NANO-SCRATCH HARDNESS AND THE LATERAL SIZE EFFECT (LSE)

This thesis is submitted for the degree of Doctor of Philosophy at the University of Leicester

by

Anna Kareer MEng
Department of Engineering
University of Leicester

Under the supervision of Professor S. V. Hainsworth
**ABSTRACT**

Nano-scratch testing has been used throughout this thesis in order to deepen the understanding of the processes occurring during the nano-scratch test, and to develop a method for calculating the nano-scratch hardness, from the quantifiable variables that are obtainable from the technique. Scratch testing on the macro scale is a well-established technique, however when reducing the scale of a mechanical test, whilst interest is focussed on the yield strength or hardness of the material, plasticity size effects must be explored. A literature survey concludes that size effects in nano-scratch testing have not been investigated in the past, thus this is the main subject of this thesis. In order to carry out this investigation a number of methods were trialled to calculate the nano-scratch hardness of pure, polycrystalline, oxygen free copper using both the edge forward and the face forward tip orientations of a diamond Berkovich indenter. The results obtained were compared to the indentation hardness and the most theoretically suitable method was adopted for later experiments carried out in this work; the technique for obtaining measurements was optimised, such that a genuine lateral size effect (LSE), whereby the nano-scratch hardness increases with decreasing scratch size, was observed. To further investigate the lateral size effect, nano-scratches were performed on a sample of single crystal copper in different work hardened states. It was observed that the nano-scratch hardness not only increases with decreasing scratch size, but also increases when the spacing between the dislocations in the material is reduced; when the level of work hardening in the sample increases, the density of dislocations increases, thus the spacing between these obstacles is reduced. In addition to this, the anisotropy of the nano-scratch hardness was investigated by altering the scratch direction in the (100) plane of the single crystal copper. It was found that the nano-scratch hardness is anisotropic and that the scratch hardness is largest when the scratch direction is parallel to the slip plane. It is known that the yield strength of a material increases with decreasing average grain size and therefore the effect of grain size on the nano-scratch hardness was considered. By reducing the grain size of pure, annealed, oxygen free copper, the nano-scratch hardness was observed to increase. In all experiments, the nano-scratch hardness values of scratches performed in the face forward tip orientation were larger than that of scratches performed in the edge forward tip orientation, when scratching the same sample condition. This suggests that scratch hardness is tip geometry dependent and in order to develop a method of calculating a tip orientation-independent scratch hardness, the shape of the indenter and the
plastic flow of material around the indenter in that orientation, must be known and incorporated into the calculation, possibly as a drag coefficient. In addition to the geometry of the plastic flow, and therefore the plastic zone size, it was found that the nano-scratch hardness is also governed by the interaction between the geometry of the indenter and the grain boundaries in the material. Finally a number of experimental issues from the nano-scratch test are highlighted and researchers are encouraged to consider these precautions when using the nano-scratch test.
TABLE OF CONTENTS

Abstract ................................................................................................................................. 2
Acknowledgements .............................................................................................................. 7
List of figure captions ........................................................................................................ 9
2. Introduction ..................................................................................................................... 16
   2.1 Indentation hardness and the size effect (ISE) ............................................................ 17
   2.2 Nano-indentation ....................................................................................................... 19
   2.3 Nano-scratch test ...................................................................................................... 21
   2.4 Research aims .......................................................................................................... 22
   2.5 Thesis structure ....................................................................................................... 24
3. Literature Review ........................................................................................................... 25
   3.1 Indentation size effect ............................................................................................. 25
   3.1.1 Berkovich / pyramidal indentation size effect .................................................... 25
   3.1.2 Spherical indentation .......................................................................................... 28
   3.1.3 Models and mechanisms ..................................................................................... 31
   3.1.4 The Nix and Gao Model (1998) ......................................................................... 32
   3.1.5 The Hall-Petch effect in indentation .................................................................... 36
   3.1.6 Slip distance theory ........................................................................................... 38
   3.1.7 Summary ............................................................................................................. 42
   3.2 Review of the scratch test ....................................................................................... 43
   3.2.1 Macroscopic scratch testing ................................................................................. 43
   3.2.2 Nano-scratch testing ........................................................................................... 45
   3.2.3 Lateral force measurement ................................................................................. 46
   3.2.4 Three-pass scratch method ................................................................................ 46
   3.2.5 Current uses of nano-scratch testing ................................................................. 48
   3.2.6 Scratch hardness measurements ........................................................................ 53
   3.2.7 Link between indentation hardness and scratch hardness .................................. 54
   3.2.8 Summary ............................................................................................................. 55
4. Experimental Techniques ............................................................................................... 56
   4.1 Nano-indenter .......................................................................................................... 56
1. Single crystal, as received (0 hours)..................................................133
2. Single crystal annealed (1 hour) ......................................................134
3. Single crystal annealed (4 hours)......................................................135
4. Polycrystalline copper, grain size 1.15µm........................................136
5. Polycrystalline copper, grain size 2.2µm ................................................................. 137
6. Polycrystalline copper, grain size 17.36µm ............................................................... 138
7. Polycrystalline copper, grain size 44.4µm ................................................................. 139
11. References ............................................................................................................. 140
ACKNOWLEDGEMENTS

I would like to express gratitude to all of the people who made completing this thesis possible. Firstly my supervisors, Professor Sarah Hainsworth who has been a role model, whom I look up to. I sincerely appreciate all of the encouragement and support she has provided me with over the last three years. Professor Nigel Jennet, for all the knowledge I have gained from him throughout my PhD during our numerous discussions at NPL (and additional discussions that I have eavesdropped on whilst sharing an office with you!). I thank you for encouraging me to 'think like a physicist' and I am sure this will be very useful in life. I would also like to say an enormous thank you to Dr Xiaodong Hou, who has been an amazing mentor throughout my PhD providing me with new ideas, good advice and lots of laughs along the way. You have made my stay at NPL both enjoyable and productive.

To all of my colleagues and the staff members from the University of Leicester Engineering department, I thank you all for your continuous help, support and guidance in addition to good company and friendly faces to work with. In particular a special thanks to Graham Clark, whom I have relied on when things haven't gone to plan in the labs, which was more often than not, and Michael Dodge for his expert advice in microscopy, hence the nickname Mike-rooscope!

I appreciate all of the support from my close friends and family who have made my time in Leicester a pleasure. I thank my Siblings, Alka Kareer and Ajay Kareer who provide me with the confidence I need to achieve my goals in life.

I would like to give a special thank you to Tristram Broadbent for all his love and support during the most difficult and frustrating of times, in particular whilst writing this thesis. I thank you for bearing with me during my bad moods and tantrums, and continuously reminding me that I am capable of achieving this.
Finally I wish to thank my parents, Baljit Kareer and Harjinder Kareer. I thank you for your love, support, encouragement and advice. You have always taught me that education is of key importance in life, therefore I dedicate this thesis to you.

The financial support provided by the DTA and the National Physical Laboratory is gratefully acknowledged.

Leicester, 2014

Anna Kareer
LIST OF FIGURE CAPTIONS

Figure 1-1 – A schematic representation of a section through an indentation showing the variables used in the Oliver and Pharr analysis [12]................................................................. 20

Figure 2-1 – Berkovich tip geometry. Original angle \( a \) was 65.03\(^\circ\), the modified Berkovich has angle \( a \) of 65.3\(^\circ\)..................................................................................................................... 25

Figure 2-2 –a. Indentation size effect in (111) single crystal copper and polycrystalline cold worked copper performed with a Berkovich diamond indenter by McElhaney et al. [17]. b. Indentation size effect observed for both nano-indentation data (open squares and crosses) and Vickers hardness data (closed triangles) of polycrystalline annealed and work-hardened oxygen-free copper by Lim et al. [18]........................................................................................................ 27

Figure 2-3 - Schematic of the spherical indentation test. Ratio of contact radius to indenter radius give the indentation strain [23]. .................................................................................................. 28

Figure 2-4 – Spherical indentation stress-strain curves of Copper; Experimental spherical indentation data (open symbols), Finite Element simulation (closed symbols), Tabor representation of uniaxial data (solid line), Hertzian elastic response (dashed line); Radius of the indenter used in each case are given in the legend.[21]. .................................................................................... 29

Figure 2-5 – Plastic strain gradient beneath an indentation. The plastic strain is large immediately beneath the indenter and is small further away creating a gradient of strain[1]..... 32

Figure 2-6 – (a) Model of geometrically necessary dislocations for a conical indentation (b) a general indentation profile (c) a spherical indentation [24]....................................................................................... 35

Figure 2-7 – (a) Edge dislocation located at A subjected to an external shear stress. (b) Edge dislocation moves to location B by dislocation glide (distance AB). (c) Plastic displacement is produced from the glide of the dislocation................................................................. 39

Figure 2-8 - (a) Scanning electron micrographs (backscattered image) of scratch tracks in a 100 nm aluminium coating on 304 stainless steel showing the stripping of the coating at the critical load with a sharp change (top scratch) and a more gradual change as the aluminium coating is
thinned (lower scratch). (b) Associated friction traces showing a sharp and gradual transition in the friction coefficient [65].

Figure 2-9 - Schematic representation of the three test segments in the three-pass scratch method. 1. is the first profile, 2. is the pre-profile over scan, 3. is the scratch segment, 4. is the post-profile over scan and 5. is the final profile scan [72].

Figure 2-10 - Cross-profile of a progressive load nano-scratch taken at the location where the normal force was 50mN with an optical micrograph of the scratch on the right hand side, showing the location of the scratch [86].

Figure 2-11 - Pre- and post- profiles and scratch penetration depth of a nano-scratch of a glass-ceramic coating [91].

Figure 2-12 - Penetration depth vs. applied load for a durable nano-tube film illustrating the critical load for coating delamination [103].

Figure 3-1 – The Agilent G200 nano-indenter and a cross-sectional diagram of the XP-NMAT [115].

Figure 3-2 – AFM scans of diamond Berkovich tip TB1178 left: 10µm x 10µm scan, right: 3µm x 3µm scan.

Figure 3-3 – AFM scans of diamond Berkovich tip TB21097 left: 10µm x 10µm scan, right: 2µm x 2µm scan.

Figure 3-4 - Force-time history for an indentation test.

Figure 3-5 - Force displacement curve for the same indentation. The hold segments are not apparent in this force-displacement curve as minimal displacement occurred. This data is used for the Oliver and Pharr method of analysis detailed in the introduction section 1.2.

Figure 3-6 - Two tip orientations used for nano-scratch experiments.

Figure 3-7 - Indenter deflection measured by the LFM probes.
Figure 3-8 - Three pass nano-scratch process for a constant load scratch test. .......................... 68

Figure 3-9 - Schematic diagram of a typical AFM system. The tip attached to the cantilever scans the sample surface; the deflection of the cantilever is measured using a laser reflected off the cantilever onto the position-sensitive photo-detector. ................................................................. 70

Figure 3-10 - Typical AFM line scan of middle region of scratch. The right shows the Z detector image from which the measurements were obtained. Measurements taken from these line-scans were the scratch depth including the pile up (vertical height from a-b, a-c), scratch depth excluding pile-up (vertical height a-d) and the scratch width (horizontal width b-c). 10 line scans were taken from each scratch and the measurements were averaged. .............................. 72

Figure 3-11 - 10µm x 10µm scans of the start, middle and of a nano-scratch performed with a normal force of 3mN in the edge forward orientation. These images were produced from the feedback signal which provides a better imaging contrast, however measurements were not obtained from this signal. ........................................................................................................ 72

Figure 3-12 - EBSD set up configuration showing the sample positioned 70˚ to the horizontal and the phosphor screen normal to the electron beam. Kikuchi bands are shown on the phosphor screen projected by the diffraction electron cones.[119]. ......................................................... 74

Figure 4-1 – a. schematic representation of the projected area, \( A_P \), of contact calculated from the projected area function at the penetration depth. One-third used for FF scratch and two-thirds used for EF scratch. b. Schematic of an AFM line scan across the scratch width / cross-section of the scratch track highlighting the area measured as the tangential area, \( A_T \). ........................................... 77

Figure 4-2 – Diagram illustrating how each of the forces, \( F_N \), \( F_L \) and \( F_R \) act on the indenter during the FF scratch and the EF scratch. \( F_L \) is always negative in the direction of the scratch. ................................................................................................................................. 77

Figure 4-3 - AFM image of the beginning of a nano-scratch performed in the EF tip orientation, with normal force of a. 3mN and b 5mN. The profiling force used was 0.2mN, which has caused significant plastic deformation which can be identified in the over-scan segment before the scratch segment. ...................................................................................................................... 78

Figure 4-4 – Comparison of scratch penetration depths measured on one of the 5 repeat scratches using direct methods from the original surface and from the pile-up height (see
Figure 26.b.) and measured by averaging the corrected penetration depth channel (instantaneous scratch depth). Direct measurements of depth of the over-scan segment from the original surface were added to the instantaneous to show the impact that the profiling force has on the residual measurement of the scratch depth for small scratches. This is negligible in larger scratches hence the residual depth is shallower than the instantaneous scratch depth, as expected. All scratches were performed in the face forward tip orientation.

Figure 4-5 - a. Depth at the maximum force (point 1 in d) for scratches of both tip orientations and the depth at maximum force for indentations performed with the same normal force b. Average corrected penetration depth from the steady state region of scratches (3 in d). c. Ratio of the depth at 2 : depth at 1 (see d). d. Typical scratch, corrected, penetration depth channel for EF case and FF case. (Error bars in a. and b. represent one standard deviation).

Figure 4-6 – Direct measurements from one of 5 repeat scratches at each normal force a. pile up height and b. scratch width of EF and FF scratches.

Figure 4-7 – Confocal microscope depth profile image of a. edge forward scratch and b. face forward scratch. Deepest point is identified by the purple colour and the highest points are shown in yellow.

Figure 4-8 – Nano-scratch hardness measured using method one. Average of five repeat experiments are shown; error bars represent one standard deviation. Scratches were performed using both tip orientations.

Figure 4-9 – Nano-scratch hardness measured using method two. Scratches were performed using both tip orientations. The dimensions of the residual scratch groove were measured for one of the five repeat scratches; this measured scratch was used for the calculation of the scratch hardness.

Figure 4-10 – Nano-scratch hardness measured using method three. Average of five repeat experiments are shown; error bars represent one standard deviation. Scratches were performed using both tip orientations.

Figure 4-11 – Nano-indentation hardness of the same sample, as a comparison to the scratch hardness measurements presented above. Average of 10 repeat experiments are shown; error bars represent one standard deviation.
Figure 4-12 – a. Normal force vs. lateral force for all nano-scratches in both tip orientations. Lateral force is dependent on tip orientation. b. Normal force vs. friction coefficient $F_l/F_n$ for both tip orientations.

Figure 5-1 - Nano-scratch hardness of single crystal copper. Average of 5 repeat experiments is shown; error bars represent one standard deviation of the mean.

Figure 5-2 - Nano-scratch hardness of single crystal copper in three heat-treated states. Right shows the face forward tip orientation and left shows the edge forward tip orientation. Average of 5 repeat experiments is shown; error bars represent one standard deviation of the mean.

Figure 5-3 - Fit to data for the 4hr-annealed condition. Least squares fit reveals the gradient and intercept for each tip orientation.

Figure 5-4 - Crystal unit cell identified from the EBSP. Angles indicating the direction of the scratches are shown (left). Indexed EBSP of the single crystal (right). With knowledge of the positioning of the sample in the SEM chamber, crystallographic directions could be identified.

Figure 5-5 - Indication of the direction in which scratches were performed in the 100 crystal plane.

Figure 5-6 – a. Nano-scratch hardness of as received, single crystal copper, scratched in different crystallographic directions using a 5mN normal force. b. corresponding coefficient of friction.

Figure 5-7- Slip plane and slip direction relative to the scratch directions shown in Figure 5-5.

Figure 5-8 - Slip observed in material subjected to a scratch force $F_R$ for three different crystallographic orientations. The dotted line each case represents the slip plane and the adjacent arrows represent the slip direction. The red arrows represent the direction of which the force is applied. $\tau_R$ is the resolved shear stress in each case, $\lambda$ is the angle between the stress direction and the slip direction, $\phi$ is the angle between the stress direction and the normal to the slip direction.
Figure 6-1- Electron Backscatter Diffraction (EBSD) inverse pole figure (IPF) colour map of a sample with 44.4µm average grain size.

Figure 6-2 - Nano-scratch hardness measurements for polycrystalline samples performed in the face forward tip orientation. Average of 5 repeat experiments are shown; error bars represent one standard deviation.

Figure 6-3 - Nano-scratch hardness measurements for polycrystalline samples performed in the edge forward tip orientation. Average of 5 repeat experiments are shown; error bars represent one standard deviation.

Figure 6-4- Average nano-scratch hardness of all nano-scratch sizes in polycrystalline samples and the well annealed single crystal from the previous chapter, plotted vs. 1/d. Error bars show the spread of data as a function of scratch size i.e. the lateral size effect within each sample.

Figure 6-5 - Schematic of a grain boundary separating two crystals with different crystallographic orientations.

6-6 - Left: Optical micrograph of a scratch with 5mN normal force, a and c face forward tip orientation, b and d edge forward tip orientation. a and b are performed on the sample with average grain size 1.15µm, c and d are performed on the sample with average grain size 44.4µm. Right: Corresponding Plot of the Penetration depth and the lateral force along the scratch distance.

Figure 7-1- Corrected penetration depth channel for scratches of varying velocities. Above the Figure the scan segments indicate 1. the First profile 2. the pre-over-scan segment 3. scratch segment 4. Post-over-scan segment 5. Final profile.

Figure 7-2- Schematic of the displacement with respect to time. Assumes each segment has a flat topography, the first profile and the final profile are the same constant load and the scratch is a constant load scratch. The velocity of each segment is the same. This is a simplified schematic; which hasn't included the over-scan segments and the retracing of the stylus back to the start position, after each segment has occurred.
Figure 7-3 - Schematic of the displacement with respect to time. Assumes each segment has a flat topography, the first profile and the final profile are the same constant load and the scratch is a constant load scratch. The velocity of each segment is the same. ................................. 115

Figure 7-4- Schematic of nano-scratches performed in the edge forward and face forward orientations when well aligned (a. and c.) and when slightly misaligned (b. and d.). .............. 116

Figure 7-5- Corrected penetration curves of two 0.5mN constant force nano-scratches in polycrystalline copper. The tip orientation differs in each case. The blue trace has a well aligned face forward tip orientation and the red has a misaligned tip orientation, shown to the left of the picture. ........................................................................................................ 117

Figure 7-6- AFM image of a non-symmetrical Berkovich indenter. ................................................. 118

Figure 7-7- Nano-indenter shaft assembly experiencing shaft rotation due to low lateral stiffness and high lateral forces. ........................................................................................................ 120

Figure 8-1 - Flow of material ahead of the indenter for each tip orientation................................. 124

Figure 8-2 - Left: Optical micrographs of a scratches with 30mN normal force, performed in both tip orientation on the sample with average grain size 44.4µm. Right: Corresponding Plot of the Penetration depth (BLUE) and the lateral force (RED) along the scratch distance...... 129

Figure 8-3 - Left: Optical micrographs of a scratches with 30mN normal force, performed in both tip orientation on the sample with average grain size 1.15µm. Right: Corresponding Plot of the Penetration depth (BLUE) and the lateral force (RED) along the scratch distance...... 130
2. **Introduction**

This thesis experimentally analyses the response of the nano-scratch test, performed using an instrumented indentation testing system. Nano-indentation testing has made it possible to understand and measure the properties of complex materials at the micro- and nano-scale by determining two fundamental material properties: elasticity and yield strength, measured through the indentation modulus and hardness respectively. In this work we aim to find a relationship between the material strength and the quantities measureable in the nano-scratch test. A detailed investigation of the deformation mechanisms occurring during the scratch process has been conducted and important factors that require consideration, when using the nano-scratch test, are highlighted.

There is a particular focus throughout this research on plasticity length-scale effects, whereby the yield strength of a material increases when the ‘size’ of a dominant dimension is reduced. Plasticity length-scale effects in nano-indentation, also referred to the indentation size effect (ISE), have been known to show a significant increase in material hardness, with a reduction of indentation size. Great efforts have been taken to generate a better understanding of the mechanisms responsible for the enhancement in hardness as the indentation size is reduced. A deeper understanding will not only aid the correction of the current implications the size effect poses, but additionally provide the capability to exploit size effects to improve the strength of materials.

In the case of the nano-scratch test, we refer to this effect as the lateral size effect (LSE). The test has not received as much attention as nano-indentation, yet it is frequently used for research and industrial purposes. It is an appropriate method to evaluate the adhesive strength of coatings or the resistance to wear in frictional contact situations, however using the test to evaluate classic material properties, such as yield strength through scratch hardness measurements, requires a better mechanistic understanding of the nano-scratch test. As a consequence plasticity size effects that arise from the test require a detailed investigation.
2.1 **INDENTATION HARDNESS AND THE SIZE EFFECT (ISE)**

Reports of plasticity size effects have arisen in several experimental situations such as torsion of thin wires, whereby the flow stress of the thinnest wires was observed to be approximately three times higher than that of the thickest wires [1] and bending of thin foils, where a significant increase in plastic work hardening was observed as the beam thickness decreased in micro-bend tests [2]. An example of a microstructural size effect is the classic Hall –Petch effect, where the strength of a material increases with decreasing grain size [3, 4]. Our interest here is plasticity size effects identified in indentation testing where the indentation hardness of a material increases with decreasing depth of the indentation, for pyramidal indenters, also referred to as the indentation size effect (ISE). In early experiments, it was assumed that these size effects were a result of metrological errors, however with the advent of the instrumented indentation system, and considerable improvements to the calibration procedures, the increase in hardness persisted.

It is appropriate to mention what the indentation hardness measurement represents. The definition of a material’s hardness is its ability to resist permanent plastic deformation, or abrasion by other bodies [5]. Indentation hardness testing involves applying a static normal force to an indenter of specific geometry to create a permanent residual impression; the hardness has a unit of pressure and is calculated by dividing the normal force applied, by the area of contact; direct optical imaging of the residual impression is required after indentation, to determine the area of contact. Macroscopic indentation tests include the Brinell hardness test; a steel or carbide ball indenter is subjected to a load of up to 3000kgf, and the Rockwell hardness test; a conical or ball indenter is subjected to a normal forces up to 150kgf. Micro-indentation tests using indenters such as the Vickers or Knoop use normal forces ranging from 10gf – 1000gf. The indenters in both tests are 4-sided sharp indenters with specific geometries. The quantitative value of hardness is dependent on the technique used for the measurement including the load.
applied, the type of test and the indenter geometry, therefore the measured values of hardness are relative and specific to the test used.

The indentation size effect was first reported in 1956 by Mott in his experiments using Vickers micro-hardness tests [6]. Vickers hardness testing uses a square-based pyramid diamond indenter to create an indentation in a material surface. The residual impression is imaged and the contact area is calculated from the known relationship between the measured diagonal of the residual impression and the geometry of the indenter. Initially it was proposed that these size effects were a result of measurement errors as it was difficult to produce clear images of such small indentations. Other early explanations for this increase in hardness were related to sample preparation complications and hardened surface layers [7], or to indenter tip blunting, which would cause a transition from a pyramidal indenter tip to a spherical tip at small contact depths [8] (we see in a later section that indentation with a spherical indenter would not be expected to remain constant with indentation depth). However, after improvements to the surface preparation technique were made and the implementation of instrumented indentation or nano-indentation, which is detailed in the following section, it was revealed that the ISE does have a real physical basis and is more fundamental than these explanations.

The ability to enhance material properties and performance is of great interest. In order to achieve higher performance of structural components, the entire bulk material must be improved. An increase in the yield strength and the toughness of components can increase their lifetime and/or enable a reduction in mass, which can often directly relate to fuel efficiency and cost saving for relevant components and industries. There is therefore a requirement to validate size effects and measurement methods to enable length-scale engineering of materials; the goal being to develop structural materials with an increased yield stress that retain their toughness [9].
2.2 Nano-indentation

Instrumented indentation testing (IIT), or nano-indentation, was introduced in the 1980's [10][11] and provided a technique from which the size of the hardness impression, or the contact area could be determined, without the necessity of directly imaging the indentation. The system allows the applied force, \( P \), and indenter displacement, \( h \), to be continuously and simultaneously recorded throughout a loading and unloading indentation cycle. An analysis of this data determines various material parameters including the material hardness and the elastic modulus.

The most common analysis method adopted was the Oliver and Pharr method, established in 1992 [12] and based on previous work by Doener and Nix [10]. The method is currently used in the instrumented indentation standard ISO14577 2002. The method was initially developed for indentation data using a Berkovich indenter (a three sided, geometrically self-similar, pyramid indenter with a half included angle of 65.3°); it was later recognized that the method could be applied to any indenter with axisymmetric geometry, including a sphere. A brief introduction to the method is given here and a more detailed explanation of the instrument is given in the experimental details section.

To determine the Young’s modulus the contact stiffness, \( S \), is derived from the slope of the unloading curve, \( dP/dh \), at the initial point of force removal. The stiffness is then used in Equation 1-1 to calculate the reduced Young’s modulus \( E_r \), which contains contributions of the sample’s elastic displacement and elastic displacements of the indenter. Using contact mechanics, and with knowledge of the elastic modulus and Poisson’s ratio of the diamond tip, it is possible to isolate the elastic modulus of the specimen.

\[
E_r = \frac{1}{2} \beta \frac{\sqrt{\pi}}{A(h_c)} S \left( \frac{1}{h_c} \right)
\]

Equation 1-1
where $A(h_c)$ is the projected area at the contact depth, $h_c$, and $\beta$ is a geometrical constant of the order of unity. A function, $f(h_c)$, must be established experimentally prior to the analysis in order to determine $A(h_c)$. The contact depth is determined using Equation 1-2, which takes into account the surface of the sample in the periphery of the indentation, which behaves elastically.

$$h_c = h_{\text{max}} - \varepsilon \frac{P_{\text{max}}}{S}$$

Equation 1-2

$h_{\text{max}}$ is the maximum indentation depth, $P_{\text{max}}$ is the maximum force applied during the indentation cycle and $\varepsilon$ is a geometrical constant, for a Berkovich tip $\varepsilon = 0.72$. Finally, hardness is defined as $H = \frac{P_{\text{max}}}{A(h_c)}$. Variables used in the Oliver and Pharr method are illustrated in the schematic in Figure 1-1.

The method is now routinely adopted for both research and industrial purposes and is highly desirable for measuring the mechanical properties of small volumes of materials; property mapping and high-temperature nano-indentation are also useful techniques. By
eliminating the requirement of directly imaging the indentation impression, nano-indentation has offered the capability of producing indentation depths as small as a few nanometers. As a consequence the 1990's brought about a resurgence of interest in the ISE [13][14].

2.3 Nano-scratch test

The development of instrumented indentation systems has provided a platform for which additional nano-mechanical test techniques can be performed, requiring only minor adaptations to the instrument. This means that the system is no longer limited to nano-indentation but also includes the capability for nano-tribological measurements such as nano-scratch and nano-wear testing. In a nano-scratch test, the stage of the instrumented indentation system is required to move the rigidly mounted sample laterally, whilst the indenter is subjected to the normal force. The use of a piezo electric motorized stage can enable this function and therefore allow the capability of a controlled, single point nano-scratch test, from which real-time normal force, vertical displacement and scratch distance can be monitored. Many systems have the supplementary function of a lateral force measurement probe, from which lateral forces during the scratch test can be observed. Nano-scratch testing is recently becoming an established nano-mechanical characterization method, which is an important technique for the assessment of the mechanical failure behaviour and adhesion strength of thin films and hard coatings. The test also provides a simulation tool of single asperity contact in tribological experiments [15]. The nano-scratch test is a flexible method that can be used to investigate wear through a multi-pass scratch method; coating adhesion through analysis of the force at which the coating delaminates in a ramped force scratch; and finally scratch resistance, or hardness through a constant force scratch.

Nano-scratch hardness is a further measurement that can be obtained from the nano-scratch test giving a quantitative measurement of a materials resistance to a laterally
applied force or sliding contact. In principle, the scratch hardness number is a more appropriate measure of the damage resistance of a material to surface damage processes like two-body abrasion than the indentation hardness. The term ‘scratch hardness’ is used frequently in the body of literature utilizing the nano-scratch technique however there is no standardized method for the calculation of the nano-scratch hardness. This is concerning considering the amount of literature that have presented data from using the technique. Furthermore, as with nano-indentation, plasticity size effects should be considered for the nano-scratch technique. The research aims of this thesis are to establish a comprehensive method for the calculation of the nano-scratch hardness and investigate the plasticity size effect in nano-scratch testing, referred to as the lateral size effect (LSE).

2.4 RESEARCH AIMS

It has been identified that a detailed investigation of the nano-scratch technique and the potential lateral size effect (LSE) is essential for the progression of the nano-scratch test to become an established, quantitative nano-mechanical characterization method. Quantitative nano-scale scratch testing could potentially increase the understanding of nano-scale plastic deformation under a single asperity contact, providing new and important information for tribological design. Since wear is often the result of an integration of many scratch responses, quantified understanding of the lateral resistance or scratch hardness of materials, obtained directly, may be a more appropriate predictor of wear resistance than indentation hardness. Similarly, quantification of material response to a laterally applied force would, perhaps, be a more appropriate measure of the damage resistance of a material to surface damage processes such as two-body abrasion, or would provide a more relevant input to models for cutting and machining processes considering the test measures a material’s resistance to a combination of indentation and lateral shear. This thesis aims to investigate this nano-mechanical test method through achieving the following research aims:
1. Develop a detailed understanding of the response of pure FCC copper when subjected to nano-scratch tests performed at various normal loads using a diamond Berkovich indenter. A number of measurements will be determined in order to investigate the nano-scratch response. These include: measurements of the penetration depth along the scratch under load and post-scratching, the lateral force and how it is affected by tip orientation and scratch distance, and the amount of pile-up and size of the plastic zone around the scratch.

2. Define a method of calculating the nano-scratch hardness using a Berkovich indenter. Various methods will be tested using combinations of the normal force, lateral force and a number of projected areas of indenter-sample contact. Hardness calculations will be presented in units of pressure using the basic equation \( H = P/A \). The resulting hardness measurements obtained from these methods will be compared to the indentation hardness of the same specimens.

3. Determine the scratch hardness of a single crystal pure copper to investigate the lateral size effect with respect to scratch size.

4. To investigate the lateral size effect (LSE) combined with other intrinsic, length scales such as the grain size and the spacing between other obstacles in the material. This will be performed by using a ‘Hall-Petch’ based analysis, involving comparisons of the nano-scratch response of scratches, performed on samples with varying grain sizes. If the grain boundaries are considered as obstacles to dislocation movement, a reduction in grain size reduces the distance between these obstructions. Similarly by increasing the density of the statistically stored dislocations, which are also considered as obstructions to dislocation movement, the space in which mobile dislocations are free to move is further reduced. The combined distance between the obstacles or the ‘slip-distance’ that is available for the mobile dislocations to move can be directly related to the increase in hardness. Applying the slip-distance theory to the nano-scratch hardness will provide an insight into the lateral size effect. These effects will be investigated to study the influence they have on the lateral size effect.
2.5 **Thesis Structure**

Chapter One of this thesis provides: an introduction to the nano-indentation and nano-scratch technique, a description of plasticity size effects that can influence the indentation hardness and describes the research aims of this thesis; primarily to investigate the lateral size effect in nano-scratch hardness of copper with a Berkovich indenter. Chapter Two presents a detailed literature survey of the indentation size effect and describes the most common models used to describe the effect. Further, the capabilities of the nano-scratch test are introduced and current uses of the nano-scratch technique are discussed. The fact that nowhere in the literature is the lateral size effect investigated is highlighted and provides motivation for this work. Next, Chapter Three provides technical details of all the experimental procedures used throughout this thesis. Chapter Four presents methods of obtaining the nano-scratch hardness and compares different methods of scratch measurement, both directly and through the nano-indenter; the aim being to attain a suitable methodology for obtaining the nano-scratch hardness. The nano-scratch hardness of a sample of polycrystalline copper is presented and the method of hardness calculation is evaluated. In Chapter Five, the scratch hardness of a single crystal of pure copper is calculated and the lateral size effect evaluated. Further, the scratch hardness of the single crystal with different degrees of work hardening are investigated to identify the effect on the lateral size effect. Chapter Six introduces another intrinsic length scale, the grain size, by investigating the nano-scratch hardness of polycrystalline copper. Chapter Seven emphasizes the importance of ensuring that the tip alignment, indenter geometry, vertical drift and lateral compliance are carefully considered in nano-scratch tests. A general discussion is presented in Chapter Eight, followed by the final conclusions and a description of future work, required to develop further understanding of the lateral size effect, in Chapter Nine.
3. Literature Review

3.1 Indentation Size Effect

3.1.1 Berkovich / Pyramidal Indentation Size Effect

As introduced previously, the Berkovich tip geometry is frequently used in nano-indentation testing. The tip is a three-sided pyramid with a self-similar geometry and originally had a centreline-to-face angle of 65.03°, producing the same depth-to-area relationship as the Vickers indenter used in micro-hardness testing. Later literature uses a modified Berkovich geometry with a centreline-to-face angle of 65.3° which matches the depth-to-projected area relationship of the Vickers indenter tip. The preference of the Berkovich geometry for nano-indentation testing arose from the ability to prepare the tip without the chisel edge tip defect, which destroys the self-similar geometry of the Vickers indenter at small depths [16]. An ideal Berkovich tip has an infinitely sharp radius, however this is impossible in practice and the tip will always have some rounding. The Berkovich indenter geometry is shown in Figure 2.1.

![Figure 3-1 – Berkovich tip geometry. Original angle $\alpha$ was 65.03°, the modified Berkovich has angle $\alpha$ of 65.3°.](image-url)
An example of the ISE whilst using nano-indentation with a Berkovich indenter was presented in experimental results obtained from experiments on single crystal (111) copper by McElhaney et al. [17]. These frequently cited results are presented below in Figure 2-2a where an increase in the indentation hardness, with reduced depth of penetration for both the (111) single crystal copper and cold worked polycrystalline copper can be identified. Another classic example available in the literature is the data obtained by Lim et al. which shows an increase in hardness with decreasing penetration depth for both Vickers hardness data and nano-indentation data of annealed and work-hardened, polycrystalline oxygen-free copper [18]. This is shown below in Figure 2-2b. The ISE is most often observed in results using geometrically self-similar indenters such as the Berkovich. It is assumed that classic continuum laws, in which there is no characteristic material length scale, can describe plasticity. As there is no length scale for the self-similar geometry of the indenter, it can be assumed that the hardness, $H$, would be independent of the depth of penetration; contradictory to what is observed in the results below. Other reports of ISE confirm that the hardness begins to significantly increase when the indentation depth is below a few microns [19].
Figure 3.2—a. Indentation size effect in (111) single crystal copper and polycrystalline cold worked copper performed with a Berkovich diamond indenter by McElhaney et al. [17]. b. Indentation size effect observed for both nano-indentation data (open squares and crosses) and Vickers hardness data (closed triangles) of polycrystalline annealed and work-hardened oxygen-free copper by Lim et al. [18]
3.1.2 SPHERICAL INDENTATION

In contrast to indentation with a self-similar Berkovich indenter during which plastic deformation is induced from an early stage in the indentation cycle, indentation with a spherical tip does not necessarily induce plastic flow from the start of contact. Additionally, the geometry of the contact changes with increasing depth of penetration [20]. Consequently, hardness is not expected to be constant with depth and therefore a more suitable parameter to measure, is the mean indentation pressure, \( P_m = \frac{P}{\pi a^2} \) at a particular contact depth. This change in geometry can generate an ‘indentation stress-strain curve’ when plotted as \( P_m \) vs. the effective indentation strain, \( a/R \), where \( a \) is the contact radius and \( R \) is the radius of the indenter, this is shown in Figure 2-3 [21]. For a particular radius indenter, \( P_m \) is expected to vary with indentation depth and therefore \( a/R \). Tabor showed that the shape of the indentation stress-strain curve of a given metal was analogous to the uniaxial stress-strain curve from a tensile test when plotted as \( P_m/2.8 \) against \( 0.2 \ a/R \) [22].

![Diagram of spherical indentation test](image)

**Figure 3-3 - Schematic of the spherical indentation test. Ratio of contact radius to indenter radius give the indentation strain [23].**

Indentation with a spherical indenter produces an equally important ISE; several studies have shown that for smaller radius spherical indenters (approximately less than 200µm), the indentation stress-strain curve moves to higher pressures. So, where it would be
expected that the value of $P_m$ obtained with different radii indenters to be the same for the same values of $a/R$, we actually see an increase in pressure with decreasing indenter radius\cite{18}\cite{24}. This is shown in Figure 2-4 below. Predicting tensile stress-strain properties from a non-destructive indentation test is highly desirable to a number of industries including oil and gas, production and power generation, therefore a thorough appreciation of spherical indentation size effects is required in order to achieve this successfully \cite{21}.

![Figure 3-4 – Spherical indentation stress-strain curves of Copper; Experimental spherical indentation data (open symbols), Finite Element simulation (closed symbols), Tabor representation of uniaxial data (solid line), Hertzian elastic response (dashed line); Radius of the indenter used in each case are given in the legend.\cite{21}](image)

Figure 2-4 shows the results presented by Spary et al. in 2006 \cite{21} who compared the experimental spherical indentation stress-strain curves to uniaxial stress-strain curves and reproduced the spherical indentation size effect by simulation in a finite element (FE) model. They developed a FE model to simulate the indentation process using parameters of which values were determined from the uniaxial test data. Inputting the uniaxial data directly into the model (solid line in Figure 2-4) reproduced the macroscopic ball indentation data (open symbol squares and circles in Figure 2-4). Changing the
dimensions of the indenter in the model did not reproduce the experimental ISE. However, it was found that by increasing the initial yield stress input into the FE model, the experimental ISE could be replicated by the model. Furthermore, the factor, by which the yield stress is increased, was found to scale with the indenter radius. The authors performed similar experiments on a range of metals, spanning a wide range of material properties, and found that the proportional increase in yield stress with indenter radius was similar for all materials tested, which implies that the observed size effect is related to a geometrical effect linked to the stress distribution beneath a spherical indenter. These results may be used to predict the spherical indentation size effect as well as extract the size-dependent indentation stress-strain data that is equivalent to the uniaxial stress-strain data.

A different type of indentation size effect was observed for spherical indentation by Shim et al. This size effect was not based on the material hardness, which depends on the yield and the work-hardening of the material, but rather on the stress required to initiate dislocation plasticity [25]. When indenting material with a spherical indenter, the onset of plastic flow is marked by a sudden displacement burst, or pop-in, in the load displacement data. This pop-in phenomenon was used to investigate the effect of indenter radius, and the effect of pre-existing dislocations in the material, on the stress required to initiate plasticity in annealed and pre-strained, single crystals of nickel. It was found that the pop-in load increases monotonically with increasing indenter radius until it reaches a plateau at approximately 5mN for the indenter radius of 17.5μm. Additionally, for the samples with pre-existing strain, the pop-in load required to initiate plasticity was measurably reduced. From the pop-in loads applied, it is possible to calculate the maximum shear stress in the highly stressed region beneath the indenter. It was found that for small indenter radii, the maximum shear stress reached an asymptotic limit; however, for large indenter radii, the shear stress decreased monotonically with increasing indenter radius. Shim et al. qualitatively reported a possible explanation for this. Plasticity is due to the movement of pre-existing dislocations and the nucleation of new dislocations; the latter of which require a much higher stress to initiate. When the radius of the indenter is small in comparison to the spacing between dislocations, the
probability that there will be a pre-existing dislocation in the highly stressed region is low. Therefore the shear stress required to nucleate new dislocations in the material, and initiate plasticity, is high. On the other hand when the plastic zone size beneath the indenter is large, i.e. an indenter with a large radius, it is likely that pre-existing dislocations will be in the highly stressed zone beneath the indenter and therefore requires a lower stress to move dislocations and initiate plasticity. By pre-straining the material and increasing the dislocation density, it is more likely that for all indenters, there will be a pre-existing dislocation in the highly stressed region beneath the indenter and therefore the stress required to initiate plasticity will be lower [25].

3.1.3 Models and Mechanisms

Experimental observations of the ISE in both pyramidal and spherical indentation led to an outbreak of research activity in the 1990’s, aiming to further characterise and explain the mechanisms controlling the ISE. The attempts of modelling can be described by two different types [26]; Mechanistically based models that rely on dislocation descriptions of hardening mechanisms [27][28][29][30][31] and phenomenological models which introduce a material length-scale parameter into conventional descriptions of continuum plasticity [1][32][33][34]. The phenomenological models are based on a concept of a plastic strain gradient, which occurs from the geometry of the loading. Figure 2-5 shows the strain gradient in an indentation where the plastic strain is high immediately beneath the indenter and gets smaller, further away from the indentation, creating a gradient of strain. Dislocation theory suggests that plastic deformation occurs from the storage, movement and generation of both statistically stored dislocations (SSD) that arise from strain, and geometrically necessary dislocations (GND) that arise from a strain gradient. In general, the gradient of strain is inversely proportional to the length-scale over which plasticity occurs and as a result, the effect of the strain gradient is more prominent at small length scales. From this understanding, strain gradient plasticity models use the gradient of strain to determine a length-scale that can be
implemented into continuum mechanics [35]. Of the various mechanistic models, the most commonly used model is the Nix and Gao model detailed below [36].

![Figure 3-5 – Plastic strain gradient beneath an indentation. The plastic strain is large immediately beneath the indenter and is small further away creating a gradient of strain.]({})

### 3.1.4 **The Nix and Gao Model (1998)**

The Nix and Gao Model [36] is a mechanism–based model that has been shown to provide a correlation between the ISE observed in pyramidal and spherical indentation, based on geometrically necessary dislocations (GND's). GND's represent an extra storage of dislocations required to accommodate the lattice curvature that arises whenever there is non-uniform plastic deformation [37]. In an indentation, a permanently plastic indentation is created on the originally flat sample. As mass must be conserved we can assume that the material originally in the indentation region is ‘pushed’ into the material beneath the sample and stored as extra planes of atoms in the original atomic lattice – i.e. GND’s. It was proposed in 1970 by Ashby that GND’s in a material would lead to an increase in material strength [38]. In 1998, Nix and Gao considered this and presented a mechanism-based model to explain the ISE in pyramidal indentation [36]. The model assumes that the GND’s underneath the indentation are contained as dislocation loops contained in a hemispherical volume, \( V = \frac{2\pi a^3}{3} \), and distributed uniformly (See Figure 2-6(a)). As the geometry of the indenter is self-similar, the angle
that the indentation makes with the surface, $\theta$, remains constant and independent of the residual plastic depth, $h_P$. The number of loops beneath the indenter is defined as $h_P/b$, where $b$ is the Burger’s vector. By integrating from 0 to $a$ it is possible to get the total length of the dislocation loops, $\lambda = \pi b a / b$. Therefore the density of the geometrically necessary dislocations is:

$$\rho_G = \frac{\lambda}{V} = \frac{3}{2bh_P} \tan^2 \theta$$

Equation 2-1

Through the Taylor hardening model [39], the dislocation density can be related to the shear strength:

$$\tau = \alpha \mu b \sqrt{\rho_T}$$

Equation 2-2

where $\tau$ is the shear strength, $\mu$ is the shear modulus, $\rho_T$ is the total dislocation density and the constant $\alpha$ is usually in the range 0.3-0.6 for face centred cubic (FCC) materials [40]. It has been shown that the actual number of dislocations that must be generated to accommodate plastic deformation is greater than the number of GND’s by a Nye factor, $\bar{\rho}$ [41], which is designed such that the total dislocation density, $\rho_T = \bar{\rho} \rho_G + \rho_S$, is approximately 1.9 where $\rho_S$ is the density of statistically-stored dislocations. Assuming that the shear strength is related to the flow stress by Mises flow rule where $\sigma = \sqrt{3}\tau$, and that the hardness is related to the flow stress by the Tabor factor $H = 3\sigma$, the model gives Equation 2-3 for the increase in hardness as a function of depth.

$$H = H_0 \sqrt{1 + \frac{h^*}{h_p}}$$

Equation 2-3
where \( H_0 = 3\sqrt{3}a\mu b\sqrt{\rho_S} \) and \( h^* = 3\bar{r}tan^2\theta/2b\rho_S \). \( H_0 \) represents the macroscopic hardness and \( h^* \) is the characteristic depth, below which the extra hardening, due to GND’s is appreciable. In 2001, Swadener et al. extended the model to indenters of various shapes, including the sphere, thus determining a model which can explain various forms of the ISE observed [24]. In Figure 2-6 (b) an example of a general indentation profile is given of which the Nix and Gao model can be extended to. The indenter is a smooth axisymmetric indenter of the form \( h = A\bar{r}^n \), where \( A \) is a constant and \( n > 1 \). The total length of the GND loops is found by integrating the number of steps on the surface and is used to find the density of GND’s as before. Most indenters used are of the form \( n = 1 \) (pyramidal or conical), \( n = 2 \) (spherical) or \( n = \infty \) (flat punch). For the flat punch case, difficulties in measuring the hardness arise from the smoothness of the punch or rounding of the edges. For the spherical case, i.e. a profile of \( h = \bar{r}^2/2R_P \) where \( R_P \) is the spherical radius of the indentation impression, the average density of GND’s is equal to:

\[
\rho_G = \frac{1}{bR_P}
\]

Equation 2-4

If a material length scale \( R^* = \bar{r}/b\rho_S \) is introduced, it is possible to derive an expression for the hardness as a function of \( R_P \) that has the same form as Equation 2-3:

\[
H = H_0 \sqrt{1 + \frac{R^*}{R_P}}
\]

Equation 2-5

From Equations 5 and 7, we see that the increase in hardness, due to the density of geometrically necessary dislocations for a conical indentation is dependent on the depth
of penetration; for spherical indentation the size effect is determined by the radius of the impression.

Although the Nix and Gao model agrees well with a large number of studies that present indentation data, it has been observed that the model breaks down when the contact size is very small [24][27]. Swadener et al. debated that assuming the GND’s are contained in a hemispherical volume, equal to the radius of the contact impression, is incorrect as it ignores the physical processes that determine the size of the plastic zone. If all GND’s contained in the hemispherical volume were of the same sign, large mutually repulsive forces would cause the dislocations to drive outwards and occupy a larger volume than is assumed. This would result in the model being limited to larger indentation depths; for the smaller depths the density of GND’s would be predicted lower than the actual value and the hardness would be overestimated [24]. Another suggestion as to why the model may break down at small indentation depths could be due to experimental artefacts. When using the continuous stiffness measurement technique (CSM),
significant errors have been observed at small indentation depths [42][43]. The model breakdown has also been interpreted as an indication that another mechanism predominates at very small depths, approximately of the order of 100μm. We have mentioned the suggestion that the GND's are spreading to a larger volume however another theory related to dislocation source-limited behaviour, that is the change in behaviour when there is a lack of indentation sources available as the deformation volume gets smaller [44][45][46]. Other authors have accounted for the expansion of the GND volume [47][48] however these explanations are empirical and require a physically based model to determine the actual size of the contact zone.

3.1.5 The Hall-Petch Effect in Indentation

The well-known Hall-Petch effect is an example of a plasticity strengthening effect that relates the yield stress, $\sigma_y$, of a polycrystalline material to the inverse square root of the grain size, $d$, through the following the relationship [3][4]:

$$\sigma_y = \sigma_0 + kd^{-1/2}$$

Equation 2-6

where $k$ is a constant and $\sigma_0$ is the yield strength of a single crystal. Despite the masses of experimental data confirming this relationship, no single theoretical explanation of this behaviour has been established [49]. There is also little knowledge of how applicable this relationship is in small structures where the structure size is approximately the same size as the grain. It has been most directly linked to the flow stress of the material but many authors have reported that the work-hardening rate has also been dependent on the inverse square root of the grain size. Copper samples with grain sizes ranging from 1μm down to single crystal copper were investigated using spherical indentation [50]. Altering the radius of the indenter and indenting samples with different grain sizes allowed the experimental control parameter of the relative size of the indentation
compared to the grain size of the sample to be investigated i.e. a ratio of the indentation size to the grain size. From this study it was found that when the grain size, \(d\), is less than six times the indenter radius of the projected area of contact, \(a\), i.e. the indentation is performed across numerous grains, the pressure is linearly related to the inverse square root of the grain size, similar to the well-known Hall-Petch relation. On the other hand, when the grain size was larger than six times the indentation contact area, it was found that the indentation size effect was dominant, where the increase in indentation pressure is independent of grain size.

It was revealed from these results, that the increase in stress due to the indentation size effect is linear with the inverse square root of the indenter radius, similar to the Hall-Petch effect, implying that the two effects are superimposed. However, it remains unclear as to how these two effects are in fact related. One approach suggested is to combine the length scales in quadrature, which would generate a new fitting parameter, \(D\), defined by:

\[
\left(\frac{1}{\sqrt{D}}\right)^2 = \left(\frac{K_1}{\sqrt{a}}\right)^2 + \left(\frac{K_2}{\sqrt{d}}\right)^2
\]

Equation 2-7

where \(K_1\) and \(K_2\) are constants and \(D\) has the unit of length. This superposition method works well for copper and has the ability to directly predict the effective hardness of different sized contacts on different grain sized materials. It also indicates that there is a single underlying principle driven by the two independent length scales.

The linkage between the grain size effect and the indentation size effect confirms that strain gradient plasticity theory is insufficient to predict size effects. The attempt to combine the two effects was further investigated using other experimental data sets that display plasticity size effects [51]. The interaction of the two length scale effects exists in the form:
\[ \frac{1}{l_{\text{eff}}} = \frac{1}{h} + \frac{1}{d} \]

Equation 2-8

where \( b \) is the indentation contact size or the structure size depending on the geometry of loading, and \( d \) is the average grain size. The observed hardness increase varies with the inverse square root of the effective length, \( l_{\text{eff}} \). It was concluded that the size effect is driven by the finite size of strained volume, whether it is limited by the grain size or the structure size. From this, it is clear that the Hall-Petch effect and the structure size effect must be due to a common physical mechanism.

An inverse Hall-Petch effect has been observed in nanocrystalline materials whereby the yield strength decreases when the grain size is below a critical value \([52][53][54]\). In very small grained material, typically grain size less than 10nm, it is understood that the grain boundaries can no longer support the pile-up of dislocations \([55][56]\). Consequently, a threshold value, for which the yield strength can be increased by decreasing the grain size, is inevitable. Experiments show that the deviation from the Hall-Petch effect occurs at a critical grain size which is larger than 10nm, where dislocation pile-up can occur \([52][57]\). This effect is known as the inverse Hall-Petch effect, of which the mechanisms are not fully understood. Throughout this thesis, nanocrystalline material will not be investigated and thus an inverse Hall-Petch effect is not likely to be observed.

3.1.6 **SLIP DISTANCE THEORY**

The slip-distance theory was initially proposed by Conrad in 1967 and is able to determine the plastic strain in a crystal using the distance moved by dislocations \([58]\). In Figure 2-7a and 2-7b, we see that the external applied shear stress causes the edge dislocation located at A, to slip a distance \( x_i \), to location B. The contribution of this single dislocation to the plastic strain is the Burgers vector, \( b \), multiplied by the slip distance \( x_i \) (distance A to B).
Figure 3-7 – (a) Edge dislocation located at A subjected to an external shear stress. (b) Edge dislocation moves to location B by dislocation glide (distance AB). (c) Plastic displacement is produced from the glide of the dislocation.

If the density of the mobile dislocations in the crystal is \( \rho_m \), with the average mean mobile path being a distance of \( \bar{x} \), then the total plastic strain, \( \varepsilon_{pl} \), is determined by Equation 2-9, which denotes the slip-distance theory.

\[
\varepsilon_{pl} = b\rho_m \bar{x}
\]

Equation 2-9

The total dislocation density in a crystal is made up of the statistically stored or sessile dislocations and mobile dislocations, of which the mobile dislocations are a fraction, \( \lambda \), of the total dislocation density i.e. \( \rho_{total} = \rho_s + \rho_m \) and \( \rho_m = \lambda \rho_{total} \). The Taylor formula for the stress increase caused by the interaction between mobile dislocations passing through the material is given by:

\[
\Delta \sigma = \alpha G b \sqrt{\rho_{total}}
\]

Equation 2-10
where $G$ is the shear modulus and $\alpha$ is the Taylor coefficient. The coefficient $\alpha$, can be interpreted to effectively scale the average distance, or mean free path, between the interacting dislocations. If the mean free path is equivalent to the inverse square root of the density of sessile dislocations, $\rho_s$, Equation 2-10 can be re-written as:

$$\Delta \sigma = Gb\sqrt{\rho_s}$$

Equation 2-11

To determine $\rho_s$, we use the expression:

$$\rho_s = \left(\frac{1-\lambda}{\lambda}\right)\rho_m$$

Equation 2-12

Using the above expression of $\rho_s$ from Equation 2-12 and the expression for $\rho_m$ given in Equation 2-9, the Taylor Equation 2-10 can be re-written to obtain:

$$\Delta \sigma(\varepsilon_{pl}) = Gb\sqrt{\left(\frac{1-\lambda}{\lambda}\right)\frac{\varepsilon_{pl}}{\bar{x}}}, \quad 0 \leq \lambda \leq 1$$

Equation 2-13

Equation 2-13 provides a relationship between the increase in stress at a particular strain, and the inverse square root of a parameter that has a unit of length. This is identical to the Hall-Petch relationship whereby the length parameter of importance is the average grain size. Similarly, as suggested by Hou et al. and mentioned previously, the increase in indentation hardness can be related to the inverse square root of the combined length scale parameter, $D$, which is a combination of all of the individual length scales acting to obstruct dislocation movement [50].
Hou and Jennett [9] have applied the slip distance theory to spherical and Berkovich indentation data of annealed oxygen-free copper using an extended version of Equation 2-7:

\[ P_m = P_0 + \frac{k_{HP}}{\sqrt{D}} \quad \text{where,} \quad \frac{k_{HP}^2}{D} = \frac{k_1}{a} + \frac{k_2}{d} + k_3\sqrt{\rho_s} \]

Equation 2-14

Here, \( P_m \) is the mean indentation pressure or hardness; \( P_0 \) is the hardness of an infinite single crystal; \( k_{HP} \) is a Hall-Petch-like constant; \( a \) is the contact radius of the indentation; \( d \) is the average grain size; \( \rho_s \) is the line density of other pinning points, voids, impurities or sessile dislocations that obstruct dislocation movement; finally \( k_1 \), \( k_2 \) and \( k_3 \) are scaling parameters with \( k_1 \) affected by indenter geometry, \( k_2 \) affected by microstructural alterations such as the texture or the number of slip planes available and \( k_3 \) is included in the equation for mathematical completeness.

Hou et al. found that there was a good agreement between the model and the experimental data, confirming that the indentation size effect and the structure size effect (SSE) or grain size effect are independent components of the same plasticity mechanism [50]. The model also allowed the interdependent contributions to the increase in hardness to be separated out into indent size, grain size and the spatial frequency of the other pinning defects. They also found that by using the different indenter geometries, spherical and Berkovich, two different levels of strain were being investigated. The equivalent uniaxial strain for a Berkovich is 7% and for spherical indenters of different radii, the depth of the indentation was selected such that the equivalent uniaxial strain was 5%. A difference in the sessile dislocations produced by the Taylor forest work-hardening, was detected in the \( k_3\sqrt{\rho_s} \) term which suggests that work-hardening can be considered as another size effect contributing to the increase in strength.
3.1.7 SUMMARY

It is clear from experimental evidence that the plasticity size effect is a fundamental material phenomenon; it is becoming increasingly important to understand and develop fully validated models that are able to predict material behaviour whilst accounting for them. The size effect causes both problems and opportunities for material scientists. At present, predictive models used for the design of components, such as finite element methods, utilise input data in the form of a true stress-strain curve obtained by uniaxial testing of bulk material, based on continuum mechanics. Continuum mechanics have been modified to include a strain gradient plasticity term, in order to describe the length-scale effect, however without verification of the validity of this modification, it is insufficient to explain material behaviour appropriately. The ISE introduced throughout this section can create numerous problems; one example is that implications are created for the calibration of indentation test systems. In conventional instrumented indentation testing (IIT) systems, errors are corrected using an estimated offset derived from a hardness reference block. However, these reference blocks are only certified for hardness at one particular indentation size and therefore will be invalid if the indentation sizes differ significantly. Additionally the indentation size effect also limits the effectiveness of property mapping using two-dimensional arrays of indentations. On the other hand, the ability to use length-scale engineering to enhance material performance is of great technological interest. The ability to achieve an increased strength in structural components would result in increased lifetime of components and/or enable a reduction in mass - which would directly relate to fuel efficiency and cost reduction. The material enhancement is applicable to a wide range of industrial sectors and therefore, there is a requirement to validate the size effect theories.
3.2 REVIEW OF THE SCRATCH TEST

Although it is considered the norm to concentrate on hardness measurements obtained from indentation testing, the ability of one material to scratch another material was originally the basis of hardness scales. The earliest established hardness scale was developed in the 1820’s by Frederich Mohs and consisted of an array of ten minerals ranging from talc (number 1) to diamond (number 10) [59]. Scratch hardness scales preceded the indentation test for a number of years until the indentation test was formalised and became the international standard for measuring hardness of materials; both for research and industrial applications [60]. The scratch test continued being used as a method that was capable of investigating controlled abrasive wear mechanisms of material surfaces and eventually became the primary test for evaluating the adhesion strength and wear rate of coatings [61].

3.2.1 MACROSCOPIC SCRATCH TESTING

The scratch test involves drawing a stylus, of specific geometry, across the surface of a sample at a controlled velocity and normal force. The scratch can either be an increasing load/ramped scratch in which the normal force increases with scratch distance or alternatively it can be a constant loaded scratch in which a constant normal force is maintained along the scratch distance. For general abrasion resistance, it is useful to use a constant force scratch whereby the scratch response of different material surfaces can be compared relative to each other [62]. The scratch width is a quantitative value that can be measured via optically imaging the scratches, post scratching. Similarly, the deformation mechanisms can be qualitatively compared [63]. Ramped load scratches have been regularly used for the assessment of the adhesive strength of coatings to their substrate [64]. In the normal configuration of the test, a diamond stylus is drawn across the coated surface under an increasing load until some well-defined failure occurs. The load at the point of failure is often termed the critical load, this is illustrated in Figure 2-
For the majority of macroscopic scratch tests, a Rockwell “C” type, conical, diamond tip is used with a 200μm tip radius. The test has limitations as the critical load depends not only on the adhesive strength of the coating to the substrate but also on several intrinsic testing conditions, such as the loading rate, scratch velocity and indenter geometry; extrinsic conditions that affect the test involve the material properties and the friction coefficient.

The friction behaviour of the surface during the scratching process can be investigated through measurements of the tangential force. The coefficient of friction can be found as the ratio of the lateral force to the normal force during the scratch process. A plot of the frictional force against the scratch distance can indicate different types of failure;
small oscillations in the measured friction can correspond to chipping of surfaces whereas larger variations can show the presence of flaking. A large inflection point in the data can mark the point of total coating failure [66]. Figure 2-8 above shows the frictional force along the scratch, the location at which the coating delaminates from the substrate can clearly be identified.

The macroscopic scratch test can provide a plethora of valuable measurements for tribologists. Surfaces that have been engineered either by deposition of hard coatings, thin films or thermal/chemical treatments have proven to increase the wear resistance for many applications. Therefore if significant intellectual input is to be made in the design of these coatings, a full understanding of the mechanical properties of the coating-substrate system is essential; information that can be easily acquired from the scratch test.

Macroscopic scratch testing has also been used to investigate the anisotropy of single crystals and the effect of grain boundaries in polycrystalline materials in order to aid tribological design [67]. From these experiments it was concluded that FCC copper is anisotropic with respect to the scratching direction, in that the width of the wear tracks were different in each case. For a single crystal of copper oriented in the (001) plane, scratches performed with a 1.6mm diameter steel ball indenter in the <100> direction and the <110> direction. It was found that when scratching perpendicular to the slip plane, the scratch track was narrower than when scratching parallel to the slip plane. In addition to this, the direction of scratching also determined the frictional response which was related to the plastic flow of material, either cutting or ploughing [67]

3.2.2 Nano-scratch testing

As mentioned previously, instrumented indentation systems have extended their test techniques ahead of purely nano-indentation to include the capability for nano-scratch testing. Essentially this involves ultra-low loads and low penetration depths during the scratch procedure. Mechanisms involved in a scratch are the elastic-plastic behaviour, the fracture behaviour and the visco-elastic behaviour in polymers. The ability to record
the normal force with a resolution of 50nN, the indenter displacement with a resolution of 0.01nm and automated positioning of the stage with a positioning accuracy of 1µm, the nano-indenter proves to be the ideal instrument for nano-scratch tests. The test is mainly used for adhesion strength measurement and mechanical failure mode determination of ceramic coatings, however it also brings the capability of nano-scale characterisation of bulk materials. With greater control and accuracy of the system than the traditional scratch tester, the nano-scratch test can simulate single asperity contact in nano-structured components and nano-devices [15].

3.2.3 LATERAL FORCE MEASUREMENT

Many systems with the nano-scratch functionality have an additional sensor known as the lateral force measurement (LFM) probe that can provide a three-dimensional, quantitative analysis. The LFM enables force detection in the x and y directions through an x-axis and a y-axis capacitive deflection gauge that can sense the lateral displacement of the indenter column. Lateral forces during the scratch can then be calculated using the stiffness of the indenter shaft, which is calibrated using a separate method [68]. It is important to have an indenter column with optimal lateral stiffness as this, combined with a high frictional sensitivity from the LFM, and would produce smooth scratch traces. The high frictional sensitivity is desirable, as this will ensure reliable quantitative frictional data [15].

3.2.4 THREE-PASS SCRATCH METHOD

It is common to use a three-pass scratch technique for a nano-scratch test. The three-pass method consists of three test segments; the first profile, the scratch segment and the final profile. This is illustrated in Figure 2-9. Stage (1) is the first profile performed at the profiling load, which should ideally be only large enough to cause elastic deformation in the surface. This segment is useful as it gives a representation of the
surface topography before the scratch has been performed. (2) and (4) are performed at the profiling load and over scan regions of the scratch segment. (3) is the scratch segment and is performed using the specified scratch forces; either a ramped force or a constant force. The penetration depth data collected in this segment is usually corrected for by subtracting the penetration depth collected in the initial scan i.e. at a specific scratch distance, x, the corrected scratch penetration depth would be (3) at distance x - (1) at distance x. This corrects for topography defects, sloping of the sample surface and roughness. (5) is the post scratch test scan which can give information about the elastic recovery of the scratch segment. Clearly the three-pass scratch method provides valuable information, which can be helpful for the data analysis. This method was not previously adopted for the macroscopic scratch test, as it was difficult to perform such small forces for the profiling segments and maintain high control and repeatability of the indenter location. Although there is no international standard for the application of a nano-scratch test, there is an ASTM standard which is applicable to paint industries, which also utilises the three-pass scratch method [69]. As with macroscopic scratch testing, the scratch segment of the test can be either a constant force scratch or a progressive load scratch in which the load increases with scratch distance. Additionally, another loading method is the repetitive nano-wear test or multi-pass scratch test. This consists of multiple scratch traces, at the scratch force during the scratch test segment shown in Figure 2-9 stage (3) and has been shown to be an effective low cycle fatigue test [70]. The low cycle nano-wear test experiments can be more informative than single pass nano-scratch tests for investigating the stress in thin films [71].
3.2.5 CURRENT USES OF NANO-SCRATCH TESTING

Published work in the field of nano-scratch testing involves determining the nanomechanical and nano-tribological properties of a range of materials both bulk materials and coated systems. These include thin metallic coatings [73] [74], diamond-like-carbon coatings [75], multilayer SiGe/Si films [76], ceramics [77], polymer films [78], powder compacts [79] and biomaterials such as human hair [80], tooth enamel [81], skin [82] and bone [83]. The use of nano-scratch enables the investigation of deformation and fracture modes, which are otherwise impossible using traditional macroscopic testing techniques due to its precise measurements at small length scales.

A regular matter of interest is the nano-scale wear mechanisms of the material, which as mentioned previously, can be studied using the multi-pass nano-wear test. By imaging the post-scratched surface and qualitatively describing the deformation mode of the scratched surface, the wear can be evaluated [74]. Under relatively low loading conditions, replicating mild abrasive wear of the surface, the scratches endure elastic and plastic deformation. The scratch test leaves a ‘groove’ in the surface accompanied by two pile-up peaks, this can be observed in the cross-profile trace in Figure 2-10. In order to define a plastically deformed scratch, the scratch width, \( w \); can be measured as the
distance between the top of the two pile up peaks, the scratch residual depth, \( p \), can be measured between the surface and the base of the scratch groove and finally the pile-up height, \( h_b \). In order to obtain these parameters, either an atomic force microscope can be used or alternatively, many IIT systems have the function of performing a cross profile, in which the tip lightly scans the surface, across the scratch, to show a profile of the cross section of the scratch [84][85].

![Figure 3-10 - Cross-profile of a progressive load nano-scratch taken at the location where the normal force was 50mN with an optical micrograph of the scratch on the right hand side, showing the location of the scratch [86].](image)

The wear volume has been used as a quantitative measure, by which the volume inside the scratch was used to describe the material losses during wear processes [87][88][89]. The volume is determined by calculating the multiple average cross-sectional area along the length of the scratch. Xia et al. used this volume measurement to determine a scratch rate, expressed as the volume of material lost per unit length of the scratch i.e. mm³/mm [89].

The contact width of scratches performed with an instrumented indentation system were calculated using a theoretical method that did not require measurements taken from direct imaging of the scratches post-experiment [90]. The method that was adopted
implied that the contact pile-up height, could be estimated from the early stages in the scratch profile measured using the indenter displacement. The contact pile-up height was representative of the pile-up material in contact with the indenter, under load, and not the maximum height of the pile-up which is usually measured post-scratching. This contact pile-up height was then used in conjunction with a cross-section, scanning probe microscope (SPM) profile across the scratch, similar to that shown in Figure 2-10, to determine the contact width at that height.

The penetration depth of the scratch and a pre- and post-scratch profile has been used by Sun et al. to provide information relating to the elastic recovery of the surface when subjected to a sliding contact, Figure 2-11 displays an example of the penetration depth as a function of the normal load in a scratch test for which the load progressively increases from 0-400mN, for a glass-ceramic material [91]. The corresponding pre- and post-scratch residual profiles are also shown. Regions I, II, and III in Figure 2-11 refer to different stages in the deformation processes in the scratch. Region I shows the elastic portion of the scratch, whereby upon force removal the penetration depth is zero, region II refers to a smooth, ramped force scratching segment until region III shows a critical event in the deformation such as coating delamination. Koumoulos et al. used this data to obtain a percentage of elastic recovery from the nano-scratch [92].

![Figure 3-11 - Pre- and post-profiles and scratch penetration depth of a nano-scratch of a glass-ceramic coating](image-url)

Figure 3-11 - Pre- and post-profiles and scratch penetration depth of a nano-scratch of a glass-ceramic coating [91].
Comparisons can be made using this data and materials have been described as having a greater ‘scratch resistance’ in cases that exhibit a lower degree of plastic deformation, or penetration depth [93][94][79]. The term ‘scratch resistance’ has been used somewhat loosely throughout the literature concerning nano-scratch. In some references the scratch resistance is a quantified measure where the scratch resistance can be calculated by dividing the normal sliding load by the area of contact [95]. Both Ahmed et al. and Ayatollahi et al. presented alterations of this equation, involving constants relating to the tip geometry being used [96][97].

In a study by Huang et al. [98] the mechanical properties of ultra-fine grained alumina ceramics were investigated using nano-scratch. In this paper, two separate calculations for scratch hardness were presented; one method gives the scratch hardness as the ratio of the normal applied load to the projected area of contact perpendicular to the normal load direction. In the same study, the scratch resistance is also defined as the ratio of the induced tangential load to the projected contact area perpendicular to the scratch direction [84]. These separate calculations give non-similar results or trends and hence could provide a broader range of information.

As mentioned above, the nano-scratch test is used mainly for testing the adhesion strength of coatings and films. Interfacial adhesion plays a crucial role in the structural stability, performance and the reliability of coating-substrate systems. A high adhesion strength can avoid delamination and cracking of the coating when exposed to stresses [99]. From determining a critical load at which the coating delaminates from the substrate, an assessment of the coating adhesion can be made [92]. The critical loads can be compared for various coatings as a measure of the adhesion and different stages of adhesion can be identified in the scratch track [100]. Furthermore, the adhesion strength or interfacial bonding force can be calculated [99]. With knowledge of the frictional behaviour, the critical load and the scratch width at critical load, Nazarpour et al. determined the critical stress at which delamination occurred and used this to give a measurement of the adhesion energy, which was also related to the thickness of the film and the elastic modulus [101].
Scratch resistance has also been related to the critical load used for testing the adhesive strength of coatings. These critical loads can be used to compare the scratch resistance of various materials; a material with a higher critical load would be considered to have a higher scratch resistance. It can be useful when severe abrasion or high loading conditions are experienced, as fracture of the surface is particularly visible in these cases, this is shown in Figure 2-12 [102][103].

Figure 3-12 - Penetration depth vs. applied load for a durable nano-tube film illustrating the critical load for coating delamination [103].

Friction data from the nano-scratch test has shown that the lateral force does not linearly increase with the applied load and therefore the coefficient of friction, taken as the ratio of the lateral force to the normal load applied, is not a constant value. This was investigated by Lafaye et al. for nano-scratch data in order to split the friction into two components, the ploughing coefficient which relates to the deformation of the surface and the adhesion coefficient [104]. Chen et al. used the friction data to identify different deformation mechanisms occurring such as the ploughing away of the material and the adhesion of the removed material to the indenter [105]. In principle the friction measured is the friction between the diamond indenter and the surface and can be viewed as a dynamic coefficient as opposed to static one [106]. Other uses of the friction data from nano-scratch tests include work by Minn et al. who compared nano-scratch friction data to macroscopic ball-on-disk data [107] and Raman et al. who used the frictional data to compare the tribology of Ti-C films with differing amounts carbon content [108].
Conical, spherical and Berkovich indenters are used for nano-scratch testing and are chosen depending on the information that is required from the experiment. Knowing the exact geometry of the tip is crucial to any nano-scratch experiment and only like-for-like testing methods, in which the same indenter geometry is used, are comparable. In addition to geometry, the Berkovich tip is sensitive to the orientation of the tip with respect to the scratch direction. The geometry of the contact zone between the indenter and the surface has a considerable influence on the deformation mode, and consequently, on the frictional behaviour. The projected area of contact along the scratch is related to the cross-section of the scratch groove and in the case of a perfectly plastic deformation, the scratch has a triangular cross-section determined by the angle of attack [88][109]. In the case of scratches performed on silicon (110) surface, the largest resistance to motion is in the face forward direction and in this case there appears to be a more pronounced scratch groove due to brittle failure, opposed to the elastic-plastic deformation in the edge forward direction where lower forces were observed [109].

Investigations of brittle materials using a nano-scratch test are advantageous when compared with macroscopic tests. Macroscopic tests feature almost instantaneous failure due to brittle deformation at the initial stages of the test. With lower contact forces and penetration depths, Huang et al. showed that ceramics can be deformed in a purely elastic manner allowing them to study the fundamental deformation mechanics of these brittle materials [84]. The potential of performing nano-scratch tests at low temperatures has been developed by Chen et al. [110] and the use of an instrumented nano-scratch technique for nano-machining has also previously been carried out [111][112].

3.2.6 SCRATCH HARDNESS MEASUREMENTS

Although scratch hardness was superseded by indentation hardness, the scratch hardness number was still standardized and used in some industries. The ASTM standard specifies that the scratch hardness number, \( H_s \), can be calculated by performing a macroscopic
scratch test with constant force, $P$, and determining an accurate value for the scratch width, $w$, measured via imaging post-scratching. With this measurement, the scratch hardness is calculated using Equation 2-15 which gives the scratch hardness number when using a conical indenter tip with apex angle $120^\circ$ and a hemispherical tip of $200\mu m$ radius whilst applying a constant, normal load, $P$, to the scratch surface [113]. A major limitation to this test is that accurate scratch width measurements can be difficult to obtain when severe surface deformation occurs at high normal forces. In addition to this, similar to the difficulty in measuring shallow indentations, there is a problem with accurately measuring the width of scratches with low applied loads. Therefore, the range of loads that are suitable for this test is limited.

$$HS_p = \frac{8P}{\pi w^2}$$

Equation 2-15

### 3.2.7 Link between Indentation Hardness and Scratch Hardness

Nano-indentation testing is able to accurately characterise classical material properties such as elasticity constants and strength at the nano-scale. Based on similar principles, it is believed that scratch hardness can be linked to strength properties. In 1950 Tabor showed that indentation hardness was approximately three times the yield stress [22]. Like indentation, scratch hardness is a measure of a material's resistance to penetration and therefore should also, to some extent, be linked to the yield stress or strength properties of the material.

A first approach to finding links between the two involves dividing the lateral force, $F_L$, required to pull the indenter through the material into two terms [22]:

$$F_L = F_p + F_a$$

Equation 2-16
Where $F_p$ is the ploughing force and $F_a$ is the adhesive force. The idea of this model is to decouple the force required to deform the material, from the force due to the friction between the indenter and the surface. The ploughing force is expected to be related to conventional indentation hardness, however Briscoe showed that the indentation hardness is different to the ploughing hardness, which renders the decoupling of the ploughing force and adhesive force less significant.

3.2.8 SUMMARY

To conclude this review of nano-scratch testing, there have been numerous methods of experimentation for a range of materials in a manner analogous to that of a macroscopic scratch test, but on a smaller scale. Due to the reduction in scale, the plasticity size effect needs to be addressed in order to fully understand and optimize the potential of nano-scratch testing. No previous studies have identified these effects conclusively, and therefore it would be useful to develop a further understanding of size effects in nano-scratch tests. As mentioned above, there is currently no single definition for the scratch hardness or scratch resistance for nano-scale applications. Standard methods are important for any mechanical test as they impact the quality and reliability of the results making further research more efficient and reproducible, which as a consequence increases validity.
4. EXPERIMENTAL TECHNIQUES

4.1 NANO-INDENTER

A nano-indenter, often referred to as an instrumented indentation system was used for both nano-indentation and nano-scratch tests. This section provides further information of the instrument including details of the test procedure and critical calibration processes.

4.2 DETAILS OF THE INSTRUMENT

The results presented throughout this thesis were obtained from experiments performed on an Agilent (formerly MTS) G200 nano-indenteter fitted with the XP Nano-Mechanical Actuating Transducer (NMAT). The G200 system is shown below in Figure 3-1 and includes a cross-sectional view of the XP NMAT head. As mentioned previously, the indenter system is required to control and continuously monitor the force and displacement throughout the indentation cycle in order to apply the analytical method developed by Oliver and Pharr [12]. The sample is placed on a stage, controlled using piezoelectric motors in the x, y directions; the height of the sample must be correct when mounting, as the vertical movement of the indenter is restricted to small displacements. An optical microscope aids the positioning of indentations, which can be controlled by the computer software. In order to avoid any external vibrations, the nano-indenteter sits on a pneumatic vibration table and is enclosed in a thermally lagged cabinet.

Control of force is performed using electromagnetic actuation via the coil/magnet assembly; high accuracy in force control is achieved from the linear relationship between the current passed through the coil and the force that is produced. The stability of the permanent magnetic field over a large distance allows force application over a large displacement. Two leaf springs are used to secure the indentation column for both stability and lateral stiffness. It is important that the sample surface is within one degree
of orthogonal alignment with the indenter in order to provide repeatable and reliable data; errors in alignment can lead to larger errors than expected due to finite lateral stiffness in transducer design [114]. High lateral stiffness is a critical design element of the NMAT and is accomplished by the doubly secured indentation shaft that prevents lateral deflection when indenting samples with surface roughness or misalignment. The final critical component of the system is the capacitance gauge, which is used for sensing the displacement. Table 1 gives the technical specification of the XP-NMAT. The system used for the experiments presented here also has an optional high load function, which enables a maximum indentation force of 10N.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range of indenter travel</td>
<td>&gt;1.5 mm</td>
</tr>
<tr>
<td>Displacement resolution</td>
<td>0.01 nm</td>
</tr>
<tr>
<td>Typical leaf spring stiffness</td>
<td>100 N/m</td>
</tr>
<tr>
<td>Maximum Load</td>
<td>500 mN</td>
</tr>
<tr>
<td>Load resolution</td>
<td>50 nN</td>
</tr>
<tr>
<td>Thermal drift rate*</td>
<td>0.05 nm/s</td>
</tr>
</tbody>
</table>

*Thermal drift rates are dependent on lab environments.

Table 1 – Technical specification of the XP-NMAT [115].

Figure 4-1 – The Agilent G200 nano-indenter and a cross-sectional diagram of the XP-NMAT [115].
4.2.1 CALIBRATION METHODS: INDENTER AREA FUNCTION AND LOAD FRAME COMPLIANCE

Two important practical considerations that need to be taken into account in order to accurately determine the materials hardness and Young’s modulus from the Oliver and Pharr analysis are the indenter tip area function and the load frame compliance. The load frame compliance is important as the displacement data consists of the displacement of the sample as well as the displacement of the load frame. It is therefore necessary to remove the displacement of the load frame before the data can be analyzed. The area function is essential for both the calculation of material hardness and the elastic modulus. Therefore the accuracy of the area function will correspond to the accuracy of the measurements obtained.

Oliver and Pharr outline a method of calibrating the system using nano-indentation [12]. The compliance, $C$, is modelled as two springs consisting of the sample compliance, $C_s$, and the load frame compliance, $C_f$:

$$ C = C_s + C_f $$

Equation 3-1

As the compliance is equal to the inverse of the stiffness, using the stiffness equation given in Equation 1-1, it is possible to write:

$$ C = C_f + \sqrt{\frac{\pi}{2E_{eff}}} \frac{1}{\sqrt{A}} $$

Equation 3-2

From Equation 3-2, it can be seen that with a constant modulus, a plot of $C$ vs. $A^{1/2}$ will produced a linear relationship, the intercept of which is a direct measurement of $C_f$. To calibrate the system, a material with low hardness needs to be used, the material selected by Oliver and Pharr was aluminium and large indentations were made into the surface.
Upon measuring these large indentations optically, a function for the area of a perfect Berkovich indenter can be presented as:

\[ A(h_c) = 24.5h_c^2 \]

Equation 3-3

The two largest indentations in aluminium were used to plot a linear \( C \) vs. \( A^{1/2} \) from which the value of \( C_f \) and \( E_{eff} \) were determined. By re-arranging Equation 3-2 the area of 6 indentations into the aluminium were found using the calculated \( C_f \) and \( E_{eff} \). This is then plotted as \( A \) vs. \( h \) and a fit to the data of the form of Equation 3-4 will give a first approximation to the tip area function.

\[ A(h_c) = 24.5h_c^2 + C_1h_c^{-1} + C_2h_c^{1/2} + C_3h_c^{1/4} \ldots \ldots + C_8h_c^{1/128} \]

Equation 3-4

Here the values of \( C_1 \) to \( C_8 \) are constants. The first term refers to a perfect Berkovich indenter and the following terms describe the tip rounding which in inevitable and unavoidable. Using the new approximation of the area function, the process is iterated until convergence is achieved.

The method used in the Agilent G200 adopts a similar method to the Oliver and Pharr method; the load frame compliance is indirectly calibrated using the load, displacement and stiffness data obtained from performing an array of indentations, with various indentation depths, on a reference material of fused silica from which the Young’s modulus is known.

The algorithm used in the Agilent G200 to determine an area function of the form given in Equation 3-4 works by inputting the nominal area function for the diamond tip (i.e. the area function of a perfect diamond with no tip rounding). The modulus of the largest indentations is calculated from Sneddon’s stiffness equation, given in Equation 1-1, and substituting the area calculated from the ‘perfect’ area function (indentations having a depth in the range of 1000nm – 2500nm). The second term of the area function is
determined by calculating the areas required to maintain the calculated modulus down to zero displacements. This process is then repeated using the new area function containing both the first and second terms of Equation 3-4 to calculate a refined modulus. The process is continued for the specified number of terms required.

The area function calibration is performed after calculating the load frame compliance and applying a correction factor to remove the additional load frame compliance.

4.2.2 **DIRECT MEASUREMENT OF INDENTER AREA FUNCTION USING AFM**

Although the method described above can be used to indirectly measure the area function of the indenter tip, it is necessary to directly measure the area function using metrological Atomic Force Microscopy (AFM). Many uncertainties are associated with using a reference material such as surface contamination or the formation of oxide layers. Similarly, using a reciprocal power series, as given in Equation 3-4, to fit the data and derive an area function produces a poor fit to the data at the apex of the indenter, where there is the most deviation from the ideal indenter shape [116]. Further details of the instrumentation and methodology of AFM are given in section 6.3, however a description of the stages required for determining the indenter area function, using traceable AFM is detailed here.

AFM uses a tip mounted on an XYZ piezo scanner to scan a stationary sample mounted on a high-resolution stage and has independent linear optical detectors on all three axis; in this case the sample we refer to is the Berkovich diamond indenter. Before performing any measurements the sample must be carefully cleaned to remove debris or dust; any indenter contamination measured in the AFM scans results in errors in the generated area function; this is a crucial step. A mechanical tip cleaning protocol, provided by Alderich-Smith et al, is followed in steps that increase in severity [116]. This cleaning process is carried out, until the desired level of cleanliness is achieved.
The diamond Berkovich indenter is mounted normal to the microscope scanning plane and initial scans are made to locate the indenter apex. In order to stabilize the system and ensure the thermal drift had reached a minimal amount, continuous scans were made; this also pushed residual debris to the edges of the scanning area. Upon stabilization of the system, the indenter was imaged. The pixel size used for the scan was 512 x 512, giving a high-resolution image. Scans were carried out in the X and Y fast-scan directions and using a scan area size initially of 10μm x 10μm followed by a higher resolution scan using a scan size of 2μm x 2μm. These parameters were selected to give a sufficient pixel resolution.

To determine the area function from the AFM data, a Matlab pixel counting software, written by NPL, was used to generate an area function of the form projected area vs. distance from the indenter apex with points in steps of 0.4nm. The area functions derived from both the 10μm x 10μm scan and the 2μm x 2μm scans were stitched together using an Excel spreadsheet, which minimized the difference between the two functions over the depth range of 50nm-250nm. This combined area function provided high resolution at the indenter apex whilst covering a large enough depth range from the indenter apex.

The area function at this point was in the form of a look-up table, however a b-spline curve was fitted to the data using NPLFIT, a public domain software suit developed by NPL to fit splines and polynomials to experimental data sets [117]. It has been shown that the area function derived from this method has lower uncertainty than the area function derived indirectly using indentation [117].

The tip originally fitted in the Agilent G200 was imaged and is shown in Figure 3-2. It can be identified that this diamond tip is not sufficient for nano-indentation; indirect calibration of this tip using indentation would identify it as a suitable Berkovich tip from which an area function could be generated. The uncertainty of this area function is likely to be large, as the tip has significantly deviated from the shape of a perfect Berkovich tip close to the apex. It was therefore necessary to purchase a new Berkovich indenter in order to carry out nano-indentation experiments. The AFM scan for the new tip is given in Figure 3-3. An area function for this tip was generated using the method outlined...
above. The surface of the new tip TB20197 appears to have a higher roughness than the tip presented in Figure 3-2. An explanation for this could be that the tip was imaged before any prior use; it is possible that performing indentations into a hard material would reduce the roughness of the surface. None-the-less, the shape of this indenter is much closer to the shape of a perfect Berkovich indenter.

Figure 4-2 – AFM scans of diamond Berkovich tip TB1178 left: 10\(\mu\)m \(\times\) 10\(\mu\)m scan, right: 3\(\mu\)m \(\times\) 3\(\mu\)m scan.

Figure 4-3 – AFM scans of diamond Berkovich tip TB21097 left: 10\(\mu\)m \(\times\) 10\(\mu\)m scan, right: 2\(\mu\)m \(\times\) 2\(\mu\)m scan.
4.3 Nano-indentation

Nano-indentation experiments were performed in order to characterise the hardness of the sample and compare the measurements to the nano-scratch tests. The basics of nano-indentation, as well as the Oliver and Pharr analysis method have previously been outlined in section 1.2. The experimental set-up of the experiment varies for each instrument; Table 2 gives a description of the inputs required for nano-indentation in the G200 system. Although the system is mounted on a vibration isolation table and housed in an environmental enclosure cabinet, all tests are set-up in advance and performed late in the evening to avoid any unnecessary disturbances from external vibrations and ensure the thermal environment is stable.
A typical indentation test has five segments, which can be depicted in the force-time history plot for an indentation test, as shown in Figure 3-4. The number for each segment corresponds to the description below:

0. The indenter approaches the test surface, at the specified approach velocity, until contact is detected. Contact is determined by an increase in the stiffness relative to the indenter column's support springs, determined by the surface approach sensitivity.

1. The indenter is driven into the surface until the max force is reached. The loading rate is determined from the time to maximum force and the maximum force.
2. The force applied to the material is held constant for the peak hold time. This will ensure materials that experience small amounts of creep should have negligible creep at the end of the dwell time.

3. The indenter is withdrawn from the sample at a rate equivalent to the loading rate until the force reaches 10% of the maximum force.

4. This force is held constant in order to determine the drift rate.

5. The indenter is fully withdrawn from the sample.

It is important to perform a minimum of 5 repeat indentations for each experiment to increase the validity of the result and an indentation location spacing of at least five times the indentation size is specified to ensure each indentation is in an area unaffected by surrounding indentations.

![Figure 4-4 - Force-time history for an indentation test.](image)
Figure 4-5 - Force displacement curve for the same indentation. The hold segments are not apparent in this force-displacement curve as minimal displacement occurred. This data is used for the Oliver and Pharr method of analysis detailed in the introduction section 1.2.

4.4 Nano-scratch

Nano-scratch experiments were performed on the Agilent G200 nano-indentation system detailed in section 3.2. The piezoelectric motors controlling the stage in the x- and y- directions allow precise movement of the sample, with a positioning accuracy of less than 2nm. The system can simultaneously perform indentations whilst moving the stage laterally. As a result, the indenter is drawn laterally across the sample surface and a controlled nano-scratch is produced, providing continuous measurements of the normal force and x-, y- and z-displacements.

The Berkovich tip shown in Figure 3-3 was used for the nano-scratch experiments. The Berkovich indenter geometry results in an orientation dependent scratch response. For the scratches performed in these experiments, two orientations were used; edge forward and face forward, shown in Figure 3-6.
The system is fitted with lateral force measurement (LFM) probes. The LFM probes measure the deflection of the indenter shaft, relative to its normal x and y position. This is shown in Figure 3-7. \( K_l \) represents the stiffness of the spring supporting the shaft and \( F \) gives the lateral force. The LFM continuously records the lateral force along the scratch track for scratches made in any direction up to a maximum lateral force of 250mN with a lateral resolution of less than 2\( \mu \)N. Scratch lengths of up to 100mm can be achieved with velocities ranging from 100nm/sec to 2mm/sec.

The experiments performed throughout this work were constant force scratches with normal forces ranging from 0.5mN-40mN. The three pass scratch method was used whereby a single-line-scan of the surface morphology is performed prior to and following the scratch segment of the test. Before and after the scratch segment a pre-scan and a post-scan, equal to 20% of the scratch length, is performed so that the
software can automatically align the data from each segment of the test. The scratch process is shown schematically in Figure 3-8. The software generates a calculated output channel, which gives the 'penetration depth', calculated by subtracting the $z$-displacement of the first profile from the $z$-displacement of the scratch segment. This gives the corrected penetration depth, which removes any surface roughness or topography influences. The required inputs for the nano-scratch test are given in Table 3.

Figure 4-8 - Three pass nano-scratch process for a constant load scratch test.
Scratch length | Total length of scratch (µm)
Scratch velocity | Speed of scratch (µm s⁻¹)
Scratch orientation | The angle of the scratch from 0° to 360° where zero is a vertical scratch beginning at the top of the sample (deg)
Maximum scratch load | Final scratch load (mN)
Starting scratch load | Beginning scratch load. If ramped scratch this is set to 0N alternatively, for a uniform loaded scratch it will be equal to the maximum scratch load (mN)
Cross profile length | Length of the profile (µm)
Profiling velocity | Speed of the indenter during the profiling (µm/s)
Load applied during profiling | Force for the profile segments (µN)

Table 3: required inputs for nano-scratch set-up.

For both the nano-indentation and nano-scratch experiments the sample must be rigidly adhered to a sample mount, designed to fit into a sample holder which can then be fitted into the piezo stage at the correct height. The location of each experiment is identified using the 10x objective optical microscope fitted to the system. Once the desired location for the experiment is selected on the sample surface, the software is able to register the co-ordinates of the stage at that position and move the stage to the same position underneath the indenter, where the experiment can begin. A calibration is required to ensure the microscope and the indenter are positioned over the same desired area.

4.5 METROLOGICAL ATOMIC FORCE MICROSCOPY (AFM)

Metrological AFM was used to directly generate an area function for the Berkovich tip and is explained in section 3.2.2. However in addition to this, metrological AFM was used to directly image the perturbed surfaces of the sample, after the nano-scratches had
been performed. The use of metrological AFM is suitable to directly measure the dimensions of nano-scratches as it has the ability to acquire three-dimensional images at an excellent resolution for relatively small nano-scratches; scratches measured using this technique were scratches with a width of less than 5µm.

![Schematic diagram of a typical AFM system](image)

**Figure 4-9-** Schematic diagram of a typical AFM system. The tip attached to the cantilever scans the sample surface; the deflection of the cantilever is measured using a laser reflected off the cantilever onto the position-sensitive photo-detector.

The most important component of the AFM is the cantilever and sharp, single-crystal silicon tip shown in Figure 3-9. The tip is rastered across the sample surface, and the force between the tip and the surface causes the cantilever to deflect according to Hooke’s law. The deflection is measured using the laser reflected off the top surface of the cantilever, onto the array of photo detectors/photodiodes; this is used as a feedback signal, which alters the tip-to-sample distance to maintain a constant force between the tip and the sample.

The piezoelectric scanning tube is used as a precise positioning stage to ensure the sample is underneath the tip. The tube scanner can move the sample in the \(x, y, \) and \(z\) directions using a single tube piezoelectric element. An advantage of the tube scanner is better vibrational isolation, resulting from the higher resonant frequency of
the single-crystal construction in combination with a low resonant frequency isolation stage.

There are two imaging modes that are used for AFM, contact mode and non-contact mode also referred to as 'tapping' mode. In contact mode, the tip is 'dragged' across the surface of the sample and the topography of the surface is measured using the feedback signal required to maintain the constant force between the sample and the surface. The distance is usually set so that there is contact between the surface and the tip, i.e. the tip is in firm contact with the solid surface. The force between the tip and the surface is a repulsive force.

Tapping mode was developed for samples that develop a liquid meniscus layer. In contact mode the tip would 'stick' to the surface causing major problems. In tapping mode the tip oscillates at an amplitude greater than 10nm. Interaction forces between the surface and the sample cause the amplitude of the oscillation to decrease, as the tip gets closer to the sample. The feedback signal controls the height of the cantilever above the sample to maintain the cantilever oscillation amplitude. In tapping mode the image is produced by imaging the force of the intermittent contacts of the tip with the sample surface. In these experiments contact mode was used.

The AFM system used was a Thermo-Microscopes 'Autoprobe' M5 AFM with a 7µm range tube scanner operating in contact mode with the Scanmaster™ closed loop scan linearising system enabled based at the National Physics Laboratory. The height data was derived from the independent z-position sensor rather than the feedback voltages; this avoids errors due to non-linearity, hysteresis and creep of the x- and y-piezo actuators. A thorough calibration of the system was performed giving a total calibration uncertainty of <1% in the x and y directions and <1.6% in the z direction at the 95% confidence level.

AFM scans were taken of each scratch at three locations: the start, middle and end, as seen in Figure 3-11. The pixel size used for each scan was 256 x 256, giving a sufficient resolution image and minimizing the time taken for each scan. Scans were carried out in
the X fast-scan directions using a scan area size of 5μm x 5μm for the smaller scratches and 10μm x 10μm for the larger scratches. The Z detector signal was used to obtain measurements of scratch width and depth using line scans as shown in Figure 3-10.

![Figure 3-10](image1)

**Figure 3-10** - Typical AFM line scan of middle region of scratch. The right shows the Z detector image from which the measurements were obtained. Measurements taken from these line-scans were the scratch depth including the pile up (vertical height from a-b, a-c), scratch depth excluding pile-up (vertical height a-d) and the scratch width (horizontal width b-c). 10 line scans were taken from each scratch and the measurements were averaged.

![Figure 4-10](image2)

**Figure 4-10** - 10μm x 10μm scans of the start, middle and of a nano-scratch performed with a normal force of 3mN in the edge forward orientation. These images were produced from the feedback signal which provides a better imaging contrast, however measurements were not obtained from this signal.

This technique is useful and provides very accurate data, however a limitation to this is that performing AFM scans on each scratch is time consuming. For small scratches with widths of around 1μm and depths of around 500nm or less AFM is necessary – however larger scratches do not require a small resolution, therefore optical microscopy methods can be used. An Olympus LEXT confocal laser scanning microscope (CLSM) was used for these measurements. The CLSM microscope is used to acquire in-focus images at
selected depths which are then stacked together to produce a 3D reconstructed image. Calibration of the depth between each image taken ensures that z-axis measurements are valid. Striations in the AFM images in Figure 3-11 indicate that the lateral stiffness of the instrument is low.

4.6 ELECTRON BACKSCATTER DIFFRACTION (EBSD)

Electron Backscatter Diffraction (EBSD) was used throughout this thesis to characterise the crystallographic orientation and microstructure of polycrystalline copper samples. EBSD is conducted using a scanning electron microscope (SEM) with an additional EBSD detector containing a phosphor screen which is fluoresced by electrons from the sample, giving the diffraction pattern used in conjunction with a CCD camera with optics for viewing the diffraction pattern on the phosphor screen. The system used was an FEI Sirion Field Emission Gun Scanning Electron Microscope (FEGSEM) with a HKL Nordlys EBSD detector.

For EBSD measurement the sample is placed in the SEM chamber at an angle of 70˚ from the horizontal position towards the diffraction camera, which is positioned, normal to the electron beam. A beam of electrons are directed at a point of interest on the sample surface, a fraction of which are inelastically scattered by the atoms within the material, to form a divergent source of electrons. Some electrons will coincide with atomic planes which satisfy the Bragg Equation [118] and these electrons are diffracted to form a set of paired large angle cones corresponding to each diffracting plane. These cones, when imaged via the camera, produce the Kikuchi bands of the EBSD pattern, which is illustrated in Figure 3-12. The centres of the bands correspond to the projection of the diffracting planes on the phosphor screen and can be indexed by the Miller indices of the diffracting crystal plane that formed it. The position of the Kikuchi bands can be found automatically with the Hough transform and the angles between the planes producing these bands can be calculated. These are compared with a list of inter-planar angles for the analysed crystal structure to allocate Miller indices to each plane. Finally
these are used to calculate the crystal orientation of the sample region that formed the image.

![Figure 4-12 - EBSD set up configuration showing the sample positioned 70° to the horizontal and the phosphor screen normal to the electron beam. Kikuchi bands are shown on the phosphor screen projected by the diffraction electron cones.][119]

A highly polished flat sample surface is required for EBSD. Sample preparation is critical as the diffracted electrons escape from only a few tens of nano-meters of depth under the sample surface. Any deformation, contamination or oxidisation on the sample surface will suppress the EBSD pattern formation. In the case of polycrystalline FCC pure copper (99.9% purity) it was necessary to mechanically polish the sample to a 1µm finish followed by electrolytic polishing at voltage of 20V and a current of 5mA for 10 seconds using a pre-mixed Sturers® D2 electrolyte.
5. **Nano-scratch hardness of pure copper**

5.1 **Methods of determining nano-scratch hardness**

The nano-scratch experiment outlined in section 3.4 consists of traversing the Berkovich indenter across the sample surface, under an applied normal force. Combinations of the following parameters affect the scratch response, the first two of which are controlled:

1. The constant normal force applied;
2. The orientation of the tip with respect to the scratch direction;
3. Interfacial friction.

The measurable quantities obtained from the nano-scratch test include:

1. The lateral force along the scratch;
2. The maximum penetration depth along the scratch which is directly related to the area of contact through the area function;
3. Scratch width;
4. Height of the pile-up either side of the scratch groove;
5. Residual penetration depth, after force removal.

Utilizing the above parameters, three methods were developed to determine the nano-scratch hardness of tests performed with a Berkovich indenter; all variations of the basic pressure calculation of \( \frac{\text{Force}}{\text{Area}} \). The three methods are detailed individually below and are shown diagrammatically in Figure 4-1 and 4-2.

Method 1, \( H_s(1) \): The first method is similar to the ASTM G171 detailed in section 2.2.6 and uses the normal force, \( F_N \), divided by the normal projected area of contact, \( A_p \). \( A_p \) is obtained from the projected area function at the scratch ‘depth’. Details of how the depth was measured are provided in the next section. Depending on the orientation of the tip during the scratch, the projected area of contact was taken as either one third of \( A_p \) for a face forward (FF) scratch, or two-thirds of \( A_p \) for an edge forward (EF) scratch.
Method 2, $H_s(2)$ : During the scratching process, the normal force, $F_{N_s}$, is applied and controlled; the tip is simultaneously traversed laterally across the sample surface causing a lateral force, $F_{L_s}$, to be exerted in the scratch direction, perpendicular to the normal force and measured via the lateral force measurement probes. Therefore, it would appear necessary to utilise the lateral force in the scratch hardness calculation, to provide a measure of the lateral resistance of the material. Hence, for method two the scratch hardness calculation uses the lateral force, $F_{L_s}$, divided by the lateral/tangential area of contact, $A_{T_s}$. The area, $A_{T_s}$, is measured directly using the AFM measurements taken from each scratch and represents the cross-sectional area, inside the triangular region bound between the top of the pile-up on either side of the scratch groove and the bottom of the scratch track (see Figure 4-1).

Method 3, $H_s(3)$ : The third method combines components of the normal force, $F_{N_s}$, and the lateral force, $F_{L_s}$, acting in the direction perpendicular to the facet(s) of the indenter to give a reaction force, $F_{R_s}$, representative of the force supporting the indenter during the scratching process. This is shown in Figure 4-2. The reaction force is divided by the surface area in contact with the material, $A_s$, to give the scratch hardness. $A_s$ is obtained from the surface area function at the scratch depth (see below) and again, either one- or two-thirds of $A_s$ is used, depending on the orientation of the tip. Ideally this calculation would include a force contribution from the interfacial friction, acting perpendicular to the reaction force, however this was excluded due to complexity of determining the interfacial friction.
Figure 5-1 – a. schematic representation of the projected area, $A_P$, of contact calculated from the projected area function at the penetration depth. One-third used for FF scratch and two-thirds used for EF scratch. b. Schematic of an AFM line scan across the scratch width / cross-section of the scratch track highlighting the area measured as the tangential area, $A_T$.

Figure 5-2 – Diagram illustrating how each of the forces, $F_N$, $F_L$, and $F_R$, act on the indenter during the FF scratch and the EF scratch. $F_L$ is always negative in the direction of the scratch.

**FF case:**
$$ F_R = -F_L \cdot (EF) \cos \theta + F_N \sin \theta $$

**EF case:**
$$ F_R = -\frac{1}{2}F_L \cdot (EF) \cos \theta \cdot 60^\circ + \frac{1}{2} F_N \sin \theta $$

$$ = -\frac{1}{2} F_L \cdot (EF) \cos \theta + F_N \sin \theta $$
5.2 DETAILS OF NANO-SCRATCH MEASUREMENT

In order to determine the most appropriate method of measuring the scratch depth, at which the contact area could be calculated from, for use in methods one and three, three-pass nano-scratches were performed on a sample of annealed, polycrystalline, pure copper with 99.99% purity. Five repeat scratches were performed for each normal force (0.5mN – 40mN) in each orientation (EF and FF). The profiling force used was 0.2mN and the velocity of both the profiling segment and the scratch segment was 10μm/sec.

From these scratches, direct measurements of the scratch depth were made using AFM and CLSM. In addition to this, the data from the corrected penetration depth channel was averaged for each scratch. These depth measurements for the FF oriented scratches are presented in Figure 4-4. Direct measurements were made for the residual scratch depth from the original surface and the residual scratch depth from the top of the pile-up (see Figure 4-1.b). Additionally, the residual depth of the over-scan segment was measured directly as this segment had caused significant deformation to the surface (see Figure 4-3).

![AFM image of the beginning of a nano-scratch performed in the EF tip orientation, with normal force of a. 3mN and b 5mN. The profiling force used was 0.2mN, which has caused significant plastic deformation which can be identified in the over-scan segment before the scratch segment.](image)

It was expected that the residual depth of the scratches from the original surface would be shallower than the corrected penetration depth channel, as direct measurements were
taken after the force had been removed and therefore would have experienced some vertical, elastic recovery. On the other hand, the penetration depth channel is a measure of the instantaneous displacement of the indenter tip, under the applied force, as a result would be deeper. This was identified for the scratches with a normal force of 10mN or larger however for the smaller scratches, this was not the case. After post-imaging and inspection of the nano-scratches (Figure 4-3), it appeared that the over-scan segments, performed with a normal force equal to the profiling force, of the scratch had left a plastically deformed surface. Ideally, the profiling segments would be performed at a force that is within the elastic limit of the material and therefore no plastic deformation would occur. Measurements of the depth of the over-scan segments, from the original surface were made for the smaller scratches and added to the depth measurements of the corrected penetration depth (shown in Figure 4-4). It can be seen that for the smaller scratches, the residual depth measured from the original surface is a combination of the residual depth of the profiling segment, plus the depth of the scratching segment, hence it appears deeper than the instantaneous scratch depth. The additional contribution is negligible in larger scratches, resulting in the residual depth being shallower then the instantaneous scratch depth, as expected.

Ideally, the scratch depth including the pile-up height would be input into the respective area functions for the surface area of contact and projected area of contact. Determining the scratch depth including pile-up is only possible using a direct measurement however, it has been observed that the direct measurement includes contributions of depth from the profiling segment, which is an over estimation of the contact depth. It would therefore seem appropriate to use the averaged, corrected penetration depth channel as the scratch depth measurement for the input into the area functions for the calculation of the scratch hardness in methods one and three.
Figure 5.4 – Comparison of scratch penetration depths measured on one of the 5 repeat scratches using direct methods from the original surface and from the pile-up height (see Figure 26.b.) and measured by averaging the corrected penetration depth channel (instantaneous scratch depth). Direct measurements of depth of the over-scan segment from the original surface were added to the instantaneous to show the impact that the profiling force has on the residual measurement of the scratch depth for small scratches. This is negligible in larger scratches hence the residual depth is shallower than the instantaneous scratch depth, as expected. All scratches were performed in the face forward tip orientation.

Figure 4.5.d shows a typical corrected scratch penetration depth channel, from which the data was averaged to give the instantaneous penetration depths presented in Figure 4.4. The red channel in Figure 4.5.d, shows the penetration depth for a scratch with a face forward tip orientation and the blue shows the edge forward case. After close inspection, it can be seen that in both channels, there is a ‘dip’ in the penetration depth, before it becomes ‘steady-state’. This is typical for all scratches performed in both tip orientations. From Figure 4.5.d we see that at point 1, where the maximum force has been reached, both the edge forward scratch and the face forward scratch have approximately the same penetration depth. The depth at point 1, or at the maximum force, is shown for all scratches and compared with the depth of an indentation performed at the same maximum force in Figure 4.5.a. This figure shows that the depth of the scratches at point 1, are unaffected by tip orientation and are approximately equal
to the indentation depth at the maximum force. This is not unanticipated as in all three cases (FF, EF, and indentation) the normal force at this stage (i.e. before the indenter has started to move laterally) is supported by all three facets of the indenter.

As the tip begins to traverse laterally across the sample, it penetrates deeper into the sample causing this ‘dip’ in the penetration curve (point 2 in Figure 4-5.d); it is no longer in contact with the back wall of the scratch track and the normal force is transferred from three facets of support to either one facet (FF case) or two facets (EF case). Figure 4-5.c. shows the ratio of the depth of the deepest point in the initial ‘dip’ (point 2) to the depth at the maximum force whereby the force is supported by three facets (point 1). The reduction in contact area, due to the reduced number of facets in contact, requires the depth to increase in order to support the same normal force. In the face forward case, the force is transferred to $\frac{1}{3}$ of the contact area and therefore the depth is expected to increase by a factor of $\sqrt{3}$. In the edge forward case, the contact area supporting the normal force reduces to $\frac{2}{3}$ of the contact area and therefore the depth is expected to increase by a factor of $\sqrt{\frac{3}{2}}$. We see in Figure 30.b. that the increase in depth follows this for both the edge forward and face forward scratches at large normal forces.

From this detailed evaluation of the penetration depth channels, it was decided that averaging the corrected penetration depth channel, was sufficient to determine a scratch penetration depth, that can be input into each of the area functions to determine the area of contact. The steady state region of the scratch track was averaged (region 3 in Figure 4-5.d) and not the entire scratch segment (i.e. 40µm - 110µm) for the penetration depths shown in Figure 4-4 for the face forward scratches, and in Figure 4-5.b for both edge forward and face forward scratches.
Figure 5-5 - a. Depth at the maximum force (point 1 in d) for scratches of both tip orientations and the depth at maximum force for indentations performed with the same normal force. b. Average corrected penetration depth from the steady state region of scratches (3 in d). c. Ratio of the depth at 2 : depth at 1 (see d). d. Typical scratch, corrected, penetration depth channel for EF case and FF case. (Error bars in a. and b. represent one standard deviation).

In the steady state region there is negligible difference between the depth of the edge forward and the face forward scratches (Figure 4-5.b). An explanation could be that the
in face forward case, the scratch behaves in a similar manner to a flat punch indentation, where a volume of material adheres to the tip, and ‘pushed’ through the sample creating the scratch groove, and not the single facet of the indenter. Thus resulting in a larger surface area for the resolved scratch force to be acting on and leaving remnant pile-up at the end of the scratch track. In the edge forward case, the material flows outwards to the sides of the scratch groove and the edge facets of the indenter glide through slip planes in the crystal. Direct measurements of the pile-up height and the scratch width, shown in Figure 4-6 confirm this. The pile-up height at either side of the scratch groove was larger for the edge forward oriented scratches and the scratch widths are similarly larger for the edge forward case. Post investigation of the scratch morphology is shown in Figure 4-7. In Figure 4-7.b there is a raised volume of material that appears to have ‘piled-up’ at the end of the scratch track. This build-up of material was not identified for the edge forward case in Figure 4-7.a.

(a)  
(b)

Figure 5-6 – Direct measurements from one of 5 repeat scratches at each normal force a. pile up height and b. scratch width of EF and FF scratches.
5.3 Evaluation of Methods Used to Calculate Nano-scratch Hardness

Scratch hardness was calculated using the measurements made from scratches in section 4.2. The three methods of calculation were used and compared. The results are shown for methods one, two and three in Figures 4-8, 4-9 and 4-10 respectively. For methods one and three, the scratch hardness values were calculated and repeated for five scratches. The error bars in Figure 4-8 and 4-10 represent a single standard deviation; the lower penetration depths have a greater degree of scatter, possibly explained by the sample roughness. As direct measurements using AFM and CLSM were only made for one of the five repeat scratches, the scratch hardness measured with method two was only calculated for one scratch. As a consequence, an average was not taken, thus results using method two are less accurate. Nano-indentation hardness measurements for the same sample are given in Figure 4-11.
Figure 5.8 – Nano-scratch hardness measured using method one. Average of five repeat experiments are shown; error bars represent one standard deviation. Scratches were performed using both tip orientations.

Figure 5.9 – Nano-scratch hardness measured using method two. Scratches were performed using both tip orientations. The dimensions of the residual scratch groove were measured for one of the five repeat scratches; this measured scratch was used for the calculation of the scratch hardness.
Figure 5-10 – Nano-scratch hardness measured using method three. Average of five repeat experiments are shown; error bars represent one standard deviation. Scratches were performed using both tip orientations.

Figure 5-11 – Nano-indentation hardness of the same sample, as a comparison to the scratch hardness measurements presented above. Average of 10 repeat experiments are shown; error bars represent one standard deviation.

In all cases, nano-scratch harness is plotted against the normal force applied. It was apparent that by increasing the normal force, the dimensions of the scratches increased proportionally and thus this was valid to investigate the lateral size effect. A full
description of the penetration depth for all scratches is provided in the Appendix. Method one was based on the macroscopic scratch hardness calculation, which has produced scratch hardness values ranging from 4GPa – 8GPa for the face forward scratches and 2GPa-5GPa for the edge forward scratches. There is a factor of two difference between the scratch hardness measured between the edge forward scratches and the face forward scratches. This factor of two difference is solely due to the contact area chosen for the analysis (either one third or two thirds) as we have identified that the difference between penetration depth for the edge forward case and the face forward case is negligible and the normal force used for this calculation is also the same for each case. We have seen that there are significant differences in the deformation mechanisms occurring in the edge forward case and the face forward case, thus this factor of two difference does not fully describe the difference between the two cases – as a consequence this method of determining scratch hardness is insufficient.

Method two gave scratch hardness values ranging from 3GPa – 5.5GPa for the face forward scratches and 1.5GPa – 3.25GPa for the edge forward scratches, which was lower than the hardness values obtained with method one. This method incorporated the lateral force, which has been identified to portray significant differences between the edge forward case and the face forward case (see Figure 4-9). It is therefore a more appropriate representation of the different deformation mechanisms occurring between the two cases. However this calculation uses direct measurements of the contact area and only one measurement was taken for each test, thus making the results less reliable. Additionally, without incorporating the normal force into the calculation we are eliminating a significant contribution to the force exerting the pressure that causes the plastic deformation. Thus method three would theoretically be the most appropriate method to use. Method three gave scratch hardness measurements of 2.5GPa-5GPa for the face forward scratches and 1.5GPa-2.5GPa for the edge forward scratches. This method combines the normal force and the lateral force to give a reaction force; representative of the force being supported by the material in the scratching process, which is then divided by the surface area in contact.
It is assumed that a material exerts the same resistance to deformation, independent of the applied force direction and therefore the hardness would be approximately the same for a static indentation and for a scratch. Subsequently, this assumption has led to the indentation hardness being selected as the key metric in wear calculations. However from this analysis, it has been confirmed that the deformation mechanisms occurring laterally, are distinctive to the orientation of the tip with respect to the scratch direction and in all cases the scratch hardness is larger than the indentation hardness.

Throughout the remainder of this thesis, method three was adopted for the calculation of nano-scratch hardness, using the average, corrected, penetration depth from the steady state region as an input into the surface area function to determine the surface area in contact. Lateral force and normal force were also averaged in the steady state region and used as inputs into the calculation of the reaction force (see Figure 4-2).

5.4 SUMMARY

A lateral size effect (LSE) has been observed in the scratch hardness measurements made using method one and method three whereby the hardness increases with decreasing
scratch size. This was not observed in the scratch hardness measurements obtained using method two. The sample used in this case was an annealed, polycrystalline copper sample of which the average grain size was approximately 20.2 µm.

According to slip-distance theory, indentation size effects are related to the size of the spacing between obstacles to dislocation glide, which is indirectly related to the amount of work-hardening the sample has undergone and the average grain size of the material. Throughout the following chapters, lateral size effects will be investigated with respect to the degree of work-hardening and grain size of pure copper samples, to generate a deeper understanding of the size dependence of nano-scratch hardness, or the lateral size effect.
6. **LATERAL SIZE EFFECT OBSERVED IN SINGLE CRYSTAL COPPER**

Nano-scratch experiments were performed on a single crystal of oxygen-free pure copper (99.9% purity) oriented in the (100) crystallographic plane (obtained from Goodfellow UK). The sample was annealed for 4 hours at 600°C in air followed by a mechanical and electro-polish in order to obtain a smooth flat surface, with negligible residual stresses. The plan orientation of the crystal was confirmed using EBSD. Nano-scratch experiments were performed in a random direction, within the (100) plane, using both face forward and edge forward tip orientations. The nano-scratch hardness was calculated using method three described in the previous chapter and results are presented in Figure 5-1 below. The full data set used to calculate the scratch hardness is provided in the appendix.

![Figure 6-1 - Nano-scratch hardness of single crystal copper. Average of 5 repeat experiments is shown; error bars represent one standard deviation of the mean.](image)

Figure 6-1 - Nano-scratch hardness of single crystal copper. Average of 5 repeat experiments is shown; error bars represent one standard deviation of the mean.
Figure 5-1 shows a lateral size effect in the data for both the edge forward and face forward case, whereby the nano-scratch hardness increases with decreasing scratch size. The nano-scratch hardness increases by a factor of two with decreasing scratch size in both the edge forward and face forward tip orientation. Furthermore, the scratch hardness of scratches performed in the face forward tip orientation is larger than the scratch hardness of scratches performed in the edge forward tip orientation, analogous to the results presented in the previous chapter. The scratch hardness is approximately one and a half times larger for the face forward tip orientation for all scratch sizes. This suggests that there is different deformation mechanism occurring in each tip orientation that has not been accounted for by resolving the lateral and normal forces.

6.1 Effect of Dislocation Density on the Nano-scratch Hardness

Prior to annealing, and after one hour of annealing, nano-scratch experiments were performed on the single crystal sample, in addition to the experiments performed after four hours of annealing. In each case, the sample was mechanically and electrolytically polished to remove any oxide that may have formed during the heat treating process. The nano-scratch hardness results from the single crystal in the three conditions are compared in Figure 5-2 below for the face forward and edge forward tip orientations.
Figure 6-2 - Nano-scratch hardness of single crystal copper in three heat-treated states. Right shows the face forward tip orientation and left shows the edge forward tip orientation. Average of 5 repeat experiments is shown; error bars represent one standard deviation of the mean.

Again, there is an evident lateral size effect observed in all three material conditions, in both tip orientations. Heat treating the sample, has reduced the scratch-hardness which is in agreement with the notion that heat-treatment of a metal would reduce the density of sessile dislocations or pinning defects in the material, thus reducing the hardness of the sample due to less obstructions to dislocation movement within the crystal. An increase in the density of obstacles present in the material is directly related to a reduction of the spacing between these obstacles, i.e. a reduced length scale in which the mobile dislocations, required for plastic deformation, can glide. This is clearly identified in the edge forward tip orientation; the well-annealed sample (after 4 hours) has the lowest hardness and the non-heat treated sample has the largest scratch hardness. However in the face forward case, the hardness values slightly overlap for the results obtained in the as received condition and after 1 hour of heat treatment, particularly at large normal forces.

Slip-distance theory, introduced in section 2.1.6, has been modified in order to combine indentation size, grain size and other pinning defects in a single, length-scale-dependent
deformation mechanism, to determine the increase in hardness [9]. This is achieved through Equation 5-1, which is a re-arranged version of Equation 2-14.

\[
P_m = P_y + \left(\frac{k_1}{a} + \frac{k_2}{d} + k_3\sqrt{\rho_s}\right)^{1/2}
\]

Equation 5-1

where \(P_m\) is the mean indentation pressure (hardness); \(P_y\) is the size-independent yield pressure; \(k_1, k_2,\) and \(k_3\) are scaling parameters; \(a\) is the indentation contact radius; \(d\) is the average grain size of the material; and \(\rho_s\) is the line density of other pinning points, thus \(\sqrt{\rho_s}\) is the average spatial frequency.

It is possible to apply slip-distance theory to the nano-scratch hardness data obtained from the single crystal to obtain values of the \(k_3\sqrt{\rho_s}\) term for each of the three sample conditions. This can indicate the density of dislocations and pinning defects in each case. As the sample is a single crystal (\(d = \infty\)), the \(k_2\) term can be ignored. A plot of the pressure squared vs. the reciprocal contact radius, yields a linear function with a gradient of \(k_1\) and intercept is \(k_3\sqrt{\rho_s}\). This is shown in Figure 5-3 for the four-hour annealed sample. The value of \(P_y\) for copper is taken as 45 MPa [9]. The two separate values of \(k_1\) for the edge forward and face forward case were used in Equation 5-1 to obtain values of \(k_3\sqrt{\rho_s}\) for each condition. These values are shown in Table 4 below. Essentially, this theory separates the lateral size effect due to scratch size from the increase in hardness due to the density of pinning defects for each tip orientation.
Face forward | Edge forward
--- | ---
$k_1$ (GPa² μm) | $k_3\sqrt{\rho_s}$ (GPa²) | $k_1$ (GPa² μm) | $k_3\sqrt{\rho_s}$ (GPa²)
As received | 2.34 | 7.79 | 0.7 | 5.72
Annealed 1 hr | 2.34 | 6.47 | 0.7 | 2.04
Annealed 4 hr | 2.34 | 1.99 | 0.7 | 0.71

Table 4 - Values of $k_1$ obtained from fitting shown in Figure 5-3 and values of $k_3\sqrt{\rho_s}$ obtained Equation 5-1 using the respective $k_1$ values for the FF and EF case.

From Figure 5-3, it is clear that there are very different gradients and as a result, values of $k_1$, for the face forward and the edge forward case. This is expected as in each case there is a different pressure distribution ahead of the indenter which would impact the contact radius, which is assumed to be related to the plastic zone size of the nano-scratch.
In the face forward case the pressure would ideally be uniformly distributed across one facet however in the edge forward case, there is a pressure gradient, which is highest at the front edge of the indenter.

The $k_3\sqrt{\rho_s}$ term represents a range of other mechanisms for pinning dislocations which act to limit dislocation mobility, thus increase hardness, other than the scratch size and distance between grain boundaries. Through the process of annealing, dislocations will annihilate, leaving a perfect atomic lattice and reduce the overall density of pinning defects in the sample. Therefore, it is expected that the value of $k_3\sqrt{\rho_s}$ would decrease with increased heat-treatment. This is observed in the measured values of $k_3\sqrt{\rho_s}$ presented in Table 4 above for both tip orientations. It is concerning that there are differences in the $k_3\sqrt{\rho_s}$ with respect to the tip orientation when scratching the same condition of sample however, referring back to Figure 5-3, it can be seen that for small values of $1/a$ the data begins to converge which, with an improved fitting may produce intercepts that are relatively close to each other.

When the scratch-hardness data obtained for the sample in the as received condition and after one hour of heat-treatment were plotted in a similar manner to Figure 5-3, each generated individual values of $k_1$ for each tip orientation, and also began to converge as the value of $1/a$ was reduced. When these individual $k_1$ values were used in Equation 5-1, the $k_3\sqrt{\rho_s}$ terms obtained did not correlate with the expected order of dislocation density in each sample. For the face forward tip orientation, however the values did correlate with the order of sample hardness observed in Figure 5-2 where the hardness of the sample exposed to an intermediate amount of heat-treatment appeared harder than the non-heat treated sample for some scratch sizes.
6.2 Effect of Crystallographic Direction on the Nano-scratch Hardness

In each of the above cases, the crystallographic direction in which the scratch was traversing, was not identified. It has been shown for macroscopic scratch testing, with a steel ball indenter, the scratch response is anisotropic [67] and therefore it is useful to investigate these effects in nano-scratch testing. Figure 5-4 shows an indexed EBSP for the single crystal in the non-heat treated condition. The plane orientation of the crystal is (100) thus the [100] direction is normal to the image. From the indexed solution, it was possible to identify the crystallographic direction and therefore, the sample was positioned such that scratches were performed in specific crystallographic directions. Scratches were performed at approximately 0º, 45º and at three interpolar angles. The scratch hardness results are given in Figure 5-6; in each direction, scratches were performed in both the edge forward and face forward tip orientation.

Figure 6-4 - Crystal unit cell identified from the EBSP. Angles indicating the direction of the scratches are shown (left). Indexed EBSP of the single crystal (right). With knowledge of the positioning of the sample in the SEM chamber, crystallographic directions could be identified.
Figure 6-5 - Indication of the direction in which scratches were performed in the 100 crystal plane.

Figure 6-6 – a. Nano-scratch hardness of as received, single crystal copper, scratched in different crystallographic directions using a 5mN normal force. b. corresponding coefficient of friction.
It is known that slip in a FCC crystal is most energetically favourable in close packed-planes, of the \{111\} type and the observed slip direction is of the \(<110>\) type. This is illustrated in Figure 5-7. For the single crystal above, the direction of slip would occur at 45°. When scratching at 0°, the slip direction is 45° to the direction of the applied force, therefore the resolved shear stress, \(\tau_R\), is large which makes it easier for the crystal to slip. This is shown in the middle diagram of Figure 5-8. When scratching at 45° the slip direction is parallel to the direction in which the force is applied, thus slip is more difficult. This is shown in the third image of Figure 5-8. Generally, in FCC materials, dislocation movement, thus plastic deformation is easiest when the slip direction is 45° to the direction of the applied force.

Therefore, scratching at an angle of 45° is expected to be the most difficult and would exhibit a larger scratch-hardness. This is the case for both the face forward and edge forward tip orientation as the hardness gradually increases as the direction moves towards the slip direction. It is evident from Figure 5-6 that the scratch hardness of the face forward tip orientation remains larger than the scratch hardness of the edge forward case, irrespective of the scratch direction.

Figure 6-7- Slip plane and slip direction relative to the scratch directions shown in Figure 5-5.
Figure 6-8 - Slip observed in material subjected to a scratch force $F_R$ for three different crystallographic orientations. The dotted line each case represents the slip plane and the adjacent arrows represent the slip direction. The red arrows represent the direction of which the force is applied. $\tau_R$ is the resolved shear stress in each case, $\lambda$ is the angle between the stress direction and the slip direction. $\varphi$ is the angle between the stress direction and the normal to the slip direction.

6.3 SUMMARY

The scratch-hardness increases with increased dislocation density when scratching with an edge forward tip orientation, however this is not the case when scratching with a face-forward tip orientation. This suggests that some other mechanism is responsible for the scratch hardness when scratching with the face forward tip orientation. An explanation could be that as the material is being forced ahead of the indenter by the angled facet of the indenter in the face forward orientation, dislocations are being generated ahead of the indenter causing the material to work-harden as the material is being scratched. It has already been identified that there is a large pile-up of material deposited at the end of the scratch track which confirms that the material is being pushed ahead of the indenter. In the sample exposed to an intermediate amount of work hardening a number of dislocation sources are already present in the material, this would facilitate the nucleation of new dislocations, increasing the rate in which dislocations are generated ahead of the indenter, which causes the large scratch hardness observed in this sample. In the sample that had not been heat treated, the dislocation density is already high and at a saturation point whereby no more dislocations can be generated. Thus, the amount of dislocations generated ahead of the indenter is less than that of the sample with one hour of heat treatment.
Furthermore, crystallographic direction with respect to the scratching direction has a significant impact of the scratch-hardness for both tip orientations. When scratching in a direction parallel to the slip direction, plastic deformation is difficult and the scratch resistance increases, whereas scratching in a direction 45° to the slip direction, deformation is favoured and the scratch hardness is reduced. As a result, scratch hardness of single crystal copper is crystallographic direction dependent and anisotropic. Ideally, in a small grained sample this effect will average out by scratching numerous grains of different crystallographic orientations. This is investigated in the next chapter.

The modified slip-distance theory used to predict the indentation size effect is not sufficient to predict the lateral size effect observed in nano-scratch hardness of single crystal copper. A further understanding of the deformation mechanisms occurring in the scratch process, particularly for the face forward tip orientation, and a description of the direction in which the scratch is traversing with respect to the orientation of the tip is required in order to develop a suitable predictive model.
7. LATERAL SIZE EFFECT OBSERVED IN POLYCRYSTALLINE COPPER

The previous chapter investigates the interaction between the lateral size effect and the effect of dislocation density on the material hardness, for single crystal copper. In this chapter an alternative internal length-scale, the average grain size, is introduced.

7.1 NANO-SCRATCH HARDNESS OF POLYCRYSTALLINE COPPER

Grain boundaries are defined as the boundary separating two grains of crystal with different orientations. The grain boundaries are known to have a strengthening effect on the mechanical behaviour of materials. The Hall-Petch relationship, described in section 2.1.5, demonstrates how the yield strength of a material is related to the average grain size of the material through Equation 2-6, \( \sigma_y = \sigma_0 + k d^{-1/2} \), where \( k \) is a constant and \( \sigma_0 \) is the yield strength of a single crystal. The Hall-Petch relationship is applicable to the indentation hardness of copper and an increase in hardness is observed when the grain size is reduced. Grain boundaries affect dislocation motion in different ways; they act as obstacles for dislocation mobility; reduce the average spacing in which the dislocation has to move, act as a source for dislocations and accommodate the inhomogeneous deformation that occurs at the grain boundaries. Additionally, each individual grain would have a different crystallographic orientation and therefore have different slip planes and directions. Assessing the effects of grain size on the nano-scratch hardness aids the investigation of the interaction between the Hall-Petch effect and the lateral size effect.

Nano-scratch experiments were performed on four polycrystalline samples of annealed, pure, oxygen free copper with average grain sizes, \( d \), of 1.15µm, 2.23µm, 17.36µm and 44.44µm. The average grain size was measured from EBSD orientation maps using the line intercept method, an example of which is given in Figure 6-1. Samples were mechanically polished and electrolytically polished prior to EBSD and nano-scratch experiments. The nano-scratch hardness measurements are shown in Figures 6-2 and 6-
3 for the face forward and edge forward tip orientation respectively. The full data set used to calculate the scratch hardness is provided in the appendix.

Figure 7-1- Electron Backscatter Diffraction (EBSD) inverse pole figure (IPF) colour map of a sample with 44.4µm average grain size.
Figure 7.2 - Nano-scratch hardness measurements for polycrystalline samples performed in the face forward tip orientation. Average of 5 repeat experiments are shown; error bars represent one standard deviation.

Figure 7.3 - Nano-scratch hardness measurements for polycrystalline samples performed in the edge forward tip orientation. Average of 5 repeat experiments are shown; error bars represent one standard deviation.
Figure 6-3 shows a defined increase in nano-scratch hardness with decreasing average grain size for scratches performed in the edge forward tip orientation. This trend is not as distinct for scratch-hardness of scratches performed in the face forward tip orientation, however the two samples with the smallest grain sizes clearly have a large scratch hardness value relative to the scratch hardness of the larger grained samples. This is in agreement with what is expected; the reduction in grain size increases the strength, and therefore the scratch-hardness of the material. Additionally in each sample there is lateral size effect observed whereby the scratch hardness increases with decreasing scratch size for both tip orientations.

7.2 Hall-Petch analysis in Nano-scratch hardness data

The Hall-Petch effect essentially predicts a linear relationship between the strength and $1/\sqrt{d}$, where $d$ is the average grain size. The nano-scratch hardness data for all samples, including the single crystal, are plotted against $1/\sqrt{d}$ in Figure 6-4 below. The scratch hardness values for the range of scratch sizes are averaged for simplicity and the error bars show the range of the size effect. There is a Hall-Petch-like linear relationship evident in the nano-scratch hardness measurements with respect to the inverse square root of the average grain size. In nano-indentation, using a spherical indenter, it has been observed that the Hall-Petch-like relationship only begins to 'take off' when the grain size is less than six times the indentation size. This means that when the indentation is small with respect to the grain size, there is little interaction of the grain boundaries with the indentation and as a result, by increasing the grain size further, there is no effect on the indentation hardness [50]. The dissimilarity of the nano-scratch test is that each scratch performed in these experiments was of 100µm in length, thus will always penetrate through some grain boundaries for all polycrystalline samples used. As a result there will always be a grain boundary-to-nano-scratch interaction and thus the Hall-Petch effect is observed for all samples. If the scratch length was reduced such that the nano-scratch was of a significant distance from the grain boundaries, it is likely that the
hardness response would be equivalent to that observed in the single crystal, i.e. there would be no effect of the grain boundaries.

The increase in scratch hardness for scratches performed in the edge forward tip orientation is smaller than the increase in hardness for the larger grained samples and the single crystal, i.e. the lateral size effect observed is to a larger degree in the single crystal and decreases with decreasing grain size. This correlates well with the proposal by Hou et al. that the length scale driving the indentation size effect is a combination of the inverse square root of the scratch size and the inverse square root of the grain size [50], which was used in the previous chapter to determine the dislocation density i.e. the length-scale controlling the size effect is of the form, \( \frac{1}{\sqrt{a}} + \frac{1}{\sqrt{d}} \). In Figure 6-4 above, for each grain sized sample, different scratch sizes are plotted. We have seen that for each

![Figure 7-4: Average nano-scratch hardness of all nano-scratch sizes in polycrystalline samples and the well annealed single crystal from the previous chapter, plotted vs. 1 / \( \sqrt{d} \). Error bars show the spread of data as a function of scratch size i.e. the lateral size effect within each sample.](image-url)
sample, the scratch hardness increases with decreasing scratch size. As grain size remains constant for each sample, when \( \frac{1}{\sqrt{a}} \) is small, the change in scratch hardness is dependent on \( \frac{1}{\sqrt{a}} \) and has a large range of scratch hardness values (a range 0.7GPa for the sample with an average grain size of 44.4µm). When \( \frac{1}{\sqrt{d}} \) is large, the contribution from \( \frac{1}{\sqrt{a}} \) is less significant and therefore the size effect observed in small grained materials is to a smaller degree (a range of 0.3GPa for the sample with an average grain size of 1.15µm). This effect was less distinct in Figure 6-4 for the face forward tip orientation however referring back to Figure 6-3 the largest grain sample has a range of 2GPa whereas the smallest grained sample has a range of 1GPa which confirms this effect is evident for both tip orientations.

7.3 INTERACTION OF GRAIN BOUNDARIES WITH THE SCRATCH TRACK

Figure 6-6 shows optical micrographs of scratches with a normal force of 5mN, performed in both tip orientations on the sample with the smallest average grain size and the largest average grain size. The corresponding penetration depth and lateral force plots, along the scratch distance, are presented to the right of each optical image.

For the large grain sample, the scratch track appears to be very smooth with variations in the penetration depth occurring as the grain boundaries are approached. From the optical images in Figure 6-6 c. and d. the contrast between the different grains allow the location of grain boundaries to be identified. Referring to the corresponding plots of penetration depth it is clear that for some crystallographic orientations, the indenter penetrates deeper than others. This correlates with what has been identified in the previous chapter, which some crystallographic orientations, with respect to the scratch direction, are easier to penetrate than others. This is particularly evident in the edge forward tip orientation and at a scratch distance of approximately 40µm. The schematic shown in Figure 6-5 demonstrates what is happening in this case; grain A has a
crystallographic orientation whereby the slip direction is approximately parallel to the scratch direction which is difficult for dislocation movement and as a result is it more difficult for the indenter to penetrate the material. As the grain boundary is approached this resistance increases and the indenter is pushed up, until the grain boundary is penetrated and the indenter is now scratching through grain B. The orientation of this crystal with respect to the scratch direction favours deformation and therefore the indenter penetrates deeper into the sample, than in grain A. This will additionally occur in the small grained material however, as the grains are smaller, the crystallographic orientation is regularly changing and as a result the indenter is not in any single grain for a long period of time, before it is pushed out again by the resistance from the next grain boundary. This gives the 'jagged' edge that is observed in optical images of scratches performed on the small grained material. The penetration depth channel averages out to appear a constant depth, without these large variations that we see in the penetration depth channel for the large grained material. Additionally, there is 'chatter' in the lateral force channel due to these fluctuations in the scratch resistance.

![Figure 7.5 - Schematic of a grain boundary separating two crystals with different crystallographic orientations.](image)

For the face forward tip orientation, in the small grained material, the 'jagged' edge is irregular, however in the edge forward tip orientation the scratch groove has uniform distribution with a continuous jagged edges. The lateral force channel for the face forward tip orientation additionally has large variances in addition to the 'chatter' caused
by the presence of grain boundaries. This could be explained by the large build-up of material ahead of the indenter which is pushed forward, increasing the lateral force, until the scratch force is large enough to penetrate through the material leaving debris towards the sides of the scratch track - hence these 'clumps' of material are observed at the edges of the scratch track for the face forward tip orientation (Figure 6-6.a). On the other hand, whilst the lateral force channel for the edge forward tip orientation exhibits the same 'chatter', it appears that the force is constant and continuous along the length of the scratch. In the edge forward case, the material is being 'cut' through, continuously and uniformly being pushed to the edges of the scratch track with regular variations due to the penetration through grain boundaries.

Figure 6-4 shows that the difference in hardness between the two tip orientations is larger for the small grained sample than the larger grained sample and single crystal. This suggests that, penetrating through grain boundaries is easier in an edge forward case than the face forward case, which again can be assumed to be a result of the 'cutting' action of the sharp pointed edge in the edge forward tip orientation. Therefore, in the small grained sample, the edge forward tip orientation is constantly cutting through the grain boundaries with ease, as opposed to the face forward tip orientation pushing an angled, facet against the grain boundaries, hence these differences are observed in the scratch hardness. However, when the grain size is large, the indenter is predominantly scratching through crystals of different orientations with infrequent grain boundaries to penetrate through. In this case it is still easier to scratch the sample with the edge forward tip orientation, as we know from scratching the single crystal which has no grain boundaries, however the difference in hardness is to less of a degree.

7.4 SUMMARY

This chapter highlights that nano-scratch experiments performed on polycrystalline samples of copper have an enhanced scratch hardness due to the presence of grain boundaries and the fact that the crystallographic orientation changes for each grain the
indenter is traversed through. The grain boundaries act as obstacles to dislocation motion, and therefore the increased frequency of grain boundaries creates a reduced distance between the obstructions to the dislocations, reducing the space in which they have to glide and increasing the scratch hardness. The scratch hardness increases with decreasing grain size, follows a Hall-Petch like relationship whereby the scratch hardness increases linearly with $\frac{1}{\sqrt{d}}$.

It can be concluded that the interaction between the indenter geometry, and therefore the mode of deformation, with the grain boundaries, significantly influences the scratch hardness, making it even harder to scratch with the face forward tip orientation when there are a considerable number of grain boundaries present.
7-6 - Left: Optical micrograph of a scratch with 5mN normal force, a and c face forward tip orientation, b and d edge forward tip orientation. a and b are performed on the sample with average grain size 1.15µm, c and d are performed on the sample with average grain size 44.4µm. Right: Corresponding Plot of the Penetration depth and the lateral force along the scratch distance.
8. IMPORTANT CONSIDERATIONS FOR NANO-SCRATCH TESTING

8.1 VERTICAL DRIFT

When performing nano-scratch experiments, vertical drift of the indenter, due to thermal expansion of the instrument or stage movements, should be taken into consideration. In a constant force scratch, on a flat sample, it is expected that the penetration depth channel would present a horizontal set of data that is seemingly ‘flat’ to the eye, ignoring the sample topography. Similarly, samples that have a tilt or uneven topography would also generate a ‘flat’ penetration depth channel, as this channel is providing data that has been corrected for, i.e. scratch displacement minus first-profile displacement at each data point along the scratch distance, \( x \). Therefore, in a constant force scratch, an apparent increase in the corrected penetration depth is unanticipated and can be considered an error. Some materials would be anticipated to exhibit viscoplasticity, however if this is not the case, it is likely that the increase in penetration depth is due to vertical thermal drift of the instrument.

Fused silica, a material that is not expected to exhibit viscoelasticity was used for the following experiments to study the impact of vertical drift on the penetration depth. Figure 7-1 shows the corrected penetration depth channels of nano-scratches performed using different scratch velocities. Three scratch velocities were used; 5\( \mu \)m s\(^{-1} \), 0.5\( \mu \)m s\(^{-1} \) and 0.05\( \mu \)m s\(^{-1} \). The scratches performed were three-pass, ramped force scratches from 0mN to 10mN with a constant profiling force of 0.1mN and total scratch length of 12\( \mu \)m (10\( \mu \)m scratch length and 1\( \mu \)m either side for over-scan segments). The profiling velocity was set at the default value of 10\( \mu \)ms\(^{-1} \) and the indenter was positioned in the face forward orientation.

In Figure 7-1, there is an evident increase in the penetration depth during the scratching segment. This is expected as the normal force applied was increasing with increasing
scratch distance. However, the over-scan segments at the beginning of the scratch and end of the scratch, where the applied normal force was constant, there is also a gradient in the penetration depth; particularly in the scratch with the slowest speed. The penetration depth in these segments were corrected for by the software which subtracts the displacement of the first-profile from the displacement of the pre-scan, for this segment of the scratch distance, however as the profiling velocity was set to the default value of 10µms⁻¹, it would not have experienced the same amount of vertical drift, hence the correction is insufficient to account for vertical drift. For the slowest scratch speed, i.e. 0.05µms⁻¹, there is a vertical drift rate of 0.5nms⁻¹. The drift rate criterion set for these scratches was the default value of 5nms⁻¹, which is evidently too high when scratching at low velocities. As a result, not only is there an increase in depth during the constant force, over-scan segments, there is also an additional, false increase in the displacement during the scratch segment, labelled 3 in the schematic at the top of Figure 7-1. This would usually be assumed to be the displacement of the indenter into the sample under the applied, normal ramped force.

![Figure 8-1: Corrected penetration depth channel for scratches of varying velocities. Above the Figure the scan segments indicate 1. the First profile 2. the pre-over-scan segment 3. scratch segment 4. Post-over-scan segment 5. Final profile.](image-url)
By setting the profiling speed equal to the scratching speed, for the three-pass scratch method, all segments would encounter the same drift. The three-pass scratch method is useful as the software subtracts the displacement of the first profile (1 in Figure 7-1) from the scratch displacement (segments 2, 3 and 4 in Figure 7-1), which is sufficient to correct for the topography of the surface and provides a measure of the scratch displacement from the original surface. However, as a function of time there are various factors that affect the vertical drift of the system. This is not corrected for by the topography correction. Figure 7-2 is a simplified schematic of a constant load scratch experiment as a function of time. It is assumed that the gradient identified in the first-profile scan is not due to the topography but is due to the vertical drift alone and that the scratch segment undergoes the same drift as the first profile scan, therefore has the same gradient. To simplify things, the over scan segments and the re-trace segments have been omitted. At the end of the first profile segment, the displacement due to drift changes the starting displacement of the scratch segment. Thus, the indenter is starting the scratch segment from the displacement at point A, but the measured scratch record is actually starting from the displacement at point B, due to vertical drift. Therefore, when the software subtracts point A from point C to give the penetration into the surface, what it is essentially measuring is the penetration displacement plus the additional displacement, due to thermal drift.

To correct this problem, a hold segment is recommended before the first-profile scan and preferably before the scratch segment. This hold segment estimates the drift rate before each of the scratch segments. Using this measurement of drift, a correction can be applied to correct the thermal drift during measurement of each segment. This process is performed prior to further analysis. A stationary hold segment is required to measure drift since when the indenter is moving, the system cannot distinguish between displacement owing to drift and displacement owing to topography.
Figure 8-2- Schematic of the displacement with respect to time. Assumes each segment has a flat topography, the first profile and the final profile are the same constant load and the scratch is a constant load scratch. The velocity of each segment is the same. This is a simplified schematic; which hasn’t included the over-scan segments and the retracing of the stylus back to the start position, after each segment has occurred.

The above is a simplified scenario. In reality the over scan time plus the retrace time generates additional errors in displacement which are presented in the schematic in Figure 7-3. A fast profiling rate with a slow scratch speed is not a sufficient solution; in the slow scratch experiments presented above, the first-profile velocity is \(10 \mu m/s\) and the scratch speeds are significantly slower. This causes both a false slope in the scratch topography, as well as an apparent offset in the scratch depth unless drift is initially corrected for. When the scratch velocity and the profiling velocity are equal but slow, then additional offsets in scratch depths will occur due to drift during the slow profiling, over scan and retrace segments. In the case of using a faster scratch velocity with an equally fast profiling speed, the absolute drift error will be reduced, but this strategy may not be possible if the material being tested is strain-rate sensitive. Waiting longer, for a better thermal equilibrium, would help reduce the total drift; and operating in a stable environment would additionally help if it is affordable and available.
Figure 8-3 - Schematic of the displacement with respect to time. Assumes each segment has a flat topography, the first profile and the final profile are the same constant load and the scratch is a constant load scratch. The velocity of each segment is the same.

8.2 TIP ALIGNMENT AND GEOMETRY

The tip alignment and geometry is a crucial consideration that must be accounted for in nano-scratch testing when using a Berkovich indenter. Figure 7-4 shows an ideal schematic of the alignment of the Berkovich tip in the edge forward and face forward tip orientations, in 7-4a. and c. respectively. Figures 7-4b. and c. shows misaligned tip orientations.
Figure 8-4: Schematic of nano-scratches performed in the edge forward and face forward orientations when well aligned (a. and c.) and when slightly misaligned (b. and d.).

It has already been observed that scratching in the face forward tip orientation is different to scratching in the edge forward orientation as each case exhibits a different stress distribution ahead of the indenter. When the tip is not well aligned, scratches assumed to be performed in the face forward and edge forward tip orientations will generate different stress distributions ahead of the indenter, to what is expected.

Figure 7-5 shows the penetration depth channels of two nano-scratches performed on a sample of polycrystalline copper with a constant, normal force of 0.5mN. One scratch was had a face forward tip orientation and the other was oriented 30º off the face forward tip orientation; tip orientation is presented schematically to the left of Figure 7-5 with an AFM z-detector image showing the indenter orientation with respect to the scratch track. There is clearly a difference in the penetration curves for the two tip orientations. For the face forward tip orientation there is a typical scratch penetration curve similar to what has already been identified earlier in this thesis. There is a distinct increase in penetration depth with increasing scratch distance which was typical for all five repeat experiments of this type. The stress distribution ahead of the indenter in this case is evidently different to both the face forward and the edge forward tip orientation. In this
situation, there will be a high stress concentration at the edge of the indenter leading the scratch. As the scratch is formed, material will be cut through by the leading edge and then flow down the facet which would also push material along, similar to the face forward tip orientation. There appears to be no steady state region for this scratch as it becomes easier to scratch as the scratch distance progresses. The morphology of the pile-up is different on either side of the scratch track, which itself is uneven in comparison to the case in which the tip is well aligned.

Furthermore, tip geometry should be considered for nano-scratch testing. Many instrumented indentation systems rely on indirect methods to calibrate the indenter from which an area function is generated; this does not contain any shape information regarding the indenter and therefore is inadequate for nano-scratch testing with a Berkovich tip. Figure 7-6 is an AFM image of a distorted Berkovich tip that had undergone indirect calibration on the instrument. Nano-scratches performed with this, non-symmetrical Berkovich indenter would generate different scratch forces to that of a

Figure 8-5- Corrected penetration curves of two 0.5mN constant force nano-scratches in polycrystalline copper. The tip orientation differs in each case. The blue trace has a well aligned face forward tip orientation and the red has a misaligned tip orientation, shown to the left of the picture.
symmetrical indenter. The influence on force would leave a non-symmetrical scratch track. Only by scanning the indenter directly using AFM has the distortion of the tip been identified. This emphasized the importance of directly measuring the tip geometry before performing nano-scratch experiments.

Figure 8-6- AFM image of a non-symmetrical Berkovich indenter.

It is unmistakably important that the tip is well aligned and symmetrical for nano-scratch testing as the experiment is orientation dependent. When using a system that is not well aligned, the assumed face forward and edge forward tip orientations would produce results that are unsatisfactory to be comparable with scratch results of materials performed in a well aligned system. Repeatability of the experiments will be problematic and scratch hardness measurements calculated using the methods presented in this thesis will contain significant errors. Thus it is crucial that the tip alignment and geometry are known prior to nano-scratch experiments. The Agilent G200 has a required input of the angle of which the scratch should performed. If the misalignment of the tip is known with respect to the shaft of the indenter, the angle of scratching can be altered to ensure that the scratch is being performed with a correct tip orientation, however this is not ideal as the main drive screws are in the x and y directions, therefore by scratching at an angle, the motors will drive the shaft in a zig-zag motion as opposed to a smooth scratch.
8.3 Lateral Compliance

High lateral stiffness is crucial for nano-scratch testing. As the indenter is traversed across the sample during the scratch process a high lateral stiffness is desirable for a smooth, uniform scratch track. If the stiffness is not adequate, the scratch track will be wavy and un-even. Referring back to the optical micrographs in Figure 6-6, specifically Figure 6-6.d, there is a distinct change in the direction of the scratch track as the indenter approaches a grain boundary at approximately 40μm and 60μm; it is possible to identify the grain boundary from the contrast changes of each grain. This is clearly a compliance issue as the lateral force increases the indenter moves to a direction that is easier to penetrate through. With a high lateral stiffness this would not be possible.

In addition to this, a low lateral stiffness will produce a false reduction in the vertical displacement of the indenter. This is shown schematically in Figure 56; if the stiffness of the shaft is low, the shaft will rotate due to the high lateral force exerted on the shaft from the material during the scratch process. As the shaft rotates under this lateral force, the central plate in the capacitance gauge will appear to have moved up by an amount, C. As a result, this would appear as a false reduction in the indenter displacement, and therefore the scratch penetration depth. It was observed in an earlier chapter, that at the early stages in the scratch, the penetration depth increases initially when the normal force is transferred from three facets of support to either one or two facets, depending on the tip orientation. The increase in penetration depth was measured and was expected to increase by a factor of $\sqrt{3}$ for the face forward tip orientation and a factor of $\sqrt{3/2}$ for the edge forward tip orientation. This was the case for large scratches, however for smaller scratches the increase in depth was less than expected; an explanation could be due to the rotation of the shaft in the early scratch stages, causing a false decrease in penetration depth. A high lateral compliance which provides the optimum frictional sensitivity is necessary for a suitable nano-scratch instrument.
Figure 8-7-Nano-indenter shaft assembly experiencing shaft rotation due to low lateral stiffness and high lateral forces.
9. General Discussion

The work conducted in Chapter four introduces three methods of calculating the nano-scratch hardness, using a Berkovich indenter positioned in the face forward and edge forward tip orientation. All three methods were variations of the basic hardness calculation of $H = P/A$ and each method was evaluated on a sample data set. It was decided that the third method was the most theoretically suitable method to use as it combined the normal force and the lateral force to generate a scratching force which was acting on the facets of the indenter during the scratching process. This method was adopted throughout, for all calculations of nano-scratch hardness. Additionally, this chapter investigated various measurement methods; direct measurements were obtained using AFM, of which direct measurements of depth were compared with displacement measurements obtained from the nano-indenter. It was concluded that averaging the corrected penetration depth channel from the nano-indenter, in the steady-state region of the scratch was a suitable measurement of scratch depth which could then be inputted into the indenter area function to determine the surface area in contact, at that depth. The steady-state region referred to is the penetration depth when the scratch has reached an equilibrium state, in which the penetration depth remains relatively constant along the scratch track, until the indenter stops and the normal force is removed. In the literature there have been numerous cases whereby the displacement data along the entire scratch track has been averaged in order to obtain an average scratch depth. This is insufficient and it is important that it is only the steady-state region of the displacement channel that is averaged, due to these large variations in the penetration depth at the early stages in the scratch.

The preliminary experiments performed on polycrystalline copper in chapter four indicated that a lateral size effect does exist in nano-scratch hardness measurements, for both tip orientations, whereby the nano-scratch hardness increases with decreasing normal force applied; normal force is directly related to a decrease in scratch size in both the scratch width, penetration depth and the height of the pile-up around the scratch.
groove. Plasticity size effects require an understanding of the underlying mechanism controlling the increase in hardness in order to develop validated models that can predict and quantify the enhancement in hardness. The nano-scratch hardness can be used as an alternative material parameter to the indentation hardness, which can quantify the resistance of a material to deformation under a sliding contact, however this is only possible when the size effects are fully understood and accounted for. Initially, size effects were thought to be a result of the tip rounding at the indenter apex in indentation testing, but this was accounted for later on. In the case of scratch hardness, either one facet was used as the contact area, in the face forward case, and two facets were used in the edge forward case however as the penetration depth becomes increasingly small, the indenter may have a spherical geometry at the apex of the indenter. In this case, the tip orientation would not change the contact area, and both orientations would be in contact with half of the spherical tip, as used for calculating the microscopic scratch hardness using conical or spherical indenters. This method was adopted for scratches with small penetration depths, however there was negligible difference in the hardness results when the contact area was changed.

The lateral size effect was further investigated on single crystal copper in three different work-hardened states. The variation of dislocation density in each work-hardened state was expected to alter the slip-distance available for dislocation movement within the sample, i.e. introducing an intrinsic material length-scale that would influence the hardness response of the material. The amount of work-hardening in the sample influenced the nano-scratch hardness for the edge forward tip orientation as expected by which the scratch hardness increased with increased amount of work hardening in the sample. On the other hand, the hardness of the scratches performed in the face forward tip orientation did not show a distinct increase in the hardness; the single crystal with the largest amount of work-hardening was largest for both tip orientations for small scratches, however for large scratches, in the face forward tip orientation the single crystal with the intermediate amount of work-hardening appeared harder. An explanation for this was that as material is pushed forward ahead of the indenter, dislocations are interacting with each other, gliding and generating more dislocations. As
dislocation nucleation is more favourable in a situation where there are already dislocation sources, i.e. the sample that had been exposed to one hour of heat treatment, dislocations with cause the material to work harden as the indenter moves through the material.

In chapter six an intrinsic structural length scale was introduced by performing nano-scratch experiments on annealed copper samples with different grain sizes, \( d \). The existence of grain boundaries is expected to act as an obstacle to dislocation movement, thus in a small grained material, the frequency of grain boundaries increases and the distance between each boundary would decrease resulting in a reduced slip-distance for dislocations. The results in this chapter confirm this as the scratch hardness when \( d \) is small are larger than the scratch hardness when \( d \) is large. The data presented in chapter six agrees with the Hall-Petch theory, whereby the scratch hardness increases linearly with \( \frac{1}{\sqrt{d}} \).

It is assumed that a material would exhibit the same resistance to deformation independent of the direction in which the force is applied, however in all cases, the hardness of scratches performed in the face forward tip orientation was larger than the hardness of scratches performed in the edge forward tip orientation, despite the fact that differences in geometry were accounted for in the force calculation. Additionally, the measured scratch hardness was always larger than the indentation hardness suggesting that the material had a higher resistance to deformation when the indenter is traversed laterally, as opposed to a static indentation. This is not unexpected as in the sliding contact, the lateral force has to overcome the resistance to plastic flow and the resistance to friction.

The force used for the scratch hardness calculation in method three combined a component of the normal force, acting perpendicular to the indenter facets, and a component of the lateral force acting perpendicular to the facets to represent the total force acting perpendicular to the facets. In reality there is an additional frictional force acting parallel to the indenter facets; this was not incorporated into the scratch hardness
calculation to reduce the complexity of the method. It was shown by Bowden and Tabor that the macroscopic origin of the friction is due to two processes; the adhesion of the solids which has a physical origin, and the deformation of the solids in contact which have a mechanical origin [120]. The coefficient of friction has been split into two terms to represent each process given by Equation 8-1.

\[ \mu = \mu_{adh} + \mu_{plough} \]

Equation 8-1

This has previously been applied to nano-scratch tests to determine the mechanical deformation dependent, coefficient of friction, independent of the adhesion friction [104]. In the calculation method for the scratch hardness, the component of the lateral force acting perpendicular to the indenter facets corresponds to the ploughing component of the friction force. The frictional force, parallel to the indenter facets, that was omitted from the analysis, could correspond to the adhesive friction. There is evidently a different deformation mechanism occurring in the two tip orientations which can explain the differences observed in the scratch hardness response of the two tip orientations. Furthermore, the plastic flow of material ahead of the indenter is different in each case. This is illustrated in Figure 8-1 below.

![Flow of material ahead of the indenter for each tip orientation.](image-url)
The plastic flow of material ahead of the indenter is dependent on the amount of viscous drag that each tip orientation would encounter. In fluid dynamics, the drag coefficient is a dimensionless quantity that quantifies the resistance of an object moving through a fluid environment. When scratching copper, the material plastically flows, and therefore can be considered as a viscous fluid. From fundamental fluid mechanics, the drag coefficient of an equilateral triangular rod moving at low speed in the edge forward orientation is 1.5 and in the face forward orientation is 2 [121]. This is not directly applicable to the case of a Berkovich indenter, however it does suggest that the coefficient of drag would be dependent on the tip orientation due to differences in viscous flow. Thus, an indenter in the edge forward tip orientation encounters a lower drag coefficient when moving through a viscous fluid than the face forward tip orientation and flow of the material ahead of the indenter would be easier in the edge forward orientation than in the face forward case, hence sliding contact in this tip orientation is much easier. This suggests that knowledge of the drag coefficient could possibly be an additional requirement for the calculation of the scratch hardness in each tip orientation, in order to generate scratch hardness measurements that are independent of tip orientation.

Figures 8-2 and 8-3 show examples of scratches performed with a 30mN normal force and 100µm scratch length, in both tip orientations on polycrystalline copper samples with average grain sizes of 44.4µm and 1.15µm respectively. The full data set obtained from these experiments was used in Chapter six however the examples selected are used to discuss the interaction of the indenter with the grain boundaries during the nano-scratch process. It was discussed in Chapter six that the larger grain sample produces scratches with a wavy scratch track in comparison to the uniform scratches produced in samples with a small grain size. This is again observed in Figures 8-2 and 8-3 and it is clear that the larger grain sample, shown in Figure 8-2 has very large variations in the scratch width as the indenter passes through grain boundaries into grains with different orientations.
In both samples, there is a large build-up of material at the end of the scratches performed in the face forward tip orientation which can be explained by the fact that material is being pushed ahead of the indenter in this case with only a small amount being pushed towards the side, creating pile-up. This is also apparent in the corresponding penetration depth channels as there is a large peak in the channel at the end of the scratch track. For the edge forward case, in both samples, the scratches have a wider scratch track as material is moving toward the sides of the indenter as it traverses through the material.

In chapter six it was identified that the difference in scratch hardness between the two tip orientations was larger in the small grained sample than in the large grained sample and single crystal. In the edge forward case, not only is it easier for material to flow ahead of the indenter, the leading sharp edge of the indenter presents the highest geometrical grain to the material and can cut through the grain boundaries with greater ease. On the other hand in the face forward orientation, material builds up ahead of the indenter, and it is this blunt volume of material that has to push through the grain boundaries; this is clearly more difficult hence the lateral resistance in this case increases. When the average grain size is large, the frequency of grain boundaries is minimal and therefore this interaction of the deformation mechanism with the grain boundaries does not have a significant effect and the flow of material ahead of the indenter dominates. On the contrary when the average grain size is small, and the density of grain boundaries is high, the edge forward tip orientation can cut through numerous grain boundaries, making this tip geometry significantly easier than the face forward tip geometry, that has to plough through a high density of ‘mesh’ of grain boundaries.

The lateral force channel along the scratch distance demonstrates this for the examples presented in Figures 8-2 and 8-3. In the large grained sample, there are very few grain boundaries and as the indenter approaches the grain boundaries, the lateral force increases until the grain boundary is penetrated. In the edge forward case, the lateral force channel is relatively smooth, with gradual increases and decreases as the grain boundaries are approached, indicating an effortless penetration through the very few grain
boundaries. On the contrary, the in the face forward case there are larger increases in the lateral force channel as the indenter penetrates through the grain boundaries.

In the small grained sample, this is happening more regularly and it is observed as a large lateral force, with frequent variations for the face forward case. In the edge forward case the lateral force of appears to be constant throughout the whole scratch distance, indicating that the frequent grain boundaries are being easily penetrated.

In the face forward case, the scratches are uneven and there appears to be chips in the scratch track, particularly for the large grained sample (See Figure 8-2.a). This occurs because the material is being pushed ahead of the indenter until at some point, the force exerted by the indenter is large enough to penetrate through the build-up of material and pushes it to the sides. In Figure 8-2.c the scratch track appears to become narrower as the scratch approaches approximately 40µm, after which the scratch track begins to widen again. From the optical micrograph, the scratch begins to narrow at the early stages in the scratch, as it approaches a grain boundary, the scratch remains narrow within the next grain, until it penetrates into the third grain and begins to widen.

The changes in morphology for the edge forward tip orientation show similar variations in the width when passing through different grains however within each grain, the scratch track remains relatively uniform. These large variation are not observed in the small grain sample shown in Figure 8-3. Clearly, the moving contact influences the mode of deformation and as a result the scratch hardness is influenced; the static, indentation hardness cannot be directly compared to the nano-scratch hardness test.

It has been discussed that the method used for calculating scratch hardness does not consider all of the factors influencing the scratch deformation, thus the absolute values obtained for the scratch hardness are different for each tip orientation. However there is a lateral size effect occurring in the scratch hardness data presented for both tip orientations, showing that the scratch hardness increases with decreasing size, the mechanisms of which cannot be modelled using the same methods as the indentation size effect due to the complexity of the moving contact. The lateral size effect needs to
be accounted for before using the nano-scratch hardness as a quantitative characterisation method of materials and a number of concerns have been highlighted in Chapter seven that should be adopted when using the nano-scratch test, in order to improve the authenticity of the results.

The wear of the indenter was briefly touched on throughout this thesis as a new tip was purchased and an AFM scan of the tip was conducted prior to any experiments with the tip. After a number of nano-scratches had been performed using the indenter in the copper samples, the tip was re-scanned. There was negligible difference in the shape of the indenter after these experiments, however if the samples that had been used were harder than copper, this is unlikely to be the case. All nano-scratch experiments on different materials were performed with a different indenter to ensure minimal damage was caused to the indenter used for these experiments.
Figure 9-2 - Left: Optical micrographs of scratches with 30mN normal force, performed in both tip orientation on the sample with average grain size 44.4µm. Right: Corresponding Plot of the Penetration depth (BLUE) and the lateral force (RED) along the scratch distance.
Figure 9-3 - Left: Optical micrographs of scratches with 30mN normal force, performed in both tip orientation on the sample with average grain size 1.15µm. Right: Corresponding Plot of the penetration depth (BLUE) and the lateral force (RED) along the scratch distance.
10. CONCLUSIONS AND FUTURE WORK

The method established for calculating the nano-scratch hardness when using a Berkovich indenter provides a theoretically acceptable method of determining the scratch hardness of materials with a Berkovich indenter. The results show that a lateral size effect does exist in the scratch hardness of a single crystal of copper. The lateral size effect shows an increase in scratch hardness with decreasing scratch size, which would need to be accounted for if the test was to be used as a quantitative material characterisation method.

The method does not generate a measure of scratch hardness independent of tip orientation and therefore when using this method, both the face forward and the edge forward tip orientation should be measured, as they give convoluted scratch hardness responses which involve various deformation mechanisms. In order to determine an orientation-independent measure of scratch hardness, it would be useful to consider the viscous drag coefficient that each tip orientation encounters as the plastic flow of the material ahead of the indenter if different for each orientation.

Scratch hardness of a single crystal sample of copper is orientation dependent as when the scratch direction is parallel to the slip direction, slip is more difficult than the case when the scratch direction is at 45° to the slip direction where slip is favoured. When scratching polycrystalline copper, the crystallographic orientation with respect to the scratch direction will change for each grain the indenter traverses through. If the material has small grains that are inhomogeneous, this will average out over the scratch distance however if the grains are large, the morphology of the scratch track appears distorted as it passes through grains with different orientations.

By introducing intrinsic length scales such as the spacing between grain boundaries and the spacing between sessile dislocations and pinning defects, the lateral size effect is affected. The smaller the spacing between these obstacles, the less slip distance the dislocations have to glide and therefore the scratch hardness increases. This is similar to
what has already been investigated for the indentation size effect however the mechanistic models that are able to predict the indentation size effect are not suitable to predict the lateral size effect.

A number of important considerations have been mentioned that are essential to ensure the nano-scratch results are valid. Solutions to these issues would provide the basis for a good practise guide, for scientists wishing to utilise the nano-scratch test for research purposes and evaluate the scratch hardness of materials.

Finally, the work presented through this thesis has highlighted that the nano-scratch test is a simple experiment that can provide a plethora of information to tribologists and material scientists. In order to utilise the nano-scratch hardness as a quantitative method for the characterisation of materials, further work is required initially to determine an orientation independent measurement of scratch hardness and finally to develop a mechanistic model that can predict and correct for the lateral size effect that exists in the results.
APPENDIX

1. SINGLE CRYSTAL, AS RECEIVED (0 HOURS)

Average penetration depth measured by the displacement of the indenter and corrected for by subtracting the displacement of the first profile, for scratches with normal forces ranging from 0.5mN - 40mN. Scratches are performed in the face forward and edge forward tip orientation.

Right: Average lateral force measured in the steady state region. Left: Average coefficient of friction along the scratch $\mu = F_L/F_N$. 
2. SINGLE CRYSTAL ANNEALED (1 HOUR)

Average penetration depth measured by the displacement of the indenter and corrected for by subtracting the displacement of the first profile, for scratches with normal forces ranging from 0.5mN - 40mN. Scratches are performed in the face forward and edge forward tip orientation.

Right: Average lateral force measured in the steady state region. Left: Average coefficient of friction along the scratch $\mu = F_L/F_N$.
3. SINGLE CRYSTAL ANNEALED (4 HOURS)

Average penetration depth measured by the displacement of the indenter and corrected for by subtracting the displacement of the first profile, for scratches with normal forces ranging from 0.5mN - 40mN. Scratches are performed in the face forward and edge forward tip orientation.

Right: Average lateral force measured in the steady state region. Left: Average coefficient of friction along the scratch $\mu = \frac{F_l}{F_N}$.
4. Polycrystalline Copper, Grain Size 1.15 μm

Average penetration depth measured by the displacement of the indenter and corrected for by subtracting the displacement of the first profile, for scratches with normal forces ranging from 0.5 mN - 40 mN. Scratches are performed in the face forward and edge forward tip orientation.

Right: Average lateral force measured in the steady state region. Left: Average coefficient of friction along the scratch $\mu = F_L/F_N$. 

[Graphs showing data distribution]
5. POLYCRYSTALLINE COPPER, GRAIN SIZE 2.2μM

Average penetration depth measured by the displacement of the indenter and corrected for by subtracting the displacement of the first profile, for scratches with normal forces ranging from 0.5mN - 40mN. Scratches are performed in the face forward and edge forward tip orientation.

Right: Average lateral force measured in the steady state region. Left: Average coefficient of friction along the scratch $\mu = F_l / F_N$.
6. POLYCRYSTALLINE COPPER, GRAIN SIZE 17.36\(\mu\)M

Average penetration depth measured by the displacement of the indenter and corrected for by subtracting the displacement of the first profile, for scratches with normal forces ranging from 0.5mN - 40mN. Scratches are performed in the face forward and edge forward tip orientation.

Right: Average lateral force measured in the steady state region. Left: Average coefficient of friction along the scratch \(\mu = F_L/F_N\).
7. Polycrystalline Copper, Grain Size 44.4 µM

Average penetration depth measured by the displacement of the indenter and corrected for by subtracting the displacement of the first profile, for scratches with normal forces ranging from 0.5 mN to 40 mN. Scratches are performed in the face forward and edge forward tip orientation.

Right: Average lateral force measured in the steady state region. Left: Average coefficient of friction along the scratch $\mu = F_L / F_N$. 
11. **REFERENCES**


