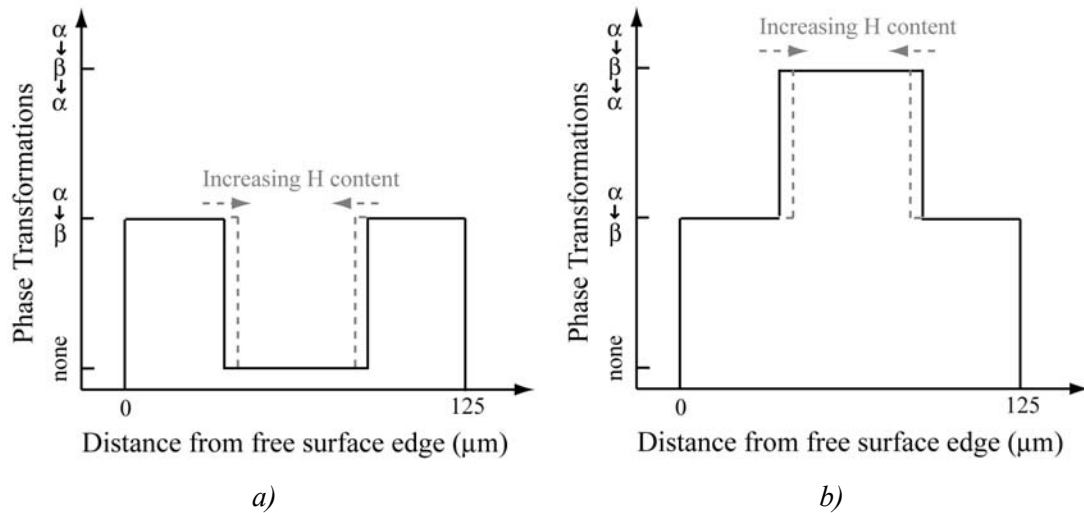


Fig. 5.29. Schematics of a) expected and b) apparent phase transformations as a function of distance from the free surface edge in hydrided palladium foils.

To suggest a mechanism for this hardening, the path by which the hydrogen outgassed must be considered (Fig. 5.30).

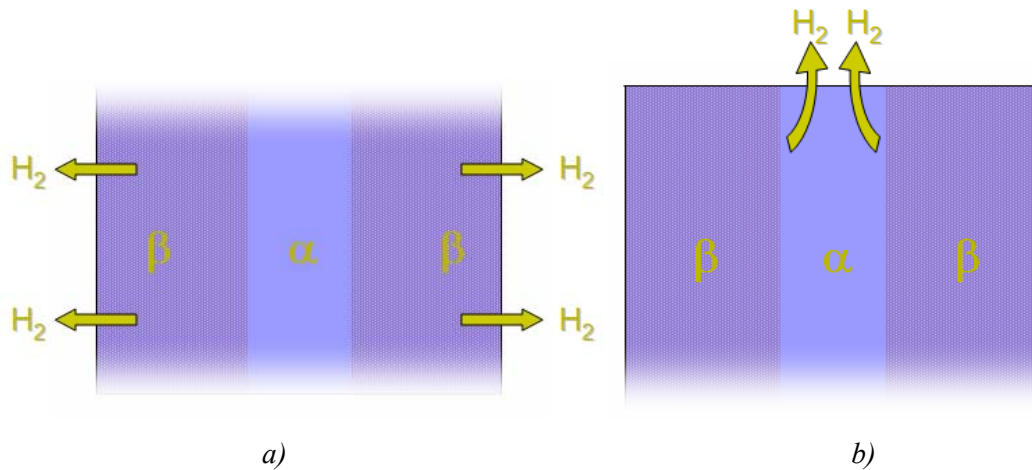


Fig. 5.30. Projected hydrogen outgassing paths for a partially hydrided specimen in a) dehydrided and b) hydrided conditions.

For the specimens in the dehydrided condition (Fig. 5.30a), the hydrogen is removed from the specimens by electrolytic action. As this is done prior to sectioning, this means the hydrogen egresses through the free surfaces of the foil. This would mean the transformed regions near the free surfaces would have experienced the greatest amount of $\alpha \rightarrow \beta \rightarrow \alpha$ phase transformations, and thus harden the most, while the α phase region in the centre remains unaffected. This is consistent with the observed characteristics.

For the specimens in the hydrided condition (Fig. 5.30b), the hydrogen appears to escape from the central α phase region of the sectioned and polished surface preferentially. To understand why this might occur, we must consider the difference in diffusion rates between the two phases (Fig. 5.31).

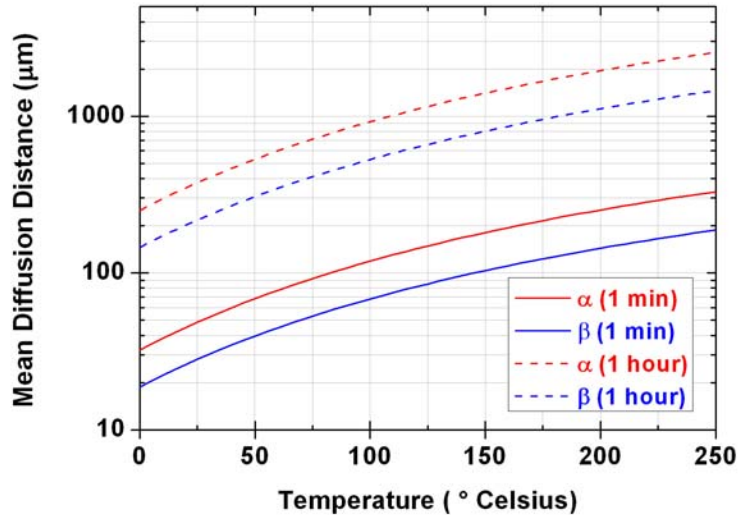


Fig.5.31. Diffusion distances for α phase and β phase palladium hydride.

Hydrogen diffuses through palladium at an extremely rapid rate (see §5.2.3). It would be possible for hydrogen to diffuse through the entire thickness of the specimens well before the indentation testing could be completed. However, since the gravimetric measurements before and after only indicated a ~3-5% Pd-H ratio loss, it is expected that surface desorption was the rate limiting step to hydrogen egress.

Since hydrogen diffuses appreciably faster in the α phase than in the β phase, it is possible that the hydrogen preferentially egresses outwards towards the polished surface of the α phase region in the centre of the specimen thickness. The rate limiting step of surface desorption might cause the local hydrogen concentration near the surface to increase above the α phase solubility and induce phase transformations. However, no surface disturbances associated with large volume mismatch phase transformations are observed in this region. Also, the sample which was fully hydrided (Fig. 5.20) suggests that the β phase regions of the partially hydrided should be harder.

5.6 Summary

The initial, annealed state of the foil samples was determined to be effectively mechanically isotropic with no significant grain shape anisotropy from rolling. Uniform indentation hardness profiles spanning the cross-section of the annealed samples confirmed this. This established the baseline response, such that any further mechanical variation observed could be attributed to the sole influence of the hydrogen treatments. No further change in grain size or morphology was observed after hydrogenation or dehydrogenation of the samples, in agreement with the literature.

Palladium hydrides were successfully synthesized via electrolytic charging to various molar ratios, and this was confirmed with X-ray diffraction, the expanded FCC lattice of the β phase was observed with lattice parameter values for different levels of hydrogen content in agreement with the literature.

Near equivalent hardness profiles for the fully hydrided foils, $\text{PdH}_{0.79}$, in both hydrogenated and dehydrogenated states suggest that all the near surface hydrogen had desorbed from the sample prior to nanoindentation. This suggested that all hydrogenated samples might have experienced similar loss. Samples in the hydrogenated condition were also observed to have expanded due to hydrogenation, as expected from the literature.

Partially hydrided samples were observed in the dehydrogenated condition to have a hardened region near the free surface edges proportional in size to the degree of hydrogenation experienced; this is attributed to the hardened (β phase) region having experienced cold work from $\alpha \rightarrow \beta \rightarrow \alpha$ phase transformations. This demonstrated the ability of nanoindentation to track the effects of hydrogen-induced phase transformations.

The (β phase) regions of the partially hydrided samples, which were observed to be hardened in the dehydrogenated condition, demonstrated limited or no significant hardening in the hydrogenated condition. However, a reversal in pile-up/sink-in behaviour was observed (Fig. 5.27b), despite similar load-displacement behaviour to

annealed samples. This could be a result of interstitial hydrogen constraining plastic flow and promoting sinking-in.

The central (α phase) regions of the partially hydrided samples, which demonstrated little significant hardening in the dehydrogenated condition, demonstrated significant hardening in the hydrogenated condition. This is attributed to hydrogen preferentially egressing through the higher diffusion rate α phase and subsequently generating cold work via $\alpha \rightarrow \beta \rightarrow \alpha$ phase transformations. The central regions of the thick foil samples demonstrated a lesser degree of hardening in the hydrogenated condition than the thin samples suggesting that scale and geometry may be a factor in the hardening mechanism. Future work might replicate these experiments on foils of varying thickness and performing indentations on sections of hydrided foils periodically as a function of outgassing time.

6

Impact Indentation of Superelastic NiTi

Superelastic behaviour is briefly reviewed. Impact indentation loading is discussed in the context of new technology allowing improved instrumentation. This is utilised to investigate the superelastic behaviour of NiTi at high strain rates.

6.1 Aims of Research

Recent progress^{41, 156-159} within the Gordon Laboratory had been successful in furthering the understanding of the behaviour of superelastic materials under nanoindentation, with one significant result being the necessity of utilising spherical indenters over a range of temperatures to quantify the amount of elastic recovery. After the development by the author of the impact indentation techniques and analysis discussed in §6.3, it was envisioned that a combination of impact indentation, elevated temperature indentation and finite element modelling might allow the characterisation of any strain rate dependence to superelasticity. This hypothesis was tested as the experimental portion of S.R. Pemberton's Part III individual project¹³⁵, which was conducted partly under the author's supervision. Finite element modelling work conducted under the supervision of J. Dean is not discussed here, since the author's involvement in its undertaking was limited. An abridged version of S.R. Pemberton's¹³⁵ review of superelasticity is provided (§6.2) in order to discuss impact indentation results (§6.4).

6.2 Review of Superelasticity

It has been over 60 years since the shape memory effect was first observed and 45 years since the first commercial application in 1963¹⁶⁰. The shape memory effect is characterised by a material's ability to return to its pre-set shape, after deformation, when heated to a temperature that causes the martensitic crystal structure to transform to the parent (austenitic) phase. Most shape memory alloys (SMAs) also exhibit superelastic (SE) behaviour, whereby the material can reversibly accommodate pseudo-elastic strains of up to 15%¹⁶¹.

Superelastic materials can sustain recoverable deformations at a transformation plateau (almost constant stress), over a considerable strain range. Unsurprisingly a wide range of applications exist, with NiTi alloys being the most industrially successful¹⁵⁸, oldest, most explored and most widely used shape memory alloy¹⁶². Business in shape memory alloys is increasing year on year¹⁶³, with applications ranging from arterial stents (where shape memory alloys allow safe insertion and self-expansion once inside the body) and orthodontics (where the application of low, continuous forces is required) to the deployment and control of space structures and eyeglass frames (where frames are desired to spring back after accidental deformation)¹⁶¹.

6.2.1 General Superelasticity

A brief overview of superelasticity is presented here; for a more in-depth description see Duerig et al¹⁶³. SMAs can easily transform to and from martensitic phases¹⁶³. Such transformations are first order thermodynamic in nature, and commonly have a temperature range where both parent and martensitic phases co-exist. A shape change occurs on transformation, which is accommodated by reversible twinning, forming martensite variants. Twin boundaries are very low energy interfaces, and hence highly mobile. Therefore they can easily respond to applied stresses, with the twin variant most favourably oriented to the stress growing preferentially¹⁶⁴, causing the formation of a single martensitic variant by detwinning¹⁶⁵.

The martensitic transformation can be stress-induced at temperatures where the parent phase is thermodynamically stable, provided less energy is involved in the transformation than required for the parent phase to deform plastically¹⁶⁶. A superelastic plateau is therefore seen after the linear elastic deformation of the parent phase as the material undergoes a martensitic transformation. Further straining can then occur by elastic deformation of the martensitic phase, followed by plastic deformation above a critical stress. On removal of stress, the transformation reverses, leading to recovery of strain and the phenomenon of superelasticity (Fig. 6.1). However, local plastic deformation may occur during the transformation on loading to accommodate martensitic formation. Small residual strains may therefore be seen on unloading, dependent on the temperature and maximum strain generated¹⁶⁷.

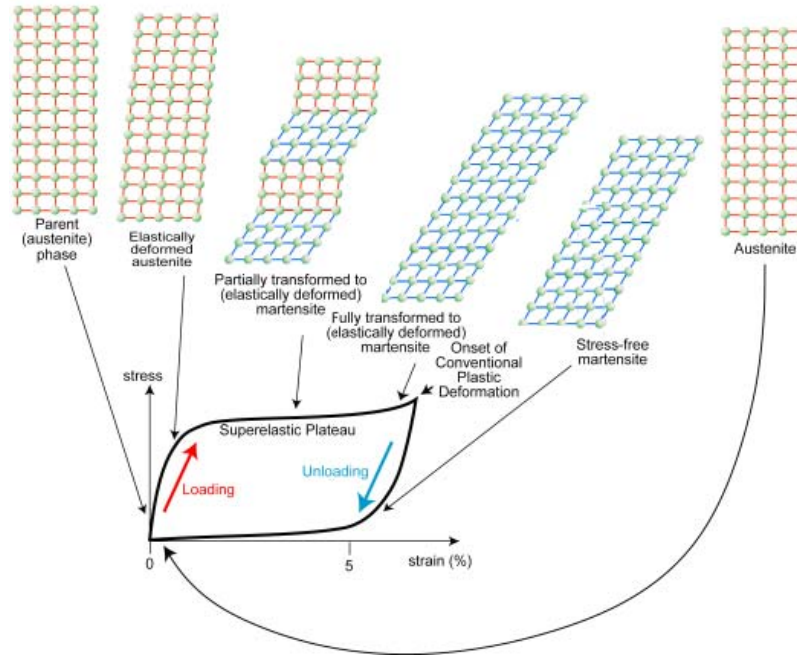


Fig. 6.1. Stages in the superelastic transformation during loading and unloading, showing changes in the structure of the crystal lattice during deformation¹⁶⁸.

NiTi is often composed of martensite at room temperature, with the martensitic transformation starting at a temperature M_S , and completing by the lower temperature M_F (Fig. 6.2). On heating, the transformation to parent phase starts at A_S and finishes on further heating to A_F ¹⁵⁸.

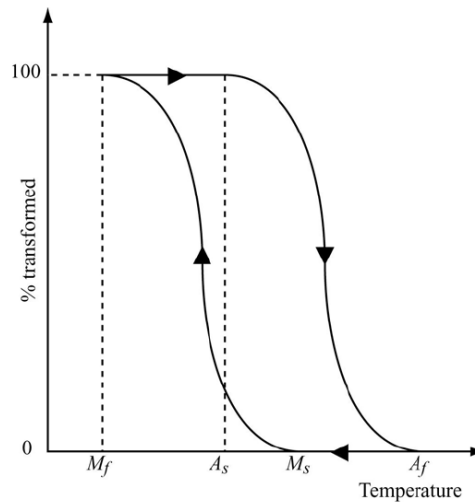


Fig. 6.2. Schematic of the changes in the percentage of parent material transformed to the martensitic structure during cooling from A_F to M_F and subsequent heating¹⁵⁸.

Above A_F large superelastic strains are achievable. This continues until a critical temperature is reached where plastic deformation of the parent phase becomes favourable. This temperature range is termed the superelastic region (Fig. 6.3). For the

full parent phase to martensitic transformation, the recoverable strain is of the order of 8% in NiTi⁴¹.

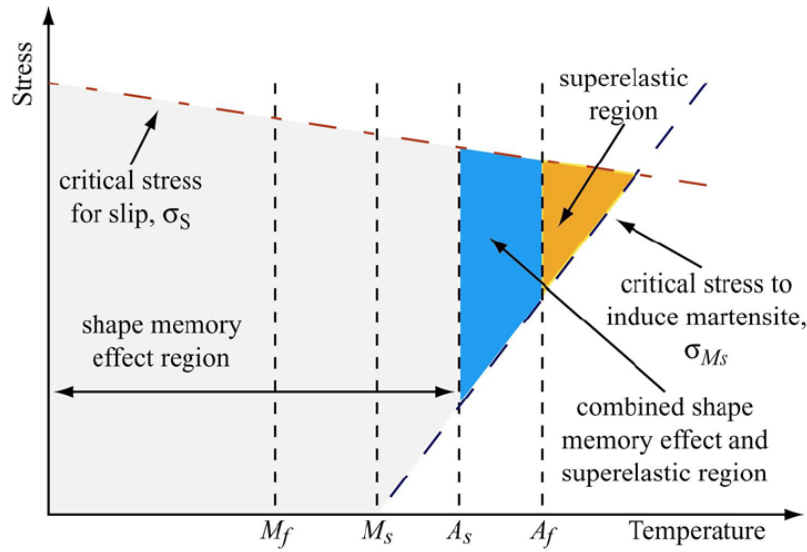


Fig. 6.3. Stress-temperature plot for a typical SMA showing the different regions of material behaviour¹⁵⁸.

6.2.1.1 Strain Rate Dependency of Superelastic Behaviour

The literature on superelastic behaviour presents conflicting results with regard to strain rate effects. Theoretically, superelastic materials are insensitive to strain rate¹⁶¹, since the formation of martensitic material and the motion of martensitic variant boundaries occur at approximately the speed of sound in the material¹⁵⁸. Indeed, some studies¹⁶⁹ have found no strain rate effects from 3×10^{-4} to 3000 s^{-1} .

A further set of workers observed no strain rate effects under quasi-static conditions, but clear strain rate sensitivity under dynamic conditions. Residual deformation and the superelastic plateau stress increase are reported by Chen et al¹⁶⁶ to increase with strain rate above 100 s^{-1} . This was again found by Adharapurapu et al¹⁷⁰, with no strain rate response seen at 0.001 s^{-1} , but observed at 1200 s^{-1} . Schmidt¹⁷¹ noted lower values of strain rate (0.002 s^{-1}) produced strain rate effects, with 20 K temperature rises seen at 0.01 s^{-1} . Similar results¹⁷² indicated an increase in plastic work and a decrease in elastic energy at higher strain rates.

A third set of papers¹⁷³ has reported established strain rate effects over the whole range of strain rates from quasi-static up to the very high strain rates seen in shock loading. Again, raising the strain rate increases the remnant strain and the martensitic

transformation stress¹⁶⁷. Additionally, the work-hardening rate increases during the superelastic plateau¹⁷⁴.

6.2.1.2 Temperature Effect on Superelastic Behaviour

A complete understanding of the relationship between stress, temperature, composition and superelasticity has not yet been achieved. However, several trends have been observed between temperature and superelasticity. Figure 6.3 describes a simple relationship between temperature and superelastic behaviour, but in experimental practice the relationship appears more complicated. Increasing the temperature was seen¹⁶⁷ to have a similar, but more pronounced, effect than increasing strain rate, increasing the remnant displacement and stress required for the martensitic transformation above A_F .

There are several reports¹⁷⁵⁻¹⁷⁷ in literature of noticeable temperature rises occurring during the tensile loading of superelastic materials. During the tensile testing of thin NiTi wires, results from Šittner¹⁷⁶ suggest that temperature rises of up to 60 K occur during cyclic loading at 80 s^{-1} . Similar loading without cycling was shown in Gadaj¹⁷⁷ to produce temperature rises of up to 10 K during the superelastic plateau. Such temperature changes occurred in narrow bands that propagated along the sample surface, corresponding to the spread of martensitic phase through the material. In a thin walled tube of NiTi under tension, similar results¹⁷⁸ were seen with a homogeneous temperature rise found during linear elasticity, followed by the initiation, propagation and growth of localized helical bands in which temperature increases were higher than the surrounding regions. Maximum temperature rises of 19 K were found.

Experimental set-up affects heat flow within a material and therefore the temperature rise found. This was examined in Shaw¹⁷⁹, where NiTi in water was found to have a lower martensitic transformation stress. Water minimised temperature changes in the material, with changes of only a few degrees seen to significantly alter the transformation stress required.

Superelastic transformations have also been observed¹⁷⁰ below the superelastic temperature range. This was thought to be due to the specimen's temperature rise as

near-adiabatic conditions were present at high strain rate. A temperature rise of between 22 and 48 °C was noted for a SMA deformed dynamically at strain rates between 1200 and 2300 s⁻¹ under similar conditions. Such a large temperature increase may have brought the alloy into its superelastic range.

6.3 Impact Loading

Impact loading is distinguished from quasi-static nanoindentation by its rapid application of load by momentum transfer. In quasi-static nanoindentation, the indenter is brought slowly into contact with the material at a load which, ideally, is miniscule compared to the maximum load achieved during indentation. Load is then steadily increased in a controlled fashion. This allows the entire load and deformation history to be captured within the load-displacement curves, so that it can be assumed that the material was initially stress-free.

Under the impact loading achievable using the MicroMaterials NanoTest system, an accelerating (impact) load is applied to the pendulum system throughout the duration of the test and only displacement, not force, can be measured as a function of time – or at least the dynamic measurement of force is a technical challenge. As the accelerating load is applied to the pendulum continuously during impact and rebound, a bouncing ball under the influence of gravitational acceleration can be considered as a representative analogue for the impact testing discussed in this work. This provides an explanation for the multiple impacts/rebounds observed during testing (Fig. 6.4). The indenter could theoretically be captured after a single impact by releasing/reversing the accelerating load after rebound, in order to generate single impact events. However, the equipment employed in this work does not yet have this capability.

Thus, the forces experienced by the sample during impact are expected to be a complex function of the accelerating load, acceleration distance, pendulum damping, and the sample response¹². The relationship of these forces to displacement will probably be similar to that observed in conventional quasi-static indentation loading, with the additional effect of any strain rate dependent response¹⁰².

6.3.1 Data Analysis

The NanoTest system impact module used in this work incorporates several different software modules for applying impact loading. Two of interest are the Multiple Impulse and Dynamic Hardness modules. These modules are similar in method of impact. The difference being that, in Multiple Impulse, at the beginning of the test the indenter is resting against the sample under the accelerating load. This produces an initial displacement prior to impact, rather than impacting a pristine surface. The Dynamic Hardness module does impact a pristine surface, having only made a very low load surface detection prior to impacting, and it has a much higher sampling rate for displacement measurement. For analytical simplicity, the data from these tests were split into separate groupings, according to their sampling rates. The Multiple Impulse module is discussed further in §7.1. It is worth noting that these two types of impact are mechanically identical. Only the data which are extracted from each test differs. This means that understanding and calibrations determined from high sampling rate data can be directly applied to an equivalent impact, i.e. the same acceleration load, indenter tip, and acceleration distance, sampled at low speed in the Multiple Impulse module.

The Dynamic Hardness module utilises a high speed data acquisition card within the MicroMaterials Ltd. NanoTest NTX series controller, which provides vastly more

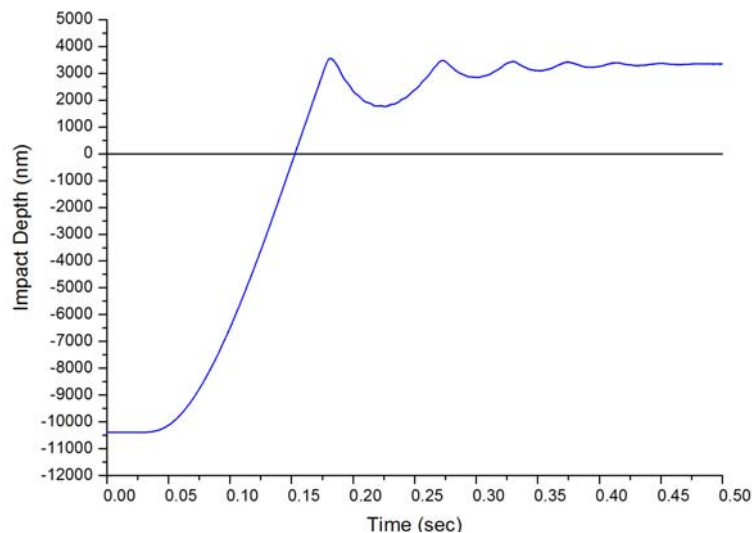


Fig. 6.4. Indenter depth as a function of time for a cube corner indenter accelerated with a force of 0.5 mN into a soda lime glass specimen.

data than the multiple impulse module. This high sampling rate data allows for the complete period of impact to be analysed, as shown in Fig. 6.4. These data illustrate that impact penetration does not occur monotonically. Instead, it can be seen that the indenter accelerates towards the sample, penetrates the sample to a certain maximum depth, rebounds off the sample, then (due to the applied force) continues to successively impact and rebound against/from the sample until settling at the final rest depth. In this particular case, the initial maximum penetration (prior to the first rebound) is approximately equal to the final rest depth, although with other types of sample the penetration can increase during the rebound regime.

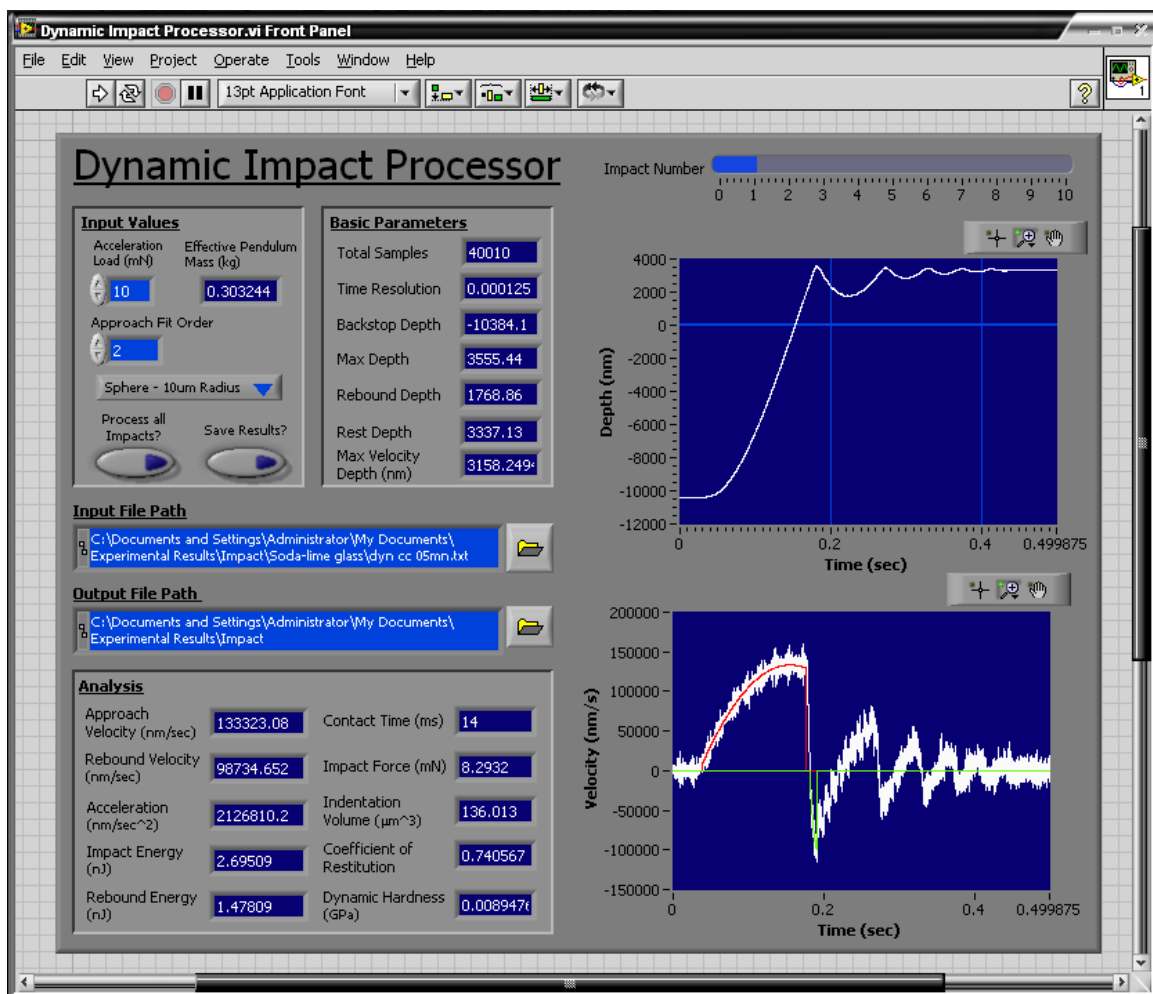


Fig. 6.5. LabVIEW virtual instrument for analysis of high sampling rate data.

The front panel of the LabVIEW virtual instrument designed for analysis of this data is shown in Fig. 6.5. It is immediately observable that a plethora of analytical parameters are determined by this program. However, several of these parameters are of more value for debugging the software than scientific analysis (e.g. total samples and time resolution). Others are very simply extracted using mean, maximum and

minimum criteria over fixed time intervals, such as the maximum depth, rebound depth, rest depth and backstop depth.

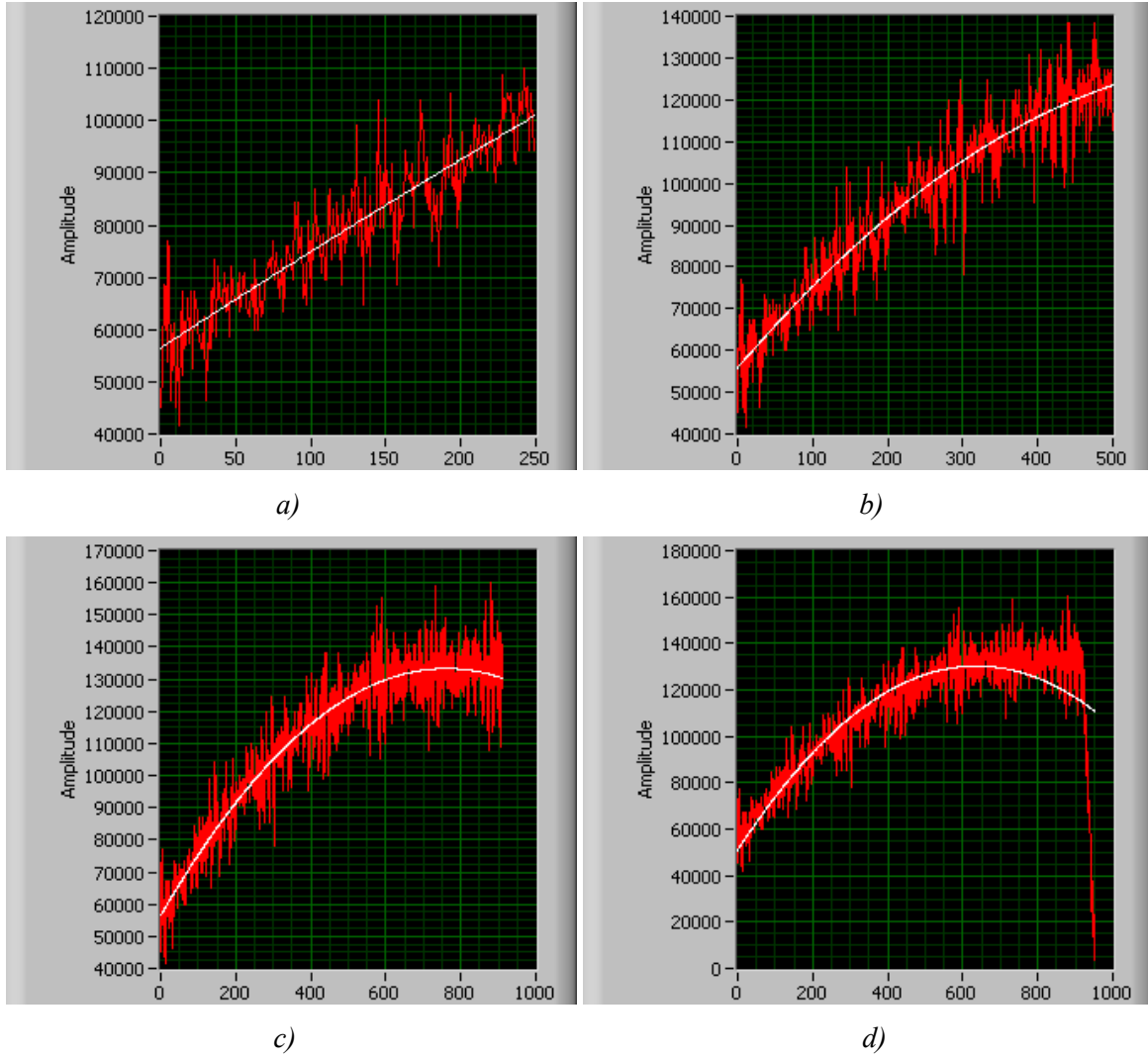


Fig. 6.6 Sample iterations of progressive data fitting algorithm for the approach velocity showing
a) 250 datapoints b) 500 datapoints c) the optimum fit at 913 datapoints
and d) the final iteration at the maximum impact depth.

Perhaps the most useful parameter that can be extracted is the impact velocity immediately before impacting the surface. This could be obtained by differentiating the time-displacement curve and finding the maximum. However, since this is a real signal, differentiation significantly increases the noise. This could be reduced by fitting the time-displacement curve and then differentiating the resulting polynomial. However, this would then make the measurements strongly dependent on the fitting parameters utilised. This is avoided by fitting the ‘noisy’ discretely differentiated data, or the velocity-time curve.

The process by which this is accomplished is somewhat complex. Since the maximum velocity occurs before the maximum depth, there is no convenient marker in the data to demarcate the time period which should be interrogated. Also, the scale of the noise in the velocity-time curve makes simple maximum criteria unusable. The algorithm developed by the author to overcome this difficulty is illustrated in Fig. 6.6 and Fig. 6.7. The algorithm begins with iteratively using a least squares polynomial fit of the time period between the take-off point (defined as the time when the impactor achieves a distance of 500 nm from the mean backstop depth) and the successive datapoints. The algorithm continues the iterative loop until the maximum depth point is reached. The optimum fit is selected by comparing the maximum velocity measured from each fit (Fig. 6.7).

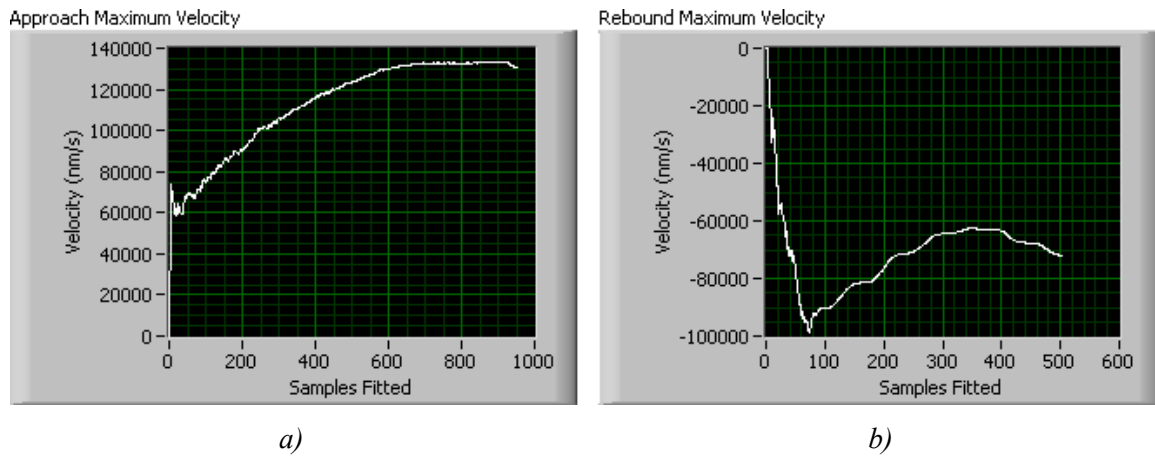


Fig. 6.7 Maximum velocities from progressive fitting algorithm with maximum velocity as a function of samples fitted (iteration number) for a) the sample approach and b) the first rebound after impact.

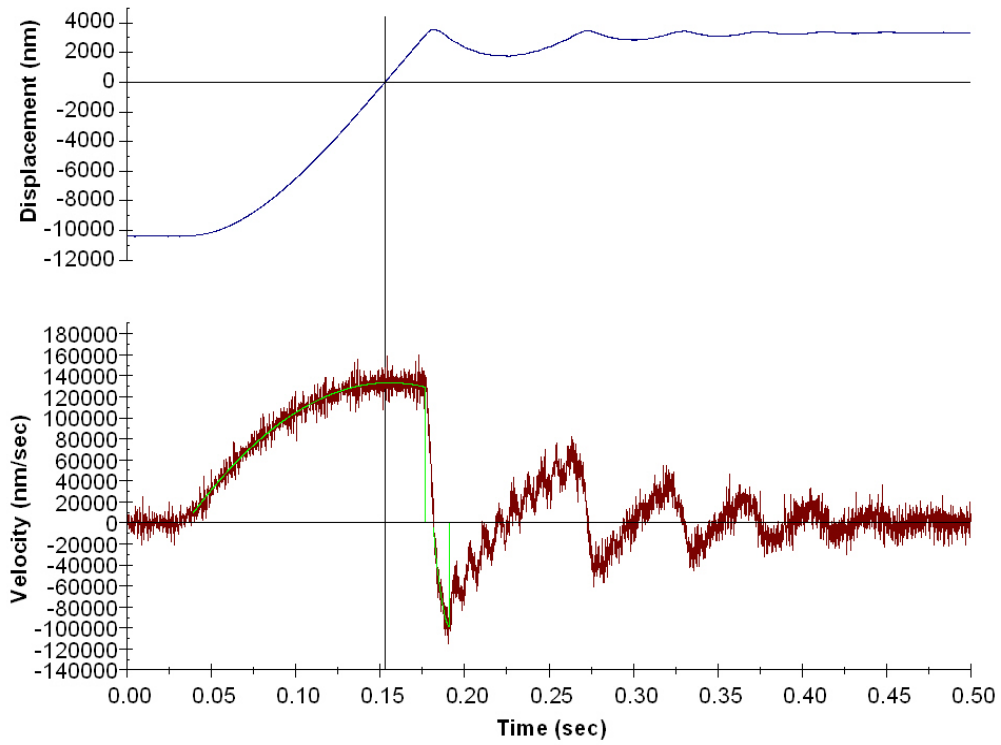
Initial noise noticeable in the maximum velocity as a function of samples fitted (Fig. 6.7a) is due to fitting of the noise as the algorithm ‘runs in’ to the larger trend in the data. The algorithm is also utilised for determining the maximum velocity attained during the rebound of the indenter from the sample (Fig. 6.7b). This maximum is negative, since positive velocity is defined as the direction of travel towards the sample. The maximum rebound velocity appears quite early, since the final iteration is defined as the point where the velocity-time curve becomes positive, which coincides with the rebound depth. This algorithm has proved particularly successful at ignoring noise over a wide range of impact velocities, and its validity as an approach is further suggested by the fact that the selected fit (which is chosen since it produces the

maximum velocity) always extends to the end of the positive portion of the velocity-time curve, even when the maximum velocity occurs significantly earlier.

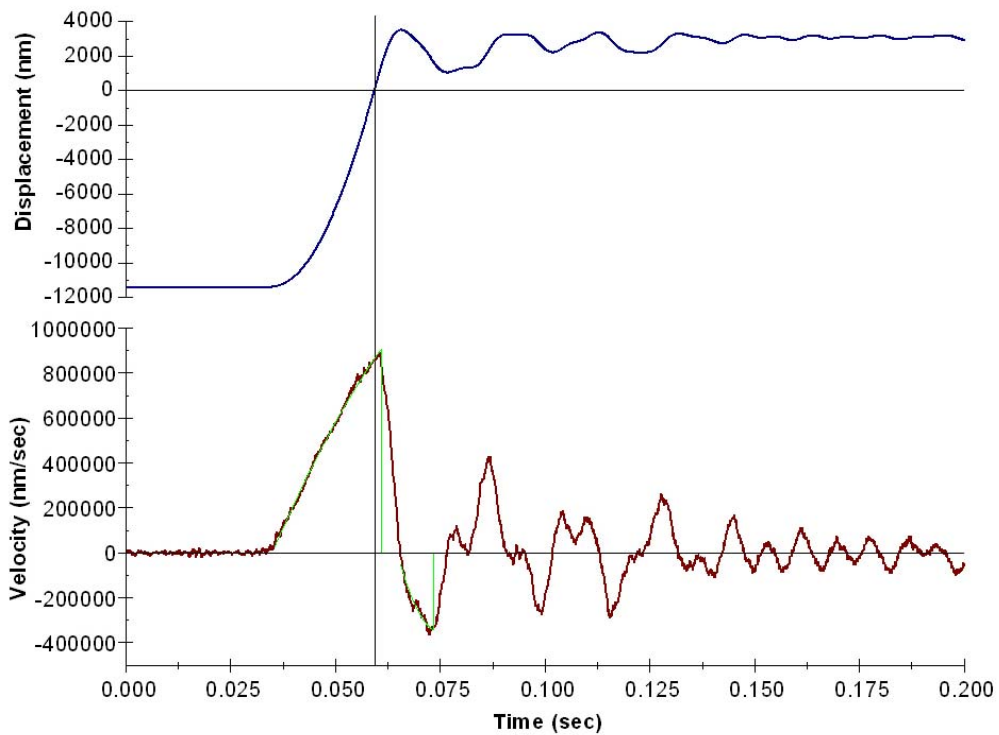
6.3.2 Dynamic Compliance

Dynamic compliance is an important consideration for instrumented impact indentation systems. As discussed in §2.1.2, normal quasi-static compliance of an indentation system can be determined using large indentations with known sample and indenter stiffness values. This quasi-static compliance is usually assumed to be a simple, linear function of displacement per applied load. Under dynamic loading, the compliance must be dependent on the impact kinetic energy, the applied accelerating force and the sample's restoring force. Due to the cantilevered pendulum design of the MicroMaterials NanoTest system, it is expected that a significant portion of the dynamic compliance occurs via beam bending of the pendulum. This bending of the pendulum during the first impact stores elastic energy within the shaft of the pendulum, which is then released when the indenter rebounds off the surface in the form of the pendulum shaft sinusoidally oscillating. This can be observed in the velocity-time curves shown in Figure 6.8.

The pendulum oscillation is most marked in Fig. 6.8a during the first rebound period, 0.2 s-0.25 s, and it is gradually damped out, to within the noise level of the signal, by 0.35 s. The oscillation is of significantly greater amplitude in Fig. 6.8b, where it is sufficient to interfere with the rebound process. This is due to the greater accelerating force (10 mN), which increased the indenter's approach velocity and thus the applied load on the pendulum shaft.



a)



b)

Fig. 6.8. Impact depth and velocity as a function of time for an a) 0.5 mN and b) 10 mN cube corner impact on soda lime glass.

6.3.3 Strain Rates during Impact

One of the more interesting features of impact loading is the high strain rates which occur within the first few moments of contact. According to Equation 2.23, for conical/pyramidal indenters, the strain rates induced in the first nanometre of penetration will initially correspond to the incident velocity of the impactor, but will rapidly fall, in a way that depends on specimen response. This is an oversimplification, since indenters are not ideally sharp and will not instantly generate their representative strain²⁶ value. However, this equation is useful for comparison purposes.

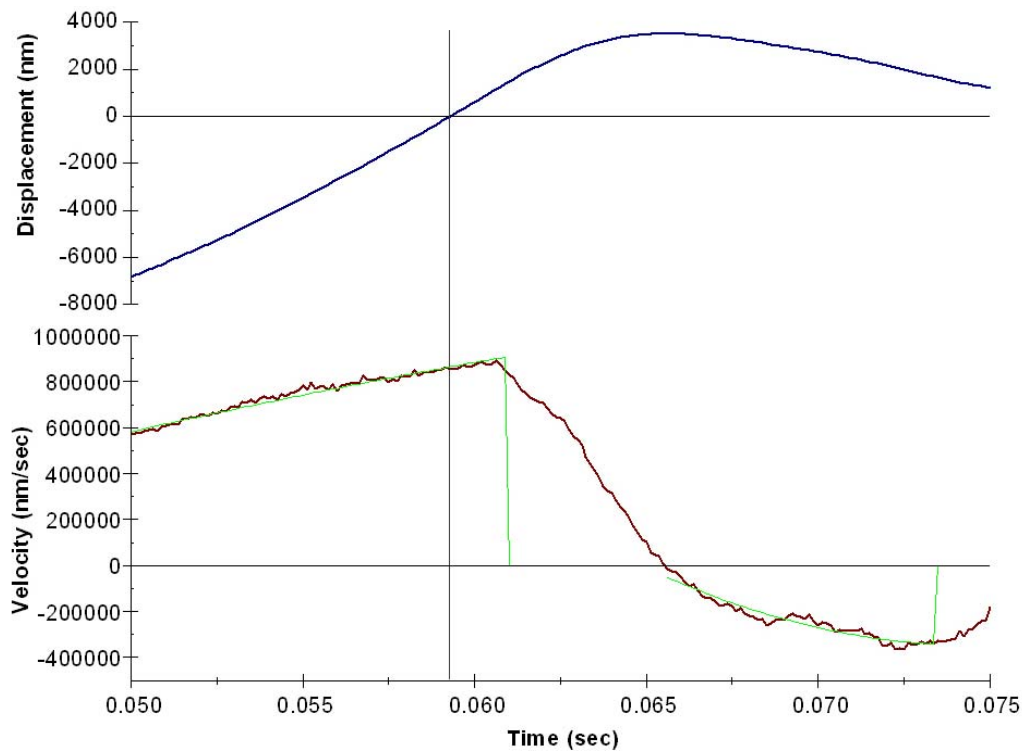


Fig. 6.9. Impact depth-time and velocity-time relationships for the initial impact and rebound period of a 10 mN cube corner impact on soda lime glass.

The time period of interest for some representative high strain rate data is shown in Fig. 6.9. Specifically, the period between the moment of contact, where displacement = 0 nm, and the moment of maximum initial penetration, where velocity = 0 nm s⁻¹. The green lines mark the fits for determining maximum incident and rebound velocity. By using the analysis discussed in §2.3.4, the displacement-time curves from this period of interest can be converted into an estimated average strain rate, as a function of time.

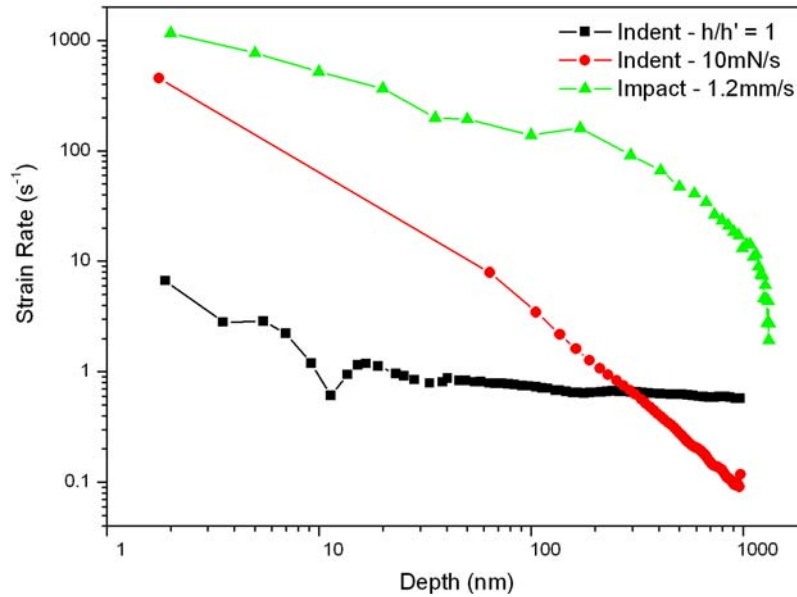


Fig. 6.10. Estimated representative strain rates, as a function of penetration depth, for various loading techniques using a Berkovich indenter on 304 steel.

This allows the strain rates during impact indentation to be compared to those acquired during conventional indentation. Figure 6.10 illustrates the difference in strain rates achieved by proportional loading rate, constantly increasing loading rate (10 mN s^{-1}) and impact loading indentation. Proportional loading rate indentation generates fairly constant indentation strain rates, but it is inherently limited by the feedback circuitry maintaining the relationship between penetration rate and penetration depth. Constantly increasing loading rates generate very high initial loading rates, but this logarithmically decreases with increasing penetration. Impact loading generates the highest strain rate values, and the highest penetration depths, but the strain rates rapidly decrease near the maximum penetration depth as the impactor is decelerated by the sample.

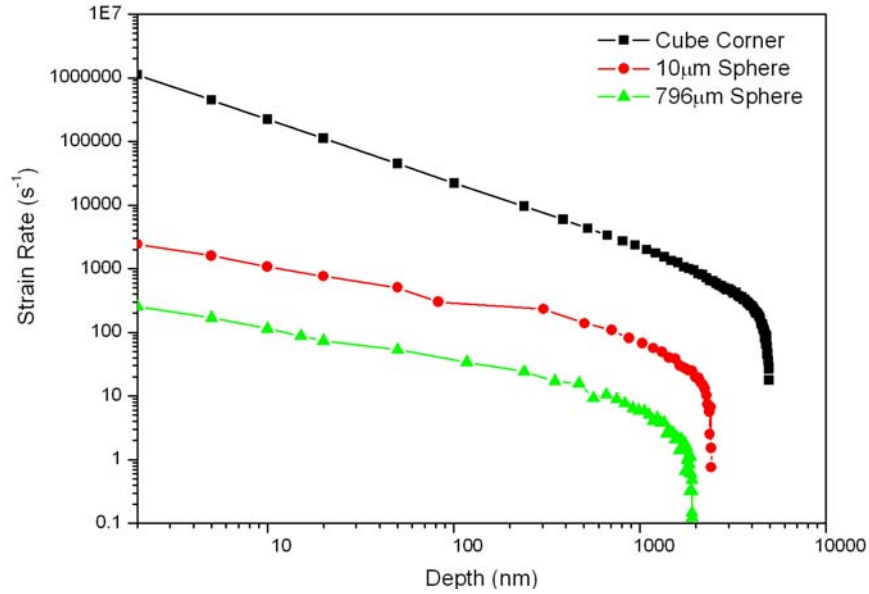


Fig. 6.11. Strain rates as a function of penetration depth for 2.2mm/sec impacts using various indenter tips on soda lime glass.

Results shown in Fig. 6.10 illustrate the trends in strain rates, as a function of penetration depth, which can be achieved using different indentation loading techniques, using a Berkovich indenter. Figure 6.11 demonstrates that the shape, particularly the ‘sharpness’, of an indenter has a strong influence on the magnitudes of the strain rates achieved during impact, as well as the maximum penetration depths.

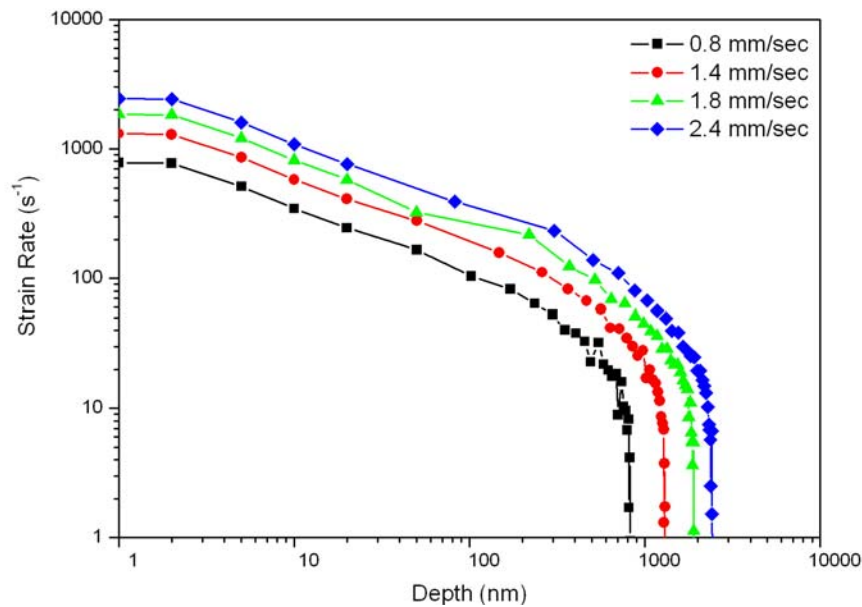


Fig. 6.12. Strain rates as a function of penetration depth for a 10 μm radius indenter tip impacting at various incident velocities on soda lime glass.

Varying tip shape has a strong influence on the strain rates achievable. However, further control over the strain rates during impact indentation can be achieved by

varying the impact incident velocity. Figure 6.12 illustrates how initial strain rate, final penetration depth, and the amplitude of the strain rate-penetration depth curve increase with increasing impact velocity.

6.4 Quasi-static and Impact Indentation of NiTi

By comparing dynamic and quasi-static indentation data, it is possible that rate-dependent behaviour can be observed. In order to achieve this, the number of experimental variables should ideally be reduced such that only the displacement rate varies between experiments. Thus, both dynamic and quasi-static experiments must use the same indenter and penetrate to the same maximum depth prior to unloading.

Superelastic nickel-titanium alloys, NiTi, are an ideal type of material for this comparison, since their properties also vary significantly with temperature, as discussed in §6.1. Figure 6.13 illustrates the behaviour of NiTi in quasi-static indentation in the three major temperature regimes. Indentations were performed to the same maximum depth (1000 nm) during the experiment.

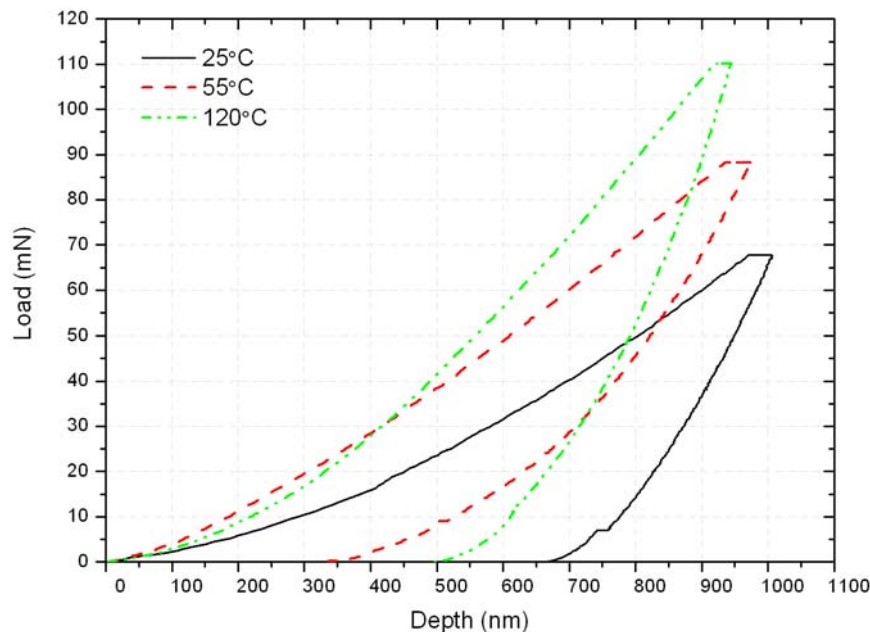


Fig. 6.13. Load-displacement relationships for quasi-static indentations on NiTi using a $10\ \mu\text{m}$ radius conospheroidal diamond tip at several different temperatures.

However, the variation in maximum depth observable is due to correcting for system compliance after indentation. At room temperature, 25°C , relatively little elastic recovery is observed, while at the Austenite start temperature, $A_S = 55^\circ\text{C}$, significant recovery occurs during unloading. At much higher temperatures above A_F , 120°C , the

specimen still displays significant recovery with a higher maximum load. Discontinuities in the unloading portion of the curves correspond to a hold period for thermal drift measurement.

One approach⁴¹ to quantifying the amount of superelastic behaviour, as a function of temperature, using quasi-static spherical nanoindentation is to plot the percentage of elastic recovery (final unloaded depth divided by maximum depth) – see Fig. 6.14. The maximum recovery appears coincident with the Austenite start temperature, A_S . The greatest recovery might be expected at the Austenite finish temperature, A_F , where all the material should initially be in the parent phase, allowing a larger proportion to transform to martensite than when below this temperature, and a lower driving force is needed for the transformation to occur than at higher temperatures, further from the martensite parent phase equilibrium temperature. However, hysteresis may be affecting the observed behaviour.

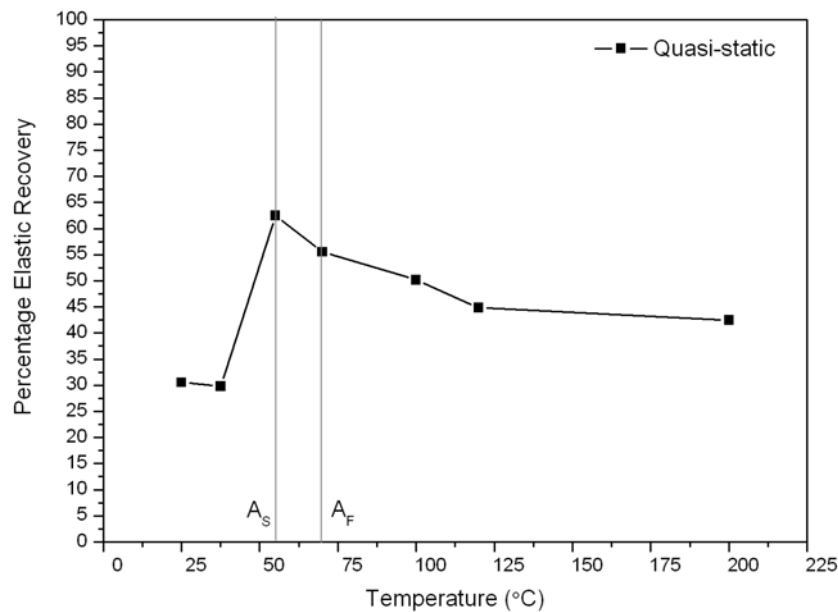


Fig. 6.14. Percentage elastic recovery as a function of temperature for a NiTi alloy.

Unfortunately, this method of comparison cannot currently be achieved using this dynamic indentation method, since the final unloaded depth is not measurable. It cannot be indirectly measured via scanning probe microscopy on the residual impressions, due to the increased deformation from the multiple impacts which occur as the pendulum rebounds as it comes to rest on the sample. Precise location of the impact indentation residual impression is also made difficult due to the large degree of elastic recovery and the spherical impression shape. Comparison of load-displacement relationships cannot be compared due to the lack of a force sensor.

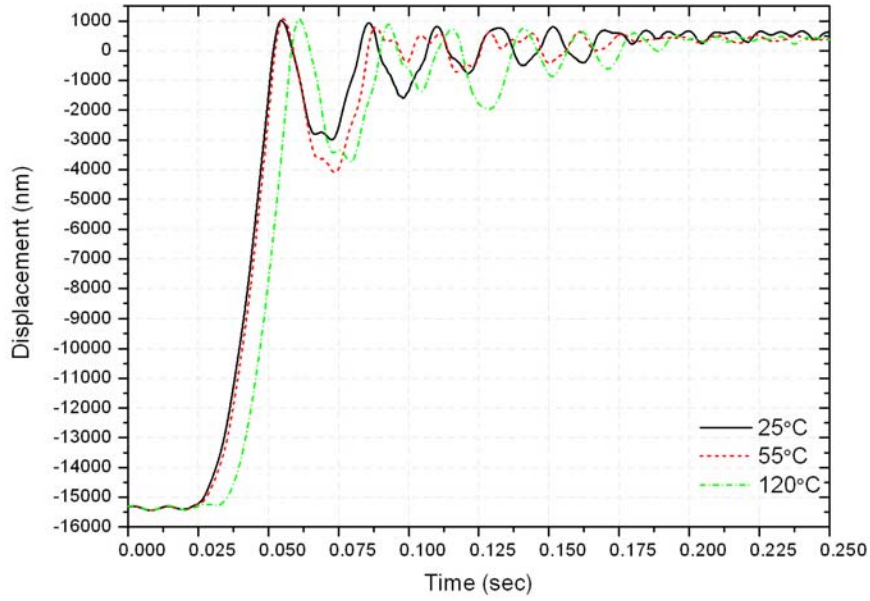


Fig. 6.15. Time-displacement relationships for impact indentations on NiTi using a $10\ \mu\text{m}$ radius conospheroidal diamond tip at several different temperatures.

This leaves time-displacement relationships from impact indentations as the only output of the test. These are shown for several different testing temperatures in Figure 6.15. It is observed that the acceleration portion of the time-displacement curves begins at different points in time from the start of the tests, but this is not presumed to have any effect on the test parameters.

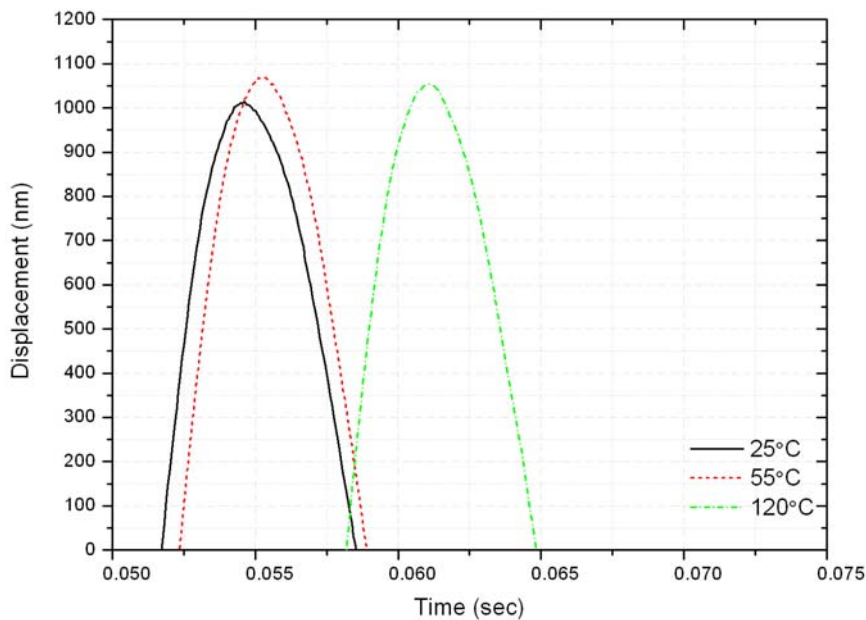


Fig. 6.16. Time-displacement relationships highlighting the contacting time period of impact indentations on NiTi at several different temperatures.

The degree of rebound observed for the different temperatures is also observed to change, as well as the oscillations accompanying subsequent impacts and rebounds as

the indenter comes to rest against the sample. It appears in Figure 6.15 that all the impacts penetrate to nearly the same depth, but closer examination (Fig. 6.16) illustrates that there is some variation.

The variation in penetration depths does not follow the same trend as the quasi-static indentations, where the load required to achieve a 1000nm penetration was seen to increase with temperature. Since the impacts all possessed the same kinetic energy, the only variation in the forces involved during impact would be the sample's response. Interestingly, the maximum impact penetration depth appears to correlate to the degree of elastic recovery observed in the quasi-static indents. This variation, which is on the order of 50 nm, is small compared to the rebound variation observed in Figure 6.15, which is on the order of a micron.

Therefore, instead of comparing the maximum and unloaded depths to determine the elastic recovery, the total and elastic energies were compared. For quasi-static indentation, this consists of determining the work of indentation, as described in §2.3.3, while for the dynamic case the incident and rebound velocities can be determined as described in §6.3.1.1. The ratio of the rebound and incident velocities is often termed the coefficient of restitution²⁵.

Following Newtonian mechanics, the kinetic energy of the pendulum is proportional to its velocity squared. The square of the coefficient of restitution is therefore equivalent to the elastic energy restored after impact over the total energy of impact. Elastic energy here is taken as energy applied to cause both standard linear elastic loading and fully reversible martensite transformations. This ratio can then be compared with indentation results for the ratio of elastic to total work, as shown in Figure 6.17.

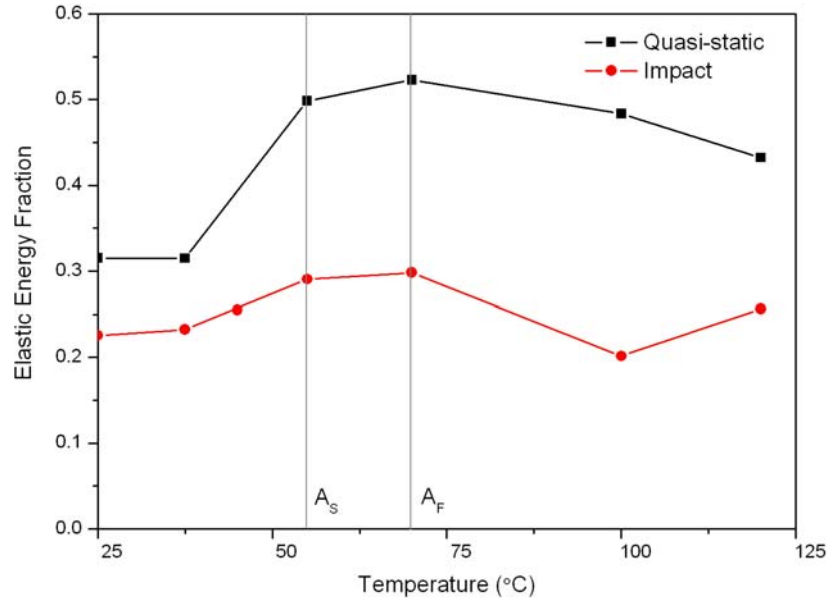


Fig. 6.17. Elastic energy fraction as a function of temperature for quasi-static and impact indentations on NiTi.

The same general trend with temperature is seen in Figure 6.17 with both impact and quasi-static indentation, indicating that the elastic to total work ratio can be used to make comparisons between impact and indentation data. Here the peak is seen at A_F as expected and discussed earlier.

It can also be seen that impact produces lower values of elastic to total work ratios. The gap between quasi-static and impact values is observed to show some temperature dependence. This is thought to be due to energy losses due to dynamic pendulum compliance, as mentioned in §6.3.2. In Figure 6.13, it is observed that the load required to achieve a given penetration depth increases with temperature. Under quasi-static conditions, this would indicate that compliance would play a greater role in deformation, which was also observed in Figure 6.13.

Since impact is a dynamic process, energy that doesn't contribute towards a stress-induced phase transformation or adiabatic heating, which is thought to account for all the energy applied in indentation, may create acoustic and elastic energy waves. This could reduce the proportion of elastic energy given back to the pendulum on rebound. However, it is also possible that the lower proportion of elastic energy for impact results may be due to the truly elastic (i.e. conventional linear elastic) response of the material. This may supply the pendulum with the impulse for rebounding from the

material, without feeling the full effect of the superelastic recovery of the material, due to the high speed of rebound.

6.5 Summary

The high sampling rate Dynamic Hardness module of the MicroMaterials NanoTest system enabled time-displacement relationships for the initial penetration and rebound of impact indentations to be acquired. A LabView analysis program was successfully implemented to rapidly extract parameters from the time-displacement relationships.

The strain rates during impact indentation were found to be higher and continue to greater penetration depth than any conventional quasi-static indentation technique. Strain rate during impact indentation was found to be strongly dependent on indenter tip radius and cone angle, which provided variability over 5 orders of magnitude. However, strain rate was found to be less dependent on impact velocity within the range of achievable velocities with the NanoTest system.

The dynamic compliance and pendulum oscillations of the indentation system were observed to be problematic to reliable depth measurement during impacts at high acceleration loads. The multiple impact/rebound cycles, caused by the continuous application of the acceleration load, as the indenter settled at the final rest depth were also problematic, since they added the possibility of additional from multiple impacts, as well as creep displacements during the period at rest depth.

The superelastic effect was characterised in NiTi by using elevated temperature, quasi-static spherical indentation using the method described by A.J. Muir-Wood⁴¹. This method was then extended using dynamic (impact) spherical indentation over the same range of temperatures. The square of the coefficient of restitution values from impact indentation was compared to the elastic fraction of the total work of quasi-static indentation, and a positive correlation demonstrating superelastic behaviour in NiTi over a range of temperatures was observed between the two methods. Lower elastic energy fractions were observed for impact indentation than quasi-static indentation. However, this cannot be attributed to a strain rate effect without accounting for dynamic compliance of the system.

7

Multiple Impact and Scratch Indentation of PEO Coatings

Multiple Impact and Scratch indentation are two modes of indentation thought to simulate wear conditions: erosion and abrasion, respectively. Both modes are examined through micro-mechanical testing of PEO coating systems and comparison to standard wear test results on them. Special emphasis is given to novel PEO coatings on Ti-6Al-4V alloys.

7.1 Aims of Research

The Gordon Laboratory has been involved in a long-term collaboration with Keronite Ltd, in development of plasma electrolytic oxidation (PEO) coatings¹⁸⁰⁻¹⁸⁴. Recent work by J.M. Paillard¹⁸⁵ on commercially pure titanium and Ti-6Al-4V alloys concluded Ti-6Al-4V is better suited to PEO processing. The next stage of this investigation was the systematic characterisation of the mechanical properties and composition of PEO coatings generated using four different electrolytes on Ti-6Al-4V conducted as A. Collier's Part III individual project¹³⁶ under the supervision of J.M. Paillard, J.A. Curran, T.W. Clyne and the author.

Nano-micro scale mechanical testing techniques, e.g. nanoindentation, are uniquely suited for experimental coating development purposes, since they can rapidly obtain a large amount of information, with minimal sample size and geometry requirements. However, interpretation of the resulting data to determine coating properties can be complex^{186, 187}. It was desired to develop an understanding of the utility and limitations of novel capability within the Gordon Laboratory to perform multiple impact and scratch indentation testing for determining micro-mechanical and wear properties of these novel coatings and related coating systems. The results of these efforts are now being prepared in a joint publication between the contributors listed above. The review provided in §7.2 is taken largely from this document, with J.A. Curran as a major contributor. Results of conventional characterisation techniques applied to the coatings are discussed in §7.3, and the results of the application of

multiple impact and scratch indentation as well as erosive and abrasive wear testing are provided in the following sections.

7.2 Review of PEO Coating Systems

Plasma electrolytic oxidation (PEO) involves the creation of relatively thick, oxide-based surface layers by oxidation of the substrate and/or deposition from the electrolyte. The high voltage fields generated across the growing oxide layer cause repeated local dielectric breakdown and plasma discharges which modify the structure of the layer. The coatings were developed primarily for wear-protection of aluminium¹⁸⁸⁻¹⁹⁸. Since it normally involves at least some conversion (oxidation) of the substrate, the interfacial adhesion tends to be superior to that of most deposited coatings^{189, 191} with critical loads for coating failure during scratch testing exceeding 100 N for thick coatings in a ductile failure mode. The plasma discharges often cause high temperature conversion of the growing coating into crystalline phases such as corundum¹⁹⁹. These phases confer higher hardness on the coating than the amorphous oxides grown during conventional anodising. PEO coatings also contain significant levels of fine-scale porosity¹⁸³ and, partly as a consequence of this, have a relatively a low global coating stiffness^{181, 184}.

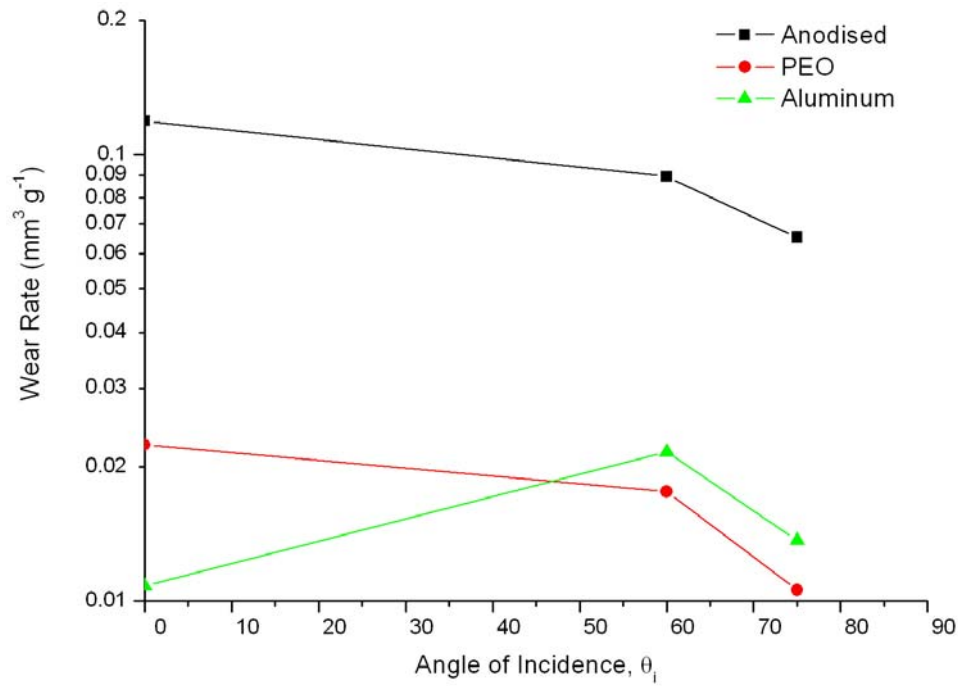
The combination of good interfacial adhesion, high hardness, permeability to fluids (giving good lubricant retention) and high compliance confers excellent tribological performance on PEO coatings in many modes of wear. In general, the wear performance is inferior under erosive or impact loading, particularly at normal incidence¹⁹⁸. Of course, this is expected with ceramic coatings, which tend to fracture under these conditions, whereas a metallic coatings or substrate tends to undergo plastic deformation. The shape, size and velocity of the erodent particles are often relevant, with large, high-speed, angular particles, incident at glancing angles, normally favouring excavation of metallic material.

While PEO coatings on aluminium and magnesium alloys are now in a relatively mature state, their development for use on titanium is still in its infancy. There has been some preliminary work in the area^{200, 201}, but there are often problems of brittleness and relatively high levels of coarse porosity, possibly associated with gas evolution. There is nevertheless considerable interest in their development,

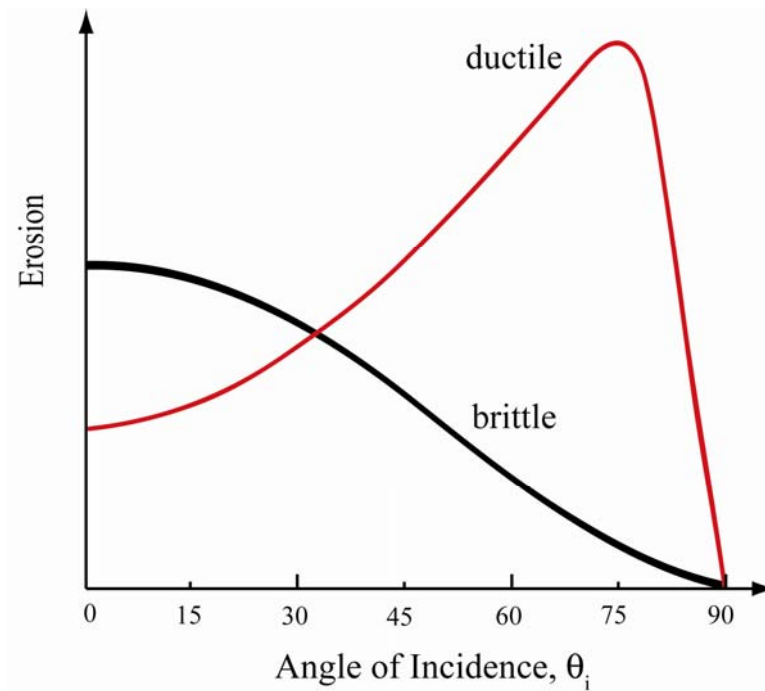
particularly in the context of biomedical applications²⁰²⁻²⁰⁶, and there have also been some reports concerning their microstructure²⁰⁷ and their resistance to corrosion and wear²⁰⁸⁻²¹¹. However, in general they are not expected to enhance the wear resistance of the substrate, which is, of course, generally expected to be superior to that of Al and Mg alloys in any event. Recent work²¹² has provided some systematic information about the structure of PEO coatings produced on Ti alloys with different electrolyte compositions. For example, it has been shown that those produced using silicate electrolytes tend to be largely composed of amorphous silica, and are hence relatively brittle.

7.2.1 Erosive Wear

There is a shortage of literature on the erosive properties of PEO coatings. Given the variability in possible processing parameters, only the more mature coating systems on aluminium alloys can be considered to be consistent between different laboratories. Only one source, Rama Krishna¹⁹⁸, of standard erosive wear test, ASTM G76, data on these coating systems was located. Within these results (reproduced in Fig. 7.1), only results for the lowest particle velocity value, 43 m s^{-1} , using $\sim 225 \text{ }\mu\text{m}$ angular silica particles, are given. This was to attempt as close to parity with indenter impact conditions as possible. However, the indenter impact velocities, at a maximum of 4 mm s^{-1} , are ~ 4 orders of magnitude slower than the 43 m s^{-1} impact velocity. The indenter impact energies (as estimated in §4.4), ranging from a few nJ to $\sim 1 \text{ }\mu\text{J}$, naturally show a similar amount of disparity to ASTM G76 energies, 36-71 mJ. Strain rates achieved by these particles are expected to be ~ 3 orders of magnitude larger, since their velocity is 4 orders of magnitude larger while the particles are only 1 order of magnitude larger in radius than the indenter tip used.



a)



b)

Fig. 7.1. Erosive wear behaviour as a function of angle of incidence in a) aluminium coating systems reproduced from Rama Krishna¹⁹⁸ and b) general trends for ductile and brittle materials²¹³.

Both brittle coating systems demonstrate decreasing wear rates with increasing angle of incidence (0° = normal incidence), while the ductile aluminium substrate demonstrates the lowest wear rate at normal incidence which then increases to a

maximum at a critical angle. For the brittle coatings, this is consistent with the reduction in the compressive strain due to the oblique incidence leading to fewer fractures. The ductile substrate absorbs most of the compressive strain through work hardening at normal incidence and fails to form sufficient shear lips to be broken off and worn away. At the higher incidence angles, the amount of displaced material which can be removed by successive impacts is increased until the critical angle for rebounding instead of cratering is surpassed. This follows the general trends²¹³ diagrammed in Figure 7.1b.

7.2.2 Abrasive Wear

Standardised abrasive wear test, ASTM G65, data for the coating systems on aluminium from the literature was found for a range of applied loads 1, 5, 10, 20 and 50 Newtons¹⁹⁸, and 130 Newtons²¹⁴. Both sources used $\sim 225\ \mu\text{m}$ silica abrasive, though one specifies it was angular silica and the other specifies rounded silica. Clifford et al gives a feed rate of 300g per minute and a rotational speed of 200rpm. Rama Krishna et al did not specify his feed rate and rotational speed. The results from Rama Krishna's work are reproduced in Figure 7.2. The results from the Clifford study were not presented in compatible units. Results for anodised aluminium are not available for loads greater than 5 N due to failure of the coating at higher loads.

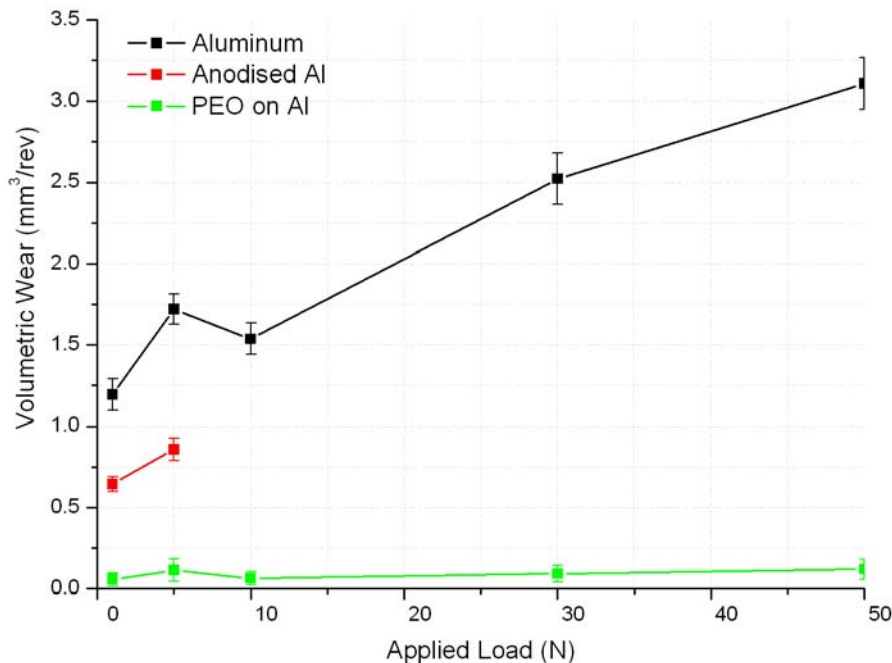


Fig. 7.2. ASTM G65 volumetric wear as a function of applied load for aluminium alloy coating systems reproduced from Rama Krishna¹⁹⁸.

7.3 Characterisation Results

The novel PEO coating systems on Ti-6Al-4V were characterised by A. Collier¹³⁶ using micrometer, scanning electron microscopy, and x-ray techniques. His results are briefly summarised here. Conventional Berkovich nanoindentation was used on coating cross sections to provide microstructural insight into discussing their multiple impact and scratch behaviour.

7.3.1 Coating Thickness and Morphology

Cross-sectional micrographs provide an estimate of the thickness of the coatings on Ti-6Al-4V (Table 7.1). There is a good agreement in the aluminate coating measurements with results obtained using a micrometer, whereas for the other coatings, the micrometer gives values that are considerably larger than the SEM measurements.

<i>Electrolyte</i>	<i>Thickness: SEM</i>	<i>Thickness: Micrometer</i>
<i>Aluminate</i>	<i>60 μm</i>	<i>56 μm</i>
<i>Phosphate</i>	<i>13 μm</i>	<i>22 μm</i>
<i>Silicate</i>	<i>60 μm</i>	<i>147 μm</i>
<i>Mixed</i>	<i>35 μm</i>	<i>103 μm</i>

Table 7.1. Thickness of PEO coatings generated on Ti-6Al-4V alloy substrates¹³⁶.

It is important to bear in mind, however, that the SEM thickness measurement cannot automatically be taken as representative, since it is only measured in one localised position and may not be indicative of the entire coating. Micrometer measurements are limited to measuring the extent to which coatings have grown outward from the original substrate surface and micrometers may exaggerate thickness measurements in surfaces with high roughness. Micrometers also cannot measure the extent to which the substrate itself may have been converted into coating.

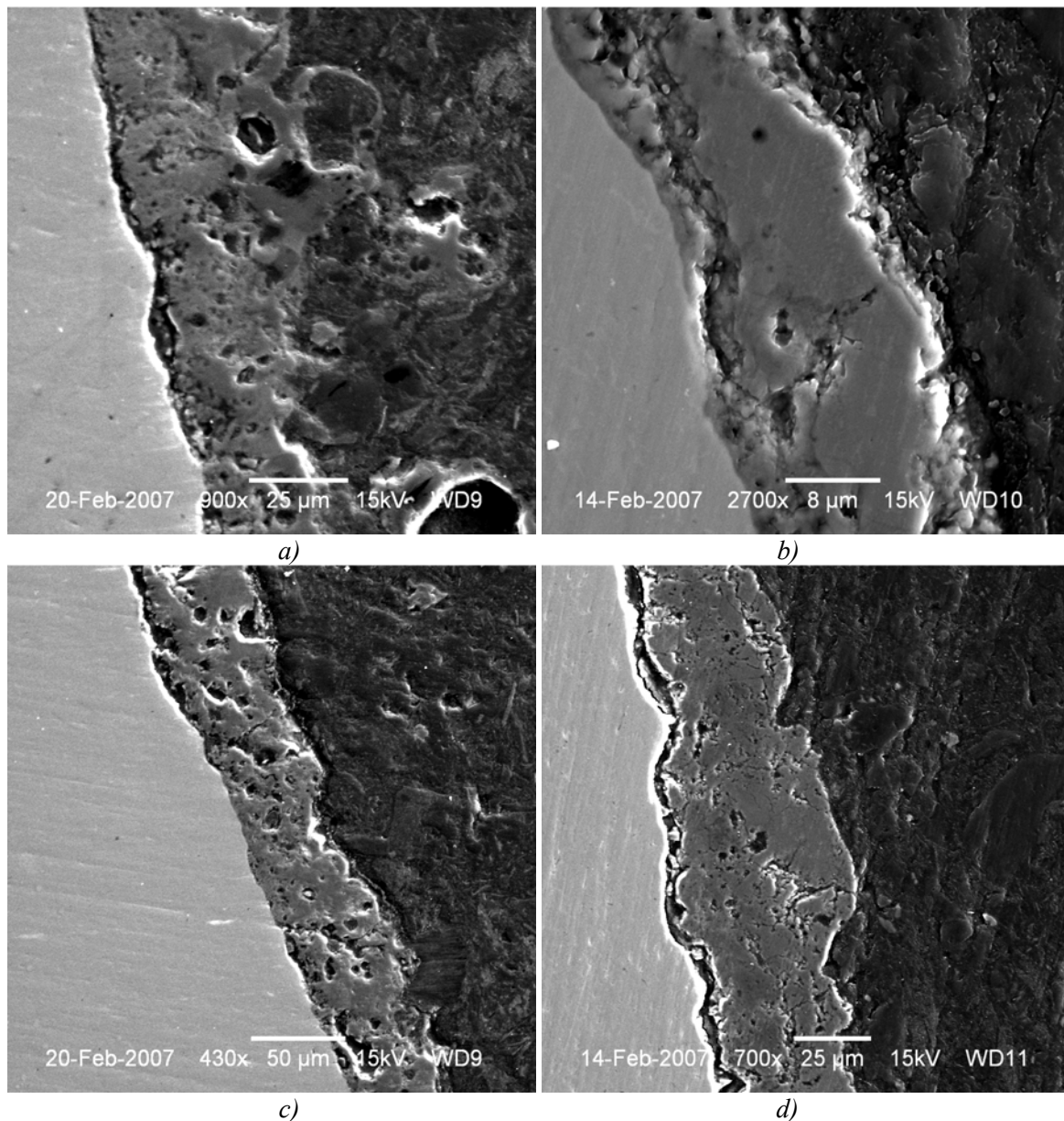


Fig. 7.3. Cross-sectional scanning electron micrographs of a) mixed, b) phosphate, c) silicate, and d) aluminate electrolyte coatings acquired by A. Collier¹³⁶.

Cross-sectional micrographs (Fig. 7.3) were chosen to be representative. All coatings display porosity on the scale of 1 to 10 μm . This is likely due to bubbles trapped during gas evolution. Phosphate (Fig. 7.3b) and aluminate (Fig. 7.3d) sections show channels running through the coating which may be the sites of discharge events during processing. The aluminate coating also appears to have debonded from the substrate. Regardless of whether this is an intrinsic property or a result of the polishing process, this indicates that the processing parameters of this particular aluminate coating have resulted in atypically low coating adhesion.

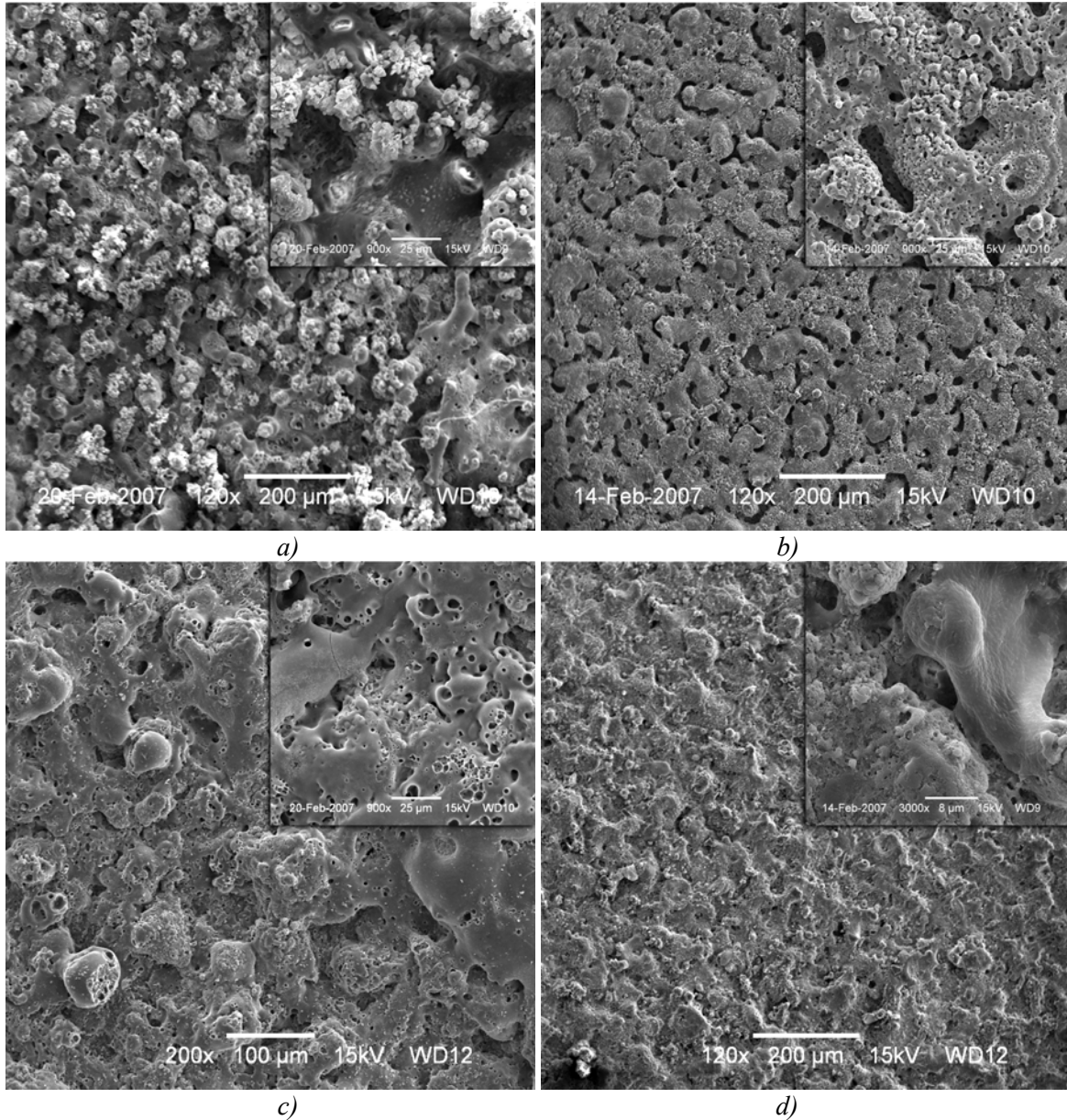


Fig. 7.4. Surface scanning electron micrographs of a) mixed, b) phosphate, c) silicate and d) aluminate electrolyte coatings [inset scale bars a, b, c = 25 μm, d = 8 μm] reproduced with permission from A. Collier¹³⁶.

The relatively low magnification images of the surfaces (Fig. 7.4) illustrate their differing morphology, roughness, and surface topology of the coatings. It is evident that the silicate and mixed electrolyte coatings have rough and irregular surfaces profiles compared to the other coatings. Pores and holes of the scale 1 to 10 μm can be observed in all of the coatings, to varying degrees. These are related to the discharges created during the processing. The phosphate electrolyte coating (Fig. 7.4b) appears to have a degree of larger scale porosity on its surface.

In the inset higher magnification images of the mixed electrolyte (Fig. 7.4a), distinct nodular and smooth regions can be observed on the surface. In the literature, coatings with similar features have been reported^{215, 216}, produced using sequential processing in silicate and phosphorus based electrolytes. Smooth regions are associated with silicate based electrolytes and nodular regions associated with phosphate electrolytes. With the mixed electrolyte (containing silicate and phosphate components together), a morphology combining these has been produced in one step. The silicate electrolyte inset (Fig. 7.4c) displays rounded pores with no "sink hole" from a discharge channel, possibly formed from evolved gas being trapped in molten material which subsequently solidifies with it inside. At higher magnification, distinct porous and glassy "fused" areas can be observed in the aluminate electrolyte (Fig. 7.4d). A possible formation mechanism for these areas is the ejection of molten material from a discharge channel, which then rapidly cooled with a glassy structure.

7.3.2 Coating Composition

By combining XRD and EDS cross sectional and surface scan data, A. Collier¹³⁶ was able to qualitatively evaluate the dominant phases present in each of the novel coatings on Ti-6Al-4V. It must be noted that PEO coatings are often inhomogeneous, and exhibit some degree of gradual 'layering'²¹⁷, with different phases appearing in different amounts at varying depths through the coating. Since the EDS probe depths are less than 1 μm , EDS surface scans give a good representation of the surface composition, without being confused by the bulk material.

<i>Electrolyte</i>	<i>Crystalline phases present</i>	<i>Approximate ratio of dominant phases in bulk</i>	<i>Approximate ratio of dominant phases at surface</i>
<i>Aluminate</i>	<i>Al_2TiO_5, α & γ-Al_2O_3, TiO_2</i>	<i>Al_2TiO_5</i>	<i>Al_2TiO_5</i>
<i>Phosphate</i>	<i>Mainly TiO_2, Al_2TiO_5</i>	<i>3-TiO_2 : Al_2TiO_5</i>	<i>3-TiO_2 : Al_2TiO_5</i>
<i>Silicate</i>	<i>TiO_2</i>	<i>4-SiO_2 : TiO_2</i>	<i>SiO_2</i>
<i>Mixed</i>	<i>TiO_2, Al_2TiO_5</i>	<i>Unknown ratio of SiO_2 and TiO_2</i>	<i>SiO_2</i>

Table 7.2. Phase compositions for PEO coatings generated on Ti-6Al-4V alloy substrates¹³⁶.

XRD results (e.g. Fig. 7.5) of all samples exhibited peaks corresponding to titanium and TiO_2 (rutile and anatase). For the aluminate, phosphate and silicate coatings, EDS scans conducted in different areas returned similar elemental ratios, suggesting that the phase compositions through the bulk of these coatings are fairly uniform. Conversely, the composition varied much more through the bulk for the mixed

electrolyte coating. The surfaces of the aluminate and phosphate coatings had almost identical compositions to that of the bulk.

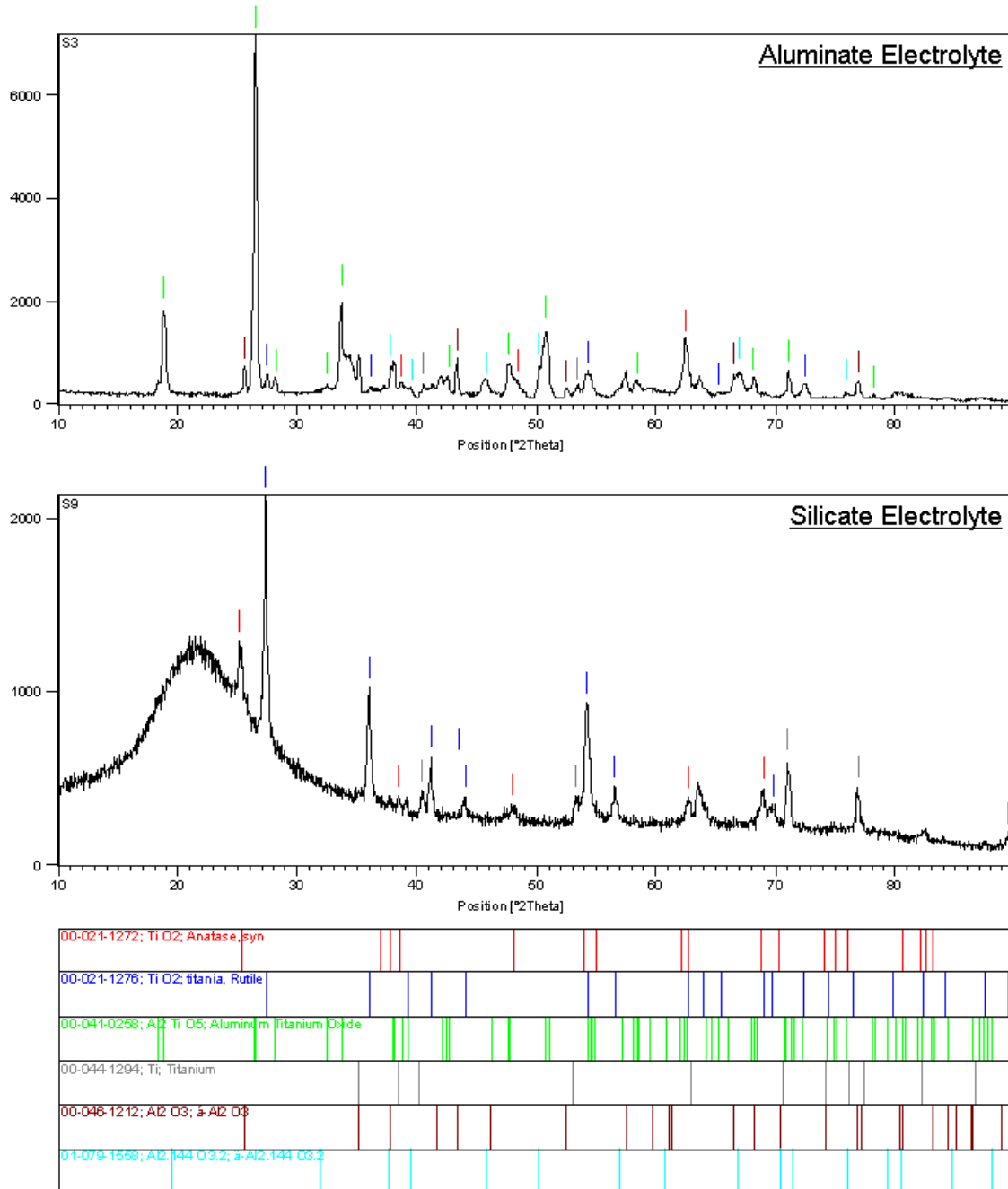


Fig. 7.5. XRD data for aluminate and silicate PEO coatings showing comparisons to reference patterns from the International Centre for Diffraction Data reproduced with permission from A. Collier¹³⁶.

The aluminate coating contained Al_2TiO_5 (aluminium titanate), $\alpha\text{-Al}_2\text{O}_3$, and $\gamma\text{-Al}_2\text{O}_3$. The proportions of the elements in the aluminate coating obtained by EDS, $\text{Al}:\text{Ti}:\text{O} \sim 2:1:6.5$, suggest that Al_2TiO_5 is the dominant phase, with smaller amounts of Al_2O_3 or TiO_2 .

In the phosphate coating, the ratio Al:Ti:O $\sim$ 1:2:6.5 suggests an approximate ratio of between 4:1 and 2:1 for TiO₂:Al₂TiO₅ (TiO₂ and Al₂TiO₅ were phases identified using XRD). However, it is clear that TiO₂ is the dominant phase, but there is a significant proportion of Al₂TiO₅ present as well. The surface of this coating had a slightly increased phosphorus content compared to the bulk. A possible explanation for this is the precipitation of salts from the electrolyte towards the end of processing.

The XRD results of the silicate (Fig. 7.5) and mixed coatings both exhibited large amorphous responses. As both of these electrolytes contained sodium silicate, the amorphous material is expected to contain silica, SiO₂²¹⁸, in addition to amorphous titania, TiO₂. EDS scans on the surface of the silicate electrolyte coating showed that the surface had a slightly higher proportion of silicon and a lower proportion of titanium, suggesting that a higher proportion of silica may be present at the surface of the coating than in the bulk.

The coating from the mixed electrolyte exhibited crystalline peaks for Al₂TiO₅ (but not alumina) despite there being no aluminium in the electrolyte. The aluminium to form this must have originated from the Ti-6Al-4V substrate. The mixed electrolyte coating has much more varied bulk EDS results, indicating that different ratios of phases exist in different areas. Surface EDS scans of this coating had much more uniformity than the bulk. Significant amounts of silicon were detected in the EDS analysis of the mixed electrolyte coatings, again suggesting the presence of amorphous silica in the outer surface of the coating. The atomic ratio of Si:O is approximately 2:7 (pure SiO₂ is 1:2), indicating that other oxide phases could be present at the surface.

7.3.3 Mechanical Properties

For all materials, accurate characterisation of the mechanical properties like hardness and elastic modulus is required for design purposes as well as prediction/explanation of performance in erosive and abrasive wear. For bulk, homogenous materials this can be determined by standard indentation on a polished surface and mechanical testing techniques on standard specimen shapes. However, for coated systems, it is desirable to know the interfacial properties and if there is any property variation through the

coating thickness. Several indentation techniques^{5, 132} and analyses have proposed for this purpose on thin ($<10\ \mu\text{m}$), hard coatings which take the adhesion and failure modes of the coatings into account. However, nanoindentation allows for sufficiently small volumes of material to be interrogated that on thick ($>10\ \mu\text{m}$) coatings the properties of a specific small area within the thickness of a coating can be determined by indentation on the coating cross section. This simple method allows for the properties of the coating to be determined as a function of distance from the substrate interface.

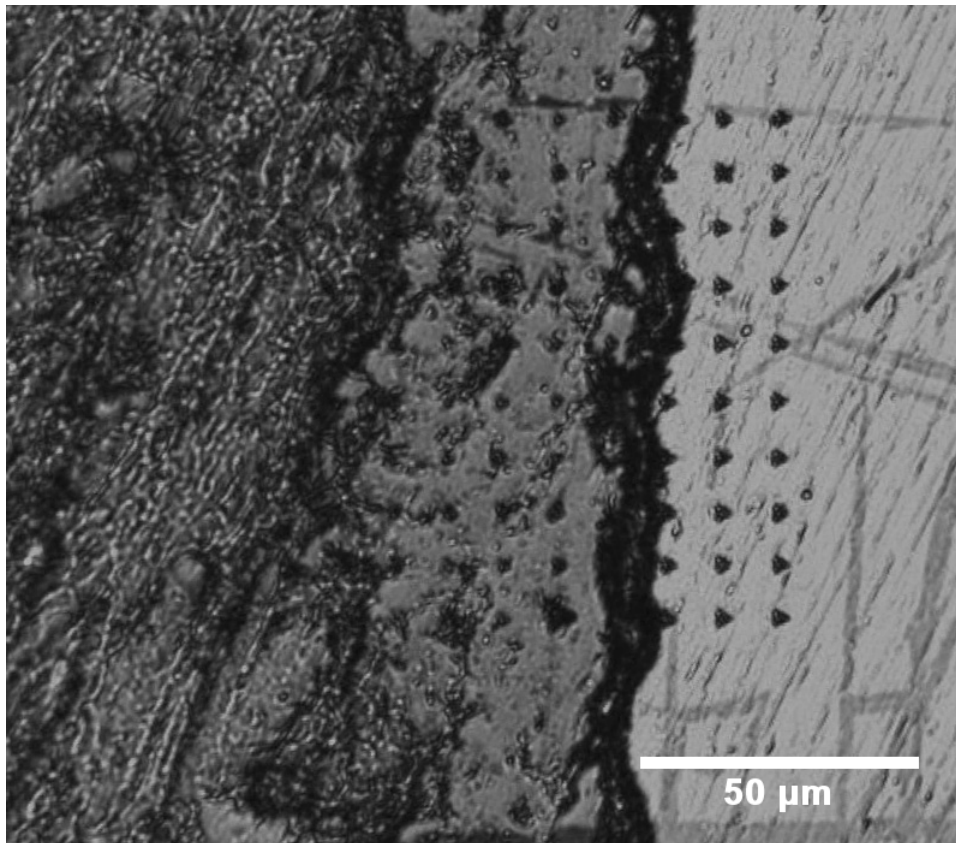
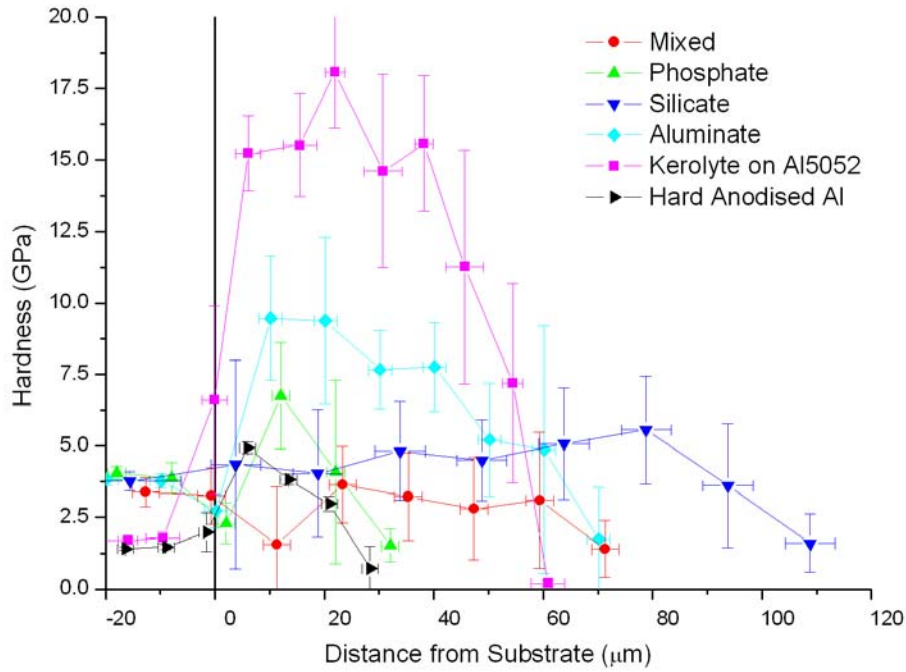
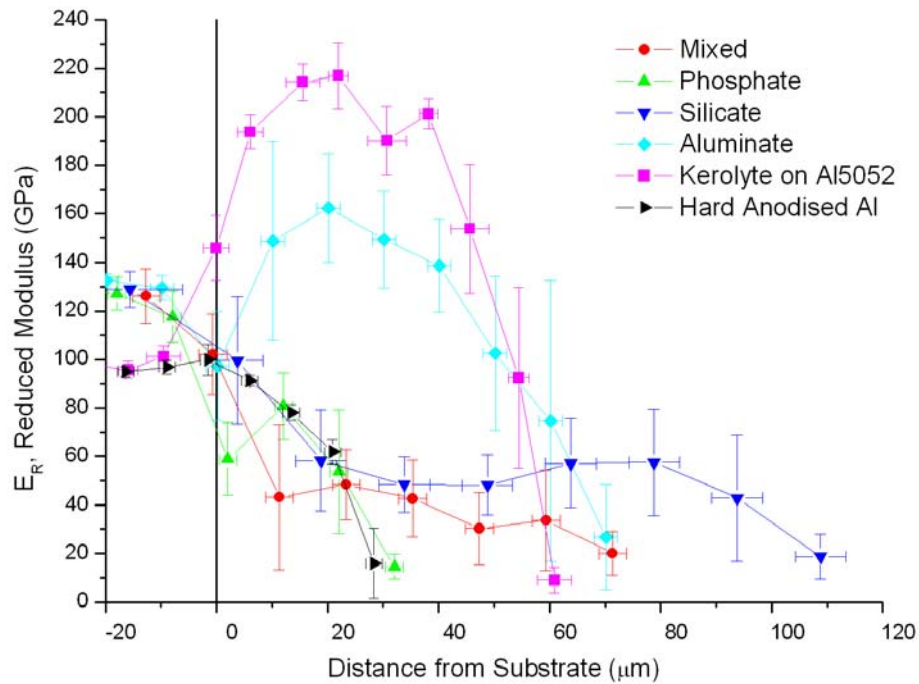


Fig. 7.6. Optical micrograph of an indentation grid on the cross section of the aluminate PEO coating on Ti-6Al-4V with the substrate on the right.

Using large arrays of 10 by 10 indents spread across a section of the coating thickness at staggered intervals (e.g. Fig. 7.6), the properties of the several coatings and the near surface of the substrates were determined as a function of distance from the substrate interface (Fig. 7.7). As indentations were made to a pre-set maximum depth, larger indentations correspond to the indentation making initial contact within a pore.



a)



b)

Fig. 7.7. Nanoindentation results as a function of distance from the substrate interface.

For results at negative distances from the substrate interface, the indents fell within the substrate materials. At distance zero, several results show a distinct depression. This corresponds to indents falling into a debond crack, thus lowering the actual contact areas. Vertical error bars correspond to the standard deviation of the results for each column of indents in the array. The large degree of scatter observed is

presumably due to the coating porosity. Horizontal error bars correspond to the deviation in distance within the rows from the irregular substrate interface. Low final values at the greatest distance from the substrate of each coating's results correspond to the thermoset mount.

The coatings on aluminium alloys displayed the greatest disparity in properties, with the PEO coating displaying the highest hardness and modulus observed of all the coatings and the anodised coating showing relatively low values. This illustrates the difference in behaviour between crystalline and amorphous alumina coatings.

Of the coatings on Ti-6Al-4V, the coating generated with the aluminate electrolyte showed the greatest hardness and modulus values. This could be attributed to the high proportion of Al_2TiO_5 within the coating. The other coating containing Al_2TiO_5 (phosphate coating) demonstrated the second highest hardness values. However, the high modulus values observed for the aluminate coating, but not in the phosphate coating (Fig. 7.4b) suggest that the alumina phases might be making a significant contribution. The lower modulus values for the phosphate coating could be due to porosity. Typically, coatings displayed the highest hardness values near the substrate and decreasing hardness with increasing distance from the substrate, possibly due to increasing porosity near the surface. Only the silicate coating demonstrated increasing hardness and modulus with distance from the surface, slightly increasing until nearing the interface with the thermoset mount. This is possibly due to the increasing content of SiO_2 observed near the surface in EDS measurements.

7.4 Multiple Impact Indentation

In §6.3 and §6.4, impact indentation was discussed focusing on single impacts on fresh surfaces of superelastic metal. The data were generated using the Dynamic Hardness module. The high sampling rate allowed the process of impact, penetration and rebound to be analysed. Low sampling rate data, for repeated impacts at a single location, can also be acquired using the Multiple Impulse module. This is thought to simulate repetitive contact wear and impact fatigue conditions.

7.4.1 Low Sampling Rate Data Analysis

A typical displacement-time relationship for a plastic material, 304L steel, using an accelerating load of 1 mN is shown in Figure 7.8. Figure 7.8b illustrates the limited sampling resolution attained by this technique.

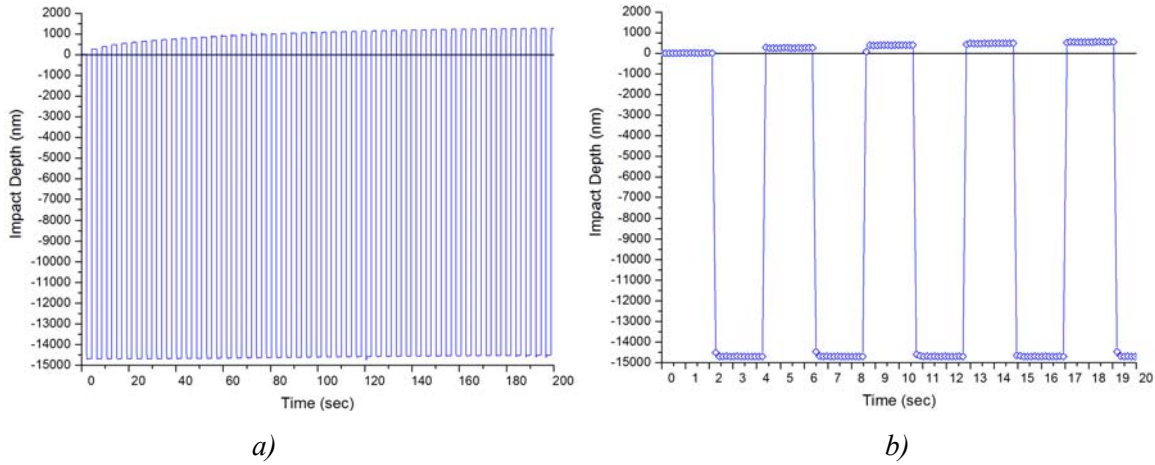


Fig. 7.8. Impact depth as a function of time over a) 200 seconds and b) 20 seconds.

Initially, the indenter rests against the sample under the applied force. It is then retracted against the solenoid. When the solenoid is released, the indenter swings forward and impacts the sample. It appears that the indenter instantly comes to rest at a fixed penetration depth and rests there under the applied force load for the entire time, against the sample. Thus, the only parameter which can be extracted from data of this type is the final rest depth, as a function of number of impacts. This process is expedited by using a bespoke LabVIEW virtual instrument (Fig. 7.9). This program parses the data and calculates the mean and standard deviation of the plateaux corresponding to the period in contact with the sample, neglecting the final and initial 20% of the plateau to avoid error from data points during the flight period. These values are then exported to an ASCII file, or, if there are multiple sets of data, the program can average the sets to extract statistical rest depth values as a function of number of impacts.

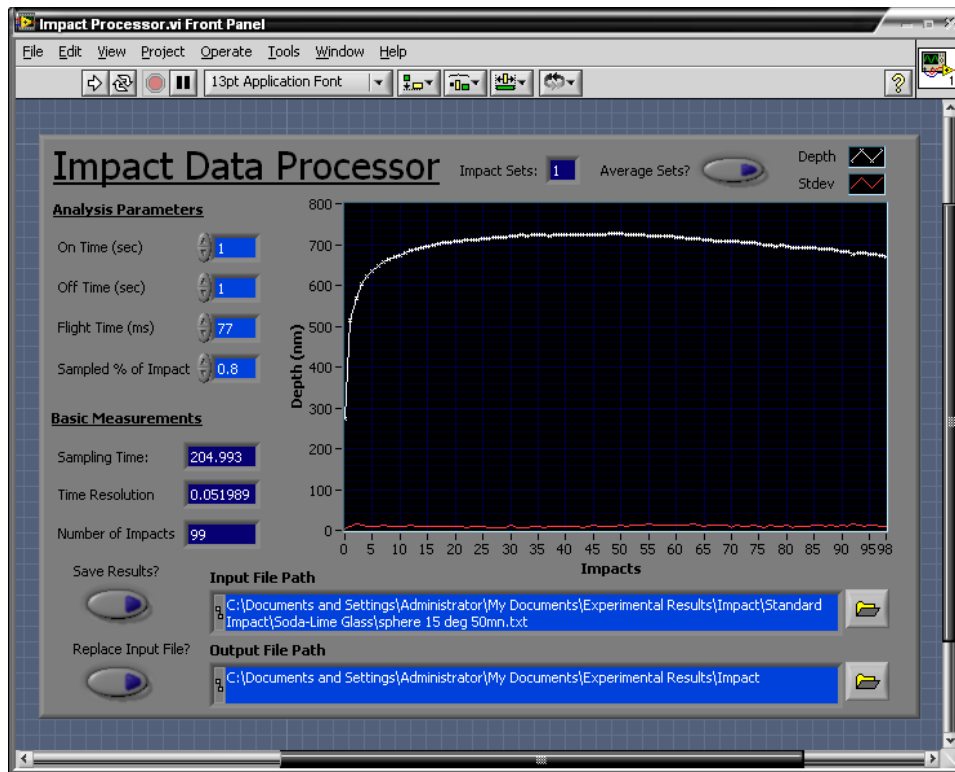


Fig. 7.9. LabVIEW virtual instrument for analysis of low sampling rate data.

By performing a series of impacts at various acceleration loads and extracting the rest depth as a function of impact number, a contour plot (Fig. 7.10a) can be generated, which illustrates the material's behaviour over a wide range of conditions.

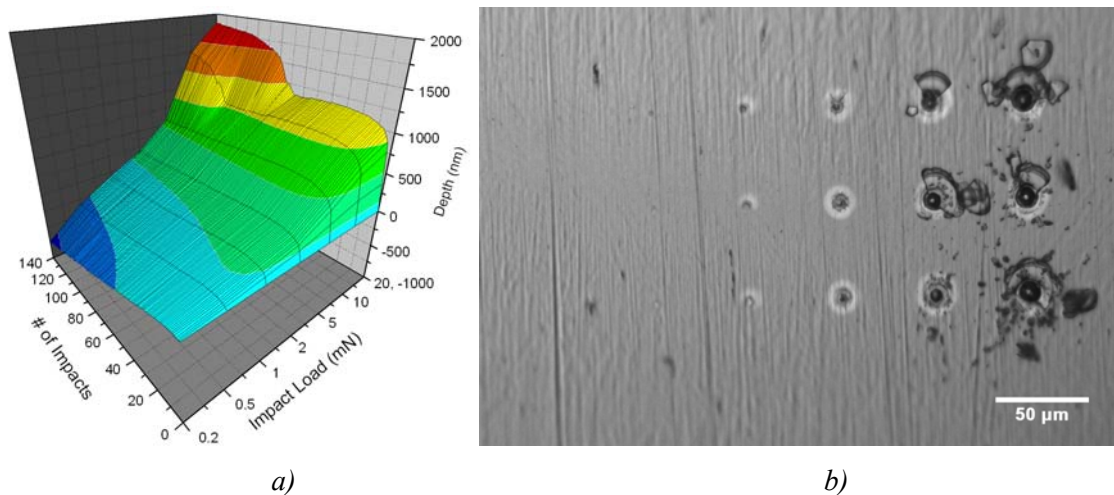


Fig. 7.10. Sample contour plot a) and corresponding optical micrograph b) from impact testing of a sol-gel coating on a steel substrate.

An example of the contour plots generated using this technique is shown in Fig. 7.10a. The data for this plot was acquired by impacting a silicate sol-gel coating on a steel substrate. Several trends can be observed in the contour plot. At low impact accelerations loads, depth initially increases and then decreases into negative values

with increasing number of impacts. This indicates that some thermal expansion or a blistering phenomenon is causing the sample to swell outwards towards the impactor. At mid-range impact loads, the depth increases with successive impacts asymptotically towards a deformation or fatigue limit depth for that impact load. At high loads, depth increases swiftly during the first few impacts and then reaches an asymptote. When depth is at an asymptote, each impact is effectively subjecting the material to rapid fatigue loading within the sample's elastic regime. After a number of these fatigue impacts, the sol-gel coating is observed to fracture and fail. This is seen in both the rapid increase in depth on the contour plots and in the corresponding micrograph of the impact test grid (Fig. 7.10b).

7.4.2 Impact Hardness Analysis

Multiple impact testing is analogous to multiple load/unload indentation testing, but with much higher strain rates and energies involved. Analysis of this testing generally falls into two categories: property extraction and fatigue observation. Fatigue observation can be accomplished by following the trends in penetration depth (Fig. 7.11a) or deformed volume (Fig. 7.11b) with increasing number of impacts. For the extraction of intrinsic properties, such as dynamic indentation hardness or modulus, it is useful to focus on the first impact, since it starts from a presumptively strain-free state. This is not actually the case with this testing, since the sample is preloaded with the applied acceleration load before the indenter is retracted for the first impact. However, it can be seen in Figure 7.11c that the largest volume increase is observed during the first impact, with successive impacts showing progressively smaller increases.

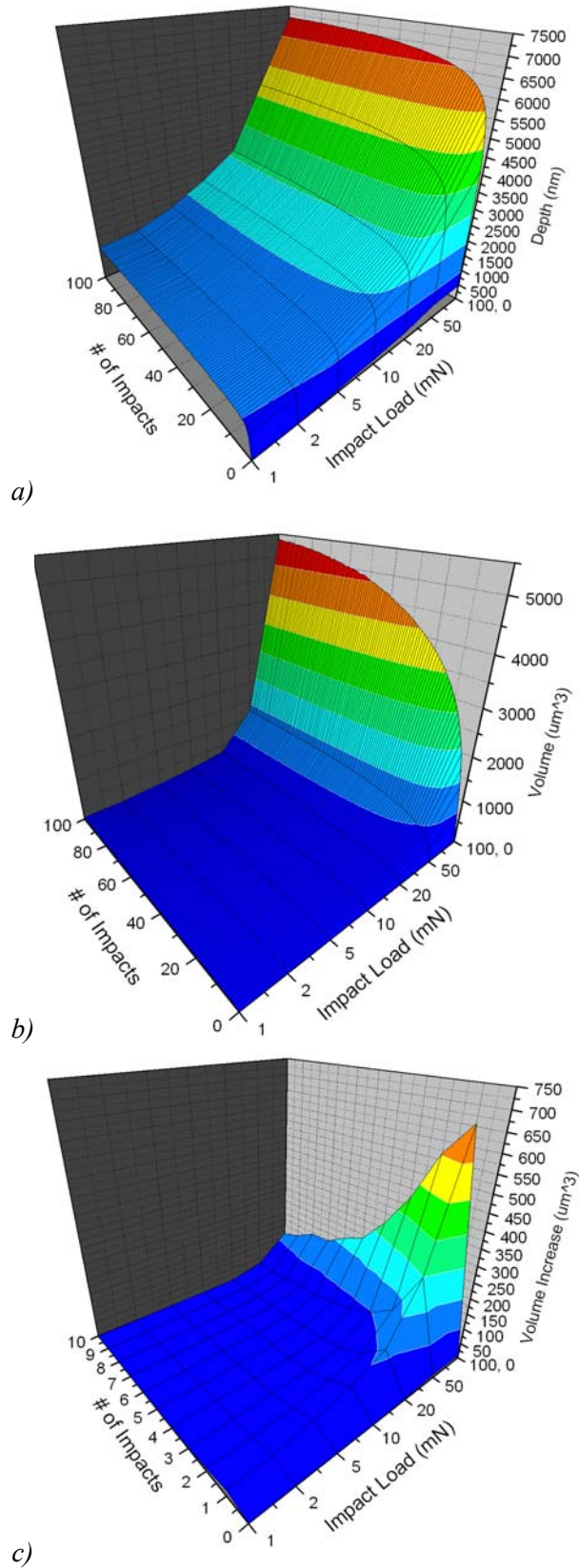


Fig. 7.11. Impact contour plots showing the relation of a) depth, b) volume and c) volume increase to impact load and number of impacts on 304L steel.

The deformed volume (Fig. 7.11b) is calculated from the rest depth using an AFM measured diamond area function for the conospheroidal indenter tip used. Since the

sample is elastically loaded with the acceleration load during the period when rest depth is measured, the sample can be expected to conform to the indenter shape. However, error may occur from pile-up or sink-in causing the depth of the contact circle to deviate from the initial surface plane. Volume increase (Fig. 7.11c) is determined from difference in depth between impacts.

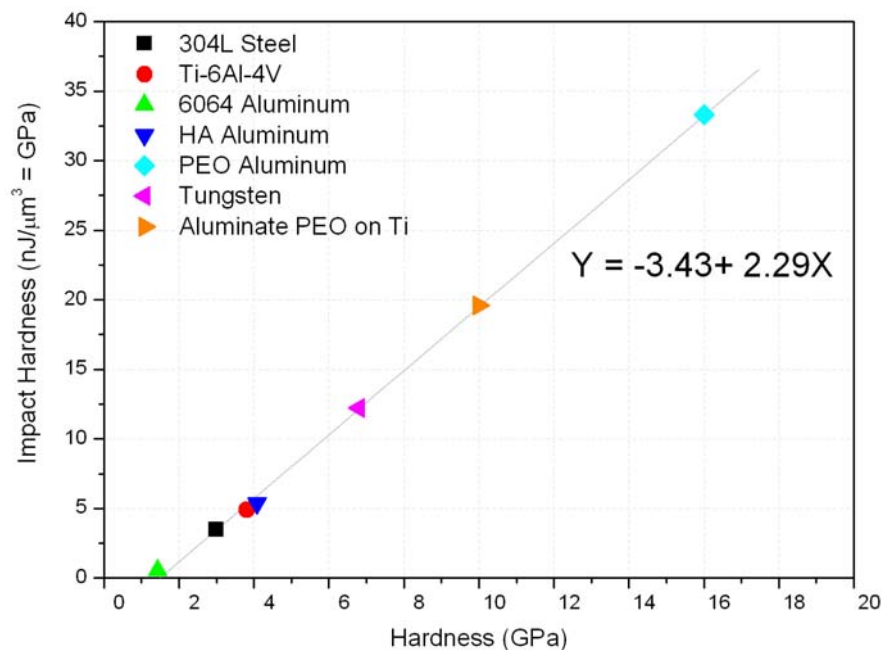
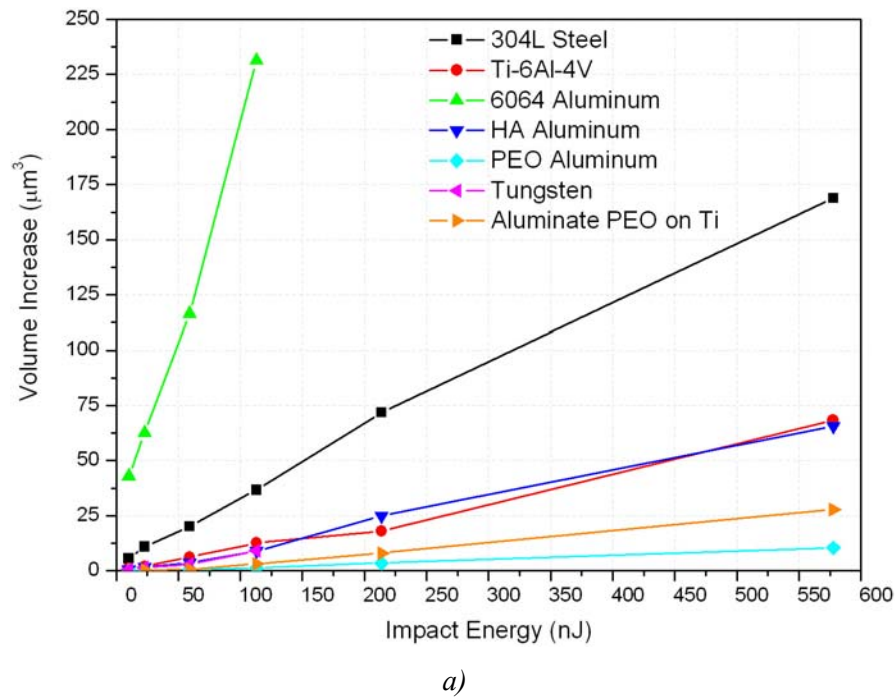


Fig. 7.12. The relation of a) volume increase from first impact to impact incident energy and b) the impact hardness to the Berkovich indentation hardness for several metals and ceramic coating.

There is interest in the relationship between the deformed volume from the first impact (or the volume increase from the first impact to the applied impact acceleration load) and the applied acceleration load, because the acceleration load is directly related to the incident impact energy (as calibrated in §4.4). The ratio of incident impact energy to maximum deformed volume is Koeppel and Subhash's¹⁰⁰ definition of dynamic hardness (Eqn. 3.3).

It is observed in Figure 7.12a that the volume increase, or deformed volume from the first impact, displays an approximately linear relation to the impact energy. By taking the inverse of the slopes of a linear fit of these data, the mean dynamic impact hardness can be determined for a range of impact energies. The impact hardness values thus determined are observed to show a linear relation to the Berkovich indentation hardness (Fig. 7.12b). However, the slope of this relation is greater than 2 and does not intersect the origin. This suggests that some additional factors, e.g. dynamic compliance and the effect of the deformation from the initial preload, need to be taken into account. A perfect correlation between impact hardness and indentation hardness is not expected, however, since impact is conducted with a spherical tip instead of a Berkovich. Also, strain rate effects would likely give rise to higher impact hardness values than indentation hardness.

7.4.3 Multiple Impact Fatigue

With increasing numbers of impacts, the behaviour significantly departs from any analogy to conventional indentation. As mentioned in §7.3.1, three behaviours are typically observed: elastic fatigue producing decreasing depth by an unknown mechanism, smooth plastic yielding, and plastic failure/fracture producing sudden increase in depth. Since comparison of contour plots is inefficient for handling large numbers of materials, Figure 7.13 displays the normalised depth values, the depth divided by the maximum depth achieved during the test, as a function of the number of impacts at 1 mN and 100 mN accelerating loads.

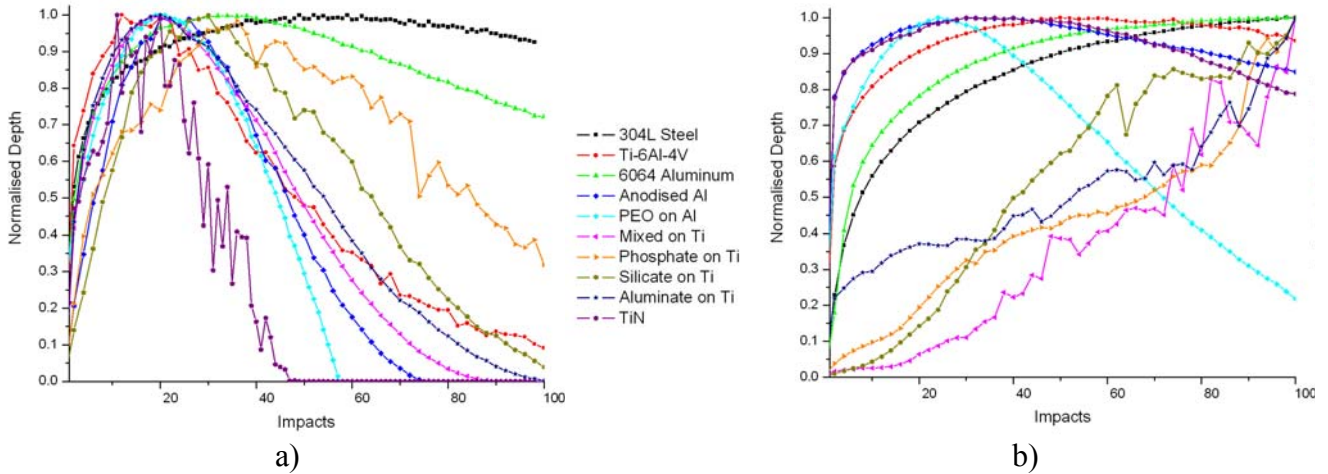
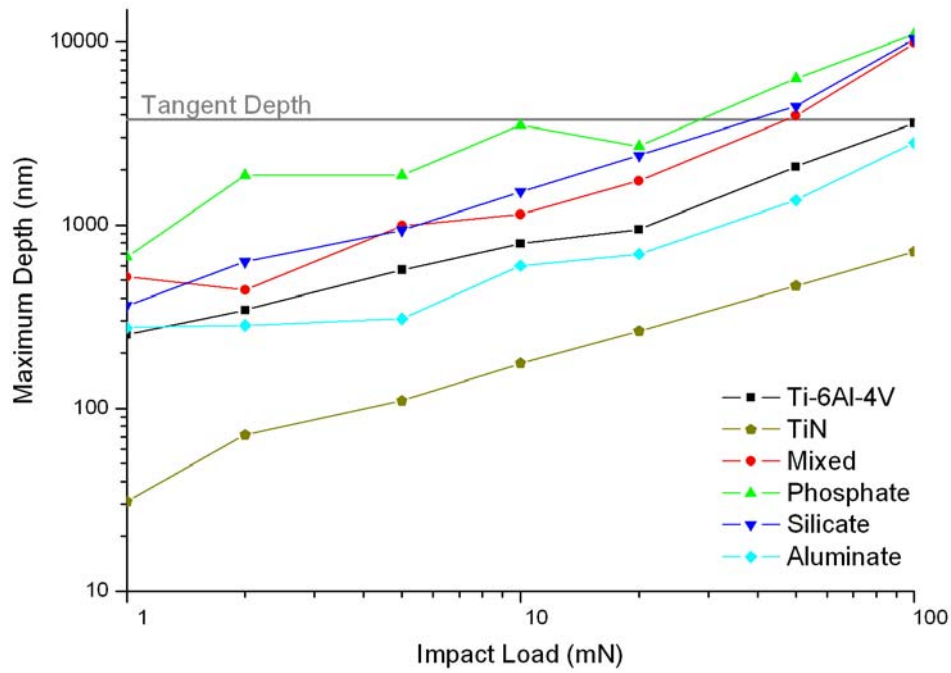


Fig. 7.13. Normalised depth as a function of number of impacts for a) 1 mN acceleration load and b) 100 mN acceleration load, for various materials.

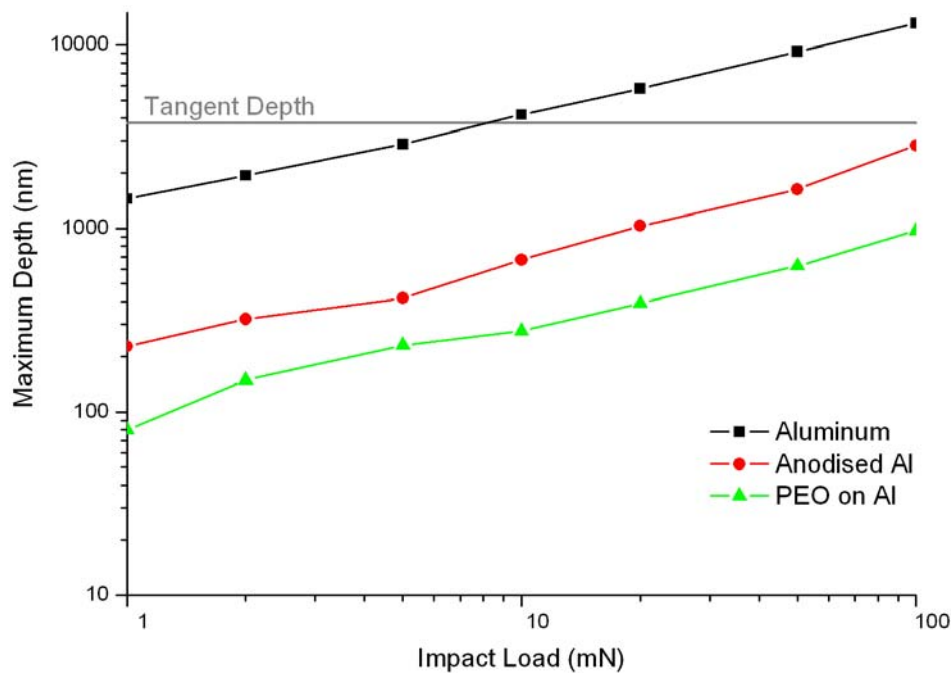
For impacts at the lowest acceleration load, 1 mN, all materials display smooth plastic yielding until some maximum depth is achieved (Fig. 7.13a). After this is reached, the impact indentation contact impression in the material is sufficiently large to be able to initially accommodate the impact force elastically. The depth then decreases by some unknown mechanism as the material is fatigued. At the highest acceleration load, 100 mN, all the PEO coatings generated on Ti-6Al-4V demonstrate the irregularly increasing depth-impact trend characteristic of micro-fractures/brittle failure. Since the data displayed are the averaged results of several datasets, the sharp increases and decreases in depth accompanying failure are not as large as can be observed in the individual datasets.

The aluminium and 304L steel samples show steady plastic deformation for the entire range of impacts. This is likely due to the penetration depths being sufficiently deep to be in the conical portion of the conospheroidal tip used, so that the indenter is effectively ‘sharper’. All other materials tested show similar behaviour to the lower acceleration loads with a maximum depth being achieved, followed by elastic fatigue.

Two parameters emerge from this comparison as relevant to the overall performance of the materials during this test: the maximum deformation achieved as a function of acceleration load and the number of impacts necessary to achieve maximum deformation. The first of these parameters, maximum depth, is shown in Figure 7.14.



a)



b)

Fig. 7.14. Maximum impact indentation penetration depth, as a function of accelerating (impact) load for a) Ti-6Al-4V coating systems and b) aluminium alloy coating systems.

For the titanium alloy coatings (Fig. 7.14a), only the aluminate PEO coating and the commercial TiN coating demonstrate superior penetration resistance to the substrate alloy. All the materials tested show power law trends of maximum depth with impact load, which plot as linear on log-log graphs. This is attributed to the effect of the conospheroidal indenter geometry used. Some deviations are observed at the highest

and lowest impact loads, with those at the highest loads being attributed to fractures/brittle failures. The phosphate coating shows different behaviour from the power law trends, which is attributed to the microstructure introducing sufficient variation that the averaging of several datasets was unable to completely remove. Values above the ideal tangent depth of the conospheroidal indenter used also have the influence of the indenter geometry acting more as a blunt cone than a sphere.

For the aluminium alloy coating systems, both coatings show significant improvements on impact penetration resistance over the substrate alloy, with the PEO coating providing the greatest resistance. The anodised coating provided similar impact penetration resistance to the Ti-6Al-4V alloy.

The first of the two parameters, maximum depth, is of obvious significance. However, the relationship of the second parameter, number of impacts to maximum depth, to performance is less clear. If the material is smoothly yielding plastically, it may be beneficial that the maximum achieved depth is at the final impact. This would mean the material is able to plastically absorb the impacts without fracture or failure and could contribute to good wear resistance. However, if the material is already fracturing or failing, this would also appear as the final depth being the maximum depth. The case of elastic fatigue is the most encouraging aspect of this parameter, since if the maximum depth occurs before the final impact then the material is able to elastically accommodate the impact force. Thus, if the maximum depth occurs prior to the final impact, it is interpreted as beneficial to performance, but if it occurs at the final impact its relation to performance is uncertain.

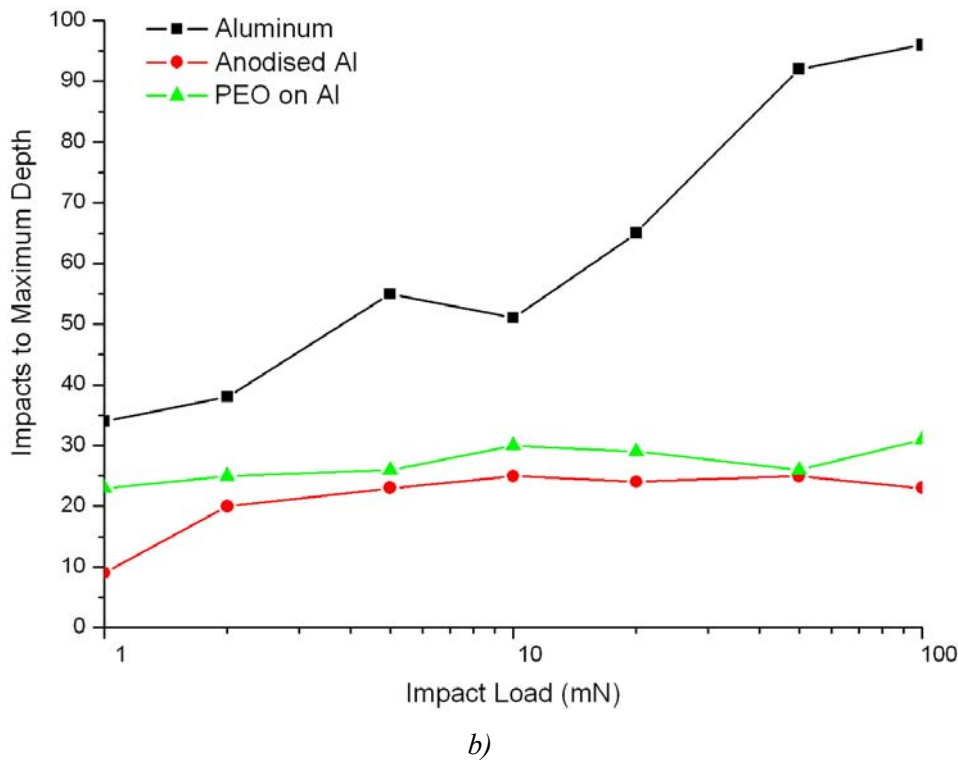
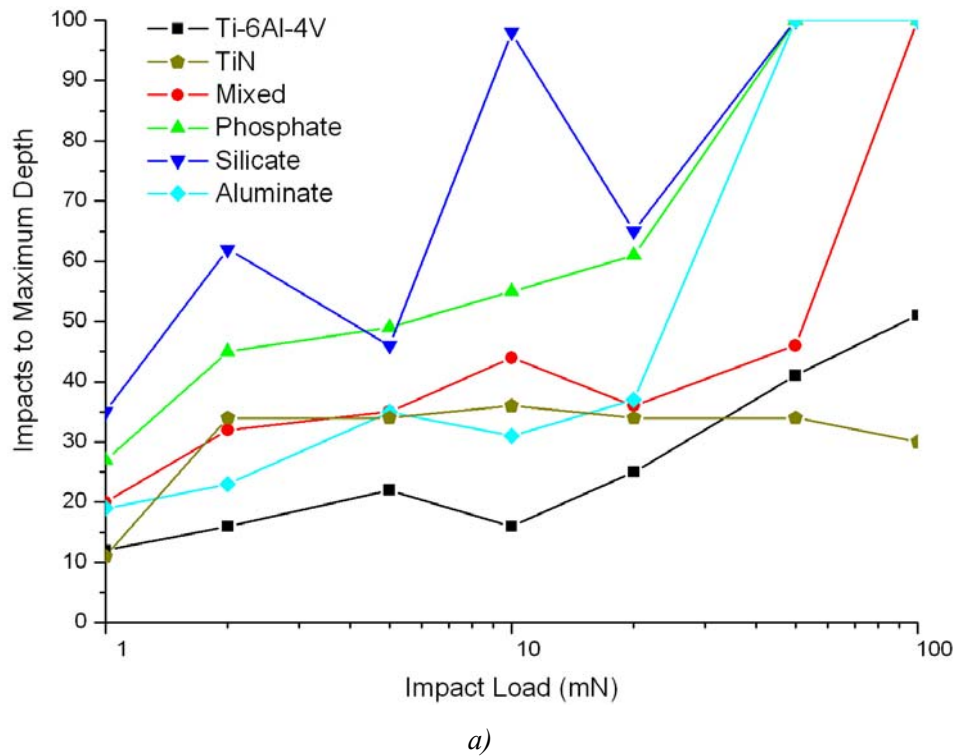


Fig. 7.15. Impacts to maximum penetration depth, as a function of indentation force for a) Ti-6Al-4V coating systems and b) aluminium alloy coating systems.

At the lowest impact loads, the maximum depths all occur before the final impact (Fig. 7.15). The number of impacts to maximum depth is observed to increase with increasing impact load for the PEO coatings on Ti-6Al-4V and for the substrate alloys. For the PEO coatings, this is attributed to brittle fractures at the high impact

loads, but for the metallic substrates it is attributed to the higher strain produced by the conical portion of the indenter geometry penetrating into the sample.

7.4.4 Impact Indentation at Oblique Incidence

There are several motivations for using oblique incidence, since erodent particles often impact obliquely and scratch indentation also effectively involves loading at an oblique angle. Several factors are relevant to adapting an indentation system for oblique incidence experiments and analysing the resulting data.

7.4.4.1 Adaptation for Oblique Testing

There are two approaches to adapting a system for oblique testing: varying the angle of the indenter approach or varying the angle of the sample orientation. Since nearly all indentation systems incorporate a rigid frame to minimise compliance, the approach of changing the orientation of the sample is usually simpler to implement.



Fig. 7.16. Sample mounts for indentation at various oblique angles.

This was accomplished by adhering the samples to mounts (Fig. 7.16) which had been sectioned at the desired angles of incidence, i.e. 15° , 30° and 45° . These mounts were then oriented such that the plane of oblique incidence was coincident with the plane of pendulum motion. This prevented any lateral forces being applied to the pendulum during impact indentation.

7.4.4.2 Measurement Corrections

For analytic simplicity, and to reduce the possibility of the indenter ‘broadside’ into the sample, conospheroidal indenters were used for all oblique incidence experiments. As mentioned in §2.3.1, conospheroidal indenters approximate to spheres until a tangent depth, is reached where a transition to conical geometry occurs. This tangent depth is a function of the indenter radius, cone angle and incidence angle:

$$h_{\tan} = R - R \cdot \sin(\varphi + \theta_i) \quad (7.1).$$

This relation is illustrated for several cone angles over the usable range of incidence angles, in Figure 7.17. This demonstrates that oblique testing at high angles of incidence, $>45^\circ$, is not feasible with conospheroidal geometries. A different geometry, such as a sphere on the end of a rod with radius much less than that of the sphere, would be required for this.

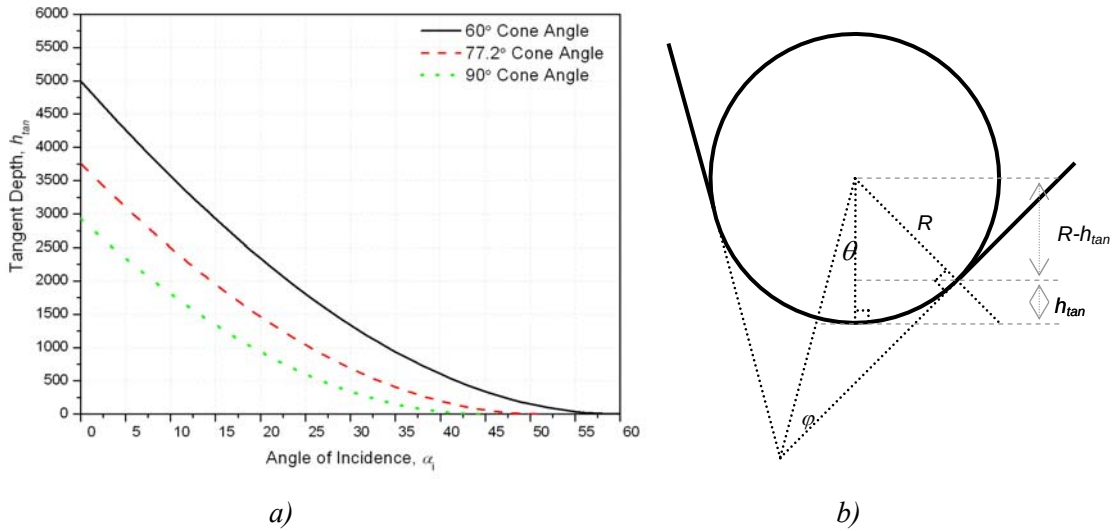


Fig. 7.17. Variation in tangent depth with angle of incidence a) for three cone angles and b) as a schematic illustration.

Another consideration necessary for analysis of data resulting from oblique incidence testing is conversion of the measured depths into the component normal and transverse displacements into the material. These are simple functions of the angle of incidence:

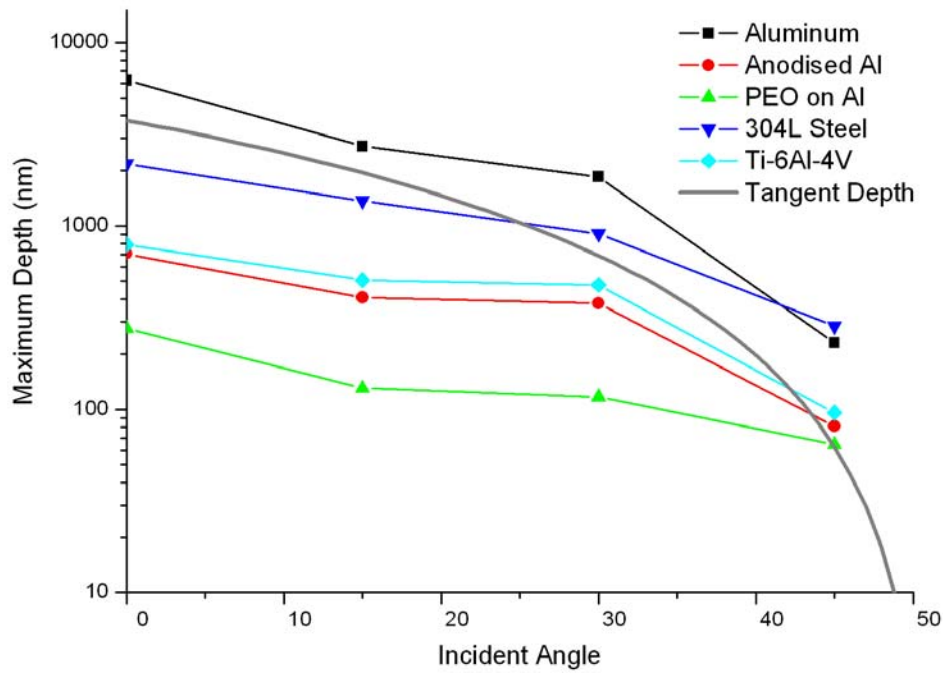
$$h_{\text{normal}} = h_m \cos(\theta_i) \quad (7.2)$$

and
$$h_{\text{transverse}} = h_m \sin(\theta_i) \quad (7.3).$$

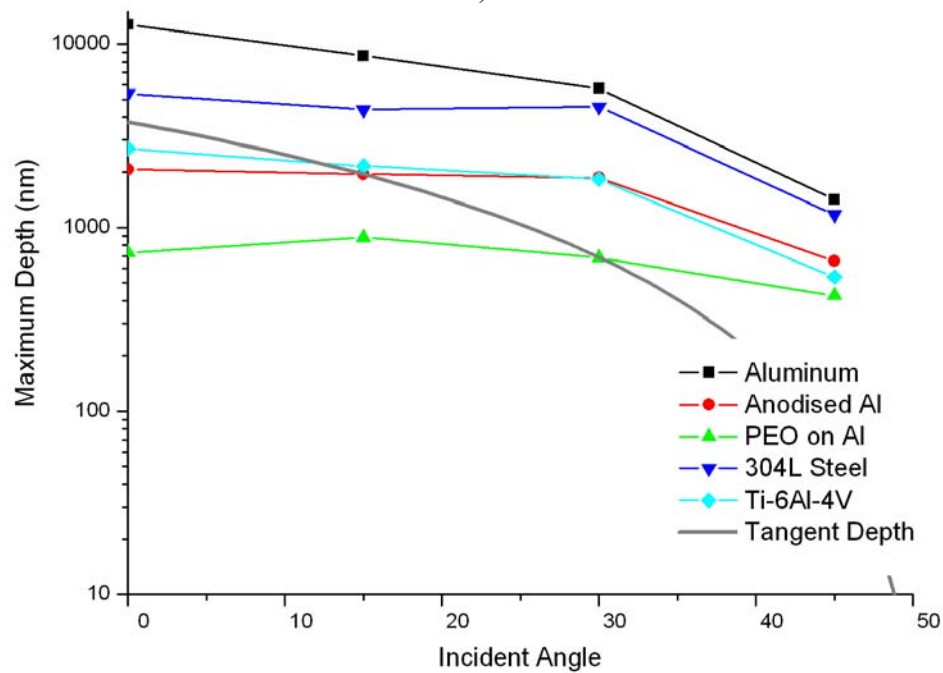
Due to the small incident angles investigated in this study, the transverse displacements are neglected in the analysis due to their comparatively small scale. The effect of incident angle on the normal displacement is focused upon instead.

7.4.4.3 Maximum Depths

As mentioned in the previous section, the tangent depth of a conospheroidal indenter decreases significantly with increasing incident angle. The ideal relation for a conospheroidal indenter with a nominal tip radius of 10 microns and a (measured) cone angle of 77.2° is shown in Figure 7.18, with the maximum depths from impact indentation.



a)



b)

Fig. 7.18. Maximum penetration depth, as a function of incident angle for a) 10 mN and b) 100 mN acceleration load.

Maximum vertical penetration depth is generally observed to decrease with increasing incident angle. In part, this can be attributed to a decrease in the normal impact force as the impact energy is increasingly split into transverse and normal components with increasing incident angle. For values greater than the tangent depth, it is useful to bear in mind that the indenter contact area increases significantly with incident angle. This

is due to the side of the conical portion of the conospheroidal indenter encountering the sample. The additional parabolic extension of the contact circle increases with increasing incident angle. This is most apparent in the results from 45° incident angle, where nearly all results are above the tangent depth, and a corresponding depression in maximum depth is observed.

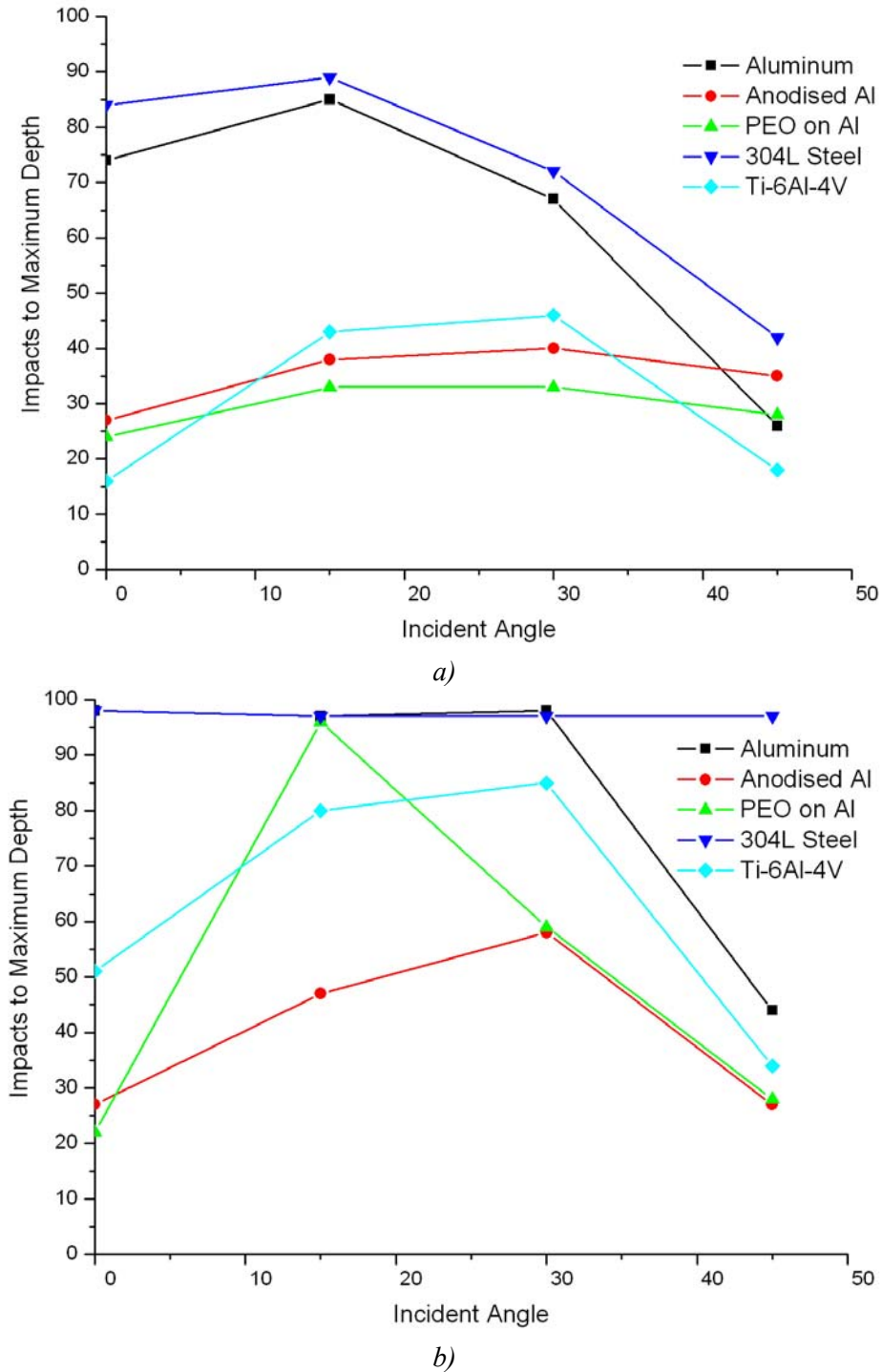


Fig. 7.19. Impacts to maximum penetration depth, as a function of incident angle for a) 10 mN and b) 100 mN acceleration load.

The effect of this increase in contact area and departure from spherical geometry is observable as a reduction in number of impacts to maximum depth (Fig. 7.19). Prior to this transition, the number of impacts to maximum depth increases with incident angle. This may be due to the additional shear force component decreasing the ability of the material to accommodate the impacts elastically. It is worth noting that the PEO coating on aluminium demonstrated an increase in maximum depth at 15° incident angle, and that maximum depth occurred at the final impact, which suggests failure/fracture.

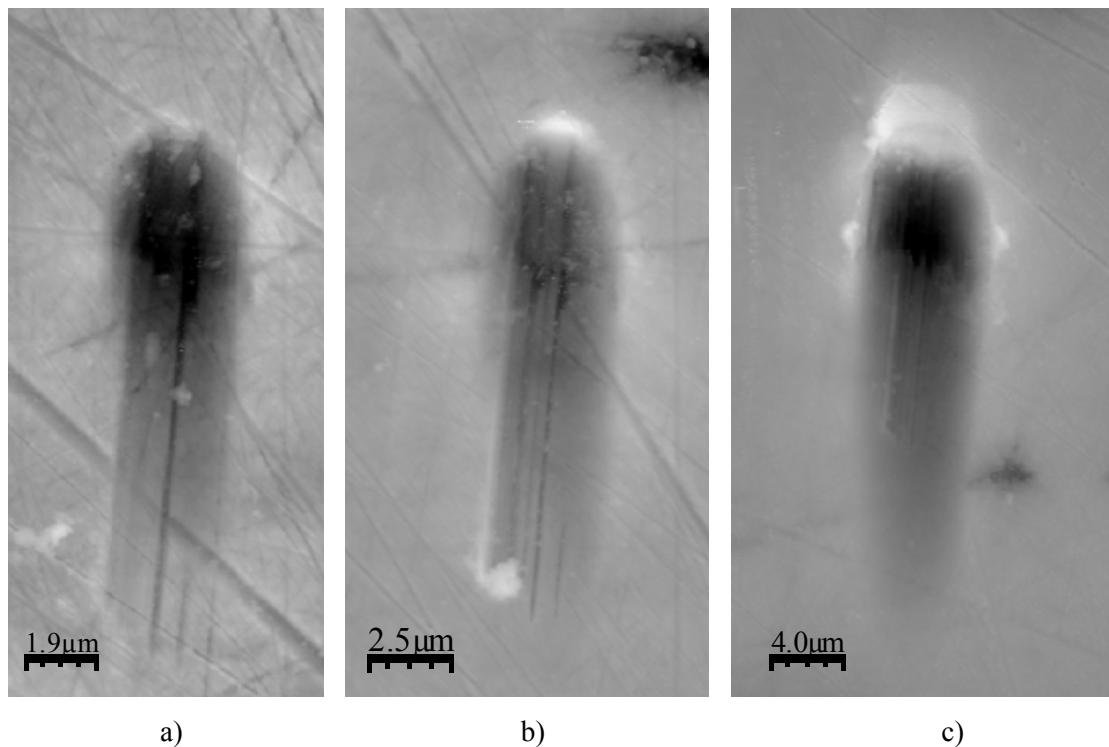


Fig. 7.20. AFM topographs of impact indentation impression at 45° incidence for a) 1 mN, b) 5 mN and c) 50 mN acceleration loads on Ti-6Al-4V.

Another aspect of impacts at oblique incidence is the asymmetric pile up around indentations. Figure 7.20 qualitatively illustrates how significant pileup is generated in front of the indenter, with comparatively modest amounts are generated laterally and none behind. The parabolic extension of contact area from the side of the cone is also observable. However, the streaks extending towards the bottom of the depression indicate that the indenter may be skidding down the sample. This would suggest that the pendulum lacks the required lateral stiffness for conducting this sort of test. If that is the case, testing at even higher angles of incidence would exaggerate this problem and possibly result in damage to the pendulum.

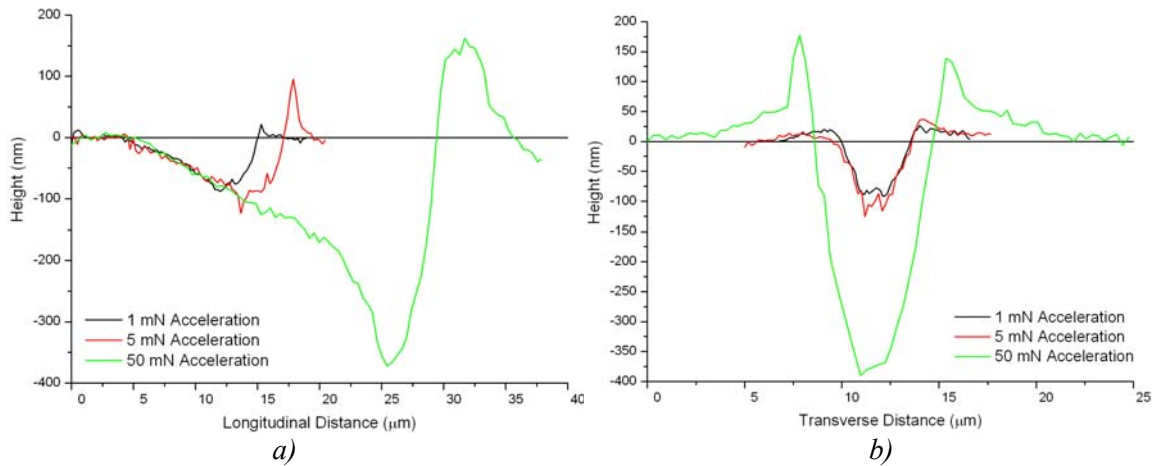


Fig. 7.21. Height profiles from AFM topographs of impact indentations on Ti-6Al-4V in the a) longitudinal and b) transverse orientations.

Figure 7.21 quantitatively illustrates the pile up around the impact indentations at 45° on Ti-6Al-4V.

7.5 Erosive Wear Behaviour

The behaviour of PEO coating systems in erosion was investigated using two different tests. The PEO coatings on Ti-6Al-4V substrates were investigated using a modified sandblasting system. Coatings on aluminium substrates are compared in §7.6 to ASTM G76 standard wear results from the literature – see §7.2.1.

7.5.1 Sandblasting of Ti-6Al-4V Coating

The results of the sandblast erosion testing of the Ti-6Al-4V coating systems conducted by A. Collier¹³⁶ are shown in Figure 7.22. The phosphate, silicate, and mixed coatings lost mass at the highest rates at the start of erosion, followed by the rate gradually decreasing until a “plateau” of erosion, corresponding to the erosion of the now exposed substrate. The aluminate coatings behaved somewhat differently, starting with a slower rate of erosion before entering a period where erosion was more rapid. The bare Ti-6Al-4V substrate gained mass, by retaining erodent fragments, at the start of testing, before eventually settling to lose mass at a rate far lower than any of the coatings.

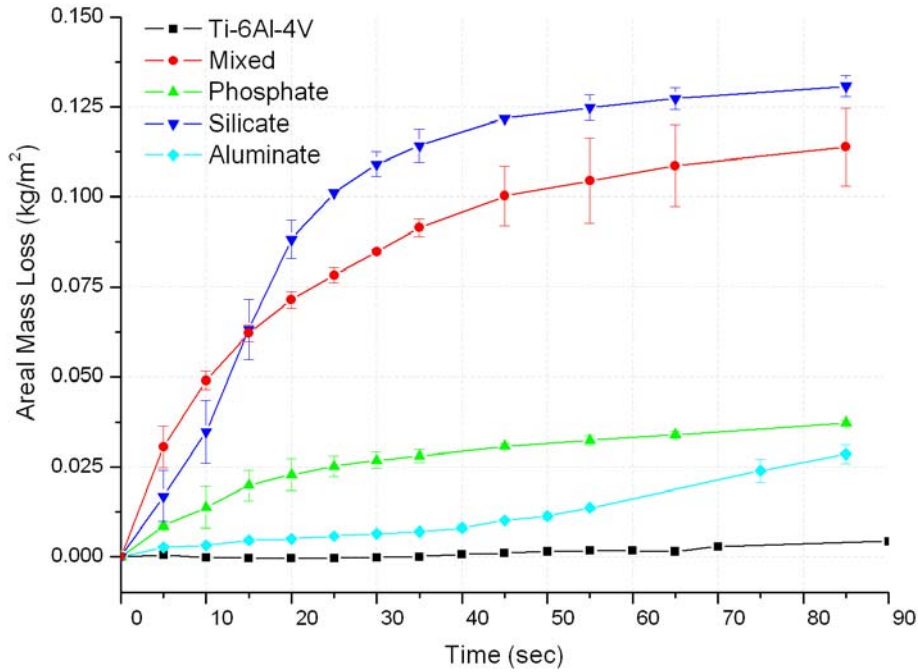


Fig. 7.22. Areal mass loss from sandblast erosion as a function of time for PEO coatings and the Ti-6Al-4V alloy substrate replotted with permission from A. Collier¹³⁶.

The initial gradients of the curves provide a good way of comparing the intrinsic erosive behaviour of the coatings. These data appears to indicate that the aluminate coating has the best erosion resistance (apart from the substrate). On a very simplistic level, it appears that coatings containing more Al_2TiO_5 and TiO_2 (i.e. aluminate and phosphate coatings) have better erosive wear properties than coatings containing SiO_2 (i.e. the silicate and mixed electrolyte coatings). The silicate coating displayed initially lower erosion rates, which then increased and finally decreased as the substrate was exposed. This is consistent with the through-thickness hardness profile observed by nanoindentation (see §7.3.3), with the harder exterior of the coating being removed more slowly, and then the softer interior being removed at a faster rate.

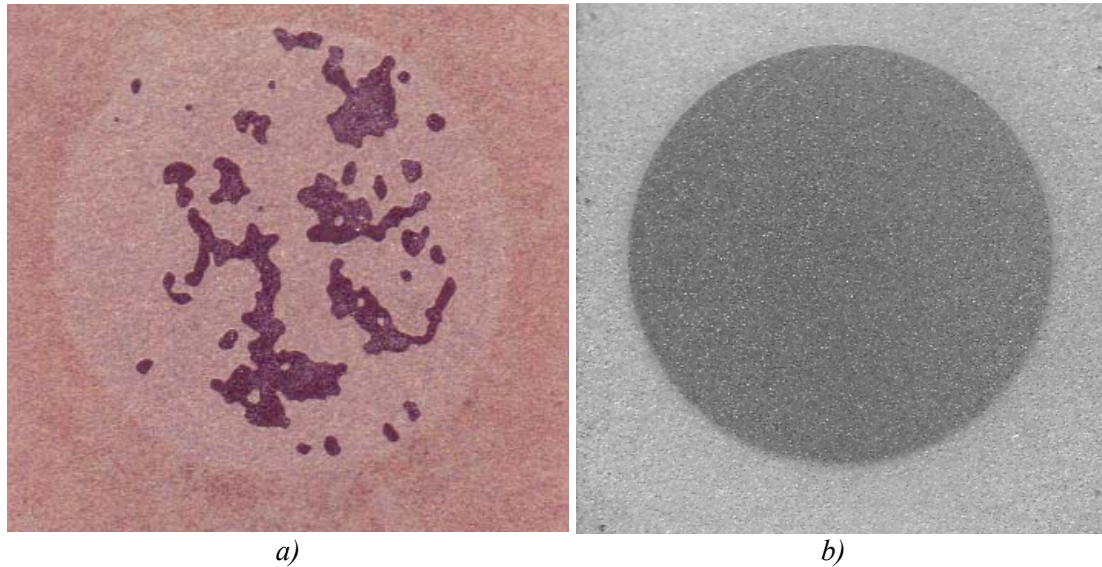


Fig. 7.23. Photographs of erosion scars on a) aluminate and b) mixed PEO coatings after 80 seconds of exposure reproduced with permission from A. Collier¹³⁶.

On a macroscopic scale, the pattern of erosion of the aluminate coating appeared to be significantly different from the others (Fig. 7.23). In addition to initial gradual erosive attrition, after 40 seconds chipping failure was also observed, until complete failure after 200 seconds (not shown in Fig. 7.22). Since Al_2TiO_5 has an anisotropic coefficient of thermal expansion²¹⁹, it is likely to have acquired internal strains and microcracks after forming at high temperature and cooling during PEO processing. These strains and cracks could be a source of the chipping failure. It was also observed in Figure 7.3d that the aluminate coating had largely debonded from the substrate, which could lead to the chipping failure via fracture of the coating.

7.6 Comparison of Wear to Multiple Impact Testing

The normalised initial slope values from the normal incidence sandblast wear testing of the Ti-6Al-4V coating systems are compared to the normalised multiple impact parameters in Figure 7.24. Since all the values are normalised to the performance of the substrate alloy, the Ti-6Al-4V appears as 1 for all tests.

The three measures show similar trends. With the exception of the phosphate coating, the number of impacts to maximum depth gives the same ranking as the sandblasting experiments. The maximum depth parameter gives a similar ranking, with the exception of the aluminate coating being ranked higher than the substrate. The phosphate coating's poor impact performance is attributed to local property variation due to its high porosity.

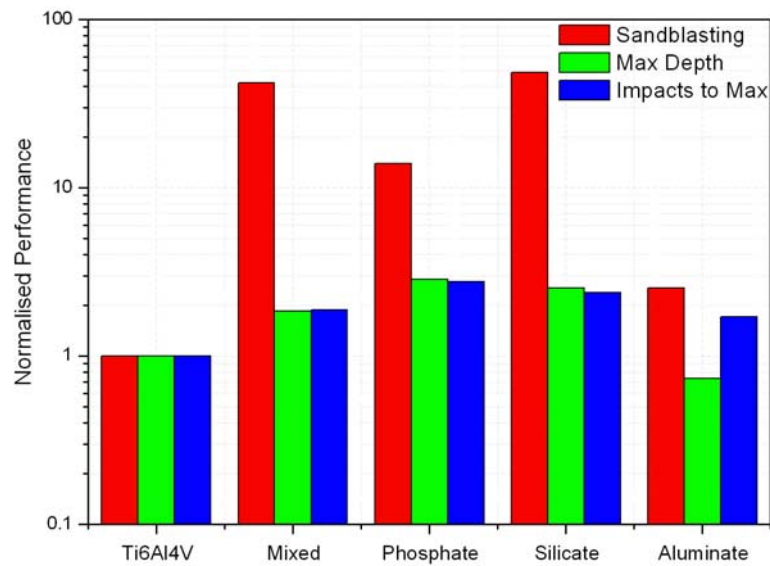


Fig. 7.24. Normalised performance for initial sandblast wear removal rates and multiple impact parameters for PEO coatings and the Ti-6Al-4V alloy substrate.

It is difficult to compare the behaviour of the aluminium alloy coatings in wear, §7.2.1, to the multiple impact behaviour. The behaviour under normal incidence is similar to that of the titanium alloy coatings with the (ductile) substrate outperforming the (brittle) coatings. The oblique incidence multiple impact testing provides useful clues towards this behaviour, especially the AFM images of residual pile up. However, the oblique incidence testing was not able to reach high angles at the energies necessary to directly compare the behaviours with the available wear test data.

7.7 Scratch Indentation

In §2.3.5, the complexity of the strain fields under normal indentation was discussed. In scratch indentation, this complexity is increased by the tangential force applied to perform the scratch. Ideally, the behaviour of a material under scratch loading could be analysed by controlling and measuring both the normal and tangential forces, while monitoring the depth of penetration and acoustic emission of the sample. However, the system utilised in the current work only allowed characterisation of the penetration depth as a function of applied normal load and displacement, with the tangential displacement being controlled via sample positioning motors. Thus, this section focuses on characterisation of the grooves produced by the scratch loading

profiles outlined in §4.5 on PEO coating systems. The possible effects of tangential translation rate and perfectly elastic scratches are also considered.

7.7.1 Displacement Rate Sensitivity

The effect of variation in lateral displacement rate was investigated on Ti-6Al-4V alloy (Fig. 7.25), using a normal load of 50 mN to ensure that no strain rate effects¹²¹ were observed for this scratch regime. Ti-6Al-4V was chosen for this purpose, since it is believed to be the most strain rate sensitive of the samples examined.

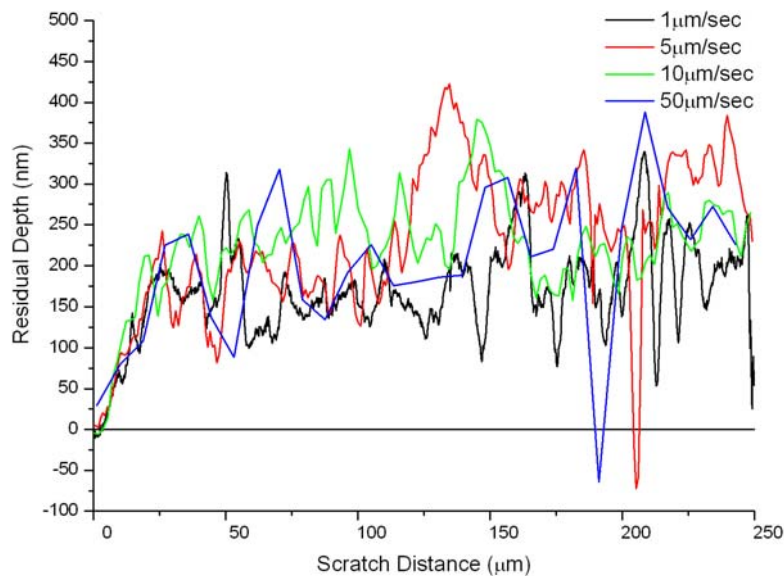


Fig. 7.25. Residual scratch depth as a function of scratch distance, for several different translation speeds, on Ti-6Al-4V alloy.

No systematic trends can be observed with mean scratch depth, as a function of lateral displacement rate. The only effect observable is that the data density decreases as the displacement rate increases.

7.7.2 Elastic Scratch Deformation

During scratch indentation, the portion of the deformation accommodated by elastic deformation (and system compliance) becomes increasingly significant as the load is reduced. This is especially the case with the (relatively large) nominally 10 μm tip radius conospheroidal indenter tip used in this work, since for small penetration depths, the strain applied by the indenter is also very small¹²⁰. It can be seen in Figure 7.26 that virtually no residual deformation occurs in scratch indentation of sodalime glass, until a certain critical load, and accompanying strain, is surpassed.

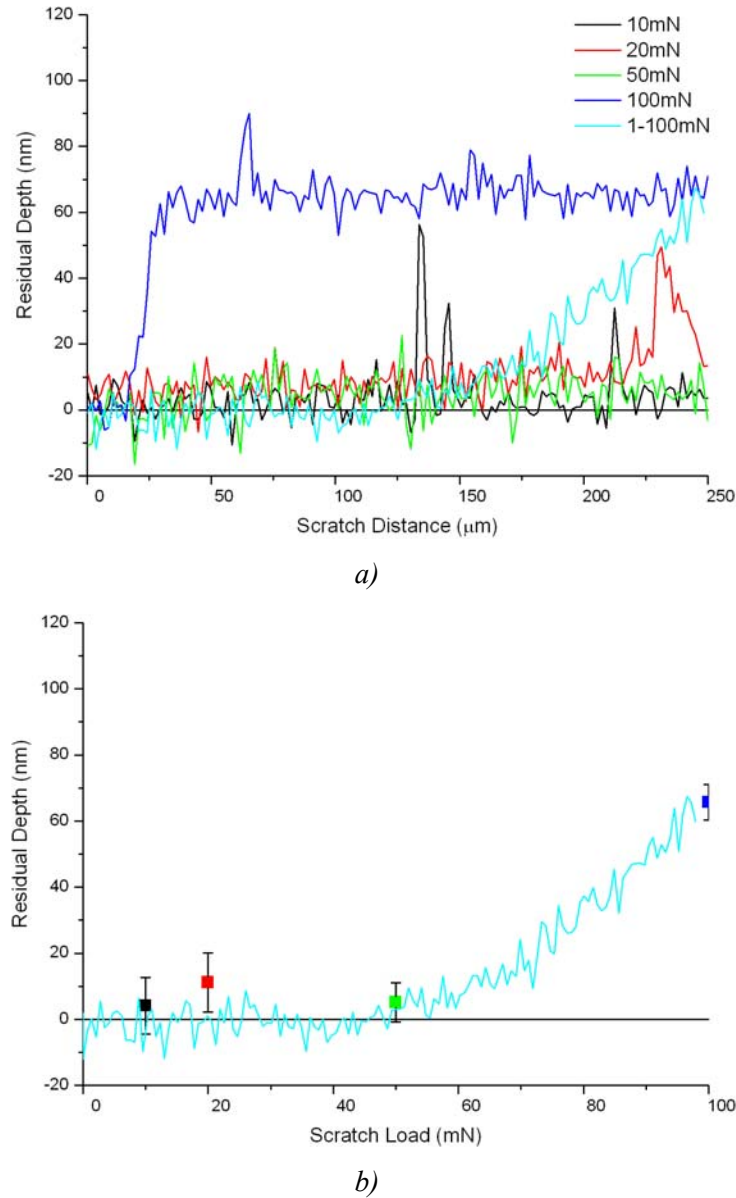


Fig. 7.26. Plastic scratch depths for a 10 μm sphere on sodalime glass as a function of a) scratch distance and b) normal scratch load.

In Figure 7.26a, other than some small perturbations, which are attributed to surface contamination and roughness, no residual deformation was observed in any of the constant load scratch indentation tests, until the load was raised to 100 mN. By comparing the mean scratch depths for each constant load scratch indentation to the constantly increasing load scratch indentation test (Fig. 7.26b), it can be seen that the minimum load for plastic deformation to occur is only slightly greater than 50 mN.

This example illustrates a limitation of the definitions of scratch hardness given in §3.3. If scratch hardness were to be calculated for the constant load scratch indentation results on glass < 100 mN, the scratch hardness values would approach

infinity. Thus, it is necessary to consider the indenter tip used in testing and possible effects of scale.

7.7.3 Scratch Indentation of PEO Coating Systems

Scratch indentation was carried out on several coating systems on aluminium and titanium alloy substrates. The substrates themselves were also tested for baseline performance standards, since coatings which do not outperform their substrates are not generally useful in abrasive wear situations.

7.7.3.1 Substrate Alloys

The residual scratch depth traces over the scratch grooves, for the tests on the titanium and aluminium alloy substrates, are shown in Figure 7.27.

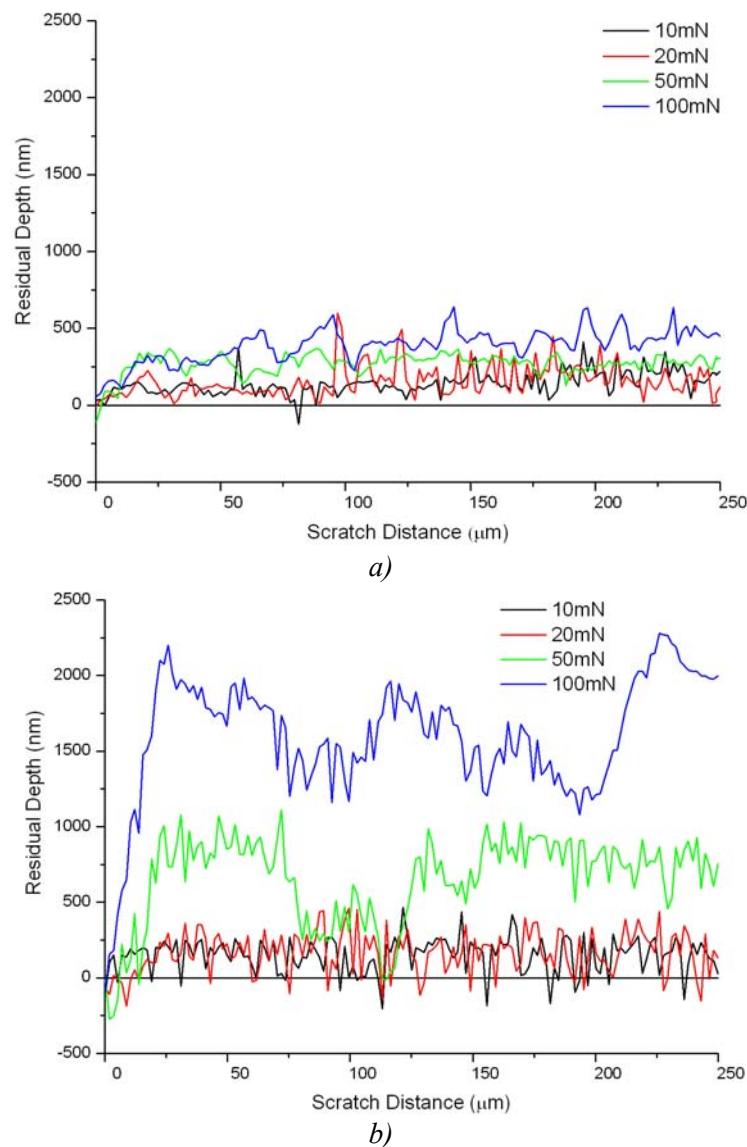


Fig. 7.27. Scratch indentation residual depth profiles for (a) a Ti-6Al-4V alloy and (b) a 6064 aluminium alloy.

The titanium alloy substrate shows much greater resistance to scratch penetration than the aluminium alloy. The titanium alloy also displays much greater uniformity in mean depth and thus much less microstructural property variation.

7.7.3.2 Coatings on Aluminium Alloys

Anodised coatings were tested to provide an additional comparative standard for performance for the PEO coatings.

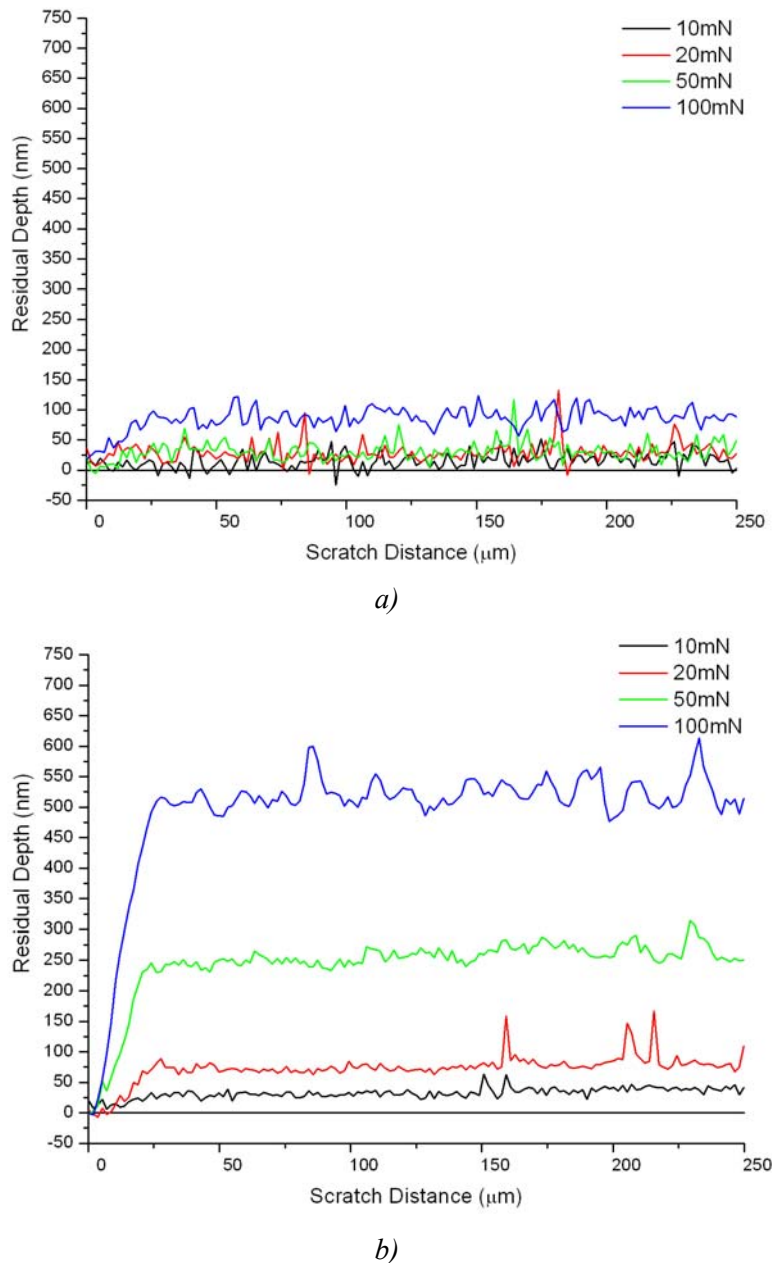


Fig. 7.28. Scratch indentation residual depth profiles for (a) a PEO coating and (b) an anodised coating on aluminium.

It can be seen in Fig. 7.28 that the PEO coating on aluminium shows significantly higher scratch penetration resistance than the anodised coating.

7.7.3.3 Coatings on Ti-6Al-4V

The scratch testing results for the coatings on Ti-6Al-4V were found to be sensitive to the coating microstructure. Relatively dense coatings, such as the anodised Al alloy, PEO coating on Al, and PEO coating on Ti-6Al-4V produced with the aluminate electrolyte, could be polished to a high finish with a flat surface for testing. The scratch profiles and resultant groove morphology from these systems were thus fairly uniform (Fig. 7.29).

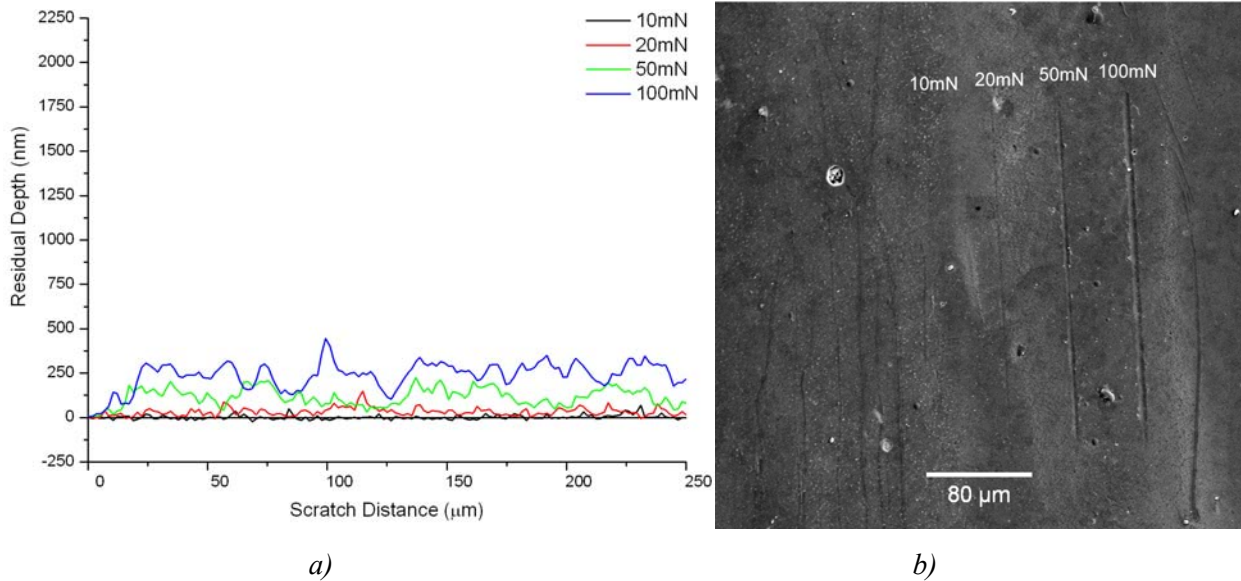


Fig. 7.29. Scratch indentation residual depth profiles for a) the aluminate PEO coating on Ti-6Al-4V and b) a SEM micrograph acquired by J.A. Curran²²⁰ of the scratches with applied normal forces labelled.

However, the PEO coatings on the Ti-6Al-4V alloy that were produced using silicate, phosphate, and mixed electrolytes contained high levels of coarse interconnected porosity, often throughout the entire thickness of the coating, which was only exposed by further polishing. During scratch testing, the indenter often penetrated these coarse pores, leading to scratch depth profiles which are irregular and variable – particularly with the larger applied loads (Fig. 7.30).

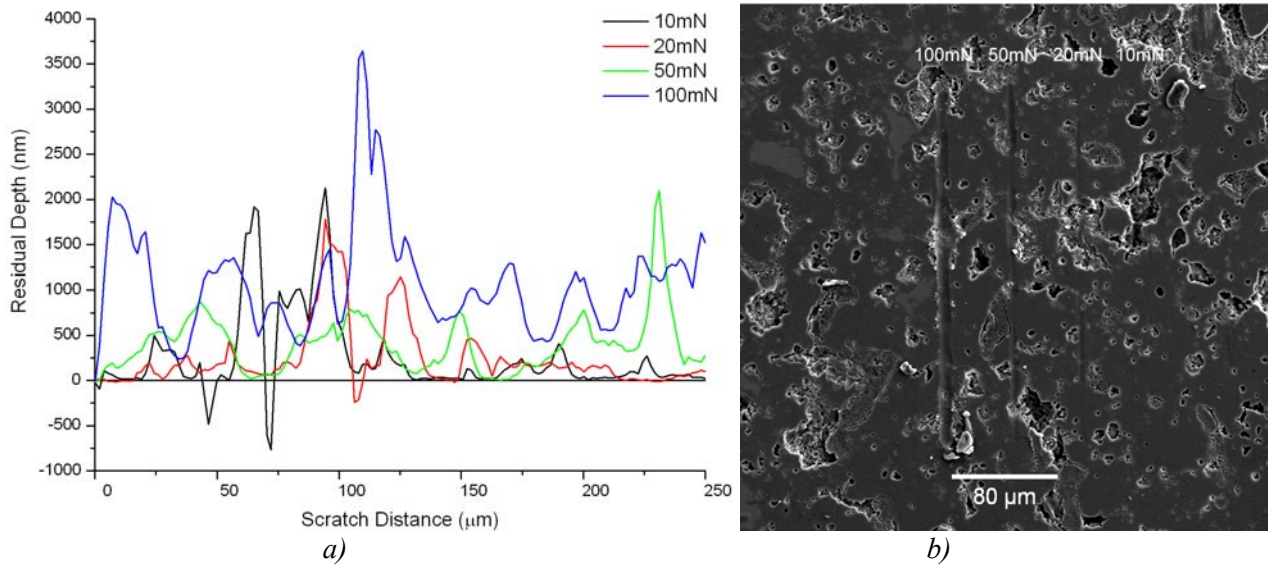


Fig. 7.30. Scratch indentation residual depth profiles for a) the phosphate PEO coating on Ti-6Al-4V and b) a SEM micrograph acquired by J. Curran²²⁰ of the scratches with applied normal forces labelled.

A comparison of residual scratch widths determined by measured scratch depth using indenter area functions and by direct measurement in SEM was performed (Fig. 7.31). Two major sources of error in determining scratch width via SEM were difficulty in locating the scratch edges due to the limited micrograph resolution (1 pixel $\sim 1/3 \mu\text{m}$) and in identifying the beginning and end points of the scratch.

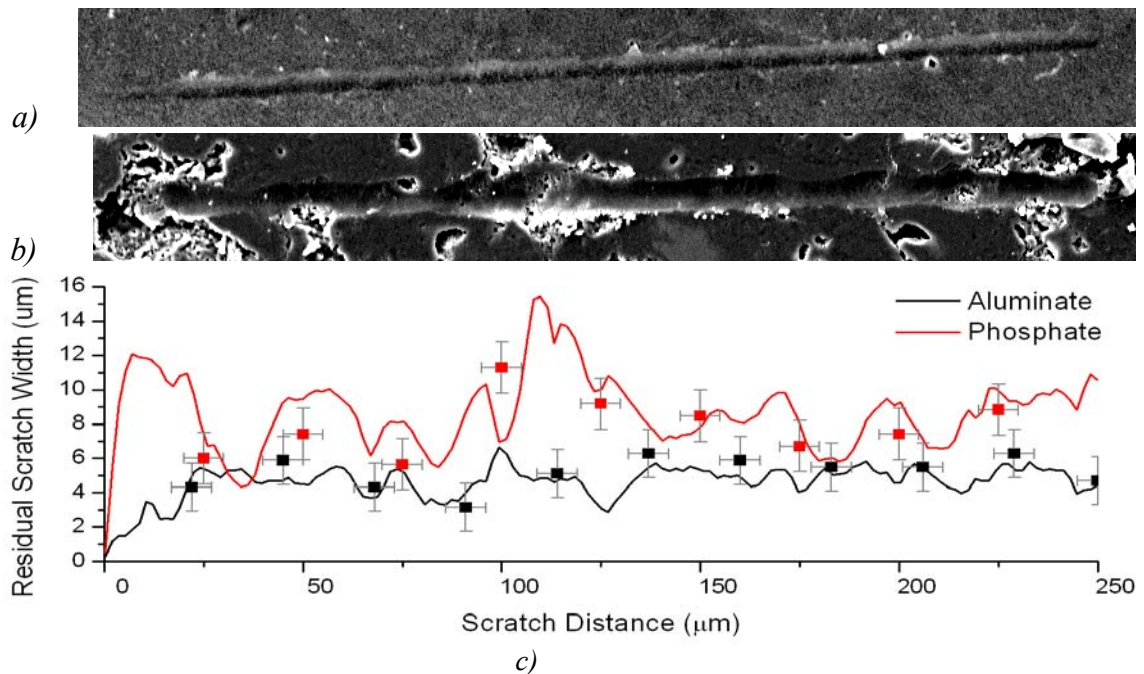


Fig. 7.31. Zoom in of SEM micrographs of 100 mN scratches on a) aluminate and b) phosphate coatings and c) a comparison of scratch width as a function of distance as measured by calculation from depth measurements (lines) and from SEM micrograph widths (markers).

Reasonably good agreement between the two methods is observed for the aluminate coating, and slightly worse agreement is seen for the phosphate coating. This is

presumed to be due to the phosphate coating's ragged edges in the micrograph. Overall the results of this comparison suggest that use of residual depth measurements to estimate scratch width and hardness is viable.

7.7.3.4 Mean Depths and Roughness

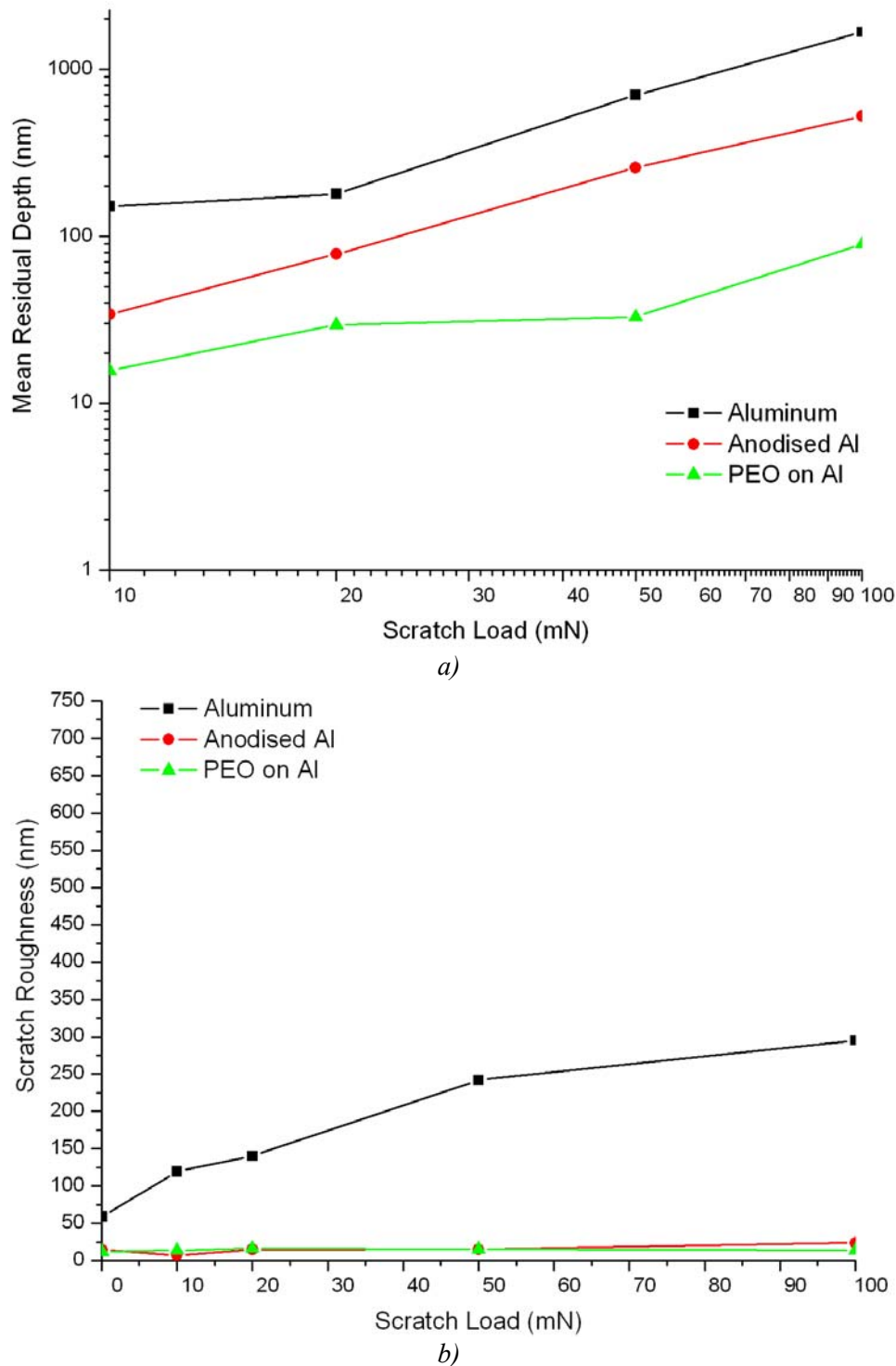
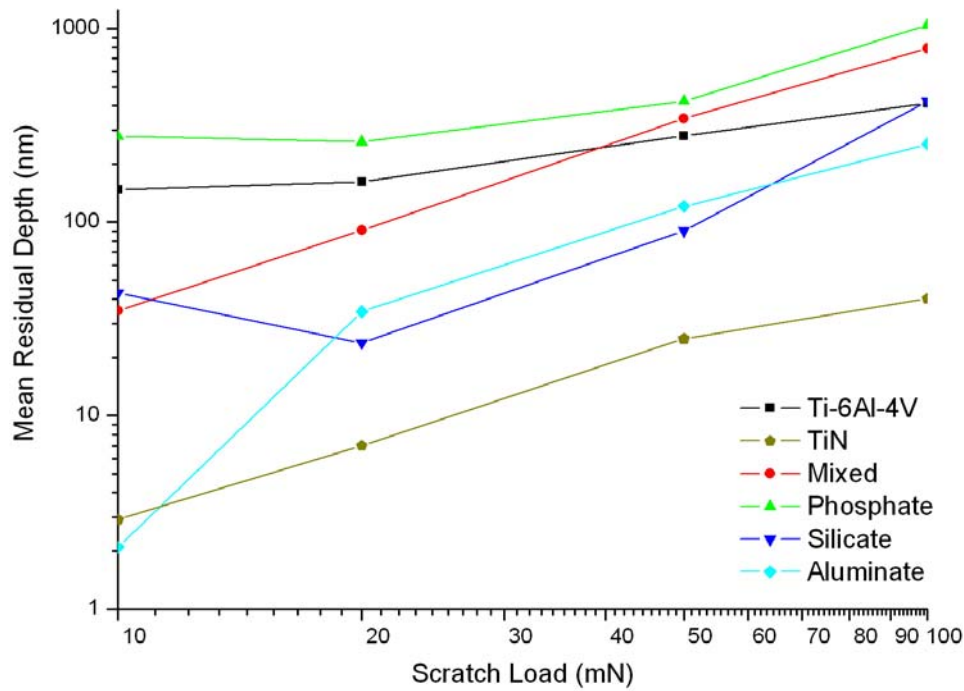


Fig. 7.32. Scratch indentation mean residual depth a) and roughness b) as a function of scratch load for coatings on aluminium alloys.

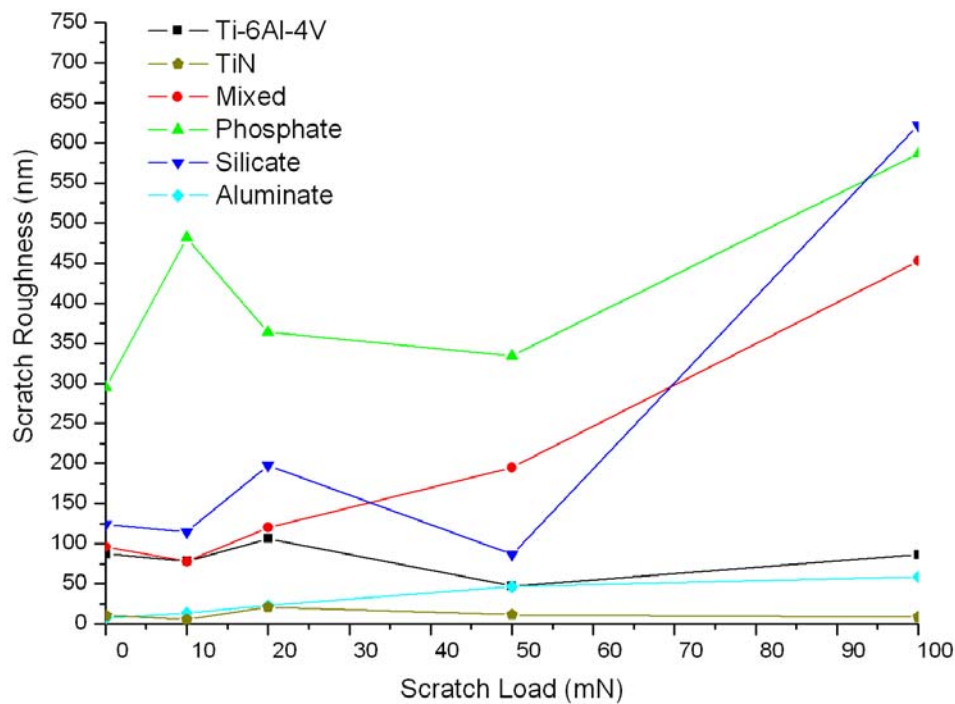
The main outcome of the scratch tests performed was the mean residual scratch depth at each indentation load. This was measured from the constant load region of the scratch: from 25-250 μm . The standard deviation of the mean scratch depths, or the scratch roughness, is also instructive for analysing the mean depths and determining the error in calculating scratch hardness values. An overview of the scratch response of the coating systems on aluminium alloys is given in Figure 7.32.

It is shown in Figure 7.32 that depth increases approximately according to a power law with the load, once the strain from the indenter has passed into the plastic regime of the material. This is roughly to be expected, since the projected contact area of the indenter increases with penetration depth according to a power law. At the lowest load, the aluminium alloy substrate yields more than might be expected from projecting from higher load results. This could be due to expulsion of absorbed species and compression of surface roughness. Similar behaviour is observed with the Ti-6Al-4V alloy substrate (Fig. 7.33). The scratch roughness of the aluminium alloy substrate was observed to significantly increase with increasing scratch load. Scatter on the PEO coating on aluminium is attributed to roughness and small scale variations, due to the very small depths involved. Both coatings are observed to significantly reduce scratch penetration, with the PEO coating showing the greatest resistance, giving residual depths an order of magnitude less than the bare substrate alloy.

Of the coatings on the titanium substrate (Fig. 7.33), it can be seen that two of the four PEO coatings, aluminate and silicate, give reduced indenter penetration, compared with the uncoated substrate. This is consistent with their high hardness values observed near the coating surface (see §7.3.3). The apparent deviation from power law behaviour of the aluminate coating at 10 mN is attributed to an almost perfectly elastic scratch, while that of the phosphate and silicate coatings is attributed to roughness. The TiN coating was found to give the highest scratch resistance.



a)



b)

Fig. 7.33. Scratch indentation mean residual depth a) and roughness b) as a function of scratch load for coatings on Ti-6Al-4V.

7.7.4 Scratch Hardness

Measurements of mean scratch depth ignore the effects of tip geometry. As discussed in §3.3, scratch indentation, as with normal indentation, is sensitive to the relative scale of tip radius for rounded indenters, as well as cone angle for sharp indenters.

Scratch hardness was calculated using Equation 3.4, with the load-bearing area being half of the projected area for the mean scratch depth, using the AFM measured diamond area function.

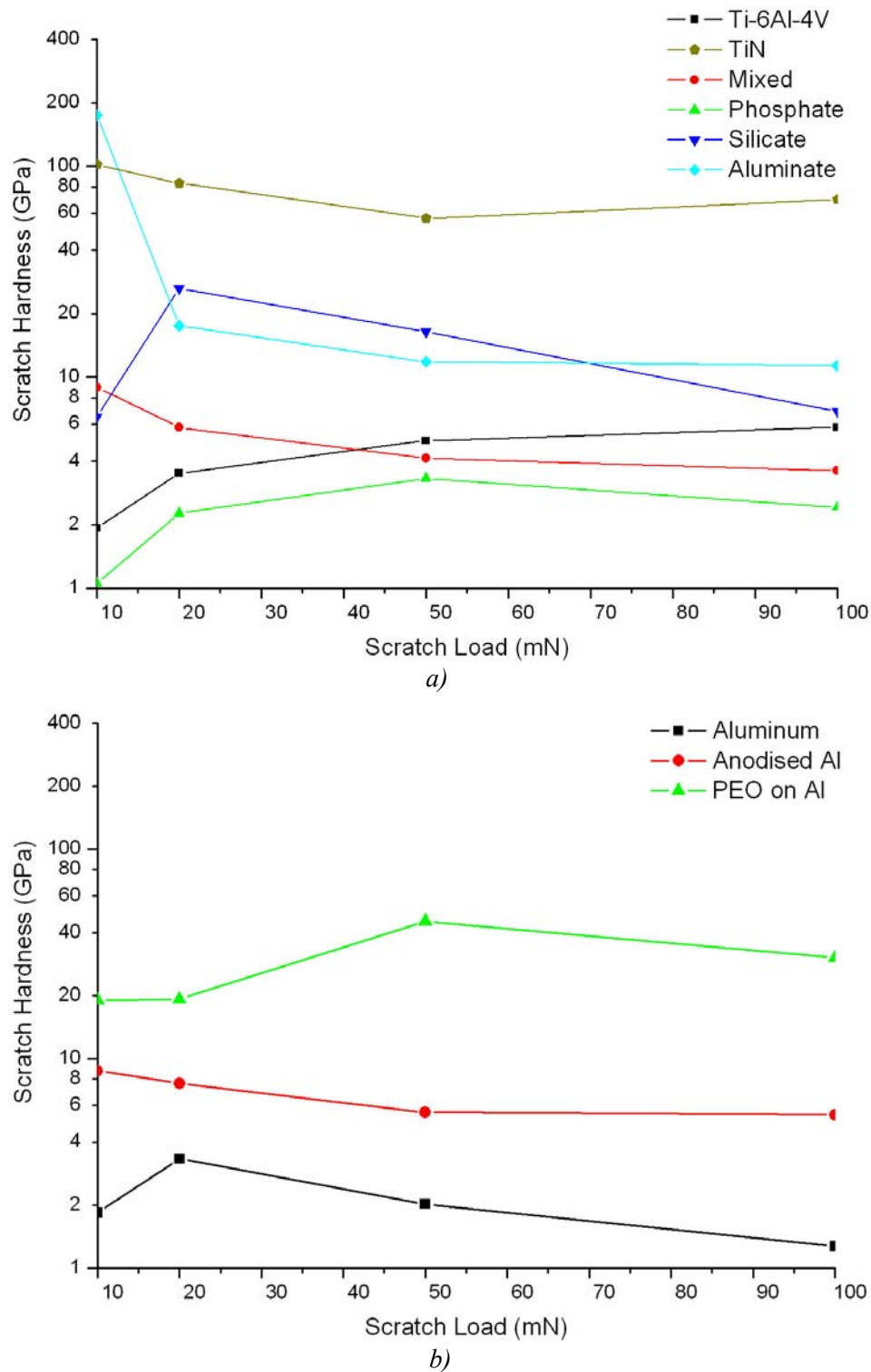


Fig. 7.34. Scratch hardness as a function of scratch load for coatings on a) Ti-6Al-4V and b) aluminium alloys.

Error bars are not included, since the scratch hardness values are calculated from the mean depth over a single scratch. Due to the extremely shallow depths (a/R) involved, it is believed that extrapolating the standard deviation of the scratch depth over the distance into scratch hardness error would overestimate the true variation between multiple scratches.

Scratch hardness values for the various coating systems are observed to vary increasingly at lower loads (Fig. 7.34). In the case of the aluminate PEO coating on Ti-6Al-4V, this appears as a significant increase in scratch hardness. However, this is attributed to a nearly elastic scratch. The drops in scratch hardness at lower loads, observed in the porous phosphate and mixed PEO coatings, are attributed to the effect of the scratch encountering pore edges, and the drops observed in the metallic substrates are thought to be related to compression of surface roughness.

7.8 Abrasive Wear Behaviour

A comparison is shown in Figure 7.35 between data obtained using ASTM G65 abrasive wheel testing (see §7.2.1) and the results of the scratch indentation testing - these two tests are similar in terms of loading geometry. Scratch results for the Al-based systems were calculated mean scratch hardness over the range of applied loads and plotted at a load of 0.1 N, the maximum scratch load applied.

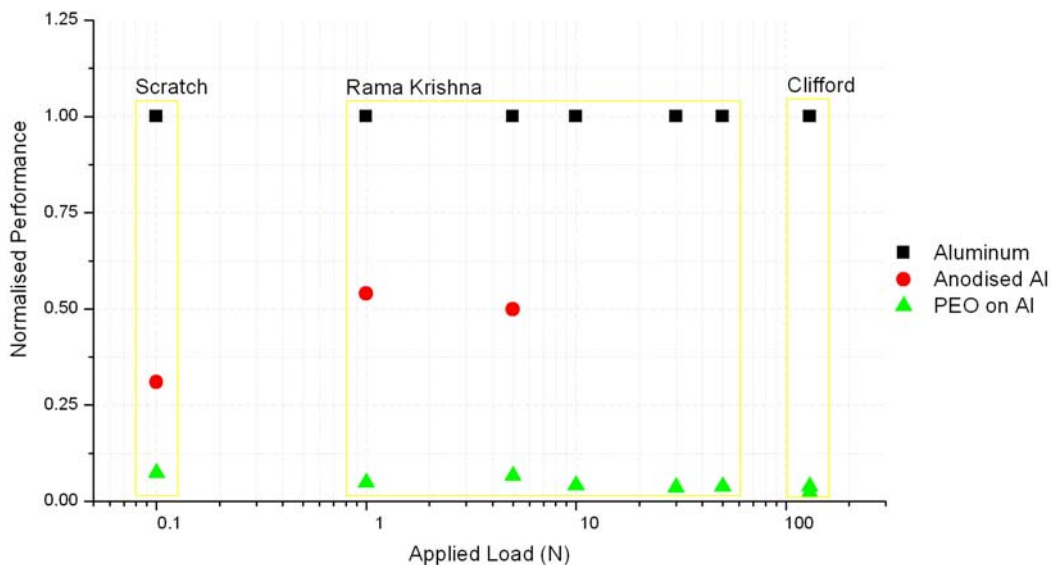


Fig. 7.35. Comparison between the response of Al-based systems to scratch indentation – load 0.1 N and abrasive wear testing – loads 1-130 N.

Normalisation was carried out with respect to performance of the uncoated aluminium substrate. It can be seen that the PEO coating shows a very similar degree of wear resistance as compared to the aluminium substrate material across all three tests, despite their varying degrees of disparity. The hard anodised coating, however, is observed to have a higher degree of deformation resistance to scratch wear. This is likely due to indentation scratch testing using a spherical tip not exploiting the brittle character of the coatings to the same degree as the larger, higher velocity particles in the abrasive wheel test.

7.9 Summary

In order to discuss the major outcomes of this chapter, it is useful to break the discussion up into four topics: the novel PEO coating materials, the multiple impact technique, the scratch technique, and comparison of multiple impact and scratch indentation to wear testing.

7.9.1 Novel Ti Coatings

The characterisation conducted by A. Collier revealed the silicate and mixed coatings consisted mainly of silicate and titania phases. These coatings also tended to be thicker for the same processing time, implying that silicate deposition significantly contributed to the thickness. Aluminate and phosphate coatings consisted of aluminium titanate (Al_2TiO_5) and titania phases. Fine porosity was observed in all of the coatings via scanning electron microscopy.

Nanoindentation testing on the cross-sections of the coatings allowed determination of hardness and modulus as a function of distance from the substrate interface for the four PEO coatings on Ti-6Al-4V alloy substrates. PEO coatings with alumina (Al_2O_3) and aluminium titanate (Al_2TiO_5) phases present were shown to have significantly higher hardness and modulus values than those containing primarily silicate and titania phases. This is consistent with the observations of Yerokhin et al²⁰⁰.

7.9.2 Multiple Impact Testing

The Multiple Impulse module of the MicroMaterials NanoTest system was used to characterise the response materials under multiple impact loading. Sampling resolution of this technique was observed to be insufficient to characterise the time-

displacement relations to the same degree as the Dynamic Hardness module discussed in Chapter 6. Impact deformation appeared to be monotonic, so the only parameter measurable by this technique was the rest depth of the indenter after impact. This rest depth includes both the plastic deformation from (multiple) impact(s) and the elastic deformation from the indenter resting on the sample under the accelerating load. A custom LabView analysis program was implemented to rapidly extract the rest depth as a function of impact number from the raw data and average the results of several datasets. The initial impact also occurs after a preload at the accelerating load, so that the surface has been effectively indented once prior to the first impact.

Three behaviours are typically observed with increasing numbers of impact indentations: elastic fatigue producing swelling or decreasing depth, smooth plastic yielding, and plastic failure/fracture. The mechanism of the ‘elastic’ fatigue which resulted in decreasing depth with increasing number of impacts is still unknown, though thermal expansion from adiabatic heating due to repeated impacts is suggested. During the initial regime of smooth plastic yielding, the initial impact indentation hardness measured from the impact energy necessary to deform a volume was observed to linearly correlate to Berkovich quasi-static indentation hardness values. However, the intercept and slope of this relation cannot be assigned to any specific dynamic effect due to the limitations mentioned in the previous paragraph.

The maximum depth achieved with multiple impacts demonstrated a power law trend with impact acceleration load, which plot as linear on log-log graphs, until the tangent depth of the conospheroidal indenter was reached. This is attributed to the effect of the indenter geometry, such that there appears to be an ultimate multiple impact hardness for each impact energy value. Impact indentation volumes scaled linearly with impact energy, which is consistent with observations of impact deformation on bulk materials by researchers as early as Martel⁹³ and Vincent⁹⁴.

The number of impacts at which maximum depth occurred was found to increase with increasing acceleration load. It remains unclear why it would require more impacts of greater energy to reach its maximum penetration depth than impacts of lesser energy. The number of impacts at which maximum depth occurred was found to correlate to

stable performance, i.e. not brittle failure, if it occurred prior to the final impact depth, as this indicated that subsequent impacts were elastically accommodated.

Of the novel PEO coatings on Ti-6Al-4V, only the aluminate demonstrated superior impact indentation penetration resistance to the substrate alloy. For the coating systems on aluminium alloys, both coatings show significant improvements on impact indentation penetration resistance over the substrate alloy with the PEO coating providing the greatest resistance.

7.9.2.1 Oblique Multiple Impacts

The NanoTest platform was adapted for conducting impacts at oblique incidence by varying the angle of the sample mount. The range of oblique incidence angles at which impact indentation could be performed was found to be limited to angles less than 45° due to the conospheroidal indenter geometry. Impact indentation at greater angles resulted in the conical portion of the indenter ‘broadside’ into the sample. The maximum vertical penetration depth was observed to generally decrease with increasing incident angle. However, the number of impacts necessary to achieve maximum depth was found to increase with increasing angle of incidence until the tangent depth of the indenter was reached.

Examination of residual impressions from oblique impacts in the AFM revealed significant amounts of asymmetric pileup at higher angles of incidence. Streaks/scratches observed within the residual impressions suggest that the lateral stiffness of the indenter was insufficient to constrain the indenter from deviating from the normal swing plane due to tangential forces from the oblique. This problem would increase in severity with increasing angle of incidence and could theoretically result in damage to the indentation system.

7.9.3 Scratch Testing

No significant variation in scratch deformation with different lateral displacement rates was observed on Ti-6Al-4V within the range of 1-50 µm/sec. Since Ti-6Al-4V is presumed to possess the greatest strain rate sensitivity of the materials tested, this suggests that strain rate effects did not influence any of the results.

No significant plastic deformation was found to occur during scratch indentation testing of sodalime glass at normal loads below 50 mN; suggesting that scratch deformation fell inside the elastic regime¹¹⁹. Since glass has a similar E/σ_Y ratio to the silicates present in the PEO coatings, this suggests that those coatings may also deform elastically at shallow depths.

Microstructural variation within the coatings was observable within the scratch profiles of coatings with large scale ($\sim 10\ \mu\text{m}$) porosity. The porosity was observed to increase the mean plastic depth achieved in the scratch indentation testing of PEO coatings, as the indenter dropped into the pores in several instances. The scratch roughness, or standard deviation of plastic scratch depth, was observed to remain constant for coatings on aluminium but increase as a function of normal scratch load for the substrate alloy. This is attributed to mechanical property variation within the microstructure manifesting. The scratch roughness of the coatings on titanium showed no dependence on load. However, the coatings with high porosity showed high roughness at all loads.

Comparison between the scratch widths determined from depth measurements and SEM observation found the two measurements in good agreement. This suggests that depths measured by the post-scratch profile scan accurately represent the scratch morphology.

The power law variation in mean depth with normal scratch load is attributed to the effect of indenter geometry, as scratch hardness values which correct for tip geometry remove this trend. The scratch hardness values observed for most material systems investigated vary between 1.5-3 times greater than their Berkovich indentation hardness values. This is consistent with the very low a/R values producing a large effective cone angle for the scratch^{119, 120}. All the coatings plastically deformed solely by ductile failure¹²⁹, which provided information on the deformation behaviour intrinsic to the coating rather a measure of its adhesion to the substrate. This was expected, since Yerokhin¹⁸⁹ observed that critical loads for coatings of this type were on the order of 100 N.

Both aluminate and silicate PEO coatings on Ti-6Al-4V were found to have superior scratch indentation hardness to the substrate alloy over the entire range of loads. Both coating systems on aluminium demonstrated higher scratch indentation hardness than their substrate alloy with the PEO coating showing the greatest value.

7.9.4 Wear Comparison

A large disparity between the sandblasting erosive performance and the maximum penetration depth from multiple impact results is observed for three of the PEO coating systems on Ti-6Al-4V. Similar disparity was observed in the behaviour of the coatings on the aluminium alloys in ASTM G76 erosive wear and in multiple impact. This is primarily attributed to two factors: the angle of incidence (Fig. 7.1b) and the disparity in impact energy as discussed in §7.2.1. The number of impacts to maximum depth appears to subjectively rank the erosive wear performance of both ductile and brittle materials which are sufficiently well bonded to their substrates. This may indicate that a similar number of impacts is required in erosive wear prior to material removal. Sandblast erosion tests showed that PEO coatings on Ti-6Al-4V which contained aluminium titanate (Al_2TiO_5) phases performed better in erosive wear. However, at normal incidence, none of the brittle PEO coatings outperformed the substrate material in erosion.

Comparison of normalised performance of coating systems on aluminium in abrasive wear to scratch hardness showed similar degrees of resistance. This indicates that both tests measured a similar wear mechanism: ductile failure of the porous coating. This agrees with the work of Gee¹³³, which indicated that scratch testing could be useful for ranking the wear behaviour within individual wear regimes. It is unfortunate that more data on the behaviour of the PEO coatings on Ti-6Al-4V in abrasive wear was not available for comparison, but for a similar correlation is suggested for them in wear test conditions similar to those used on the coatings on aluminium.

8

Conclusions & Future Work

The following conclusions were derived from the work carried out in this investigation of nanoindentation under dynamic conditions. Plans for possible future work are also discussed.

8.1 Indentation of Pd-H System

With reference to the original research aim of detecting differences in mechanical behaviour between pure palladium and palladium saturated with hydrogen, it was found that dynamic hydrogen egress under ambient conditions likely precluded direct measurement. A nanoindentation system capable of operation under high hydrogen overpressures would be required to meet this aim with certainty.

The possible exception to this is the β phase regions of the partially hydrided samples; where a reversal in pile-up/sink-in behaviour was observed (Fig. 5.27b) while similar load-displacement behaviour was achieved. This could be a result of interstitial hydrogen constraining plastic flow and promoting sinking-in.

During the course of the investigation, two additional significant phenomena were observed: the progression of the β phase as a discrete region and the high hardening observed in the hydrided α phase region. The first of these observations might be predicted from the literature, but it is not believed to have been demonstrated conclusively in previous work. The second observation, the high hardening observed in the hydrided α phase region, is suggested to be related to hydrogen outgassing. Nanoindentation results from the fully hydrided/dehydrided sample demonstrated very similar hardness profiles in both hydrogenated and dehydrogenated conditions; suggesting that the near-surface hydrogen had escaped prior to indentation.

In order to firmly establish a relationship of this phenomenon to outgassing, future work might involve performing indentations on sections of hydrided foils periodically as a function of outgassing time. Since the phenomenon was observed to decrease in

magnitude in the thicker foil (Fig. 5.25), systematically replicating these experiments on foils of varying thickness might also prove instructive.

8.2 Impact Indentation of Superelastic NiTi

The impact indentation technique developed shows considerable promise as a tool for investigation of high strain rate properties of material over a range of temperatures. There are still significant limitations to be overcome before it can be successfully utilised as such. The superelastic effect was observed at a high strain rate ($\sim 1000 \text{ s}^{-1}$) using this technique. However, it could not be accurately quantified, due to dynamic compliance issues and multiple rebounds disturbing the residual impression.

Use of a simpler dynamic indentation system, such as that of Lu et al¹⁰², would have avoided these difficulties. However, it would also require further modification for operation at elevated temperature to be suitable for the purposes of this investigation.

Uncertainties concerning the dynamic compliance of the indentation system made it difficult to obtain reliable depth measurement during impacts at high acceleration loads. Integration of a force sensor into the system is proposed for future work, in order to resolve this issue. A system for catching the pendulum after the first impact/rebound cycle will need to be implemented, so that the residual impression will be the result of a single impact.

8.3 Multiple Impact and Scratch Indentation of PEO Coatings

In order to discuss the major outcomes of this chapter, it is useful to break the discussion up into four topics: the novel PEO coating materials, the multiple impact technique, the scratch technique, and comparison of multiple impact and scratch indentation to wear testing.

8.3.1 Novel Ti Coatings

The combination of the characterisation conducted by A. Collier and micro-mechanical testing allowed determination of which phases provided improved mechanical performance within the four PEO coatings on Ti-6Al-4V alloy substrates produced using a variety of electrolytes. PEO coatings with alumina (Al_2O_3) and aluminium titanate (Al_2TiO_5) phases present were shown to have significantly higher

hardness and modulus values than those containing primarily silicate and titania phases consistent with the observations of Yerokhin et al²⁰⁰. This corresponded to the aluminate demonstrating superior impact indentation penetration resistance, scratch hardness and sandblast erosive wear performance than the other coatings and, in many cases, to the substrate alloy.

8.3.2 Multiple Impact Testing

The multiple impact capability introduced by the MicroMaterials Ltd. Nanotest system is believed to be unique. It allows the rapid application of multiple impact indentations while measuring the final penetration depth. Previous studies of this capability were limited to determining the probability of failure of thin coating systems. The implementation of a custom LabView analysis program to rapidly extract the rest depth as a function of impact number from the raw data and average the results of several datasets allowed analysis of this test to an unprecedented level.

Two flaws in this test's ability to characterise plastic deformation as a function of multiple impacts are intrinsic to the method of application of load. The initial impact occurs after a preload at the accelerating load, so that the surface has been effectively indented once prior to impact. The final resting depth measured during this test occurs while the indenter is held against the sample by the accelerating load. This means the depth measured is a combination of plastic depth from impacts and elastic deformation under loading. Removal of the preload and measurement of the residual depth after impact by a very low load indentation/surface finding procedure are improvements to this test which the author would recommend to MicroMaterials Ltd.

Three behaviours were typically observed with increasing numbers of impact indentations on both metals and ceramics: 'elastic' fatigue producing swelling or decreasing depth, smooth plastic yielding, and plastic failure/fracture. The initial impact indentation hardness measured from the impact energy necessary to deform a volume was observed to linearly correlate to Berkovich quasi-static indentation hardness values. The maximum impact indentation penetration depth achieved during multiple impact testing appears to scale with indentation hardness. However, these relations cannot yet be directly established to dynamic or quasi-static indentations due to the limitations mentioned in the previous paragraph.

All the materials tested show power law trends of maximum depth with impact acceleration load, which plot as linear on log-log graphs until the tangent depth of the conospheroidal indenter was reached. This was shown to relate to the tip shape of the indenter, such that indentation volume scaled linearly with impact energy, which is consistent with observations of impacts on bulk materials by researchers as early as Martel⁹³ and Vincent⁹⁴.

The number of impacts at which maximum depth occurred was found to increase with increasing acceleration load. It remains unclear why it would require more impacts of greater energy to reach its maximum penetration depth than impacts of lesser energy.

8.3.2.1 Oblique Multiple Impacts

The flexibility of the NanoTest platform allowed simple adaptation for conducting impacts at oblique incidence. The range of oblique incidence angles at which impact indentation could be performed was found to be limited to angles less than 45° due to the conospheroidal indenter geometry. Even within this range, however, it appears that the lateral stiffness of the indenter was insufficient to constrain the indenter from deviating from the normal swing plane. The maximum vertical penetration depth is observed to generally decrease with increasing incident angle, however the number of impacts necessary to achieve maximum depth was found to increase with increasing angle of incidence until the tangent depth of the indenter was reached.

8.3.3 Scratch Testing

The scratch hardness values observed for most material systems investigated vary between 1.5-3 times greater than their Berkovich indentation hardness values. This is consistent with the very low a/R values producing a large effective cone angle for the scratch^{119, 120}. All the coatings deformed solely by ductile failure¹²⁹, which provided information on the deformation behaviour intrinsic to the coating rather a measure of its adhesion to the substrate. This was expected, since Yerokhin¹⁸⁹ observed that critical loads for coatings of this type were on the order of 100N. Microstructural variation within the coatings was observable within the scratch profiles with large scale (~10 µm) porosity was observed to increase the mean plastic depth of PEO coatings.

Both aluminate and silicate PEO coatings on Ti-6Al-4V were found to have superior scratch indentation hardness to the substrate alloy over the entire range of loads. Both aluminium coating systems demonstrated higher scratch indentation hardness than their substrate alloy with the PEO coating showing the greatest value.

8.3.4 Wear Comparison

A large disparity between the sandblasting performance and the multiple impact results is observed for three of the PEO coating systems. This is primarily attributed to two factors which were discussed in §7.2.1: the difference in behaviour between ductile and brittle materials with angle of incidence and the 4 orders of magnitude disparity in impact energy. It was observed in Figure 7.13 that, at higher impact loads, the coatings begin to fail in a more brittle manner. It is possible that, at the significantly higher impact energies of sandblasting, the coatings are failing in a very brittle manner, yielding high wear rates. The substrate alloy, however, is still able to accommodate the impacts in an elastic/plastic manner. This offers a possible explanation for why the mixed and silicate coatings perform so poorly: the high energy impacts readily fracture the amorphous silica coatings.

Thus, while the multiple impact indentation testing may be of use for the ranking of developmental coatings, it is clear that further work is necessary to firmly establish a correlation with standard impingement tests. This work is envisioned to involve correlation of impacts distributed over an area repeated impacts in a single location and comparison of impact indentation to a conventional wear test with similar impact energies, e.g. a falling sand test.

Comparison of normalised performance of aluminium coating systems in abrasive wear to scratch hardness showed similar degrees of resistance. This indicates that both tests measured a similar wear mechanism: ductile failure of the porous coating. This agrees with the work of Gee¹³³, which indicated that scratch testing could be useful for ranking the wear behaviour within individual wear regimes. It is unfortunate that more data on the behaviour of the PEO coatings on Ti-6Al-4V in abrasive wear was not available for comparison, but for a similar correlation is suggested for them in wear test conditions similar to those used on the aluminium coatings.

References

1. Mohs, F., *Grundriss der Mineralogie*. 1822, Dresden.
2. *Hardness Conversion*. Gordon England 2008 [cited; Available from: http://www.gordonengland.co.uk/hardness/hardness_conversion_1c.htm].
3. Mott, B.W., *Micro-indentation hardness testing*. 1956, London: Butterworth's Scientific Publications. 272.
4. Hainsworth, S.V., McGurk, M.R., and Page, T.F., *The effect of coating cracking on the indentation response of thin hard-coated systems*. Surf. Coat. Techn., 1998. **102**: p. 97-107.
5. Korsunsky, A.M., McGurk, M.R., Bull, S.J., and Page, T.F., *On the hardness of coated systems*. Surface and Coatings Technology, 1998. **99**: p. 171-183.
6. Ma, Q.C., D. R., *Size dependent hardness in silver single crystals*. J Mater Res, 1995. **10**: p. 853-863.
7. Nix, W.D. and Gao, H., *Indentation size effects in crystalline materials: a law for strain gradient plasticity*. Journal of the Mechanics and Physics of Solids, 1998. **46**: p. 411-425.
8. *Liquid Cell Indentation*. 2006 [cited 2006 June]; Available from: http://micromaterials.co.uk/liquid_cell.htm.
9. Beake, B., Goodes, S., and Smith, J., *Nanoscale materials testing under industrially relevant conditions: high-temperature nanoindentation testing*. Zeitschrift fur Metallkunde, 2003. **94**(7): p. 1-7.
10. Lucas, B.N. and Oliver, W.C., *Indentation Power-Law Creep of High-Purity Indium*. Metall. Mater. Trans., 1999. **30A**: p. 601-610.
11. Schuh, C.A., Mason, J.K., and Lund, A.C., *Quantative insight into dislocation nucleation from high-temperature nanoindentation experiments*. Nature Materials, 2005. **4**: p. 617-621.
12. Constantinides, G., Tweedie, C., Holbrook, D., Barragan, P., Smith, J., and Van Vliet, K., *Quantifying deformation and energy dissipation of polymeric surfaces under localized impact*. Materials Science and Engineering A, 2008. **489**: p. 403-412.
13. Page, T.F., Oliver, W.C., and McHargue, C.J., *The Deformation Behaviour of Ceramic Crystals Subjected to Very Low Load (Nano)Indentations*. J. Mater. Res., 1992. **7**: p. 450-473.
14. Oliver, W.C. and Pharr, G.M., *An Improved Technique for Determining Hardness and Elastic Modulus Using Load and Displacement Sensing Indentation Experiments*. Journal of Materials Research, 1992. **7**(6): p. 1564-1583.
15. Axen, N., Botton, G.A., Lou, H.Q., Somekh, R.E., and Hutchings, I.M., *Incorporation of nitrogen in sputtered carbon films*. Surf. Coat. Technol., 1996. **81**: p. 262.
16. Doerner, M.F. and Nix, W.D., *A method for interpreting the data from depth-sensing indentation instruments*. Journal of Materials Research, 1986. **1**(4): p. 601-609.

17. Hainsworth, S.V., Chandler, H.W., and Page, T.F., *Analysis of nanoindentation load-displacement loading curves*. J. Mat. Res., 1996. **11**(8): p. 1987-1995.
18. Cheng, Y.-T. and Cheng, C.-M., *What is indentation hardness?* Surface and Coatings Technology, 2000. **133-134**: p. 417-424.
19. Bull, S.J., *Extracting hardness and Young's modulus from load-displacement curves*. Zeitschrift für Metallkunde, 2002. **93**: p. 870-874.
20. Cheng, Y.-T. and Cheng, C.-M., *Scaling, dimensional analysis, and indentation measurements*. Materials Science and Engineering: R: Reports, 2004. **44**(4-5): p. 91-149.
21. Oliver, W.C. and Pharr, G.M., *Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology*. Journal of Materials Research, 2004. **19**: p. 3-20.
22. Fischer-Cripps, A.C., *Critical Review of analysis and interpretation of nanoindentation test data*. Sur. Coat. Technol., 2006. **200**: p. 4153-4165.
23. Pharr, G.M.a.B., A., *Understanding Nanoindentation Unloading Curves*. J Mater Res, 2002. **17**: p. 2660-2671.
24. Chudoba, T. and Richter, F., *Investigation of Creep Behaviour Under Load During Indentation Experiments and its Influence on Hardness and Modulus Results*. Surface & Coatings Technology, 2001. **148**: p. 191-198.
25. Tabor, D., *The Hardness of Metals*. 1951, Oxford: Clarendon Press.
26. Atkins, A.G. and Tabor, D., *Plastic Indentation in Metals with Cones*. J Mech Phys Solids, 1965. **13**: p. 149-164.
27. Basu, S.M., A.; Barsoum, M.W., *On the determination of spherical nanoindentation stress-strain curves*. J Mater Res, 2006. **21**(10): p. 2628-2637.
28. Field, J.S. and Swain, M.V., *Determining the mechanical properties of small volumes of material from submicrometer spherical indentations*. Journal of Materials Research, 1995. **10**: p. 101-112.
29. Fischer-Cripps, A.C., *A review of analysis methods for sub-micron indentation testing*. Vacuum, 2000. **58**: p. 569-585.
30. Herbert, E.G., Pharr, G.M., Oliver, W.C., Lucas, B.N., and Hay, J.L., *On the measurement of stress-strain curves by spherical indentation*. Thin Solid Films, 2001. **398**: p. 331-335.
31. Field, J.S. and Swain, M.V., *A simple predictive model for spherical indentation*. Journal of Materials Research, 1993. **8**(2): p. 297-306.
32. Sneddon, I.N., *Int. J Eng. Sci.*, 1965. **3**: p. 47.
33. Fischer-Cripps, A.C., *Simulation of sub-micron indentation tests with spherical and Berkovich indenters*. Journal of Materials Research, 2001. **16**(7): p. 2149-2157.
34. Fischer-Cripps, A.C., *A simple phenomenological approach to nanoindentation creep*. Materials Science and Engineering, 2004. **A385**: p. 74-82.
35. Bolshakov, A. and Pharr, G.M., *Influences of pileup on the measurement of mechanical properties by load and depth sensing indentation*. J Mater Res, 1998. **13**(4): p. 1049-1058.
36. Stone, D.S., Yoder, K.B., and Sproul, W.D., *Hardness and elastic modulus of TiN based on continuous indentation technique and new correlation*. Journal of Vacuum Science & Technology A - Vacuum, Surfaces, and Films, 1991. **9**(4): p. 2543-2547.

37. Joslin, D. and Oliver, W.C., *Analyzing data from continuous depth-sensing microindentation tests*. J Mater Res, 1990. **5**(1): p. 123-126.
38. Cheng, Y.T. and Cheng, C.M., *Relationships between hardness, elastic modulus, and the work of indentation*. App. Phys. Lett., 1998. **73**(5): p. 614-617.
39. Hutchings, I.M. and Kusano, Y., *Analysis of nano-indentation measurements on carbon nitride films*. Surface & Coatings Technology, 2003. **169**: p. 739-742.
40. Cheng, Y.T. and Cheng, C.M., *Scaling, dimensional analysis, and indentation measurements*. Materials Science and Engineering: R: Reports: A Review Journal, 2004. **44**: p. 91-149.
41. Muir Wood, A.J. and Clyne, T.W., *Measurement and Modelling of the Nanoindentation Response of Shape Memory Alloys*. Acta Materialia, 2006. **54**(20): p. 5607-5615.
42. Chaudhri, M., *Strain Hardening around Spherical Indentations*. Physica Status Solidi A, 2000. **182**: p. 641-652.
43. Chaudhri, M., *Subsurface Strain Distribution Around Vickers Hardness Indentations in Annealed Polycrystalline Copper*. Acta Materialia, 1998. **46**(9): p. 3047-3056.
44. Murthy, T., Huang, C., and Chandrasekar, S., *Characterization of deformation field in plane-strain indentation of metals*. Journal of Physics D: Applied Physics, 2008. **41**(7).
45. Prchlik, L., Pisacka, J., and Sampath, S., *Deformation and strain distribution in plasma sprayed nickel-aluminum coating loaded by a spherical indenter*. Metallurgical and Materials Transactions A, 2003. **360**: p. 264-274.
46. Mesarovic, S.D. and Fleck, N.A., *Spherical indentations of elastic-plastic solids*. Proc. R. Soc. Lond. A, 1999. **455**: p. 2707-2728.
47. *DataSure Package*, MicroMaterials Ltd. and NPL.
48. Fischer-Cripps, A.C.K., P.;Veprek, S., *On the measurement of hardness of super-hard coatings*. Sur. Coat. Technol., 2006. **200**: p. 5645-5654.
49. Abadias, G., Dub, S., and Shmegeera, R., *Nanoindentation hardness and structure of ion beam sputtered TiN, W and TiN/W multilayer hard coatings*. Surf. Coat. Technol., 2006. **200**: p. 6538-6543.
50. Kulkarni, A.A.B., B, *Nano/picoindentation measurements on single-crystal aluminium using modified atomic force microscopy*. Materials Letters, 1996. **29**: p. 221-227.
51. Soifer, Y.M.V., A.;Rapoport, L., *Nanoindentation size effect in alkali-halide single crystals*. Materials Letters, 2002. **56**: p. 127-130.
52. Schöberl, T.G., H.S.;Fratzl, P., *Measurements of mechanical properties in Ni-base superalloys using nanoindentation and atomic force microscopy*. Mat Sci & Eng, 2003. **A363**: p. 211-220.
53. Bull, S.J., Page, T.F., and Yoffe, E.H., *An Explanation of the Indentation Size Effect in Ceramics*. Philosophical Magazine Letters, 1989. **59**(6): p. 281-288.
54. Nix, W.D. and Gao, H., *Indentation size effects in crystalline materials: a low for strain gradient plasticity*. Journal of the Mechanics and Physics of Solids, 1998. **46**(3): p. 411-425.
55. Fleck, N.A. and Hutchinson, J.W., *Strain gradient plasticity*, in *Advances in Applied Mechanics, Vol 33*. 1997. p. 295-361.

56. Fleck, N.A. and Hutchinson, J.W., *A reformulation of strain gradient plasticity*. Journal of the Mechanics and Physics of Solids, 2001. **49**(10): p. 2245-2271.
57. Fleck, N.A., Muller, G.M., Ashby, M.F., and Hutchinson, J.W., *Strain Gradient Plasticity: Theory and Experiment*. Acta Metall. et Mater., 1994. **42**(2): p. 475-487.
58. Matthews, J.W. and Crawford, J.L., *Accommodation of misfit between single-crystal films of nickel and copper*. Thin Solid Films, 1970. **5**(3): p. 187-198.
59. Dunstan, D. and Bushby, A., *Geometrical Contribution to Yield Strength in Small Volumes*. Materials Research Society Symposium Proceedings, 2003. **778**: p. U9.10.1.
60. Dunstan, D. and Bushby, A., *Theory of deformation in small volumes of material*. Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences, 2004. **460**(2050): p. 2781-2796.
61. Greer, J.R. and Nix, W.D., *Nanoscale gold pillars strengthened through dislocation starvation*. Physical Review B, 2006. **73**(24).
62. Shan, Z.W., R.K., M., Syed Asif, S.A.S., Warren, O.L., and Minor, A.M., *Mechanical annealing and source-limited deformation in submicrometre-diameter Ni crystals*. Nature Materials, 2008. **7**: p. 115-119.
63. Vlassak, J.J. and Nix, W.D., *Measuring the elastic properties of anisotropic materials by means of indentation experiments*. J. Mech. Phys. Solids, 1994. **42**(8): p. 1223-1245.
64. Atkins, A., *Hardness and Deformation Properties of Solids at Very High Temperatures*. Proceedings of the Royal Society. London, Series A., 1966. **292**: p. 441.
65. Atkins, A.G., Silverio, A., and Tabor, D., *Indentation Hardness and the Creep of Solids*. J. Inst. Met, 1966. **94**: p. 369-378.
66. Westbrook, J., *The temperature dependence of hardness of some common oxides*. Rev Hautes Temper et Refract, 1966. **3**(1): p. 47-57.
67. Sherby, O.D. and Armstrong, P., *Prediction of Activation Energies for Creep and Self-Diffusion from Hot Hardness Data*. Metallurgical Transactions, 1971. **2**(12): p. 3479-&.
68. Merchant, H.D., Murty, G.S., Bahadur, S.N., Dwivedi, L.T., and Mehrotra, Y., *Hardness-Temperature Relationships in Metals*. Journal of Materials Science, 1973. **8**(3): p. 437-442.
69. Naylor, M.G.S., *The Effects of Temperature on Hardness and Wear Processes in Engineering Ceramics*. 1982, University of Cambridge.
70. Naylor, M.G.S. and Page, T.F., *Microstructural Studies of the Temperature-Dependence of Deformation Structures around Hardness Indentations in Ceramics*. Journal of Microscopy-Oxford, 1983. **130**(JUN): p. 345-360.
71. Hirsch, P.B., Pirouz, P., Roberts, S.G., and Warren, P.D., *Indentation Plasticity and Polarity of Hardness on {111} Faces of GaAs*. Phil Mag B, 1985. **53**(3): p. 759-784.
72. Sohal, G.S. and Pearce, R., *Activation-Energies for the Deformation of Superplastic Alloys and Their Phases Derived from Hot Microhardness Studies*. Journal of Materials Science, 1987. **22**(7): p. 2327-2331.
73. Twigg, P.C. and Page, T.F., *The Temperature-Variant Hardness Response of Duplex Tbc's*. Thin Solid Films, 1993. **236**(1-2): p. 219-224.
74. Knight, J.C., Page, T.F., and Chandler, H.W., *Thermal-Instability of the Microstructure and Surface Mechanical-Properties of Hydrogenated*

- Amorphous-Carbon Films*. Surface & Coatings Technology, 1991. **49**(1-3): p. 519-529.
75. Serbena, F.C., Williams, W.S., and Roberts, S.G., *High-temperature microhardness study of the brittle-ductile transition in titanium carbide*. Hard Materials, 1995: p. 17-25.
76. Kutty, T.R.G., Ravi, K., and Ganguly, C., *Studies on hot hardness of Zr and its alloys for nuclear reactors*. Journal of Nuclear Materials, 1999. **265**(1-2): p. 91-99.
77. Pitchford, J.E., Stearn, R.J., Kelly, A., and Clegg, W.J., *Effect of Oxygen Vacancies on the Hot Hardness of Mullite*. J. Am. Ceram. Soc., 2001. **84**: p. 1167-1168.
78. Yonenaga, I. and Suzuki, T., *Indentation hardnesses of semiconductors and a scaling rule*. Philosophical Magazine Letters, 2002. **82**(10): p. 535-542.
79. Sastry, D.H., *Impression creep technique - An overview*. Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing, 2005. **409**(1-2): p. 67-75.
80. Lund A.C., H.A.M., Schuh C.A., *Incipient Plasticity during nanoindentation at elevated temperatures*. Applied Physics Letters, 2004. **85**(8): p. 1362-1364.
81. *Multi-range Nanoprobe*. [cited 2006 June]; Available from: <http://www.hysitron.com/PDF/MN-01b.pdf>.
82. *Temperature Stage: Controlled Temperature Characterization*. [cited 2006 June]; Available from: <http://www.hysitron.com/PDF/0102-002.pdf>.
83. Hay, J. *Application Note: Actuation & Sensing*. 2004 [cited 2006 June]; Available from: http://www.mtsnano.com/pdf/appnote_actuation_layout_v2.pdf.
84. Kramer, D.E., Yoder, K.B., and Gerberich, W.W., *Surface constrained plasticity: oxide rupture and the yield point process*. Philosophical Magazine A, 2001. **81**(8): p. 2033-2058.
85. Volinsky, A.A., Moody, N.R., and Gerberich, W.W., *Nanoindentation of Au and PT/CU thin films at elevated temperatures*. Journal of Materials Research, 2004. **19**(9): p. 2650-2657.
86. Schuh, C.A., Mason, J.K., and Nieh, T.G., *New regime of homogenous flow in the deformation map of metallic glasses: elevated temperature nanoindentation experiments and mechanistic modelling*. Acta Materialia, 2004. **52**: p. 5879-5891.
87. Smith J.F., Z.S., *High Temperature Nanoscale Mechanical Property Measurement*. Surface Engineering, 2000. **16**(2): p. 143-146.
88. Beake, B. and Smith, J., *High-temperature nanoindentation testing of fused silica and other materials*. Philosophical Magazine A, 2002. **82**(10): p. 2179-2186.
89. Xia, J., Li, C.X., and Dong, H., *Hot-stage nano-characterisations of an iron aluminide*. Materials Science and Engineering, 2003. **A354**: p. 112-120.
90. Evans, T. and Phaal, C. *The Kinetics of the Diamond-Oxygen Reaction*. in *Proceedings of the 5th Conference on Carbon*. 1961.
91. Field, J.E., *The Properties of Natural and Synthetic Diamond*. 1992: Academic Press.
92. Evans, T., *Changes Produced by High Temperature Treatment of Diamond*, in *The Properties of Diamond*, J.E. Field, Editor. 1979, Academic Press: New York. p. 403-424.

93. Martel, R. in *Commission des Methodes d'Essai des Materiaux de Construction*. 1895. Paris.
94. Vincent, J.H., Proc. Camb. Phil. Soc., 1900. **10**: p. 332.
95. Tabor, D., *A simple theory of static and dynamic hardness*. Proceedings of the Royal Society A, 1948. **192**: p. 247.
96. Tirupataiah, Y. and Sundararajan, G., *A dynamic indentation technique for the characterization of the high strain rate plastic flow behaviour of ductile metals and alloys*. J Mech Phys Solids, 1991. **39**(2): p. 243-271.
97. Sundararajan, G. and Tirupataiah, Y., *The localization of plastic flow under dynamic indentation conditions: I. Experimental results*. Acta mater., 2006. **54**(3): p. 565-575.
98. Sundararajan, G. and Tirupataiah, Y., *The localization of plastic flow under dynamic indentation conditions: II. Analysis of results*. Acta mater., 2006. **54**(3): p. 577-586.
99. Subhash, G., Koeppel, B., and Chandra, A., *Dynamic indentation hardness and rate sensitivity in metals*. J Eng Mat and Tech, 1999. **121**: p. 257-263.
100. Koeppel, B. and Subhash, G., *Characteristics of residual plastic zone under static and dynamic Vickers indentations*. Wear, 1999. **224**: p. 56-67.
101. Anton, R. and Subhash, G., *Dynamic Vickers indentation of brittle materials*. Wear, 2000. **239**: p. 27-35.
102. Lu, J., Suresh, S., and Ravichandran, G., *Dynamic indentation for determining the strain rate sensitivity of metals*. J Mech Phys Solids, 2003. **51**: p. 1923-1938.
103. Andrews, E., Giannakopoulos, A.E., Plisson, E., and Suresh, S., *Analysis of the impact of a sharp indenter*. Int J Solids and Structures, 2002. **39**: p. 281-295.
104. Giannakopoulos, A.E. and Suresh, S., *Determination of elastoplastic properties by instrumented sharp indentation*. Scripta Materialia, 1999. **40**(10): p. 1191-1198.
105. Nobre, J., Dias, A., and Gras, R., *A study on elasto-plastic impact friction*. Wear, 1999. **230**: p. 133-145.
106. Nobre, J., Dias, A., and Gras, R., *Resistance of a ductile steel surface to spherical normal impact indentation: use of a pendulum machine*. Wear, 1997. **211**: p. 226-236.
107. Beake, B., Goodes, S.R., and Smith, J.F., *Micro Impact Testing: A New Technique for Investigating Thin Film Toughness, Adhesion, Erosive Wear Resistance and Dynamic Hardness*. Surf. Eng., 2001. **17**(3): p. 187-192.
108. Beake, B., Goodes, S., Smith, J., Madani, R., Rego, C., Cherry, R., and Wagner, T., *Investigating the fracture resistance and adhesion of DLC films with micro-impact testing*. Diamond and Related Materials, 2002. **11**: p. 1606-1609.
109. Beake, B., Garcia, M., and Smith, J., *Micro-impact testing: a new technique for investigating fracture toughness*. Thin Solid Films, 2001. **398-399**: p. 438-443.
110. Beake, B., *Evaluation of the fracture resistance of DLC coatings on tool steel under dynamic loading*. Surf. Coat. Techn., 2005. **198**: p. 90-93.
111. Beake, B. and Smith, J., *Nano-impact testings - an effective tool for assessing the resistance of advanced wear-resistant coatings to fatigue failure and delamination*. Surf. Coat. Techn., 2004. **188-189**: p. 594-598.

112. Beake, B., Lau, S., and Smith, J., *Evaluating the fracture properties and fatigue wear of tetrahedral amorphous carbon films on silicon by nano-impact testing*. Surf. Coat. Techn., 2004. **177-178**: p. 611-615.
113. Beake, B. and Ranganathan, N., *An investigation of the nanoindentation and nano/micro-tribological behaviour of monolayer, bilayer and trilayer coatings on cemented carbide*. Materials Science and Engineering: A, 2006. **423**: p. 46-51.
114. Beake, B., Smith, J., Gray, A., Fox-Rabinovich, G., Veldhuis, S., and Endrino, J., *Investigating the correlation between nano-impact fracture resistance and hardness/modulus ratio from nanoindentation at 25-500C and the fracture resistance and lifetime of cutting tools with $Ti_{1-x}Al_xN$ ($x=0.5$ and 0.67) PVD coatings in milling operations*. Surface & Coatings Technology, 2007. **201**: p. 4585-4593.
115. Bierbaum, C., Iron Age, 1920. **106**: p. 1.
116. O'Neill, H., *The Hardness of Metals and Its Measurement*. 1934, London: Chapman and Hall.
117. Wu, T., *Microscratch and load relaxation tests for ultra-thin films*. Journal of Materials Research, 1991. **6**(2): p. 407-426.
118. Michler, J., Rabe, R., Bucaille, J.-L., Moser, B., Schwaller, P., and Breguet, J.-M., *Investigation of wear mechanisms through in situ observation during microscratching inside the scanning electron microscope*. Wear, 2005. **259**: p. 18-26.
119. Williams, J.A., *Analytical models of scratch hardness*. Tribology International, 1996. **29**(8): p. 675-694.
120. Brookes, C., Green, P., Harrison, P., and Moxley, B., *Some observations on scratch and indentation hardness*. J. Phys. D: Appl. Phys., 1972. **5**: p. 1284-1295.
121. Briscoe, B.J., Evans, P.D., Pelillo, E., and Sinha, S.K., *Scratching Maps for Polymers*. Wear, 1996. **200**: p. 137-147.
122. Hainsworth, S.V., Bull, S.J., and Page, T.F. *Scratch deformation response of thin CN_x coatings at ultra-low loads*. in *Proceedings MRS Spring Meeting*. 1998. San Francisco.
123. Heavens, O., J. Phys. Radium, 1950. **11**: p. 355.
124. Benjamin, P. and Weaver, C., *Proceedings of the Royal Society*. London, Series A., 1960. **254**: p. 163.
125. Laugier, M., *The development of the scratch test technique for the determination of the adhesion of coatings*. Thin Solid Films, 1981. **76**: p. 289-294.
126. Laugier, M., *An energy approach to the adhesion of coatings using the scratch test*. Thin Solid Films, 1984. **117**: p. 243-249.
127. Burnett, P. and Rickerby, D., *The relationship between hardness and scratch adhesion*. Thin Solid Films, 1987. **154**: p. 403-416.
128. Bull, S., Rickerby, D., Matthews, A., Leyland, A., Pace, A., and Valli, J., *The use of scratch adhesion testing for the determination of interfacial adhesion: the importance of frictional drag*. Surface and Coatings Technology, 1988. **36**: p. 503-517.
129. Bull, S., *Failure modes in scratch adhesion testing*. Surface and Coatings Technology, 1991. **50**: p. 25-32.

130. Bull, S.J. and Berasetegui, E.G., *An overview of the potential of quantitative coating adhesion measurement by scratch*. Tribology International, 2006. **39**(2): p. 99-114.
131. Bull, S.J. and Rickerby, D.S., *Multi-pass scratch testing as a model for abrasive wear*. Thin Solid Films, 1989. **181**: p. 545-553.
132. Bull, S.J., *Can scratch testing be used as a model for the abrasive wear of hard coatings?* Wear, 1999. **233-235**: p. 412-423.
133. Gee, M.C., *Low load multiple scratch tests of ceramics and hard metals*. Wear, 2001. **250**: p. 264-281.
134. ASM, *Metals Handbook*. 10th ed, ed. L.A. Abel, et al. Vol. 2. 1990, Materials Park, Ohio: American Society of Metals.
135. Pemberton, S., *Investigation of Superelastic Behaviour in a NiTi Shape Memory Alloy at High Strain Rates*. 2008, University of Cambridge.
136. Collier, A., *The Erosion Resistance of Plasma Electrolytic Oxide Coatings on Titanium*. 2007, University of Cambridge.
137. Curran, J.A., *Personal Communication with J. Wheeler*. 2008.
138. Lewis, F., *The Palladium-Hydrogen System*. 1967, New York, NY: Academic Press.
139. NASA Earth Fact Sheet. [cited 2009; Available from: <http://nssdc.gsfc.nasa.gov/planetary/factsheet/earthfact.html>].
140. Wicke, E. and Brodowsky, H., *Hydrogen in Palladium and Palladium Alloys*, in *Hydrogen in Metals II*, G. Alefeld and J. Völkl, Editors. 1978, Springer-Verlag: Berlin. p. 73-151.
141. Schirber, J. and Morosin, B., *Lattice constants of β -PdH_x and β -PdD_x with x near 1.0*. Phys. Rev. B, 1975. **12**(1): p. 117-118.
142. Worsham, J.J., Wilkinson, M., and Shull, C., *Neutron-diffraction observations on the palladium-hydrogen and palladium-deuterium systems*. J. Phys. Chem. Solids, 1957. **3**: p. 303-310.
143. Owen, E. and Jones, J., *The palladium-hydrogen system*. Proceedings of the Physical Society, 1937. **49**: p. 603-610.
144. Goldschmidt, H.J., *Interstitial Alloys*. 1967, London: Butterworths.
145. Goltsov, V., *The phenomenon of controllable hydrogen phase naklep and the prospects for its use in metal science and engineering*. Materials Science and Engineering, 1981. **49**: p. 109-125.
146. Graham, T., *On the absorption and dialytic separation of gases by colloid septa*. Philosophical Transactions of the Royal Society of London, 1866. **156**: p. 399-439.
147. Völkl, J. and Alefeld, G., *Diffusion of Hydrogen in Metals*, in *Hydrogen in Metals I*, G. Alefeld and J. Völkl, Editors. 1978, Springer-Verlag: Berlin. p. 321-344.
148. Seymour, E., Cotts, R., and David Williams, W., *NMR measurement of hydrogen diffusion in β -Palladium hydride*. Phys. Rev. Lett., 1975. **35**(3): p. 165-167.
149. Kirchheim, R., *Interaction of hydrogen with dislocations in palladium-I. activity and diffusivity and their phenomenological interpretation*. Acta Metallurgica, 1981. **29**: p. 835-843.
150. Jamieson, H., Weatherly, G.C., and Manchester, F., *The $\beta \rightarrow \alpha$ phase transformation in palladium-hydrogen alloys*. Journal of the Less-Common Metals, 1976. **50**: p. 85-102.

151. Goltsova, M., *Reverse hydride transformations in the Pd-H system*. International Journal of Hydrogen Energy, 2006. **31**: p. 223-229.
152. Zhironov, G., Goltsova, M., and Shatalova, G., *Hydrogen phase naklep influence on palladium grain and fine structures*. international Journal of Hydrogen Energy, 2006. **31**: p. 231-236.
153. Peisl, H., *Lattice Strains Due to Hydrogen in Metals*, in *Hydrogen in Metals I*, G. Alefeld and J. Völkl, Editors. 1978, Springer-Verlag: Berlin. p. 53-73.
154. Fabre, A., Finot, E., Demoment, J., and Contreras, S., *Monitoring the chemical changes in Pd induced by hydrogen absorption using microcantilevers*. Ultramicroscopy, 2003. **97**: p. 425-432.
155. Anderton, C., Strother, N., Pote, J., Foley, R., Rebeiz, K., Nesbit, S., and Craft, A., *Influence of partial hydride formation/decomposition on the mechanical properties of palladium*. Scripta Mater., 1996. **35**(8): p. 1013-1018.
156. Muir Wood, A.J., Gergely, V., and Clyne, T.W. *Indentation characteristics of superelastic nickel-titanium wires and a preliminary study of copper-bonded joints between them*. in *Smart Structures and Materials 2004: Active Materials: Behavior and Mechanics*. 2004. San Diego: SPIE.
157. Muir Wood, A.J., You, J.-H., and Clyne, T.W. *Nanoindentation response of superelastic materials*. in *Smart Materials, Nano-, and Micro-Smart Systems: Smart Materials III*. 2004. Sydney: SPIE.
158. Muir Wood, A.J., *Indentation of Shape Memory Materials*, in *Department of Materials Science*. 2005, University of Cambridge.
159. Muir Wood, A.J., Sanjabi, S., Fu, Y.Q., Barber, Z.H., and Clyne, T.W., *Nanoindentation of Binary and Ternary Ni-Ti-based Shape Memory Alloy Thin Film*. Surface & Coatings Technology, 2008. **202**: p. 3115-3120.
160. Perkins, J., *Shape Memory Effect in Alloys*. 1975, New York: Plenum Press.
161. Auricchio, F., Taylor, R.L., and Lubliner, J., *Shape-memory alloys: macromodelling and numerical simulations of the superelastic behavior*. Computer Methods in Applied Mechanics and Engineering, 1997. **146**: p. 281-312.
162. Pelton, A.R., Hodgson, D., and Duerig, T.W., *Proceedings of SMST 94: The First International Conference on Shape Memory and Superelastic Technologies*. 1994.
163. Duerig, T., Melton, K.N., Stöckel, D., and Wayman, C.M., eds. *Engineering aspects of shape memory alloys*. 1990, Butterworth-Heinemann.
164. Auricchio, F. and Taylor, R.L., *Shape-memory alloys: modelling and numerical simulations of the finite-strain superelastic behavior*. Computer Methods in Applied Mechanics and Engineering, 1997. **143**: p. 175-194.
165. Entemeyer, D., Patoor, E., Eberhardt, A., and Barveiller, M., *Strain Rate Sensitivity in Superelasticity*. International Journal of Plasticity, 2006. **16**: p. 1269-1288.
166. Chen, W.W., Wu, Q.P., Kang, J.H., and Winfree, N.A., *Compressive Superelastic Behavior of a NiTi Shape Memory Alloy at Strain Rates of 0.001-750 s⁻¹*. Int J Solids and Structures, 2001. **38**: p. 8989-8998.
167. Nemat-Nasser, S. and Guo, W.-G., *Superelastic and Cyclic Response of NiTi SMA at Various Strain Rates and Temperatures*. Mechanics of Materials, 2006. **38**: p. 463-474.

-
168. Clyne, T.W. *DoITPoMS TLP - Superelasticity and the Shape Memory Effect*. 2007 [cited 2008; Available from: http://www.doitpoms.ac.uk/tlplib-dev2008/superelasticity/shape_memory1.php].
169. Lui, *TiNi Shape Memory Alloys*, in *Shape Memory Materials*, C.M.W. K. Obsuka, Editor, CUP: Cambridge. p. 49-96.
170. Adharapurapu, R.R., Jiang, F., Vecchio, K.S., and III, G.T.G., *Response of NiTi Shape Memory Alloy at High Strain Rate: A Systematic Investigation of Temperature Effects on Tension-Compression Asymmetry*. *Acta Materialia*, 2006. **54**: p. 4609-4620.
171. Schmidt, I., *A Phenomenological Model for Superelastic NiTi Wires Based on Plasticity With Focus on Strain-Rate Dependency Caused by Temperature*. *Journal of Engineering Materials and Technology*, 2006. **128**: p. 279-284.
172. Tobushi, H., Shimeno, Y., Hachisuka, T., and Tanaka, K., *Influence of Strain Rate on Superelastic Properties of TiNi Shape Memory Alloy*. *Mechanics of Materials*, 1998. **30**: p. 141-150.
173. Millett, J.C.F., Bourne, N.K., and Gray, G.T., *Behaviour of the Shape Memory Alloy NiTi during One Dimensional Shock Loading*. *J. Applied Physics*, 2002. **92**: p. 3107-3110.
174. Nemat-Nasser, S., Choi, J.-Y., Guo, W.-G., and Isaacs, J.B., *Very High Strain-Rate Response of a NiTi Shape-Memory Alloy*. *Mechanics of Materials*, 2005. **37**: p. 287-298.
175. Nemat-Nasser, S., Choi, J.Y., Guo, W.-G., Isaacs, J.B., and Taya, M., *High Strain-Rate, Small Strain Response of a NiTi Shape-Memory Alloy*. *Journal of Engineering Materials and Technology*, 2005. **127**: p. 83-89.
176. Šittner, P., *Characterisation, Modelling and Application of the Functional Behaviour of Thin NiTi Wires*, in *Cambridge Centre for Micromechanics Seminar*. 2008: Cambridge University.
177. Gadaj, S.P., Nowacki, W.K., Pieczyska, E.A., and Tobushi, H., *Temperature Measurement as a New Technique Applied to the Phase Transformation Study in a TiNi Shape Memory Alloy Subjected to Tension*. *Archives of Metallurgy and Materials*, 2005. **50**(3): p. 668.
178. Favier, D., Louche, H., Schlosser, P., L.Orgéas, Vacher, P., and Debove, L., *Homogeneous and Heterogeneous Deformation Mechanisms in an Austenitic Polycrystalline Ti-50.8 at.% Ni Thin Tube under Tension. Investigation via Temperature and Strain Fields Measurements*. *Acta mater.*, 2007. **55**: p. 5310-5322.
179. Shaw, J.A. and Kyriakides, S., *Thermomechanical aspects of NiTi*. *Journal of the Mechanics and Physics of Solids*, 1995. **43**: p. 1243-1281.
180. Curran, J.A., *Thermal and Mechanical Properties of Plasma Electrolytic Oxide Coatings*. 2005, University of Cambridge: Cambridge, UK.
181. Curran, J.A. and Clyne, T.W., *Thermo-physical Properties of Plasma Electrolytic Oxide Coatings on Aluminium*. *Surf. & Coat. Techn.*, 2005. **199**: p. 168-176.
182. Curran, J.A. and Clyne, T.W., *The Thermal Conductivity of Plasma Electrolytic Oxide Coatings on Aluminium and Magnesium*. *Surf. & Coat. Techn.*, 2005. **199**: p. 177-183.
183. Curran, J.A. and Clyne, T.W., *Porosity in Plasma Electrolytic Oxide Coatings*. *Acta Materialia*, 2006. **54**: p. 1985-1993.

184. Curran, J.A., Kalkanci, H., Magurova, Y., and Clyne, T.W., *Mullite-rich plasma electrolytic oxide coatings for thermal barrier applications*. Surface and Coatings Technology, 2006. **201**(21): p. 8683-8687.
185. Paillard, J., *PEO processing of titanium*. 2008, University of Cambridge.
186. Bull, S.J., *Nano-indentation of coatings*. Journal of Physics D-Applied Physics, 2005. **38**(24): p. R393-R413.
187. Page, T.F. and Bull, S.J., *Measuring and modelling the instrumented indentation (nanoindentation) response of coated systems*. Philosophical Magazine, 2006. **86**(33-35): p. 5331-5346.
188. Voevodin, A.A., Yerokhin, A.L., Lyubimov, V.V., Donley, M.S., and Zabinski, J.S., *Characterisation of Wear Protective Al-Si-O Coatings formed on Al-based Alloys by Micro-arc Discharge Treatment*. Surf. & Coat. Techn., 1996. **86-7**(1-3): p. 516-521.
189. Yerokhin, A.L., Nie, X., Leyland, A., Matthews, A., and Dowey, S.J., *Plasma Electrolysis for Surface Engineering (Review)*. Surf. & Coat. Techn., 1999. **122**(2-3): p. 73-93.
190. Dearnley, P.A., Gummersbach, J., Weiss, H., Ogwu, A.A., and Davies, T.J., *The sliding wear resistance and frictional characteristics of surface modified aluminium alloys under extreme pressure*. Wear, 1999. **225**: p. 127-134.
191. Nie, X., Leyland, A., Song, H.W., Yerokhin, A.L., Dowey, S.J., and Matthews, A., *Thickness Effects on the Mechanical Properties of Micro-Arc Discharge Coatings on Aluminium Alloys*. Surf. & Coat. Techn., 1999. **116-119**: p. 1055-1060.
192. Gnedenkov, S.V., Khrisanfova, O.A., Zavidnaya, A.G., Sinebrukhov, S.L., Gordienko, P.S., Iwatsubo, S., and Matsui, A., *Composition and Adhesion of Protective Coatings on Aluminum*. Surf. & Coat. Techn., 2001. **145**(1-3): p. 146-151.
193. Tian, J., Luo, Z.Z., Qi, S.K., and Sun, X.J., *Structure and Antiwear Behavior of Micro-arc Oxidized Coatings on Aluminum Alloy*. Surf. & Coat. Techn., 2002. **154**(1): p. 1-7.
194. Nie, X., Meletis, E.I., Jiang, J.C., Leyland, A., Yerokhin, A.L., and Matthews, A., *Abrasive Wear/corrosion Properties and TEM Analysis of Al₂O₃ Coatings Fabricated using Plasma Electrolysis*. Surf. & Coat. Techn., 2002. **149**(2-3): p. 245-251.
195. Rama Krishna, L., Somaraju, K.R.C., and Sundararajan, G., *The Tribological Performance of Ultra-hard Ceramic Composite Coatings obtained through Microarc Oxidation*. Surf. Coat. Techn., 2003. **163-164**: p. 484-490.
196. Barik, R., Wharton, J.A., Wood, R.J.K., Stokes, K.R., and Jones, R.L. *Erosion and Erosion-corrosion Performance of Plasma Electrolytic Oxidation (PEO) Deposited Al₂O₃*. in *Tri-Service Corrosion Conference*. 2003. Las Vegas (November 2003): Navmar Applied Science Corp., Chester, PA.,
197. Wei, T., Yan, F., and Tian, J., *Characterisation and Wear and Corrosion-resistance of Microarc Oxidation Ceramic Coatings on Aluminum Alloy*. J. Alloys and Compounds, 2004. **389**: p. 169-176.
198. Rama Krishna, L., Sudha Purnima, A., and Sundararajan, G., *A comparative study of tribological behavior of microarc oxidation and hard-anodized coatings*. Wear, 2006. **261**: p. 1095-1101.
199. Yerokhin, A.L., Lyubimov, V.V., and Ashitkov, R.V., *Phase Formation in Ceramic Coatings During Plasma Electrolytic Oxidation of Aluminium Alloys*. Ceramics International, 1996. **24**: p. 1-6.

200. Yerokhin, A.L., Nie, X., Leyland, A., and Matthews, A., *Characterisation of Oxide Films produced by Plasma Electrolytic Oxidation of a Ti-6Al-4V alloy*. Surf. & Coat. Techn., 2000. **130**(2-3): p. 195-206.
201. Yerokhin, A.L., Leyland, A., and Matthews, A., *Kinetic aspects of Aluminium Titanate layer formation on Titanium Alloys by Plasma Electrolytic Oxidation*. App. Surf. Sci., 2002. **200**(1-4): p. 172-184.
202. Dong, Q., Chen, C.Z., Wang, D.G., and Ji, Q.M., *Research status about surface modification of biomedical Ti and its alloys by micro-arc oxidation* Surface Review and Letters, 2006. **13**: p. 35-43.
203. Song, H.J. and Park, Y.J., *Fabrication of BaTiO₃ films on titanium by microarc oxidation method and improvement of bioactivity by electric poling treatment*. Materials Letters, 2007. **61**: p. 3473-3476.
204. Wei, D., Zhou, Y., Jia, D., and Wang, Y., *Characteristic and in vitro bioactivity of a microarc-oxidized TiO₂-based coating after chemical treatment*. Acta Biomaterialia, 2007. **3**: p. 817-827.
205. Zhu, L., Ye, X., Tang, G., Zhao, N., Gong, Y., Zhao, Y., Zhao, J., and Zhang, X., *Biomimetic coating of compound titania and hydroxyapatite on titanium*. J. Biomedical Materials Research, 2007. **83A**: p. 1165-1175.
206. Sul, Y.T., *The significance of the surface properties of oxidized titanium to the bone response: special emphasis on potential biochemical bonding of oxidized titanium implant*. Biomaterials, 2003. **24**: p. 3893-3907.
207. Hou, T. and Zhang, J.Z., *Porous films on surface of titanium prepared by low voltage micro arc oxidation*. Surface Engineering, 2007. **23**: p. 169-172.
208. Wang, Y.M., Lei, T.Q., Guo, L.X., and Jiang, B.L., *Fretting wear behaviour of microarc oxidation coatings formed on titanium alloy against steel in unlubrication and oil lubrication* Appl. Surface Science, 2006. **252**: p. 8113-8120.
209. Yao, Z.P., Jiang, Z.H., and Wang, F.P., *Study on corrosion resistance and roughness of micro-plasma oxidation ceramic coatings on Ti alloy by EIS technique* Electrochimica Acta, 2007. **52**: p. 4539-4546.
210. Yao, Z., Jiang, Z., Wang, F., and Hao, G., *Oxidation behavior of ceramic coatings on Ti-6Al-4V by micro-plasma oxidation* J. Materials Processing Technology, 2007. **190**: p. 117-122.
211. Habazaki, H., Onodera, T., Fushimi, K., Konno, H., and Toyotake, K., *Spark anodizing of β -Ti alloy for wear-resistant coating*. Surface and Coatings Technology, 2007. **201**(21): p. 8730-8737.
212. Paillard, J.M. and Curran, J.A., *Unpublished X-Ray diffraction work (specimen supplied by Keronite Plc.)*. 2008.
213. Hutchings, I.M., *Tribology : Friction and Wear of Engineering Materials*. Metallurgy & Materials Science. 1992: Edward Arnold.
214. Clifford, S.M., Curran, J.A., Shipway, P.H., and Clyne, T.W. *Abrasive Wear Testing of Steel and Plasma Electrolytic Oxidation-treated Aluminium*. in *IoM3 Materials Congress*. 2006. Carlton House Terrace, London.
215. Matykina, E., Doucet, G., Monfort, F., Berkani, A., Skeldon, P., and Thompson, G.E., *Destruction of coating material during spark anodizing of titanium*. Electrochimica Acta, 2006 **51**: p. 4709-4715.
216. Matykina, E., Monfort, F., Berkani, A., Skeldon, P., Thompson, G.E., and Chapon, P., *Tracing locations of new coating material during spark anodizing of titanium*. Philosophical Magazine, 2006. **86**(1): p. 49-66.

- 217. Xue, W., Deng, Z., Ma, H., Chen, R., and Zhang, T., *Microstructure and phase composition of microarc oxidation coatings formed on Ti-6Al-4V alloy in aluminate solution*. Surface Engineering, 2001. **17**(4): p. 323-326.
- 218. Wang, Y.M., Jiang, B.L., Lei, T.Q., and Guo, L.X., *Microarc oxidation coatings formed on Ti6Al4V in Na₂SiO₃ system solution: Microstructure, mechanical and tribological properties*. Surface & Coatings Technology, 2006. **201**(1-2): p. 82-89.
- 219. Dworak, W. and Fingerle, D., *Ceramic Materials for Engines*. British Ceramic Transactions and Journal, 1987. **86**(6): p. 170-178.
- 220. Curran, J.A., *Personal communication*. 2008.