Deformation Behaviour of NiCo Multilayers with Modulated Microstructures

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
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Abstract
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Metallic multilayers, which possess a material architecture of modulated coarse-grained and nanocrystalline features stacked in a laminate configuration, represent an ideal structure to study the influence of abrupt heterogeneities on deformation behaviour. While the deformation mechanisms of homogeneous coarse-grained and nanocrystalline materials are well documented, it is not clear from the current literature how these mechanisms may interact in a heterogeneous structure, and how these interactions manifest in the measured mechanical properties. The objective of this thesis is to characterize the dominant deformation mechanisms in NiCo multilayers with modulated microstructures. More specifically, a targeted study is performed to understand the influence of interfacial plastic interactions between multilayer features on the overall deformation behaviour. For this purpose, a wide range of multilayer architectures, which possess varying fractions of coarse-grained-nanocrystalline interfaces, are manufactured. The mechanical properties of these multilayers are measured using uniaxial tensile testing and nanoindentation, and the as-deposited structures are characterized through a combination of electron microscopy and crystallographic analysis. Interestingly, the flow stress of the multilayers is observed to significantly exceed rule of mixtures expectations as the fraction of structural interfaces is increased. These results indicate a strong contribution of interfacial effects to the overall deformation behaviour. Inspired by these findings, targeted molecular dynamics simulations are performed on representative architectures to investigate interfacial deformation mechanisms. Based on molecular dynamics simulations, a novel deformation mechanism, whereby strain relaxation is achieved in nanocrystalline fea-
tures through emission of deformation twins into the coarse-grained microstructure, is elucidated. Consequently, the coarse-grained microstructure undergoes dynamic grain size refinement, leading to an increase in the intragranular boundary density. This deformation behaviour effectively reduces the dislocation mean free path of coarse-grained features, subsequently enabling additional strengthening. Based on the observed deformation mechanisms, a generalized phenomenological model is developed to predict multilayer work hardening, delivering significant improvements to rule of mixtures estimates. The emergence of deformation twinning in coarse-grained features is a unique consequence of microstructure modulation. This result offers a pathway to engineer deformation mechanisms and tailor mechanical performance through heterogeneous architectural design.
To Crystal and family
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List of Symbols and Acronyms

$\gamma$  The surface energy of a faulted area (mJ/m$^2$)

$\gamma_g$  The cumulative crystallographic shear strain due to slip (mm/mm)

$\gamma_{isf}$  The intrinsic stacking fault energy (mJ/m$^2$)

$\gamma_t$  The shear strain accommodated by deformation twinning (mm/mm)

$\gamma_{usf}$  The unstable stacking fault energy (mJ/m$^2$)

$\gamma_{utf}$  The unstable twinning fault energy (mJ/m$^2$)

$\varepsilon_f$  The elongation to failure (mm/mm)

$\varepsilon_{nu}$  The non-uniform elongation of a tensile coupon (mm/mm)

$\varepsilon_p$  The plastic strain in true terms (mm/mm)

$\varepsilon_t$  True strain (mm/mm)

$\varepsilon_u$  The uniform elongation of a tensile coupon (mm/mm)

$\bar{\Lambda}$  Average twin spacing (nm)

$\bar{\Lambda}_d$  Dislocation mean free path (nm)

$\bar{\lambda}$  Average twin thickness (nm)

$\lambda_b$  The width of a slip band (nm)

$\rho$  The stored dislocation density ($m^2$)

$\sigma_t$  True stress (MPa, GPa)

$\sigma_{YS}$  The yield strength (MPa, GPa)
\( \sigma_{\text{UTS}} \)  The ultimate tensile strength (MPa, GPa)

\( \tau \)  The applied shear stress (MPa, GPa)

\( A \)  The contact area in an instrumented indentation experiment (\( \mu \text{m}^2 \))

\( a_0 \)  The lattice parameter (nm)

\( b \)  The Burgers vector (nm)

\( C \)  The contact compliance in an instrumented indentation experiment (nm/\( \mu \text{N} \))

\( d \)  The grain size (nm, \( \mu \text{m} \))

\( d_{111} \)  The interplanar spacing of \{111\}-type slip planes (nm)

\( E \)  Elastic modulus (GPa)

\( E_r \)  The reduced modulus of contact in an instrumented indentation experiment (GPa)

\( F \)  The twin fraction

\( G \)  Shear modulus (GPa)

\( h \)  The instantaneous depth of the indenter tip in an instrumented indentation experiment (nm)

\( h_c \)  The indenter depth of contact at maximum load in an instrumented indentation experiment (nm)

\( h_p \)  Residual depth of indentation (nm)

\( L_o \)  The initial length of a tensile coupon. Also serves as one of the laboratory reference axes (nm).

\( M \)  The Taylor factor

\( N_T \)  The number of twins in a grain

\( n^i \)  The number of perfect dislocations in a slip band along slip system \( i \)

\( n_{TB} \)  The twin boundary density (nm\(^{-1} \))

\( P \)  The instantaneous load in an instrumented indentation experiment (\( \mu \text{N} \))

\( R_a \)  Reduction in area ratio
$S$ The contact stiffness in an instrumented indentation experiment ($\mu$N/nm)

t The thickness of a layer in a ML (nm, $\mu$m)

$t_\eta$ Thickness ratio, defined as the fraction of $t_{NC}$ to the ML unit cell thickness, $t_{NC} + t_{CG}$

$t_o$ The initial thickness of a tensile coupon. Also serves as one of the laboratory reference axes (mm).

$W_o$ The initial width of a tensile coupon. Also serves as one of the laboratory reference axes (mm).

AFM Atomic force microscopy

ARB Accumulative roll bonding

BF Bright field

BSE Backscatter electron

CG Coarse-grained

CNA Common neighbour analysis

CS Centrosymmetry

DF Dark field

DFT Density functional theory

DIC Digital image correlation

EAM Embedded atom method

EBSD Electron backscatter diffraction

EDX Energy dispersive X-ray spectroscopy

FCC Face-centered cubic, as in a crystal unit cell

FIB Focussed ion beam

GBE Grain boundary engineering

GBS Grain boundary sliding
GPFE Generalized planar fault energy
HCP Hexagonal close-packed
HP Hall-Petch
HV Vickers hardness number
KM Kocks-Mecking
LAMMPS Large-scale Atomic/Molecular Massively Parallel Simulator
MD Molecular dynamics
ML Multilayer
NC Nanocrystalline
OVITO Open Visualization Tool
PED Pulsed electrodeposition
ROM Rule of mixtures
SE Secondary electron
SEM Scanning electron microscopy
TEM Transmission electron microscopy
TWIP Twinning induced plasticity
UFG Ultrafine-grain
XRD X-ray diffraction
esf extrinsic stacking fault
isf Intrinsic stacking fault
kMC Kinetic Monte Carlo
tf Twin fault
Chapter 1

Introduction

The performance of metallic materials is dictated by the competition of deformation mechanisms, whose interplay manifests as the host of mechanical properties measured in laboratory experiments. From the perspective of materials engineering, a deformation mechanism describes the rules and morphology by which a structure evolves in response to applied loadings. An understanding of deformation mechanisms therefore presents a pathway for the design and engineering of effective material structures. In a general materials sense, the capacity for deformation is typically determined by ductility, which may be considered as a macroscopic observation of material plasticity. As a descriptor of deformation, plasticity may be broadly defined, and does not connote a specific deformation mechanisms. More accurately, plasticity then describes the convolution of deformation mechanisms which contribute to material deformation. A systematic categorization and rigorous characterization of deformation mechanisms therefore leads to a decoupling of plasticity, a complete understanding of deformation processes, and permits engineering of mechanical behaviour.

The process of understanding deformation mechanisms may be most logically initiated from consideration of elementary deformation processes. Within the context of face-centered cubic (FCC) metals, dislocations are the elementary carriers of material plasticity, representing a quantum of material deformation. Dislocations serve as a means of dissipating stored internal energy, permitting for a transition from homogeneous elasticity, towards localized plastic deformation. In this manner, the aggregate glide behaviour of dislocations on the atomic-scale dictates the flow of material on the macro-scale. An excellent overview of dislocation basics is available from Hull and Bacon [1]. Additionally, Hirth and Lothe [2] provide a more comprehensive text which covers an in-depth mathematical treatment of dislocations. Generally, the mechanical behaviour of a metal is largely determined by the multiplication and interaction of dislocations.
and these interactions have a strong length-scale aspect associated with their ultimate manifestation in mechanical properties. For example, the Hall-Petch (HP) effect [3] is a well known hardening mechanism with a strong length-scale dependence, whereby a metal’s yield strength may be greatly increased through the refinement of microstructure and subsequent reduction in grain size. Under HP hardening, grain refinement leads to a reduced dislocation pile-up at grain boundaries and lower interfacial back-stresses, which effectively hinders the onset of large-scale plastic flow. However, as grain sizes approach the amorphous limit, traditional dislocation pile-up accommodated plasticity is superseded by competing grain boundary-mediated deformation mechanisms, which leads to material softening and creates the so-called inverse HP effect [4]. The length-scale dependency of active deformation mechanisms may be captured schematically through a deformation mechanism map, which is a graphical tool that is utilized to understand the combinations of material state parameters (e.g., grain size, temperature, strain rate) that define transitions between deformation behaviour. Figure 1.1 illustrates the influence of competing deformation mechanisms on yield strength and their relation to grain size, which leads to the observed trends in hardness measurements. These deformation mechanisms illustrated in the figure are referred to in a very broad sense, and are discussed in greater detail in subsequent Chapters. The inverse HP effect highlights an important aspect of materials engineering, whereby structural changes in the organization of material can alter the interplay between active deformation mechanisms and consequently cause a drastic change in mechanical behaviour. Therefore, the pursuit and investigation of structure-property relationships such as the HP effect remains an active area of research within the discipline of materials science and engineering.

1.1 Motivation

Engineering of metals may be broadly considered as an effort to introduce beneficial structural modifications into a material that improve physical properties. Beginning with a pristine infinite lattice, the introduction of microstructural constraints such as precipitates, grain boundaries, and other defects represent structural barriers to the free-glide of dislocations. Each of these defect structures has a length-scale aspect associated with its impact on deformation behaviour, which provides a pathway for materials engineering. Specifically, the manifestation of different deformation mechanisms arises as a result of the differences between the size of microstructural obstacles and the characteristic length-scales of plasticity carriers (e.g., dislocation loop diameter, stacking fault ribbon widths). Figure 1.2 provides a schematic of the various microstructure obstacles and the
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Figure 1.1: A deformation mechanism map for the HP effect in FCC metals. The shape of the HP curve has been found to be general for a large number of FCC metals, although the exact slopes and positions of peak yield strength differ between materials. A more detailed description of deformation mechanisms is provided in subsequent Chapters. This figure has been adapted from a deformation mechanism map provided by Cheng et al. [5].

relevant defect structures whose interplay serves to alter the dislocation glide behaviour of engineered metals. The symbols for each defect structure are described in the figure caption and deviate from the nomenclature catalog. An excellent review of the size effects in materials, which examines many aspects of microstructural constraints and their impact on hardening, has been published by Arzt [6]. Within this context, HP hardening embodies one of the simplest structural modifications which may be introduced to affect the mechanical behaviour of an engineering material. Generally, the existence of structural discontinuities in a microstructure (i.e., grain boundaries) impede free-glide, creating a sessile field of dislocations and an interfacial stress which must be overcome by additional loadings for continued material plasticity. Additional structural complexities may also be achieved by considering the configuration of grain boundaries present in a material. For example, interface engineering implements a host of thermomechanical treatments which increase the relative fraction of low energy grain boundaries in a
Figure 1.2: A schematic illustrating the various microstructural obstacles and constraints which are applied in materials engineering. These microstructure parameters are the grain size $D$, grain boundary width $\delta_b$, precipitate spacing $L$ and radius $R$. Defect structures such as a dislocation loop of radius $d$ and stacking fault ribbons of width $w$ also can impede the movement of glissile dislocations. Electronic configuration parameters such as magnetic domain walls of width $\delta$ also impose length-scale dependencies on physical properties. The symbols used in this figure are defined as presented in the original text. This figure is reprinted from [6] with permission.

material, leading to additional improvements in physical properties. Overviews of grain boundary engineering (GBE) principles are available from Randle [7] and Watanabe [8].

In general, grain refinement technologies and thermomechanical treatments may be considered as top-down philosophies which utilize traditional materials processing techniques in their implementation. As a result, HP hardening techniques and GBE principles may only be typically applied in a non-targeted fashion. Specifically, changes in microstructures due to materials processing manifest as smooth structural transitions. The effects of grain size interface engineering are therefore distributed throughout a microstructure without any locality, leading to a homogeneous material response and a convoluted observation of deformation mechanism. However, with the rise of additive manufacturing techniques, additional levels of manufacturing complexity may be engineered into material architectures, leading to the possibility of heterogeneous microstructures with discontinuous features and unique structure-property characteristics. As an example, multilayers (ML)s , represent a modulated material architecture, whereby specified thicknesses of material are periodically layered through additive processes to form a
1.1. Motivation

bulk microstructure (e.g., [9]). Control of individual layer thicknesses therefore permits an unparalleled degree of microstructure design flexibility, which enables the investigation of a number of unique deformation behaviours and structure-property relationships. The length-scale dependent deformation mechanisms of conventional ML structures are available in a review by Misra et al. [10]. In traditional MLs, immiscible metallic species are selected for layering, whereby the geometric confinement by layer interfaces of imperfect coherency leads to a number of unique scale-dependent plastic responses. The ML architecture, combined with additive manufacturing principles, therefore represents an ideal platform to investigate the influence of length-scale on the deformation behaviour of confined material volumes. Leveraging the concept of a modulated microstructure, this thesis examines the effect of length-scale on the deformation behaviour of metallic MLs with alternating coarse-grained (CG) and nanocrystalline (NC) features. In this manner, the interplay of deformation mechanisms which are active in heterogeneous microstructures may be systematically examined via controlled additive manufacturing. Figure 1.3 provides a schematic of the ML architecture template. The grain sizes \(d\) and thicknesses \(t\) of the NC and CG layers are indicated. In this context, NC crystals are considered

\[d_{\text{CG}}\]

\[t_{\text{NC}}\]

\[t_{\text{CG}}\]

\[d_{\text{NC}}\]

**Figure 1.3:** A template of the proposed ML architecture. The length-scale dependencies of deformation mechanisms may be studied by varying the grain size \(d\) and layer thickness \(t\) of the CG and NC layers.
to have grain sizes < than 100 nm and CG is a broad term that refers to any crystal features larger than 100 nm.

This work may be considered as a fundamental study which expands upon the mechanistic knowledge of dislocation-based plasticity in homogeneous microstructures to include the effects of abrupt structural heterogeneities. CG and NC features are explicitly selected for study as there exists a great wealth of knowledge for the deformation behaviour of each respective microstructure in a homogeneous sense. However, it is not known from the available literature how deformation mechanisms interact when these features are implemented in a heterogeneous manner. In order to reduce the number of engineering variables, the average grain sizes of NC and CG features are fixed in all experimental studies undertaken in this thesis work. Additionally, the MLs are manufactured to be monolithic (i.e., of a single chemistry), such that complexities arising from interfacial incoherency due to incommensurate lattices and/or secondary phase formation effects are significantly mitigated. This study may be succinctly rationalized as a fundamental investigation of the mechanical behaviour of relatively soft CG features which are confined within a heterogeneous microstructure of comparatively hard NC features.

1.2 Thesis objectives and outline

This work represents the first systematic investigation of monolithic multilayers with modulated microstructures. As a result, a multi-pronged analytical approach combining both experimental characterization and theoretical modelling has been undertaken during the course of this thesis. The overall objective of the current thesis is to understand the influence of length-scale on the interplay of deformation mechanisms in the ML structure. In this regard, it may be reasonably assumed that extremely thick NC and/or CG layers behave as bulk homogeneous samples and that the overall response of the ML may be estimated using simple rule of mixtures (ROM) assumptions. However, it is expected that NC and CG deformation mechanisms interact at layer interfaces and it is therefore of a fundamental materials science interest to investigate the competition between these deformation behaviours and the transitional length-scale at which this effect begins to dominate the mechanical response of the entire ML. Specifically, this thesis investigates:

1. The mechanical behaviour of MLs possessing different fractions of CG and NC features

2. The correlation between the measured mechanical properties of the ML and the dominant deformation mechanisms
3. The deformation mechanisms which underpin plastic interactions at CG-NC interfaces

4. Parametric studies of ML architectural design which may be leveraged to improve and tailor mechanical properties

The current thesis is organized into nine subsequent chapters. Chapter 2 presents a detailed review of the relevant background information and existing literature on deformation mechanisms in FCC metals, including a discussion of length-scale transitions in deformation behaviour. Additionally, the available literature on the deformation behaviour of MLs is also critically analyzed. Chapter 3 overviews methodology and materials preparation, while the following six Chapters present a thorough experimental characterization of the MLs as well as the results of analytical and computational modelling of ML deformation behaviour. Chapter 4 provides a base characterization of the NC and CG constituents as well as layer measurements for the prepared ML samples. In Chapters 5 and 6, an extensive mechanical characterization of the ML samples is performed using a combination of electron microscopy analysis, uniaxial tensile testing, and indentation studies. A molecular dynamics (MD) model is constructed in order to investigate the atomistic origins of the deformation behaviour of the ML architecture in Chapter 7. Furthermore, an phenomenological model is expanded and implemented in Chapters 8 and 9 in order to predict the experimental ML behaviour. Chapter 10 is reserved for concluding remarks and suggestions for future work.

One of the significant contributions in this work, which is not a direct result for dissemination in the thesis body, is the development of customized codes to perform computational simulations. The library of code written for this thesis represents the culmination of over two years of effort, and may be considered as a unique set of tools for computational simulation. These codes are not openly available to the scientific community in the literature, but, may be obtained by contacting the author directly.
Chapter 2

Background and Literature Review

In the following sections, the literature relevant to this thesis is critically reviewed. This review is subdivided into two primary sections. In the first section, the pertinent background information and a discussion of the deformation mechanism literature as it relates to FCC metals is provided. Specifically, a discussion of the role of dislocations in deformation mechanisms is delivered. In this background, the effects of physical material properties, loading configurations, and structural length-scales on the competition between deformation mechanisms are discussed. Secondly, a review of the existing literature regarding the design of heterogeneous microstructures is undertaken. The scope of this section is broad and overviews the relevant developments in the studies of heterogeneous microstructures, which lead to the multilayer design architecture. Subsequently, a scientific chronology of theoretical and experimental developments in the study of multilayer structures is delivered. The objectives of this literature review are two-fold. Primarily, it is the goal of this section to provide the reader with sufficient background information regarding the deformation mechanisms which are relevant to the interpretation of the forthcoming results. Also, this review is designed to provide the reader with a critical analysis of the current body of literature regarding multilayer materials within the context of the stated goals of this thesis work.

2.1 Deformation mechanisms in FCC materials

As the focus of this thesis is an understanding of the length-scale effects on deformation behaviour in heterogeneous microstructures comprised of modulated features, this section of the literature review may be most logically begun with a discussion of the relevant deformation mechanisms. The literature regarding deformation mechanisms in FCC metals is extremely broad and cannot be realistically analyzed within the confines of
2.1. Deformation mechanisms in FCC materials

Therefore, it is important to first establish a number of simplifying restrictions which may be used to refine the scope of the literature search. These considerations are consistent with the problem outline as defined in Chapter 1. Namely, the review in this thesis is limited to deformation mechanisms in a monophase material which exhibit a significant grain size effect, which is critical to understanding the deformation behaviour of the CG and NC layers in the ML architecture. See Figure 1.3 for a schematic of the relevant architectural features considered as contributors to different deformation behaviours. In a general sense, this review may be considered as a discussion of the length-scale effects of planar defects (i.e. interfaces and grain boundaries). Deformation mechanisms involving secondary phases, and interactions with solute, interstitials, or vacancies, are not considered. Additionally, transitions in deformation mechanisms as a function of other state variables, such as temperature and strain rate, are not considered. For an excellent review of deformation mechanisms and the influence of state variables, please see the text from Frost and Ashby [11].

Under these considerations, a discussion of deformation mechanisms in FCC materials may be be most logically initiated with the role of the dislocation in deformation. As a elementary carrier of plasticity, dislocations represent the fundamental building blocks of deformation mechanisms in FCC materials, and the manner in which dislocations are nucleated and interact along crystallographic slip planes determines the progression of deformation. The dislocation represents a critical structure which serves as a highly-localized mobile dissipater of homogeneously stored elastic energy in a loaded material. Ignoring the effects of structural modifications such as grain boundaries, and considering deformation within the context of a single crystal, a discussion of dislocation-mediated deformation mechanisms may be reduced to consideration of two important behaviours: dislocation slip and deformation twinning.

2.1.1 Basics of dislocation slip and deformation twinning

Dislocation slip and deformation twinning represent competing deformation mechanisms in FCC metals. In the former, $<110>$-type perfect dislocations (or extended dislocations formed from dissociated $<112>$-type leading/trailing Shockley partial pairs) are emitted from a dislocation source along crystallographic slip planes, leading to a shearing of the lattice whose overall amount of slip is defined by the magnitude of the $<110>$ Burgers vector ($b$). Figure 2.1 illustrates the glide of a edge type dislocation across a single crystal. As shown in the figure, the glide of a perfect dislocation across a microstructure creates a quantum of slip upon absorption of the defect at a free surface.
Furthermore, the lattice registry is only locally disrupted by the dislocation core and there are no permanent registry faults after the dislocation has been absorbed at a free surface. Dislocation slip may be applied in a homogeneous or inhomogeneous fashion. Specifically, when perfect dislocations are emitted along the same crystallographic slip plane, the slip is cumulative, leading to large deformation. However, perfect dislocations need not be confined to a single slip plane. In this context, the glide of dislocations along multiple slip planes in a single slip system in a region of a crystal forms a slip band. There are a total of 12 possible slip systems in the FCC lattice, which represent the crystallographic permutations of the 4 \{111\}-type slip planes and the 3 \langle1\bar{1}0\rangle-type slip directions in each slip plane. A cumulative crystallographic shear strain ($\gamma^i_g$) along an arbitrary slip system $i$ may be calculated using the following relation:

$$\gamma^i_g = \frac{n^i b_{1\bar{1}0}}{\lambda_b}$$  \hspace{1cm} (2.1)$$

where $n^i$ represents the number of dislocations in a slip band of slip system $i$ and $\lambda_b$ is the width of the slip band. See Ref. [12] for a description of the relevant slip-planes and slip-directions involved in each slip system $i$. The macroscopic uniaxial extensional strain, which homogenizes the effects of crystallographic slip on multiple slip systems, may then be calculated through consideration of the Taylor factor ($M$) [13] as:

$$\gamma = M\varepsilon$$  \hspace{1cm} (2.2)$$

where $\varepsilon$ represents the macroscopic uniaxial strain. In this context, $M$ defines the ratio of the cumulative crystallographic slip in many slip systems to the measured uniaxial extensional strain. There are a minimum of 5 independent slip systems that are needed to accommodate the independent components of the cubic strain tensor (reduced from six by the requirement of constancy of volume). Taylor assumed that the combination of crystallographic shears activated during deformation are those which minimize the total shear strain energy. By definition, the ratio of the cumulative crystallographic slip to the extensional strain is the Taylor factor for a single crystal. Taking an average of textures in a polycrystal aggregate, $M$ is typically assumed in the literature to have a value of 3.06.

Under normal stacking conditions, \{111\}-type planes in an FCC material follow an ABCABCABC stacking sequence. This stacking sequence represents the relative stacking of \{111\} planes along the \langle111\rangle packing direction. The landscape of the \{111\} closed-packed plane permits the stacking of additional \{111\} planes into two variant
2.1. Deformation mechanisms in FCC materials

Figure 2.1: An edge dislocation glides across a single crystal which is subjected to an external shear stress. Upon exiting the crystal, a slip step in the crystal is visible. The magnitude of the lattice displacement across the slip plane is equal to $b$. This figure has been adapted from the original source [1].

positions, which are denoted as the ‘B’ and ‘C’ interstitial sites. Figure 2.2 presents a schematic of the ABC stacking sequence and the interstitial packing sites which are available for population in the FCC lattice. Twinning is observed in an FCC crystal when stacking faults (regions of a local hexagonal close-packed (HCP) lattice stacking, ABAB) disrupt the normal sequence and form bounded regions which possess a stacking of relative mirror symmetry. For example, the lattice sequence of FFHFFHFFFF, where F and H represent local planes of FCC and HCP stacking, respectively, has a ABCBACBABC stacking sequence. In this stacking pattern, the red characters represent stacking faults within regions of a local HCP lattice. The planes contained between these faults possess a reversed stacking sequence (i.e., CBAC) and represent a twinned region.

Deformation twinning manifests in a FCC crystal when a reversal of stacking is facilitated by the glide of $<11\overline{2}>$-type Shockley partial dislocations along adjacent slip planes in a slip system. The magnitude of the $<11\overline{2}>$ Shockley partial represents the exact relative displacement required to displace atoms within a $\{111\}$ close-packed plane to a different interstitial site (e.g., B site $\rightarrow$ C site), consequently altering the stacking sequence. In this manner, the progressive glide of Shockley partials disrupts the normal stacking sequence, and the boundaries of the slipped region form stacking faults with the surrounding matrix material. This process may be envisioned as the application of a homogeneous shear along a region of material in a crystal. The strength of this homogeneous shear is equal to the magnitude of the Shockley partial dislocation and the width of the twinned area is defined by the number of slip planes involved in shearing. Figure 2.3 illustrates the relative shift in atoms due to progressive glide of Shockley par-
2.1. Deformation mechanisms in FCC materials

Figure 2.2: A schematic of ABC packing in an FCC lattice. The relevant crystallographic directions are noted for perspective. Two variants of interstitial packing are available for stacking in the FCC lattice. These variants are denoted as ‘B’ and ‘C’ in the figure.

tial dislocations on adjacent slip planes. As the deformed region grows, the morphology of the twin becomes evident and a number of structural defects are created. Beginning with the first instance of Shockley partial glide, the stacking sequence is found to be CACABC, when the stacking direction is upwards relative to the figure. The red letters highlight the region of faulted stacking. The resulting structure is known as an intrinsic stacking fault (isf) and this defect may be envisaged as a structure where a \{111\} slip plane has been removed from stacking (e.g., in this example, the B plane). Glide of an additional Shockley partial on the immediately adjacent plane leads to a stacking sequence of CACBCA and an extrinsic stacking fault (esf), which may be considered as the insertion of an extra \{111\} slip plane (blue) into the deformed region. Finally, glide of a third Shockley partial leads to the formation of a fully developed twin fault (tf) which is shown in green and possesses a stacking sequence of CACBAB. Table 2.1 provides a summary of the planar fault structures and their relative stacking sequences.

Due to the homogeneous nature of shear in deformation twinning, the shear strain which may be accommodated by this deformation mechanism is uniformly distributed across the defective region. The shear strain accommodated by twinning (\(\gamma_t\)) on a particular twinning plane may be calculated as the ratio of magnitude of the Shockley partial dislocation (\(b_{112} = a_o / \sqrt{6}\), where \(a_o\) is the lattice parameter) and the interplanar spacing (\(d_{111}\)) of \{111\}-type slip planes, which is equal to \(a_o / \sqrt{3}\). Therefore, a quanta of shear
2.1. Deformation mechanisms in FCC materials

Figure 2.3: The growth of a deformation twin due to progressive glide of Shockley partial dislocations on adjacent slip planes. The crystallographic directions are provided for perspective. An isf is created from the glide of an initial \(<1\bar{1}2\>\)-type Shockley partial (red stroke). Subsequent glide of an additional dislocation on the slip plane of immediate adjacency leads to the formation of an esf (blue stroke). A fully developed tf is formed from the glide of a third Shockley partial (denoted by green stroke). The deformation twin may grow further in this fashion through the nucleation and glide of additional Shockley partials. A perspective drawing of the FCC cell is provided. The transparency of the atoms in the perspective drawing illustrates relative position into the plane of the image. Please note, the perspective atoms are not drawn to proper scale, such that the \(<110>\) directions are not visibly close-packed. Atoms in the deformation twinning schematic are not drawn with a 3D perspective.

Strain accommodated by deformation twinning is calculated as \(\gamma_t = 1/\sqrt{2}\). The relationship between macroscopic strain during uniaxial tension experiments and \(\gamma_t\) may also be described in terms of the Taylor factor as in Eq. 2.2.

From a deformation mechanism perspective, the major differences between dislocation slip and deformation twinning may be understood through a consideration of the organizational changes in microstructure which result from each deformation mode. Since dislocation slip occurs without any requirements for registry faults, a microstructure may slip homogeneously or the deformation may unfold in a localized manner along a singular slip plane. Conversely, deformation twinning must occur incrementally along adjacent slip planes in a homogeneous manner in order to preserve the mirror symmetry requirements of this deformation mechanism. Additionally, deformation twinning requires the emission of leading Shockley partial dislocations exclusively. On the other
2.1. Deformation mechanisms in FCC materials

Table 2.1: Stacking sequences of the planar faults formed by glide of Shockley partial dislocations on adjacent slip planes. See the main text for the meanings of the colour stroke.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Number of Shockley partials</th>
<th>Lattice sequence</th>
<th>Stacking sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>isf</td>
<td>1</td>
<td>FHHFFF</td>
<td>CACABC</td>
</tr>
<tr>
<td>esf</td>
<td>2</td>
<td>FHFHFF</td>
<td>CACBCA</td>
</tr>
<tr>
<td>tf</td>
<td>3</td>
<td>FHFFHF</td>
<td>CACBAB</td>
</tr>
</tbody>
</table>

On the other hand, dislocation slip can be achieved using \(<\overline{1}10>-type perfect dislocations or \(<\overline{1}12>-type leading/trailing Shockley partial pairs, provided that the stacking fault ribbon is sufficiently narrow to prevent the formation of localized twins. Figure 2.4 illustrates some of the key morphology differences between dislocation slip and deformation twinning.

2.1.2 Competition between dislocation slip and deformation twinning

In order to provide context for a study of interactions between deformation mechanisms, it is pertinent to review the factors which lead to competition between deformation processes. In absence of the structural complications associated with polycrystalline materials, the relative competition between dislocation slip and deformation twinning in a single crystal may be understood through the consideration of the interplay between two state parameters: namely, the orientation of driving forces relative to the crystallographic directions involved in deformation, and the energy barriers resisting the nucleation of the mechanism-defining dislocation. In the former, the projected shear stress along the various pertinent crystallographic directions is relevant in determining which deformation mechanism is preferred due to applied loading. Determination of the influence of loading orientation on the dominant deformation mechanism may be best illustrated through consideration of a sharp edge crack under a Mode I loading scenario. An edge crack is the ideal format for investigating the influence of loading geometry as the stress concentrations at the crack tip are sufficiently high, such that energetic barrier differences between each deformation mechanism are somewhat mitigated. The problem of dislocation nucleation from a crack tip is considered to be a classic problem in the materials science literature and was first mathematically treated using the tools of a Peierls definition of a dislocation in a seminal paper from Rice [15]. As reported by Weertman and Weertman [16], crack tip dislocation emission may manifest as crystallographic slip in the form of perfect dislocations or through crack tip twinning due to the nucleation of successive leading Shockley partials. A number of multiscale studies using both discrete MD simulations
2.1. Deformation mechanisms in FCC materials

Figure 2.4: A schematic of a distorted FCC lattice after homogeneous application of $\frac{a_0}{6} <11\bar{2}>$(a,b) and $\frac{a_0}{2} <110>$(c,d) shears. The shears have been applied to each $\{111\}$ plane of atoms between the black arrows. The configuration in (b) exhibits deformation twinning due to the glide of leading Shockley partial dislocations. However, the configuration in (d) does not exhibit any irregularities in the stacking sequence and possesses a perfect lattice registry, which is characteristic of dislocation slip. Additional atoms have been added to illustrate the differences in the microstructures due to each deformation mechanism. This image has been reprinted from its original source [14] with permission from Elsevier.

Combined with concurrent continuum mechanics methods have investigated the crack tip problem [17–19] as it relates to dislocation slip and deformation twinning. The role of temperature [20] and loading rate [21] have been investigated in separate studies from Warner et al., which have elucidated the role of thermal activation in these deformation processes. Perhaps, the most comprehensive study of the influence of crystal geometry on the active deformation mechanism has been performed by Yamakov et al. [22]. In this study, the researchers report the influence of slip plane orientation and slip direction on the active deformation mechanism. Notably, Yamakov et al. [22] report that the orientation of the slip plane relative to the far-field loading is inconsequential in determining the active deformation mechanism. However, when the $<11\bar{2}>$ crystallographic direction is oriented perpendicular to the crack tip front, deformation twinning is prevalent. Con-
versely, dislocation slip is dominant in simulations where the $\langle 1\bar{1}0 \rangle$ direction is oriented in this manner. This effect may be rationalized by consideration of the projected shear stresses along each direction. In the first case, the $\langle 1\bar{1}2 \rangle$ is parallel to the direction of maximum load projection. In this manner, the emission of leading partial dislocations is preferred. However, the emission of a trailing partial is not preferred as the trailing Burgers vector must, as required to form an extended $\langle 1\bar{1}0 \rangle$ dislocation, be directed at $60^\circ$ to the crack tip front, which is a geometrically unfavourable orientation for emission.

In the latter configuration, emission of a dissociated dislocation is preferred as leading and trailing partials directions are both located at $30^\circ$ relative to the crack tip perpendicular, making them equally favourable for activation. Figures 2.5 and 2.6 illustrate the crystallographic parameters used to orient crystals in the study of Yamakov et al. [22] as well as the resulting deformation mechanism from each simulated configuration. Please see the captions for descriptions of the figure symbols. The orientation parameters $\theta$ and $\phi$ illustrated in Figure 2.5 should not be confused with the angles used in Schmid factor calculations [23], although they do represent an analogous description of crystallographic configuration.

The energetic barriers resisting deformation processes may be elegantly described using a generalized planar fault energy (GPFE) surface, as originally defined in the seminal
2.1. Deformation mechanisms in FCC materials

Figure 2.6: Snapshots of the simulation cell after loading to the indicated stress intensity factor (defined as $K_I = \sigma \sqrt{\pi a}$ MPa, where $\sigma$ is the applied far-field loading, and $a$ is the edge crack length). The nucleation of deformation twins is evident in (a), (b) and (c) which possess orientation parameters ($\theta, \phi$) of $(35.26^\circ, 0^\circ)$, $(54.74^\circ, 0^\circ)$, and $(70.53^\circ, 0^\circ)$, respectively. Conversely, full dislocation slip is observed in (d), (e), and (f). The simulation configuration parameters for these microstructures is $(35.26^\circ, 30^\circ)$, $(54.74^\circ, 30^\circ)$, and $(70.53^\circ, 30^\circ)$, respectively. This image has been reprinted from its original source [22] with permission from Elsevier.

Paper from Vítěk [24]. The GPFE represents a visualization of a planar surface in terms of a potential energy landscape, whereby the energetic barriers resisting the shuffling of atomic planes along specific crystallographic directions are fully defined. Within the context of deformation mechanisms, the energy barriers resisting dislocation slip and deformation twinning may be extracted by taking slices of the GPFE surface along the appropriate deformation pathway. Figure 2.7 depicts a typical GPFE surface of the $\{111\}$ slip plane in Al. The GPFE surface may be envisaged as representing the potential energy barrier associated with shearing of adjacent $\{111\}$ slip planes along any of the in-plane crystallographic directions. The energetics associated with dislocation slip for
2.1. Deformation mechanisms in FCC materials

Figure 2.7: The GPFE surface of Al after Vítek [24]. The potential energy landscape may be envisaged as representing the potential energy barriers for the shearing of adjacent \{111\} slip planes. This image has been reprinted from its original source [24] with permission from the Taylor & Francis group.

example, may be determined by taking the GPFE surface contour along the pathway of extended dislocation glide, where the \langle1\bar{1}0\rangle Burgers vector is recovered from leading/trailing Shockley partial dislocation glide along slip-conjugate \langle1\bar{1}2\rangle directions (e.g., \(\frac{a_0}{2} [1\bar{1}0] \rightarrow \frac{a_0}{6} [1\bar{2}1] + \frac{a_0}{6}[2\bar{1}\bar{1}]\)). The GPFE of a \{111\} surface may be readily calculated using analytical formulations of interatomic binding potentials (e.g. Vítek [24] uses the potential of Pick [25]), providing a powerful first-principles-based methodology for understanding deformation energetics. In deformation twinning, the deformation process occurs across multiple slip planes, necessitating the consideration of multiple GPFE surfaces whose interactions during shearing are not tractable using analytical approaches. Recently, atomistic simulation methodologies such as density functional theory (DFT) calculations and MD simulations have been utilized to reconstruct the GPFE pathway for deformation twinning and also dislocation slip. For example, GPFE curves for deformation twinning have been calculated using DFT simulations for a number of common FCC metals such as Ag [26], Al [27], Au [26], Cu [26–29], Ni [27, 30], Pb [26], and alloys such as Cu-Al [28, 29]. The GPFE curves for each deformation mechanism may be determined via DFT through the application of \(a_o/\sqrt{6}<1\bar{1}2>\) shears to a pristine crystal on the appropriate slip planes (i.e., on the same plane for dislocation slip and on adjacent planes for deformation twinning). This shearing process is analogous to the emission and glide of a corresponding number of Shockley partial dislocations. The energy introduced into the system as a function of the displacement represents the excess surface energy
2.1. Deformation mechanisms in FCC materials

Figure 2.8: An example of GPFE curves for dislocation slip (red line) and deformation twinning (blue line). In this figure the terms $\gamma_{usf}$, $\gamma_{sf}$, and $\gamma_{utf}$ refer to the unstable stacking fault, stacking fault, and unstable twinning fault energies, respectively. $r_o$ symbolizes the lattice parameter. These terms are discussed in greater depth in forthcoming Chapters. This image has been reprinted from its original source [31] with permission from the Nature Publishing group.

associated with the disruption in interplanar registry, and may be used to directly calculate the GPFE. Figure 2.8 provides a schematic of a typical GPFE curve for deformation twinning and dislocation slip, which is formed using this methodology. Please see the figure caption for a description of the symbols used. In the case of dislocation slip, the deformation pathway follows the stacking fault curve, whereby the surface energy is returned to a pristine condition upon the restoration of a perfect registry and stacking sequence across the slip surface. Deformation twinning is represented in the figure by the blue curve. Notably, the surface energy does not return to a pristine condition due to the existence of planar faults in the crystal after the application of a rigid homogeneous shear of strength $a_o/\sqrt{6}$ on two adjacent slip planes.

Within the context of the GPFE curve, the competition between dislocation slip and deformation twinning may be understood through consideration of the relative magnitudes of the unstable stacking fault ($\gamma_{usf}$) and the unstable twinning fault ($\gamma_{utf}$) energies. After the formation of a stacking fault, the GPFE curve bifurcates due to the divergent deformation processes associated with each deformation mechanism. As discussed by Tadmor and Hai [32], the competition between dislocation slip and deformation twinning
2.1. Deformation mechanisms in FCC materials

at a crack tip may be described by a ‘twinnability’ parameter, which is related to the ratio of the unstable fault energies. In this regard, as the unstable twinning fault energy approaches the unstable stacking fault energy, the likelihood of deformation twinning increases from an energetic’s perspective. Tadmor and Bernstein [33] later expanded the application of the twinnability parameter to include deformation competition at grain boundaries by treating the intergranular region as a sharp edge crack and homogenizing their model through a representative volume element approach. It should be noted that a comparison of unstable fault energies in this context is only relevant to the discussion of deformation mechanism competition because these processes are considered as initiating at the same source (e.g., a crack tip in [32]). Therefore, the twinnability parameter should be considered within this caveat. Generally, when the source of deformation is not fixed, the stacking fault energy ($\gamma_{sf}$ in Figure 2.8) is usually a better indicator of the comparative deformation energetics between dislocation slip and deformation twinning, as it describes the energetic penalty incurred by the latter process as a result of the introduction of planar fault structures.

2.1.3 Intragranular and boundary-mediated mechanisms

The preceding section has established the considerations required to understand competition between dislocation slip and deformation twinning. However, the specific morphologies by which these deformation mechanisms manifest within a microstructure has not been clarified. Specifically, the method by which dislocations nucleate and aggregate within a microstructure becomes relevant to understanding the various morphologies which may be adopted by a deformation mechanism as well as the potential pathways by which deformation mechanisms may interact. In general, dislocation nucleation and interaction mechanisms, as they pertain to deformation, may be broadly classified as intragranular or boundary-mediated phenomena. A discussion of deformation mechanism morphology within the context of microstructure is also pertinent to this review in the sense that the role of grain boundaries with respect to deformation mechanisms may also be introduced. This facilitates an easy transition towards an eventual discussion of structural considerations, whereas deformation mechanisms were previously examined only in the context of single crystals. For the purposes of this thesis, an explicit discussion of dislocation nucleation and multiplication from Frank-Read [34] type sources is omitted. For a review of this concept, please see the work of Dieter [35]. The primary focus of this section is to specifically address the various intragranular and boundary-mediated morphologies of deformation twinning. A discussion of dislocation slip in this context is
2.1. Deformation mechanisms in FCC materials

not within the scope of this review.

The most recognized morphology of an intragranular deformation twin is formed through a pole mechanism by the prismatic glide of elements in a long jog dislocation, as originally described by Venables [36]. Figure 2.9 illustrates the prismatic glide mechanism proposed by Venables for the nucleation and growth of an intragranular deformation twin in FCC materials. The dislocations in the figure are described using Thompson notation. A 2D projection of the Thompson tetrahedron is provided for the reader’s reference in Figure 2.10. For a detailed explanation of Thompson notation, please see this report from Nix [37]. Consider a dislocation $\mathbf{AC}$ which is jogged along $\mathbf{CB}$ (Figure 2.9a). The jog may dissociate into a $\langle 11\bar{2} \rangle$ Shockley partial dislocation $\alpha \mathbf{C}$, and a sessile $\langle 111 \rangle$ Frank partial $\alpha \mathbf{A}$, in the plane of the jog (Figure 2.9b). The Shockley partial $\alpha \mathbf{C}$ is free to glide under the applied loadings and rotate about the poles $X$ and $Y$. After a near complete revolution of the Shockley partial, a unit jog has been created at $N_2$ which reforms the twin source at $T_2$ (Figure 2.9c). It is important to note that the segments of the Shockley partial pinned at $N_1$ and $N_2$ have opposite Burgers vectors of $\alpha \mathbf{C}$ and $-\alpha \mathbf{C}$, respectively, due to the antiparallel orientation of their dislocation lines. Normally the segments along $RS$ would annihilate as in a Frank-Read dislocation multiplication mechanism. However, due to the presence of the jog line, the segment pinned at $N_2$ is forced below the $N_1N_2$ line by climb, as indicated in Figure 2.9c. Recombination of the Shockley and Frank partials along $RN_2$ reforms the full dislocation $\mathbf{AC}$, which is free to further dissociate in the slip plane directly adjacent to the original jog line at $T_2$ (Figure 2.9d). After a revolution of the Shockley partial dissociated at $T_2$, the segment pinned to the $Y$ pole is again forced by glide under the jog line. In this instance, the segment is able to annihilate with the partial dislocation segment from the previous revolution event (Figure 2.9e), leaving an uninterrupted helical prismatic glide morphology and a deformation twin embryo. Permutation of this deformation mechanism leads to the growth of the deformation twin along the $X-Y$ pole (Figure 2.9f). Variants of the prismatic glide mechanism are reported in [39, 40]. Other notable intragranular twinning theories which do not explicitly rely on this prismatic glide mechanism are found in reports from Cohen and Weertman [41], Fujita and Mori [42], Mahajan [43], Niewczas and Saada [44], and Mahajan and Chin [45]. A comprehensive review of intragranular deformation twinning morphologies is available from Christian and Mahajan [46].

Deformation twinning via emission of Shockley partial dislocations from grain boundaries was first predicted in MD simulations [47] and later verified experimentally by high resolution electron microscopy [48, 49]. As a homogeneous deformation process, deformation twinning requires the glide of Shockley partial dislocations on adjacent slip planes.
2.1. Deformation mechanisms in FCC materials

Figure 2.9: The prismatic twinning mechanism as proposed by Venables [36]. See the main text for a description of the deformation events in each subfigure. This image has been reprinted from its original source [36] with permission from the Taylor & Francis group.
2.1. Deformation mechanisms in FCC materials

With respect to grain boundaries, it is statistically unlikely for the atomic configurations along the grain boundary to permit the nucleation and emission of a Shockley partial on every slip plane. This consideration gives rise to the need for a partial multiplication mechanism which can provide an energetically favourable source of twinning partial dislocations. One possible mechanism for the multiplication of partial dislocations involves cross-slip of screw-type Shockley partial dislocations, as proposed by Zhu et al. \[49\]. Figure 2.11 provides a schematic of the partial dislocations and assumed microstructure configuration relevant to this cross-slip multiplication mechanism. Referring to the notation in the figure, the full dislocation can dissociate readily into partials under the following reaction: $b \rightarrow b_1 + b_2$. The partial $b_1$ possesses a pure screw character and may easily cross-slip to an adjacent (11$\bar{1}$) plane, where it dissociates in the following reaction: $b_1 \rightarrow b + (-b_2)$. $-b_2$ remains at the grain boundary. Subsequently, $b$ may again dissociate into $b_1$ and $b_2$, replenishing the screw partial dislocation $b_1$, and permitting the propagation of the reaction on additional slip planes. Meanwhile, the mixed $b_2$ partial dislocation is free to glide towards the grain interior, extending the stacking fault and widening the deformation twin. The glide of $b_2$ Shockley partials on successive
2.1. Deformation mechanisms in FCC materials

Figure 2.11: A square grain with a dislocation \( b \) and line parallel to the grain boundary. This configuration is proposed as the starting point for a cross-slip partial dislocation multiplication mechanism. See main text for a description of this process. This figure is reprinted from the original source [49] with permission from AIP Publishing LLC.

slip planes creates a kink of 141° at the boundary between a twin and a matrix, which is twice the angle between two \{111\} slip planes. This yields the grain morphology which is schematically shown in Figure 2.12a and mirrors experimental morphology observations in deformation twinning in NC materials (Figure 2.12b). A number of additional grain boundary-mediated deformation mechanisms involving deformation twinning have been proposed which result in varying degrees of macroscopic strain in the deformed grain morphologies. For example, mechanisms which rely on a number of dislocation reactions involving Shockley partials to form deformation twins have been reported to generate grain morphologies with no observable kink (i.e., zero macroscopic strain) [50].

In addition to grain boundaries, existing planar faults and twin boundaries within a microstructure can also facilitate the growth of deformation twins. For example, Zhu et al. [51] have reported a novel twinning mechanism whereby a stacking fault may grow into a deformation twin through capture and dissociation of incoming Shockley partial dislocations. Figure 2.13 illustrates this deformation process. As shown in the figure, a stacking fault on plane (d) interacts with a Shockley partial \( C\beta \) which approaches on a zone-conjugate slip plane (b) (Figure 2.13a). Free-glide of the incoming Shockley partial is halted by the stacking fault, leading to dissociation by the following reaction: \( C\beta \rightarrow \)}
2.1. Deformation mechanisms in FCC materials

Figure 2.12: (a) A schematic of the grain morphology resulting from the glide of $b_2$ type Shockley partial dislocations during deformation twinning. A grain boundary kink of 141° exists at the interface between the twin and the matrix. This morphology has been observed in deformation experiments performed on NC Cu (b). Subfigures (a) and (b) are reprinted from the original works [49, 50], with permission from AIP Publishing LLC and the American Physical Society.

Figure 2.13: The formation of a deformation twin through partial dislocation reaction with a stacking fault after Zhu et al. [51]. See the main text for a description of this process. This figure is reprinted from the original work [51] with permission from Elsevier.

$C\delta + \delta\beta$, where $\delta\beta$ is a stair-rod dislocation (Figure 2.13b). The product $C\delta$ Shockley partial is free to glide to the right to nucleate a deformation twin. The sessile stair-rod dislocation may then further dissociate into two Shockley partials by the reaction: $\delta\beta \rightarrow \delta C + C\delta$. The partial $\delta C$ then glides to the left of the image to widen the existing deformation twin on plane (d). The Shockley partial $C\delta$ is then able to repeat these dissociation reactions to further thicken the deformation twin. Although this dissociation process is energetically unfavourable, the application of sufficient stress can provide access to this deformation pathway. In this manner, a deformation twin may continue to thicken by reactions of Shockley partials and twin boundaries on zone-conjugate slip planes. Experimental evidence of this specific morphology of deformation twinning has been reported in the literature [51] for NC Cu deformed through high pressure torsion experiments. A high resolution electron microscopy image of this deformation twin mor-
2.1. Deformation mechanisms in FCC materials

Figure 2.14: A high resolution electron microscopy image of a deformation twin in NC Cu believed to be formed by the mechanism described in [51]. This figure is reprinted from the original work [51] with permission from Elsevier.

A number of variations of this deformation twinning mechanism have been proposed in the literature, including V-shaped twins formed via dislocation reaction and cross-slip [51–53]. Additionally, a dislocation rebounding mechanism has been [54] proposed. In this mechanism, the elastic field of a partial dislocation is reflected at grain or twin boundaries, assisting in the nucleation of twinning partials of opposite Burgers vectors. Successive reflections at opposing grain boundaries leads to the growth of a deformation twin. A comprehensive review of boundary-mediated deformation twinning is provided by Zhu et al. [55].

2.1.4 Other deformation mechanisms

Beyond deformation twinning and dislocation slip there are a number of grain boundary-driven deformation mechanisms which are known to occur in NC FCC materials at the smallest grain sizes. It is relevant to this literature review to briefly discuss other grain boundary-driven deformation mechanisms before beginning an analysis of the effects of length-scale. Grain boundary-driven deformation mechanisms may be distinguished from conventional dislocation slip and deformation twinning in that they describe processes by which deformation is accommodated purely at the grain boundary, and they do not directly rely on the lattice glide of dislocations. Grain boundary sliding (GBS) is one of the most studied grain boundary-driven deformation processes. In GBS, macroscale
Figure 2.15: The GBS process as envisaged by Sutton and Balluffi [56]. This particular GBS mechanism relies on the glide and pile-up of grain boundary dislocations at triple junctions. These grain boundary dislocations may not be considered as true lattice dislocations as they break the translational symmetry of the FCC lattice. This figure is reprinted from the original text of Koch et al. [57].

deformation is accommodated through the localized boundary shear of a neighbourhood of grains. There are a number of competing theories regarding the exact mechanism of GBS. For example, Sutton and Balluffi [56] propose a dislocation-based GBS mechanism whereby the glide and accumulation of intergranular boundary dislocations permit the movement of triple junction nodes in a microstructure. Figure 2.15 illustrates the mechanism of Sutton and Balluffi [56]. As shown in the figure, a grain boundary dislocation with a Burgers vector in the plane of the boundary glides towards a triple junction at AB. According to Koch et al. [57], these grain boundary dislocations can not be considered true lattice dislocations as they possess Burgers vectors which break the translational symmetry of the FCC lattice (e.g. $b = a_0/5$). The accumulation of these grain boundary dislocations then leads to a displacement of the triple junction. Conversely, a number of investigators [56, 58–60], have proposed a thermally activated shear mechanism, whereby a shear-driven shuffling of atoms occurs at a grain boundary where there is greater free-volume for microstructure reorganization. This processes has found some computational support in MD studies of NC Ni [59]. It is not clear, from the available literature, if the localized shear processes described by [56, 58–60] is the method by which grain boundary
dislocations are generated in the mechanism of Sutton and Balluffi [56]. In both processes, deformation is facilitated by diffusion at the grain boundary rather than lattice slip. In contrast to dislocation slip and deformation twinning, GBS may therefore be considered as a diffusion-driven deformation process. Due to the relatively higher fraction of grain boundaries in NC materials, GBS is expected to better compete with lattice-driven deformation mechanisms. Notably, GBS is known to facilitate superplasticity at relatively high strain rates and low temperatures compared to analogous coarse-grained materials. This superplasticity effect in NC materials has been reported in a number of experimental studies [61–64].

In addition to GBS, grain rotation is a closely related grain boundary-mediated process which has been suggested as a deformation mechanism in NC materials. Experimental evidence for grain rotation has been reported in a number of studies (e.g., Ke et al. [65] and Shan et al. [66]). In contrast to GBS, which involves the shuffling of atoms in the intercrystalline region, grain rotation involves a coordinated global rotation of a crystal lattice. Since grain rotation requires the global movement of a lattice, it is generally only observed at the smallest of grain sizes (e.g., $d < 6$ nm for Pt [67]).

It should be noted that some of the earliest deformation mechanisms suggested for nanocrystalline materials are diffusion-based processes such as Nabarro-Herring [68, 69] and Coble creep [70]. Although typically associated with high temperature and long timescale deformation in conventional coarse-grained materials, the strong inverse correlation with grain size for Nabarro-Herring and Coble creep (second and third power relations, respectively), increases their relative contributions to overall deformation within the context of NC materials. Indeed, Wang et al. [71] have shown that the contributions of diffusion-based creep (as well as GBS) to the mechanical response of electrodeposited NC is significant even at room temperature and within the timescale of a conventional tensile test. For an excellent review of boundary-mediated deformation mechanisms in NC materials, see the review by Morris [72].

2.1.5 Length-scale effects in the nanometer regime

Having reviewed the relevant deformation mechanisms and the morphologies by which they may manifest, a discussion of the effects of length-scale (i.e., grain size) on these processes may now be initiated. The influence of length-scale is expected to be critical to assessing the interactions of deformation mechanisms in heterogeneous microstructures. Conventional understanding of the competition between dislocation slip and deformation twinning in coarse-grained materials states that the latter processes is impeded at smaller
Deformation mechanisms in FCC materials

Grain sizes [73–75]. This suggests that deformation twinning is not likely to play a role in HP hardening at small grain sizes. The HP slopes for both dislocation slip and deformation twinning in a number of materials has been summarized by Meyers et al. [74]. El-Danaf et al. [75] reported a much higher twin density in samples of α-brass with grain sizes of 250 μm than in samples with 9 and 30 μm grains. Additionally, Meyers et al. [76] observed extensive twinning in 117 and 315 μm Cu samples, but not samples with average grain sizes of 9 μm.

Figure 2.16 schematically shows the slopes of HP relations for a FCC material under each of these deformation processes. As shown in the figure, the shear stress (τ) required for deformation twinning grows at a comparatively greater rate than for dislocation slip. This disparity between the flow stresses is amplified at smaller values of d. It should be noted that the exact physical rationale for this trend is not well understood and has been established purely from experimental observation [77]. A natural conclusion from the above discussion is that dislocation slip is dominant in small grains and deformation twinning is not relevant to deformation mechanisms at the grain sizes which are investigated in the multilayer structures prepared for this thesis work (<1 μm). However, an extensive body of experimental (e.g., see the review from Zhu et al. [55]) and comput-

![Figure 2.16: The flow stress (τ) relations for deformation twinning (blue) and dislocation slip (red) as it relates to grain size. Twinning becomes less accessible at smaller values of d. This figure is adapted from the original work of Zhu et al. [55].](image-url)
2.1. Deformation mechanisms in FCC materials

Tetralogical (e.g. see the review from Wolf [78]) literature highlights twinning as one of the most important deformation mechanisms in NC materials. Additionally, heterogeneous deformation from grain boundary sources is reported to play a dominant role in deformation, replacing deformation from intragranular sources as the primary deformation accommodation mechanism.

To understand this contradiction, the length-scale competition between the grain size and the dislocation splitting distance must be considered. Generally, as the grain size of a NC microstructure approaches the splitting distance of an extended dislocation, the tendency for a material to undergo deformation twinning from grain boundary dislocation sources increases, supplanting Frank-Read dislocation slip as the dominant deformation mechanism. The grain size at which a cross-over in deformation mechanism occurs is influenced primarily by the stacking fault energy of the specific FCC material under consideration. From an energetics perspective, the stable splitting distance of extended dislocations is inversely correlated with the stacking fault energy parameter [2]. Therefore, as the stacking fault energy increases, the width of the stacking fault ribbon decreases due to the comparatively higher specific energy penalty levied by the planar defect. In this regard, materials with lower stacking fault energies, such as Cu \( (d_{\text{twin}} \approx 100 \text{ nm} [79]) \), exhibit pronounced deformation twinning at larger grain sizes in comparison to high stacking fault energy materials such as Al \( (d_{\text{twin}} \approx 10 \text{ nm} [80]) \). While stacking fault energy can be used to rationalize the length-scale crossover between dislocation slip and deformation twinning in a general sense, it cannot explain the shift in dislocation source from the Frank-Read mechanism towards heterogeneous grain boundary emission.

To understand this shift, the length-scales associated with pile-up from traditional intragranular sources must be considered. Due to the significant repulsive stresses associated with lattice dislocations in a pile-up configuration, intragranular sources can be assumed to not be significantly active in grains with diameters less than twice the critical distance between two dislocations. According to Wang et al. [81], this value can be estimated as \( \approx 20 \text{ nm} \). It should be noted that this value represents a theoretical estimation of pile-up distances which does not account for residual stress fields which are present in a NC microstructure [82]. Practically, Frank-Read dislocation sources are not active in grains less than 1 \( \mu \text{m} \) in diameter [2]. Under these considerations, grain boundary sources are disproportionately active in the deformation of NC materials and serve as the dominant emission source from which dislocations are nucleated.

The cross-over between deformation mechanisms is widely believed to manifest in material properties through the inverse HP relationship, which was described in Chapter 1. The inverse HP effect was initially controversial, with a number of conflicting hard-
2.1. Deformation mechanisms in FCC materials

In some studies, researchers reported a monotonic hardening with grain size, whereas other investigators observed softening at extreme grain sizes (i.e., the inverse HP effect). In an attempt to explain these discrepancies, Fougere et al. [83] proposed that the inverse HP effect arose as a consequence of materials processing conditions. These researchers argued that a monotonic hardening trend is achieved in as-prepared samples (e.g., Ref. [84]), whereas the inverse HP effect is observed when a single sample is successively annealed to increase the grain size for subsequent hardness measurements (e.g., Ref. [4]). Indeed, initial investigations into HP hardening in the NC regime were complicated by difficulties in producing reliable samples. For example, Nieman et al. [85] could not show a clear grain size dependence for yield strength in NC Pd samples formed from an inert gas condensation process due to premature brittle fracture of the Pd samples, which was attributed to sensitivity to sample flaws created during materials processing [86]. These sample preparation issues have been largely resolved through the implementation of manufacturing processes which yield void-free NC materials. For example, Palumbo et al. [87] and El-Sherik et al. [88] have demonstrated reliable softening in as-prepared fully-dense NC NiP and Ni electrodeposited foils, entrenching the inverse HP effect as the strength-limiting feature in grain size refinement.

Targeted MD simulations serve as a high-resolution platform to provide a atomic-scale observation of the influence of grain size on competing deformation mechanisms in the inverse HP effect. In this regard, a number of MD investigations have shown a transition from grain boundary-mediated dislocation-based plasticity (i.e., both dislocation slip and deformation twinning) towards localized grain boundary deformation processes (e.g. GBS) [89–92]. Schiotz et al. [93] considered a wide range of grain sizes varying from 5 to 50 nm in NC Cu and observed a complete transition from dislocation-mediated plasticity towards grain boundary mechanisms. Notably, the scale of this study also provided access to a MD-based assessment of the inverse HP effect. Consequently, Schiotz et al. [93] identified $\approx 10$ nm as the critical grain size in NC Cu at which a maximum strength is measured. Furthermore, the investigators provided a direct link between transition in deformation mechanism to grain boundary processes and the grain size associated with maximum strength, thus elucidating the physical processes underpinning the inverse HP effect. Yamakov et al. [94] quantified and generalized these results to include chemical (i.e., stacking fault energy) effects along with structural (i.e., grain size) in the assessment of competing deformation mechanisms.

Figure 2.17 provides a generalized deformation mechanism map for NC FCC materials after Yamakov et al. [94], which considers the effects of applied stress, stacking fault
2.1. Deformation mechanisms in FCC materials

Figure 2.17: A deformation mechanism map for NC FCC materials after Yamakov et al. [94]. Please see the main text for an explanation of the figure. This figure is reprinted from the original work of Yamakov et al. [94], with permission from the Nature Publishing Group.

energy, and grain size. According to Yamakov et al. [94], the deformation of NC FCC materials may be unambiguously described using two dimensionless parameters, namely: reduced stress $\sigma/\sigma_\infty$ and reduced inverse grain size $r_o/d$. The former dimensionless parameter describes the ratio of applied stress $\sigma$ to the theoretical shear-strength of the material $\sigma_\infty = K\gamma_{\text{isf}}$, where $K$ depends on the elastic moduli of the material and the Shockley partial character, and $\gamma_{\text{isf}}$ is the intrinsic stacking fault energy [2]. Conceptually, $\sigma_\infty$ may be considered as the stress required to bring Shockley partials to an infinite separation, or as the loading required to shear an entire $\{111\}$ slip plane in the $<11\bar{2}>$ crystallographic direction. The latter parameter is the ratio of the zero-load dislocation dissociation distance $r_o$ to the grain size $d$. Based on these parameters, the map is partitioned into three regions. The nucleation relationship $1/d$ describes the required stress to nucleate dislocations from a grain boundary in a NC material [5], and separates
2.2. Heterogeneous microstructures

Grain boundary-mediated deformation (e.g., from GBS) from dislocation-based plasticity. The dissociation distance of Shockley partials under an applied load, and defines the line $d = r$, which separates dislocation slip from partial slip (i.e., deformation twin precursors).

According to Hirth and Lothe [2], $r$ may be calculated as a function of the above parameters:

$$r = \frac{r_o(\gamma_{isf})}{1 - \sigma/\sigma_{\infty}(\gamma_{isf})}$$

(2.3)

The map proposed by Yamakov et al. [94] is an elegant representation of the competition between deformation mechanisms in NC materials. However, the current theory does not consider other state parameters of microstructure which may influence the dominance of particular deformation mechanisms. For example, this approach assumes that the boundary characters of each grain in the microstructure are identical. In a realistic microstructure, deformation is expected to proceed from areas of high free volume at the grain boundary, which amplify the applied stress-field in a manner similar to a crack-tip [33]. This notion adds considerable parametric complexity to the mapping of deformation mechanisms and remains an open theme for investigation.

2.2 Heterogeneous microstructures

Heterogeneities in microstructures are represented by a large number of engineered material offerings. In a broad materials sense, heterogeneous structures can refer to any material system which possesses distinguishable microstructure features. In this regard, composite materials, multi-phase materials, functionally graded materials, and biomaterials can all be regarded as heterogeneous material systems. In this portion of the review, the focus of the literature survey is limited to a discussion of monophase metallic systems whereby heterogeneities arise primarily from differences in lattice organization. In this structural context, heterogeneity is defined as microstructures populated by grain sizes which deviate significantly from the expected log-normal distribution [95]. This definition includes material systems with bimodal or duplex grain size distributions. This section specifically focuses on studies whereby NC and CG features have been incorporated into a microstructure. The engineering motivation for this form of microstructure design is to leverage strength gains from HP hardening in the NC grains with the inherent high ductility of CG crystals. The goal of this section is to establish the limitations of these methods in delivering architectured materials, which may serve as a platform for the targeted study of the length-scale effects on the deformation mechanisms in heterogeneous...
2.2.1 Metallic systems with bimodal microstructures

A discussion of heterogeneous microstructures may most logically be initiated through consideration of the thermomechanical processing technologies, which may be leveraged to embed structural inhomogeneities within a material system. For example, Wang et al. report in separate studies [96, 97] a cryorolling and heat treatment process by which a bimodal microstructure consisting of NC and CG grains may be introduced into a bulk Cu sheet. The processes relies on the abnormal grain growth and subsequent secondary recrystallization of NC grains which were produced during cryorolling. Figure 2.18 shows a bright field transmission electron micrograph of the resulting microstructure. Interestingly, the effects of this bimodal microstructure are synergistic, resulting in improved material toughness, which falls outside the envelope established for Cu. However, due to the uncontrolled distribution of recrystallized grains in this microstructure, an explicitly parametric study of trends in deformation as they relate to the CG volume fraction cannot be conducted. Bimodal microstructures have also been reported for aluminum-based alloys prepared by cryomilling, followed by warm compaction [98] or hot isostatic pressing treatments [99–101]. Similarly, asymmetric rolling paired with partial recrystallization annealing treatments has also been shown to deliver bimodal microstructures in Ti [102] and Al-Mg alloys [103]. Notably, Wu et al. [102] have provided an industrial-scale method by which heterogeneous lamella of CG crystals may be recrystallized within

Figure 2.18: A bright field transmission electron micrograph of the bimodal Cu microstructure. This figure is reprinted from the original work [97], with permission from the Nature Publishing Group.
an ultrafine-grain (UFG) matrix of Ti, leading to significant improvements in mechanical properties and strain hardening over conventional CG Ti. Bimodal material architectures may also be formed using techniques which do not rely on partial recrystallization of the microstructure. Chen et al. [104] have reported a bimodal UFG-NC microstructure populated by a high density of growth twins in Ni formed through chemical vapor deposition.

In general, the mechanical properties of the materials formed using the described methods were found to be improved due to the presence of bimodal crystal features. Conversely, bimodal microstructures produced from partial recrystallization of electrodeposited NC Ni are reported to suffer a substantial drop in elongation to failure under uniaxial tension [105]. This embrittlement during heat treatment is likely due to the segregation of sulphur impurities along the boundaries of recrystallized grains [106]. Although microstructures formed from these processes generally exhibit excellent mechanical properties, heterogeneous material architectures produced using these non-targeted treatments are not suitable for the current study. Specifically, the discussed manufacturing processes may only be homogeneously applied to a material, impairing the ability for precise microstructure control, which limits the possibility for a parametric study of deformation. In this regard, the unique structure-property relationships and deformation mechanisms of heterogeneous microstructures with abrupt discontinuities in structural features may not be studied.

2.2.2 Deformation behaviour of metallic multilayers

A targeted length-scale study of deformation mechanisms in heterogeneous microstructures requires material architectures which provide a pathway for direct parametric study. The ML concept represents an ideal format, whereby layer thicknesses may be controlled through additive manufacturing principles, permitting a controlled study of length-scale. The following section briefly reviews the relevant published literature pertaining to the deformation behaviour MLs.

MLs are a layering of alternating material structures and represent an architecture which may be engineered to improve the relative mechanical properties of the constituent material components [107–110]. In traditional ML architectures, immiscible metallic species are selected for layering such that geometric confinement imposed by layer interfaces is augmented by lattice misfit between constituents, leading to increases in interfacial barrier strength [111, 112]. Figure 2.19 depicts a bright field transmission electron micrograph of a Cu/Nb ML with layer thicknesses of 0.8 and 20 nm. The relation-
Figure 2.19: A bright field transmission electron micrograph a Cu/Nb ML with layer thicknesses of \( t = 0.8 \) (a) and 20 (b) nm. This figure is reprinted from the original work [113], with permission from Elsevier.

The relationship between strength and layer thickness \( (h) \) in MLs by dislocation pile-up mechanisms \( (\sigma_{YS} \propto h^{-1/2}) \) is analogous to HP strengthening \( (\sigma_{YS} \propto d^{-1/2}) \). The layer thicknesses in a ML may be refined in order to encourage specific dislocation-based strengthening mechanisms. For example, experimental and atomistic simulations have shown that as layer thicknesses reach into the nanometer regime, interfacial confinement effects suppress traditional Hall-Petch hardening and dislocation pile-up phenomena [114–116]. At these length scales, conventional dislocation-based plasticity is supplanted by dislocation confinement and transmission within individual layers, leading to significant gains.
in mechanical strength that exceed Hall-Petch predictions [114–116]. Once layer thicknesses approach sizes comparable to a dislocation core (\(\sim 1–2 \text{ nm}\)), interfacial barrier strength has been shown to reduce, promoting interlayer dislocation transmission and, consequently, a reversal of strength improvements from geometric scaling effects [117], which is similar in principle to the inverse HP effect. Figure 2.20 schematically shows the transition of deformation mechanisms with ML layer thickness.

Although the presence of nanoscale geometric features in metallic MLs have led to impressive improvements in strength, as discussed by Anderson et al. [108], confinement from a high density of interfacial misfit dislocations may lead to notable decreases in ductility and a ductile-brittle transition in fracture behavior. For example, uniaxial tensile tests of Cu/Ag MLs show a two-fold decrease in elongation to failure at layer thicknesses of less than 40 nm when compared against monolithic samples of the same materials [118]. A similar finding was echoed in a tensile investigation of Cr/Cu MLs [119], where the dislocation storing capability of the relatively ductile Cu constituent becomes compromised at layer thicknesses less than 100 nm. In nanoscale Cu/Au and Cr/Cu MLs, these reductions in elongation to failure are observed to create fracture surfaces exhibiting brittle failure [120]. Ultimately, lattice mismatch at interfacial structures

\[ \sigma \propto \ln(h/b)/h \]

\[ \sigma \propto h^{-1/2} \]
in traditional MLs are generally detrimental to plastic flow, making preservation of the intrinsic ductility of such material architectures problematic. Additionally, in the case of hard-soft nanostructured MLs such as Cr/Cu, material elongation is further handicapped by a significant decrease in the dislocation storage capability of the Cu layer at nanometer thicknesses [120]. In a notable exception to this property trend, Mara et al. [121] have reported a measurement of ultra-high strength and a ductility of greater than 0.25 true strain in 5 nm Cu/Nb ML pillars under compressive loading. It is unclear from this study, however, if similar strains may be achieved under tensile loading.

The current body of literature regarding MLs serves as an excellent basis for the consideration of deformation mechanisms in heterogeneous microstructures. However, as the vast majority of ML studies are directed on structures with dissimilar layering species, a purely structure-based assessment of deformation behaviour has not been performed. Furthermore, the concept of grain size modulation through NC and CG layering has been largely ignored in the structural design of MLs. Currently, there exists only a single set of studies on single-chemistry MLs with modulated grain sizes in the literature [122–124]. However, as reported by Kurmanaeva et al. [122], these NiFe MLs are multi-component and possess both FCC and BCC phases, which raises the complication of interphase lattice misfit and again convolutes a purely structure-based investigation. Therefore, an unambiguous assessment of length-scale as it relates to interacting deformation mechanisms in heterogeneous microstructures with CG and NC features is absent from the literature, and represents the primary motivation for this thesis work. The ML architecture presented in Figure 1.3 provides an ideal format to examine the effects of length-scale and serves as the structural template for the experimental, computational, and analytical techniques which are implemented in this thesis work.

2.3 Chapter summary

The current chapter has provided an overview of the relevant background material pertaining to dislocation-based deformation mechanisms in FCC materials. In this context, the important deformation mechanisms which are active in coarse-grained and nanocrystalline materials have been overviewed. A specific focus on the process of deformation twinning has been presented, as it proves relevant in the future chapters of this thesis. Additionally, the existing literature on the deformation behaviour of heterogeneous structures, including bimodal and multilayer materials has been critically reviewed.
Chapter 3

Materials and Methods

The purpose of the following chapter is to provide background regarding the manufacture of the ML materials and the characterization methods by which they are examined in this thesis. The discussion begins with a consideration of the strengths and drawbacks of ML manufacturing techniques and continues with an overview of the experimental, computational, and analytical methodologies which are implemented in the forthcoming analysis.

3.1 Multilayer manufacturing techniques

Due to the architecture of the ML structure, these materials cannot be readily manufactured using traditional top-down techniques. Additive manufacturing practices, however, are ideally suited for ML manufacture as they offer unparalleled engineering control over thicknesses and relative volume fractions of ML constituent layers. MLs with dissimilar layer chemistries have been produced using a variety of additive vapor deposition techniques, such as ion beam [125] and magnetron sputtering [113], electron beam deposition [126], and other evaporative techniques [127], which offer precise control of individual laminate thicknesses at the atomic length-scale. However, these techniques typically have very low deposition rates ($\approx 1 \, \mu\text{m/hr}$) and do not offer a method to explicitly control grain size, making them not appropriate for the current study. More recently, accumulative roll bonding (ARB) has emerged as a mechanical process by which bulk MLs may be manufactured. For example, dissimilar MLs formed from Zr/Nb [128] and Cu/Nb [129] have been manufactured using an ARB process. However, since ARB relies on severe plastic deformation for grain size refinement, the process inherently does not provide a robust or easily controllable pathway for the fabrication of heterogeneous microstructures. For an extensive review of ML manufacturing techniques, please see the review.
from Was and Foecke [130].

### 3.1.1 Pulsed electrodeposition of MLs with modulated microstructures

Electrodeposition (or electroplating) is an electrochemical process by which metallic species are dissolved at an anode, transmitted through a conductive electrolyte bath, and deposited on a cathode through the application of an electric field. It has been used to deposit dissimilar MLs composed of Ni-Cu with good success [110, 131]. Pulsed electrodeposition (PED) is a particularly attractive additive process which offers a high degree of microstructure control through manipulation of the applied electric pulse profile as well as a relatively high deposition rate (> 100 μm/hr). The process is highly scalable, permitting the manufacture of bulk free-standing foils. Electrodeposition is a versatile manufacturing technique, and may be used to deposit nanocrystalline metal, alloy, and multiphase films composed of Au [132], Co [133], CoP [134], CoCu [135], Cu [136], Ni [88], NiFe [137], NiCo [138], and NiP [139]. This list is not exhaustive but serves to indicate the wide range of materials which may be deposited using electrodeposition. The main components of a typical electrodeposition apparatus are provided in Figure 3.1.

NC foils are readily manufactured by PED through pulse profile shaping, and through the use of bath additives. The pulse duration, current density, polarity, and duty cycle are all parameters which may be modified to precisely control the grain size and uniformity of the deposited microstructure. Generally, the process parameters modified in the deposition of NC films serve to alter the deposition kinetics to encourage grain nucleation over grain growth. The basics of PED as it relates to NC films are available in patents and published literature from Erb [141], Erb and El-Sherik [142], and El-Sherik and Erb [143]. Figure 3.2 presents the parameters which may be modified in a pulse plating waveform. In general, the pulse intensity and duration as well as the duty cycle may be controlled through alteration of $J_p$, $T_{on}$, and $T_{off}$ (see the figure). These waveform parameters are critical in the deposition of NC microstructures as they serve to maintain the required chemical gradients in the boundary layer surrounding the cathodic surface during PED. Modifications to the pulse plating parameters may be programmed at any time during deposition, permitting the fabrication of modulated microstructures with NC and CG features. Additionally, the periodic switching of pulse plating recipes offers a pathway to create ML structures, where the relative duty cycle of NC and CG recipes may be used to deposit constituent layers with excellent thickness control. The implementation of PED for ML manufacture has been explored by Chan et al. [144] for CG-UFG NiFe
MLs, showing a clear modulation of grain sizes with well defined layers. Given its scalability, high deposition rate, and excellent microstructure control, PED represents an ideal process, by which MLs with targeted architectures may be manufactured.

For this thesis work, NiCo ML samples were manufactured using a proprietary PED process developed by Integran Technologies Inc. The reasons for selecting NiCo for this study are two-fold. First, the addition of Co is known to lower the stacking fault energy in the Ni system [145–147], which increases the likelihood of competition from deformation twinning during mechanical loading. Second, nickel-rich NiCo MLs are all expected to be in the FCC phase as these metallic species exhibit perfect solid solubility at chemistries greater than 40 wt% Ni [148], precluding complications in analysis arising from the formation of secondary phases. Therefore, the NiCo system possesses the ideal characteristics for a targeted analysis of ML layer thickness effects on active deformation mechanisms.
3.2 Experimental testing methods

The following section describes the experimental methodologies which are implemented in this thesis work. The working principles of the various electron microscopy and crystallographic analysis techniques employed in this thesis are discussed. Additionally, mechanical testing protocols such as uniaxial tensile testing and nanoindentation, as well as image processing techniques such as digital image correlation are also described. For the purposes of brevity, only the major experimental techniques used in this thesis are discussed in this section.

3.2.1 Scanning and transmission electron microscopy

As an analytical tool for high-resolution imaging of materials, electron microscopy is most commonly utilized in two formats: scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In the former technique, electrons are accelerated and focused into a probe which is typically $<$ 10 nm in diameter and is rastered across a surface of interest. Imaging is achieved by the collection of electrons which are

![Figure 3.2: A schematic of a typical pulse plating waveform. $T_{on}$ and $T_{off}$ determine the pulse duration and off-time respectively. $J_p$ is the peak current density of the applied electric field and $J_m$ is the average current density. This figure is reprinted from its original source [143], with permission from Springer.](image-url)
3.2. Experimental testing methods

Figure 3.3: A diagram of beam-specimen interactions in SEM analysis. \( \lambda \) represents the mean free path of the incoming probe (B). Arrows indicate ionization events and the release of an SE. The path of the incoming probe is elastically scattered and emerges as a BSE. This figure has been reprinted from the original text [149].

emitted from the bombarded surface and contrast arises from differences in the electron signal due to sample interactions. The emitted electrons are classified into two major categories: secondary electrons (SE), which are created due to ionization of the radiated target surface (energies typically \(< 50 \text{ eV}\) ), and backscatter electrons (BSE), which are created through high angle elastic scattering interactions of the probe beam with the sample. Due to their low energy, SEs have a shallow escape depth and provide good topographic contrast, whereas BSEs provide excellent elemental and crystallographic contrast due to increased elastic interactions with higher Z materials and differential channeling cross-sections for various crystallographic planes. The resolution of an SEM image is ultimately limited by the beam-specimen interaction volume, which defines the effective region of electron emission due to probe radiation. Figure 3.3 provides an illustration of the beam-sample interactions in SEM analysis. For an excellent text regarding the use of SEM, please see Ref. [149].

In contrast to SEM, TEM relies on the differential electron transparency of materials as its contrasting mechanism. Due to this requirement of electron transparency, the incident beam must be accelerated to extremely high voltages (generally \(> 100 \text{ kV}\) ) and samples of interest must be sufficiently thin (typically less than 100 nm thick) such that a high yield of transmitted electrons may be collected to form an image. There are two primary imaging modes used in TEM analysis: namely, dark field (DF) and bright field (BF). In DF imaging, electrons which have undergone elastic scattering events during
3.2. Experimental testing methods

Figure 3.4: A ray diagram for BF and DF imaging conditions. The objective aperture is placed in the path of the direct beam for BF imaging (a), and it is placed in the path of a diffracted beam for DF imaging (b). This figure has been reprinted from the original text [150]. It should be noted that this schematic is presented purely for illustrative purposes. In normal DF imaging, the incident beam is tilted such that the diffracted beam is aligned to the optical axis of the TEM. This helps reduce spherical aberrations in imaging.

progression through a sample are collected while the unscattered electrons are ignored. In its most primitive mode of operation, this selective filtering is achieved through the use of an objective aperture which physically blocks the transmitted beam, permitting image formation from select diffracted electrons. Therefore, DF imaging is highly sensitive to diffraction effects and provides excellent crystallographic contrast, whereby selected structures may be imaged with high contrast by configuring the TEM beam to bring the target planes into a near Bragg condition. Under a Bragg condition, the Ewald sphere of reflection is oriented to intercept the reciprocal lattice at points corresponding to the desired diffracting planes, permitting observation of the scattered beams. Conversely, in BF imaging only the unscattered electrons are collected to form an image. BF contrast arises primarily from differences in transmission behaviour between materials of different phases, although it does provide some crystallographic contrast in a manner similar to the channeling effect in the BSE signal in SEM imaging. Figure 3.4 provides a schematic of a ray diagram for the BF and DF imaging modes. For more information, please see the text from Williams and Carter [150] which is the authoritative resource on TEM.

In addition to imaging, electron-sample interactions in the SEM and TEM may be
3.2. Experimental testing methods

utilized to perform spectroscopy analysis. Energy dispersive X-ray spectroscopy (EDX),
for example, is an elemental analysis technique whereby characteristic X-rays (e.g. Kα, Kβ, Lα) may be collected to determine the chemical composition of a sample. The precise energies of each characteristic X-ray varies by element, therefore providing a basis for characterization. The technique relies on the ejection of inner shell electrons and formation of electron holes through specimen-beam interactions. The migration and decay of higher energy electrons into the electron holes then leads to the emission of a characteristic X-ray. The emitted X-rays may then be collected and analyzed to determine the specimen composition. This technique may be leveraged with beam-rastering (SEM) to provide a high resolution elemental map of a target specimen.

3.2.2 Crystallographic analysis

The wave-nature of the electron beam in the SEM and TEM may be leveraged to perform diffraction analysis on crystalline specimens. For example in the SEM, electron backscatter diffraction (EBSD) analysis is a popular technique which can be used to determine the orientation relationships between the important crystallographic directions of a specimen microstructure and the relevant laboratory axes. In EBSD, the Bragg scattering of BSEs is utilized to determine crystallographic orientation. In practice, a specimen is tilted at a large angle relative to the incident electron beam (usually 70°) to increase the BSE signal. BSEs emergent from the specimen surface at a Bragg condition constructively interfere, forming a complex of interference patterns which are each associated with diffraction from a particular crystallographic plane. These interference patterns may be envisaged as a series of cones of diffracted electrons which emanate from the measurement site. These cones each have an interior angle of nearly 180°, due to the low Bragg angles associated with electron diffraction. These patterns are imaged by a phosphor screen which is placed in the path of the scattering front. The interference patterns appear as bands of contrast on the phosphor screen which are known as Kikuchi bands. The width and orientation of the Kikuchi bands are directly related to the underlying crystallography of the measurement point, and may be indexed in order to ascertain the orientation of the crystal relative to the measurement axes. Figure 3.5 provides a schematic of the working principle of EBSD as well as an example of an EBSD pattern with a network of Kikuchi bands visible. Further information regarding EBSD may be found in the text of Goldstein [149].

In the TEM, crystallographic analysis may also be achieved using diffraction effects from specimen-beam interactions. In contrast to the backscatter diffraction in the SEM,
3.2. Experimental testing methods

Figure 3.5: (a) The setup for EBSD analysis inside an SEM. The tilted specimen is exposed to the electron beam. A diffraction cone from a single crystallographic plane is shown. The front of this cone is intercepted by a phosphor screen and the interference pattern appears as a line of contrast. The interior angle of the cone is close to 180° and is not drawn-to-scale here for illustration purposes. The simultaneous capture of several diffraction cones leads to the formation of the EBSD pattern shown in (b). The width and relative orientation of Kikuchi bands may be used to determine the orientation of the important crystallographic directions relative to the measurement axes. This figure has been reprinted from the original text [149].

Diffraction analysis in the TEM relies on the interference of the transmitted (direct) electron beam. During TEM observation, the incident beam is elastically scattered from interactions with the planes of a crystalline specimen. Constructive interference of the scattered electrons is achieved at angles which satisfy the Bragg condition for a particular set of crystallographic planes. These coherent wavefronts of diffracted electrons appear as specular ‘reflections’ which may be detected by a phosphor screen or camera which is placed in the path of the transmitted electron beam. The distance of the diffracted spots from the transmitted beam is directly related to the screen-sample distance, and the parameters in Bragg’s law, such as the wavelength of the incident electron beam and the interplanar spacing of the diffracting crystallographic planes. These spots may be indexed, which then provides information regarding the orientation of the sample relative to the electron-beam. Figure 3.6 provides the working principle of transmitted diffraction within a TEM. See the caption for a description of the symbols. Further information regarding diffraction analysis in the TEM may be found in the text of Williams and Carter [150].

In addition to electrons, X-rays may also be used to perform diffraction analysis. X-
Figure 3.6: A schematic representation of diffraction in a TEM. The incident beam is diffracted from planes \((hkl)\) at an angle of \(2\theta\) relative to the direct beam, which is twice the Bragg angle. The direct beam and diffracted beam spots are separated by a distance \(R\) at a sample-detector distance of \(L\). \(d\) in this figure refers to the interplanar spacing of \((hkl)\) and should not be mistaken for the grain size. This figure has been reprinted from the original text [150].

Ray diffraction (XRD) is the oldest of the crystallographic analysis techniques. It operates from same principles of Bragg diffraction as electron diffraction and therefore is not re-viewed here in great detail. The primary difference between XRD and electron diffraction is the wavelength of the incident radiation. Electrons typically possess wavelengths on the order of picometers whereas X-rays operate at wavelengths in the Angstrom range. The reader is referred to the definitive text from Cullity for further information regarding XRD [151].

3.2.3 Mechanical testing protocols

Uniaxial tensile testing and digital image correlation

Uniaxial tensile testing is a mechanical deformation process by which a material is subjected to unidirectional loadings from a rigid testing frame. Generally, uniaxial tensile testing is considered as a “weakest-link” assessment of mechanical properties, as
all areas of a tensile specimen may be subjected to equal loadings provided the specimen is designed with a uniform cross-section. The loadings may be applied at a constant velocity or loading rate, or using a combination of these schemes. The mechanical response of a material is represented in normalized values of load and extension (i.e., stress and strain), in order to permit comparison of mechanical properties between specimens of differing cross-sectional dimensions. The stress-strain response of a typical metal is provided in Figure 3.7 along with schematics of the material cross-section at each stage of loading. As shown in the figure, the initial stages of loading exhibit a linear relation. This portion of the stress-strain curve represents the elastic response of the material and the slope of this curve is the elastic or Young’s modulus ($E$). The non-linear portion of the stress-strain curve represents the plastic response of the material. As indicated in the insets in the figure, the cross-section of the tensile specimen undergoes a series of changes

![Figure 3.7](image-url): A typical stress-strain response of a metal loaded under uniaxial tension. Please see the main text for a discussion of these symbols. This figure has been reprinted from the original work [3].
during plastic loading. The initially uniform specimen, begins to deform in a highly localized “neck” region after reaching the peak load (point M in the figure), whereby ultimate fracture is observed to occur (point F in the figure). The stress at the peak load corresponds to the ultimate tensile strength of the material (point TS in the figure), which represents the maximum stress that this material can endure without undergoing fracture. For further details, please see Ref. [152].

In a stress-strain test, stress is measured through the use of a load cell, which is a force transducer that typically relies on a resistance change in an internal strain gauge to measure applied force. Engineering stress may then be directly determined through consideration of the undeformed cross-sectional area of the tensile specimen. The measurement of strain is somewhat of a more complicated proposition. Due to compliance of the loading frame, which may be considered as an elastic spring in a series configuration with the tensile specimen, the displacement of the loading segments cannot be used to determine the applied strain with perfect accuracy. The error between the measured frame displacement and the true applied strain is magnified as the applied load increases, making the testing of NC metals particularly problematic. However, methods to extract applied strains exist which do not depend explicitly on measurement of frame displacement. For example, digital image correlation (DIC) is a non-contact method that does not suffer from frame compliance error and can be leveraged to resolve 3D surface strains during deformation. Under DIC, images are captured of a specimen during deformation by a camera system, which are then processed by a computer. Using image recognition algorithms, the computer can detect relative displacements in a tensile sample by tracking the trajectories of characteristic features. These characteristic features permit a meshing of the tensile sample images into a series of facets. Tensile samples may be coated with a “speckle” pattern prior to deformation to increase the number of features for detection. Figure 3.8 illustrates the process of determining strain using DIC. Referring to the figure, once the sequence of images taken during deformation is meshed into a consistent set of facets, the coordinates \((x', y')\) of Q' may be directly determined by using the following relations (2D case):

\[
x' = x + u_x + \frac{\delta u_x}{\delta x} \Delta x + \frac{\delta u_x}{\delta y} \Delta y \tag{3.1}
\]

\[
y' = y + u_y + \frac{\delta u_y}{\delta x} \Delta x + \frac{\delta u_y}{\delta y} \Delta y \tag{3.2}
\]

In this formulation, the extensional \((\varepsilon_x\ \text{and} \ \varepsilon_y)\) strains as well as the shear strain \((\varepsilon_{xy})\) are represented by the relative displacement between P’ and Q’ and may be mathematically
3.2. Experimental testing methods

Figure 3.8: The basics of DIC analysis. Characteristic features from a speckle pattern are used to facet the surface of a tensile sample via image processing algorithms. The relative displacements between points in facets is used to measure the applied strain during deformation.

defined as:

\[
\varepsilon_x = \frac{\delta u_x}{\delta x} \quad (3.3)
\]
\[
\varepsilon_y = \frac{\delta u_y}{\delta y} \quad (3.4)
\]
\[
\varepsilon_{xy} = \frac{\delta u_x}{\delta y} + \frac{\delta u_y}{\delta x} \quad (3.5)
\]

For a more detailed discussion of DIC analysis, please see Ref. [153].

Nanoindentation testing

The elastic moduli of materials may be measured using instrumented nanoindentation equipment. In general, during instrumented nanoindentation testing, a hard indenter tip of known mechanical properties and a precisely manufactured geometry is plunged into a test sample and the resulting displacement and force on the indenter tip are recorded. The most commonly used tip geometry in nanoindentation is the Berkovich tip, which has
the profile of a triangular-based pyramid with an interior half angle of 65.27° (measured from indenter axis to pyramid-face flat). The elastic modulus of an indented sample may be determined using the method of Oliver and Pharr [154], which is the most commonly used methodology for mechanical property assessment via nanoindentation. Figure 3.9 provides a cross-sectional schematic of the important parameters used in Oliver-Pharr analysis and also provides a typical load-displacement profile from an indentation experiment. From contact mechanics, the indenter tip and test surface made be considered as two springs in a series configuration. The reduced modulus of contact \( E_r \) is related to the individual moduli of the indenter tip and test sample by the relation:

\[
\frac{1}{E_r} = \frac{(1 - \nu^2)}{E} + \frac{(1 - \nu_{tip}^2)}{E_{tip}}
\]  

(3.6)

where \( E \) and \( \nu \) are the Young’s modulus and Poisson’s ratio for the sample, and \( E_{tip} \) and \( \nu_{tip} \) are the equivalent parameters for the indenter. \( E_r \) may be calculated from nanoindentation data as:

\[
E_r = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A}}
\]

(3.7)

where \( A \) is the area of contact, \( \beta \) is a geometric constant equal to 1.034, and \( S \) is the tangent modulus of the load-displacement curve upon unloading from the maximum load, as shown in Figure 3.9b. The area of contact \( A \) depends on the indenter geometry and is a function of the contact depth \( (h_c) \). For a perfect Berkovich indenter, the contact area may be estimated as \( A(h_c) = 24.5h_c^2 \). Referring to Figure 3.9, at maximum load \( h_c = h_{max} - h_s \) and \( h_s = \varepsilon P_{max}/S \). \( \varepsilon \) is a geometric constant which typically takes on a value of \( \varepsilon = 0.75 \) for a Berkovich indenter. Higher order polynomial forms of the area tip function may be implemented to compensate for an indenter with small geometric flaws, such a tip blunting or rounding effects. These imperfections tend to be only significant at very low indentation loads (< 5 mN). However, if compensation for tip geometry is required, the area tip function must be iteratively solved. This process involves performing nanoindentation tests at several loads on a sample, followed by iterative calculation of \( A(h_c) \) from Eq. 3.7. Additionally, compliance effects from the indenter frame are typically accounted for in nanoindentation testing. However, the indenter equipment used in this thesis independently accounts for frame compliance, and therefore these effects are not considered here. Under testing programs where indentation loads are sufficiently high and the influence of frame compliance is separately compensated, the elastic modulus may then be directly determined explicitly through calculation of \( S \) and \( A \) at max load and solving Eqs. 3.6 and 3.7. In this calculation, the effects of material pile-up
Figure 3.9: (a) A cross-sectional schematic of the important parameters used in Oliver-Pharr analysis. (b) A typical load-displacement curve for a nanoindentation test. Please see the text for a discussion on the Oliver-Pharr method which is commonly implemented to extract the elastic modulus from the unloading curve of an instrumented indentation experiment. This figure has been reprinted from the original work [154] with permission from Cambridge University Press.
around the tip during indentation are not explicitly accounted for. For materials which undergo significant pile-up, direct imaging of the indent impression is required to ascertain the exact contact area. For additional information regarding mechanical property measurement from instrumented indentation experiments, please see the original work of Oliver and Pharr [154].

3.3 Computational methods

In the following section, a general discussion of the computational methods implemented in this thesis work is undertaken. Specifically, details regarding the approach used to generate microstructures for MD simulations and an overview of the kinetic Monte Carlo (kMC) method are provided. The modulus and stacking fault energy of the NiCo interatomic potential used in MD simulations has been characterized for validation purposes. The in-house MATLAB codes which were written to create MD microstructures and conduct kMC simulations are available from the author upon request.

3.3.1 Generation of microstructures for polycrystalline MD simulations

In this subsection, the methodologies used to create supercell configurations for MD simulations are discussed. This discussion begins with the strategies used to generate a physically realistic microstructure and continues with a thorough validation of the atomic configurations. Additionally, the interatomic potential used during MD simulations is examined. The first consideration when developing atomic configurations for polycrystalline MD simulations is the method by which microstructure may be formed. In this regard, there are a number of different strategies to form microstructure. The main criterion for microstructure generation is that the scheme by which grains are generated should yield a fully dense partitioning of a volume, that is comprised of closed convex hulls which are connected by a network of interfacial planar regions and triple junction nodes. The Voronoi tessellation is recognized as one of the most popular volume partitioning algorithms for the formation of microstructures and has been leveraged in several polycrystalline MD studies [59, 155–159]. Based on the assignment of randomized points within a volume, the Voronoi tessellation partitions space into a fully-dense distribution of convex polyhedra, which can be used to form the hulls of grains in a microstructure. Additionally, a particularly attractive feature of the Voronoi tessellation is the ability to specify the average grain size of the microstructure \textit{a priori} by controlling
3.3. Computational methods

Figure 3.10: Voronoi tessellations in 3D (a) and 2D (b). The seeds used in the partitioning scheme are shown as black points. The original cubic/square cell to be partitioned is outlined. (c) Replicas of (b) are translated along the horizontal and vertical directions of the unit cell, highlighting the preservation of periodicity.

the seed density within the partitioning volume. In this thesis work, Voronoi tessellations were performed using the Voro++ library developed by Rycroft [160]. Figure 3.10 shows examples of 2D and 3D Voronoi tessellations generated using the Voro++ library. The black points in Figure 3.10a and b represent the Voronoi seeds, which form the basis of the partitioning scheme and the cube/square represents the partitioned volume/area. Although the partitioning does not appear to be fully dense, this scheme was implemented to enforce periodic boundary conditions. As shown in Figure 3.10c, when replications of the 2D Voronoi cells are considered, a fully-dense partitioning of the volume is achieved.

A histogram of the distribution in polyhedra sizes for a very large 2D Voronoi tessellation with a targeted grain size of 20 nm is presented in Figure 3.11a, showing good agreement in statistical terms. In this measurement, the grain size is considered to be the average of the caliper dimension of the polyhedra. It was found that the caliper dimension measurements collected yielded similar results to other measurement strategies such as the line-intercept method of Mendelson [95]. The distribution of grain sizes is log-normal, which can be seen by the cumulative distribution function (CDF) and quantile-quantile plots provided in Figures 3.11b and c.

Having established a reasonable model for a grain, it becomes necessary to develop a scheme to populate each grain with atoms. In this regard, the scale of simulations becomes a primary consideration. Current computational hardware limitations restrict MD simulations to less than \( \approx 10 \) million atoms. For a fully 3D microstructure, this restriction limits the scale of the supercell to approximately 10000 nm\(^3\), or \( \approx 20 \times 20 \times 20 \) nm for a supercell of equal dimensions. For the purposes of modeling MLs, these length-scale limitations are rather problematic. However, the use of quasi-3D microstructures,
3.3. Computational methods

Figure 3.11: (a) A histogram of sizes for 1848 grains produced by the Voronoi tessellation. The measured average grain size is $20.2 \pm 0.1$ nm (Standard Error), which is in good agreement with the target of 20 nm. (b) A cumulative distribution function plot of a nominal log-normal distribution along with the actual measurement based on the distribution in (a). (c) A quantile-quantile plot of the histogram data for a log-normal distribution. The data largely follows a linear trend, indicating that the Voronoi tessellation can produce a log-normal grain size distribution.
3.3. Computational methods

Figure 3.12: A pole figure for a quasi-3D microstructure with a [110] sacrificial dimension. This sacrificial dimension acts as a zone axis for all the grains in the microstructure, as required to enforce periodic boundary conditions on the supercell. The red marks indicate the positions of the simulated crystal poles relative to the observation frame.

whereby one of the supercell dimensions is sacrificed to expand the lateral size of the simulation, is a common approach implemented to combat length-scale limitations. For metals, where dislocation-based processes are of highest interest, the size of the sacrificial dimension can be reduced to $\approx 2$ nm without introducing spurious forces through periodic replications of a supercell [22]. However, the sacrificial dimension must be orthogonal to the active slip system during deformation to avoid periodic image artifacts.

The implementation of a sacrificial dimension raises additional restrictions on the MD supercell. Due to periodicity requirements, the texture of the lateral grains is restricted to a common zone axis which must be shared by all grains in the microstructure to prevent stacking faults through the periodic images of the supercell. Figure 3.12 illustrates a stereographic projection of the poles for a quasi-3D microstructure where the [110] direction is chosen as the sacrificial dimension. For the remainder of this thesis, all microstructures discussed are of a quasi-3D geometry due to the length-scale requirements of the MD simulations.

In order to populate the Voronoi polyhedra with atoms, a grain-filling scheme was programmed into MATLAB, whereby extremely large single crystals with the appropriate
3.3. Computational methods

Grain texture were generated. The single crystals were generated based on a FCC lattice motif with a lattice parameter of 0.352 nm. The crystals were designed to be bigger than the largest caliper dimension of each of the grains in the microstructure such that atoms which fall outside the convex hull may be trimmed from the final atomic configuration. A deletion scheme was also used to remove one atom from a pair of interfacial atoms whose interatomic distance was found to be less than the closed-packed distance of an FCC structure \( a_0/\sqrt{2} \). The intragranular regions were observed to have perfect FCC coordinations for every microstructure generated. Figure 3.13 illustrates a planar view of a quasi-3D microstructure (from Figure 3.10b) which has been populated with atoms \( d_{NC} = 20 \text{ nm} \). The sacrificial dimension is perpendicular to the paper plane. The structure is observed to be fully dense and possesses a well connected grain boundary network, with triple junctions comprising the majority of the microstructure nodes. However, some quaternary nodes are visible in the topology. It should be noted that the relative fraction of quaternary nodes is expected to be higher in a quasi-3D structure due to the dimensional restrictions placed on allocation of Voronoi seeds. The atoms are colored using the common neighbour analysis (CNA) algorithm, with green indicating an atom in perfect FCC configuration and black representing atoms in a defective position (i.e., at a grain boundary or triple junction). The proper enforcement of periodicity in the supercell is evident in the figure.

While it is difficult to quantitatively assess the grain boundary configurations created by the grain-filling algorithm, it is possible to compare the fraction of intercrystalline atoms in the supercell against analytical expectations. Based on the work of Palumbo et al. [161] for grains with a tetrakaidecahedron shape, the volume fraction of intercrystalline atoms \( V_{IC} \), i.e. atoms which exist at a grain boundary or triple junction) may be calculated as:

\[
V_{IC} = 1 - \left[ \frac{d - \Delta}{d} \right]^3
\]

(3.8)

where \( d \) is the grain size and \( \Delta \) is the assumed grain boundary thickness. The CNA algorithm may be used to identify intercrystalline atoms in MD supercells. Figure 3.14 provides a comparison of Eq. 3.8 for different assumed grain boundary thicknesses with the results of the CNA algorithm applied to MD supercells with \( d_{MD} = 5-25 \text{ nm} \). A lower limit of \( \Delta = a_0/\sqrt{2} \approx 0.25 \text{ nm} \) was established for these calculations and the MD supercell was constructed using the method discussed previously. The standard embedded atom method (EAM) interatomic potential of Mishin et al. [162] was used to validate this grain-filling scheme.

As shown in the figure, the MD data follows the same trend as the analytical ex-
3.3. Computational methods

Figure 3.13: An example of a quasi-3D microstructure generated using the Voro++ library and MATLAB grain-filling program in top and side views. The sacrificial dimension is shown as the side view. Atoms coloured in green possess a perfect FCC coordination whereas atoms in black are in a defective position (i.e., at a grain boundary). All grains in this microstructure share a common [110] axis, which is perpendicular to the plane of the page.

Expectations and falls between $\Delta = 0.25$-0.5 nm. It should be noted that in experiments, the grain boundary thickness is typically taken to be $\approx 1$ nm [161]. One possible interpretation for the discrepancy between MD simulation and experimental measurements of grain boundary thickness lies with the measurement technique. The CNA algorithm considers the local neighbourhood of an atom to determine if it is in a defective position. This determination considers only the existence and coordination of the nearest neighbours, and is insensitive to interatomic distances. In this regard, the CNA algorithm is highly robust, and can accurately identify phases in high temperature materials where bonding distances fluctuate rapidly due to thermal oscillations. However, due to this behaviour, the CNA algorithm may only capture the grain boundary core atoms. The algorithm is not sensitive to minor dilations of the lattice, which are expected to exist in regions near a grain boundary. Atoms existing in these regions are therefore omitted from intercrystalline calculations. Conversely, experimental measurements of grain boundary thickness typically involve high-resolution TEM microscopy or bulk resistivity
measurements which can capture dilatory lattice effects near interfaces. Therefore, the differences between the MD measurements and experimental values of grain boundary thickness reflect the sensitivity of each technique to changes in the lattice. For more information regarding the CNA algorithm, please see the work from Faken and Jónssson [163]. The centrosymmetry (CS) parameter represents an alternative determination of atomic packing which may also be used to identify grain boundary atoms in MD. Unlike the CNA algorithm, the CS parameter is highly sensitive to small changes in interatomic spacing and may be used to better identify intercrystalline regions. CS is a continuous parameter, and therefore may be coloured using a colormap. One drawback, however, is that it is very sensitive to thermal vibrations and can easily false-identify intragranular atoms as existing in a defective position. Further information regarding the CS parameter and its determination may be found in Ref. [164]. Figure 3.15 provides a high resolution image of a grain boundary taken from a MD supercell. The boundary is coloured using both CS and the CNA algorithm, illustrating the differences between these two atomic packing parameters.
Figure 3.15: (left) A grain boundary coloured using the CS parameter. In this color mapping, blue atoms are in a FCC condition and atoms which are coloured red have the highest CS value, representing an area of high lattice disorder. False-positives are evident in the intragranular region. (right) The same grain boundary coloured using the CNA algorithm. In this visualization, green atoms are considered to be in perfect FCC coordination, whereas white and red atoms represent atoms in the “other” and hexagonal close-packed conditions, respectively. Based purely from an examination of the atomic colouring, the differences in the grain boundary thicknesses between the two techniques are apparent. Two extended dislocations are also visible in the bottom right corner of each image.

3.3.2 Validation of the interatomic potential

In this thesis, the interatomic interactions are modeled using a relatively new potential from Purja Pun et al. [165]. Although not explicitly designed for the exact NiCo compositions which are targeted in this study, atomic configurations generated using this potential remain stable with perfect solid solution and maintain the proper FCC unit cell and lattice parameter. For validation purposes, a number of basic checks of the mechanical response of the potential were undertaken. As previously mentioned, the solid solution effects were not found to considerably stiffen the experimental samples relative to pure Ni. Therefore, the elastic modulus of MD supercells loaded under the NiCo potential was evaluated and compared against the known value for CG Ni. Microstructures with average grain sizes varying from 5 to 25 nm were produced using the methods described previously and then mechanically tested under constant stress uniaxial loading in MD simulations. Figure 3.16 presents the elastic modulus measurements of these microstructures. As shown in the figure, the MD results are relatively comparable to the CG expectations for polycrystalline Ni (207 GPa [166]). Discrepancies between MD and experimental expectations may be rationalized through consideration of the simplifying assumptions engaged when forming the MD supercells. Primarily, the restriction
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Figure 3.16: The elastic moduli measurements for the MD microstructures with average grain sizes ranging from 5 - 25 nm. The CG modulus of 207 GPa [166] is also noted for comparison. Measurement discrepancies believed to be due to the limited number of grains in the 20 and 25 nm supercells as well as grain size softening effects in the 5 nm simulation are noted in the figure.

of grain texture to a shared [1\bar{1}0] zone axis creates a statistical bias towards the stiffer crystal directions (e.g. \langle111\rangle) and eliminates the possibility of a truly randomized sampling of moduli. This effect is perhaps most dramatically seen in the 20 and 25 nm samples, where only 19 and 13 grains respectively, comprise the entire microstructure due to length-scale limitations. Additionally, it has been reported by Zhou et al. [167], that the large intercrystalline fraction at the smallest grain sizes can serve to soften the elastic response of a NC material. This effect also appears to be present in the MD data collected for the 5 nm microstructure.

In addition to the modulus, the GPFE curve of the NiCo potential should be validated in order to ensure that it can properly predict deformation mechanisms. Unfortunately, the GPFE for the NiCo system is currently not reported in the literature. However, a supercell of pure Ni may be constructed and tested using the NiCo potential to compare against other published results. Figure 3.17 provides the GPFE curve for deformation twinning in Ni. The GPFE curve was calculated by applying a homogeneous \(a_\alpha/6\langle112\rangle\) shear along adjacent \{111\} slip planes in a Ni single crystal. The MD results were
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Figure 3.17: The GPFE curve for pure Ni calculated using the NiCo potential from Purja Pun et al. [165] and the Ni potential of Mishin et al. [162]. The experimental and DFT values for the GPFE energies are obtained from Carter and Holmes [168] and Jin et al. [169], respectively. Deformation twinning is simulated by applying a homogeneous $a_0/6\langle112\rangle$ shear along adjacent $\{111\}$ slip planes in a pristine Ni single crystal (a) to form an isf (c) and eventually an esf (e). Atoms are coloured using the CNA algorithm as discussed previously. Green indicates atoms in a perfect FCC configuration, whereas red and white refer to atoms in a local hexagonal close-packed or “other” coordination, respectively.

obtained using the NiCo with a fully Ni composition [165] and with the potential of Mishin et al. [162]. The supercell configuration at each critical stage of deformation is provided. These atomic snapshots are paired with labels to the energies of the faulted surface on the GFPE curve. The atomic colouring uses the CNA algorithm as described previously. DFT data for the GPFE is obtained from Jin et al. [169] and experimental data for the intrinsic stacking fault energy is reported by Carter and Holmes [168] to be $\approx 130 \text{ mJ/m}^2$. As shown in the figure, the shearing of the pristine crystal in (a) progresses to an isf at (c) and finally to an esf at (e). An excellent agreement between MD, DFT, and experimental data is obtained for the $\gamma_{\text{isf}}$, however the MD potential from Mishin et al. [162] seems to overestimate the unstable stacking and twinning fault energies when compared to the DFT data. Conversely, the NiCo potential is in reasonable agreement with the first-principles reports for all pertinent GPFE curve energies.
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The various benchmarks involved in validating the NiCo potential are summarized below:

- The NiCo potential was found to deliver a stable FCC lattice at all temperatures required for MD simulations in this thesis, consistent with experimental studies.

- The lattice parameter of the NiCo potential was found to be \( \approx 0.36 \text{ nm} \), which is in excellent agreement with the experimental value (0.352 nm) calculated from XRD measurements (see Chapter 4).

- The measurements for the elastic modulus in the NC microstructures were found to be in reasonable agreement with the experimental value (213 GPa, see Chapter 4) and the expectations for bulk Ni (207 GPa) \footnote{166}. Deviations from these values are attributed to MD supercell size effects at higher grain sizes and grain size softening at lower grain sizes.

- When set to a pure Ni chemistry, the NiCo potential recreates the GPFE curve of Ni (as determined by DFT) with excellent accuracy. A direct comparison to the GPFEs of NiCo is not available in the literature.

3.3.3 MD tensile simulations

MD tensile simulations are performed in this thesis using the freely available Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) \footnote{170}. The LAMMPS input files used to conduct these simulations are provided in Appendix A. All simulations are conducted with a timestep of 1 fs, with periodic boundary conditions imposed on all three dimensions of the MD supercell. Visualization of atomic topologies is achieved using the Open Visualization Tool (OVITO) \footnote{171}. Tensile simulations are achieved through the implementation of two LAMMPS algorithms. In the first portion of the simulation, the MD supercell generated using the customized MATLAB code is subjected to an energy minimization scheme followed by a controlled anneal and equilibration. Annealing of the MD supercell is achieved through heating the microstructure from 0 K to 773 K over a 20 ps ramp, and then holding at temperature for 200 ps. The anneal is terminated through cooling to 1 K over a 20 ps period and equilibrating the system pressure for an additional 50 ps. During relaxation, the system temperature and pressure are controlled using the Nosé-Hoover isothermal-isobaric ensemble as available in LAMMPS. For all stages of system relaxation, a zero-pressure target was applied to each of the supercell boundaries.
Uniaxial tensile simulations are performed in this thesis using a stress-controlled loading scheme. In this mechanical testing protocol, the zero-load condition imposed by the simulation ensemble is altered to progressively increase the external stress along the loading direction. Loads are applied in increments of 100 MPa, which represents $\approx 1-2\%$ of the tensile strength of the samples measured in this thesis. The load increments are applied over an interval of 1 ps, followed by an isobaric equilibration of 10 ps at the new load level. The equivalent average applied engineering strain rate is calculated to be in the range of $\approx 1-2 \times 10^8$/s. A zero-load is maintained along the remaining two system directions in order to account for Poisson effects. The engineering strain is calculated by monitoring the normalized change in length of the total simulation cell and the true strain ($\varepsilon_t$) is calculated directly from this value. Stress is calculated from temporal averaging of the combined per-atom values, which are determined using the Virial theorem [172]. The Virial stress may be considered as a discrete, atomic-scale equivalent of the continuum-level true stress ($\sigma_t$) [173]. All tensile simulations were performed at a system temperature of 1 K. Figure 3.18 illustrates the work flow of the MD simulations under the relaxation and tensile algorithms.

The purpose of the relaxation procedure is to significantly reduce the number of unstable Voronoi cells within the microstructure. Qualitatively, unstable Voronoi cells refer to structures which possess with highly acute interior angles and high connectivity.
3.3. Computational methods

(i.e., greater than tertiary) nodes. Figure 3.19a,b shows atomic snapshots of a NC MD supercell \(d_{NC} = 10\) nm after initialization and equilibration. Inspection of the two figures shows that a number of grain boundary structures have been annealed during relaxation and low and high angle grain boundary structures are observed to exist within the annealed supercell (Figure 3.19c,d). A number of needle-shaped Voronoi cells have been blunted and several high connectivity nodes have been annealed although some regions of high node connectivity still exist. As previously noted, the relative fraction of high connectivity nodes is larger in the quasi-3D supercell relative to a fully 3D structure.

To give context to the effect of the relaxation on the MD supercell, the total \(E_{atom}\) and potential per-atom energies \(U_{atom}\) of the system during annealing and equilibration are provided in Figure 3.19e. As shown in the figure, the energies of the simulation cell are gradually reduced, reaching a plateau during the late stages of annealing. Upon termination of annealing and equilibration, the internal energy of the structure drops significantly, and is found to be lower than before structural relaxation (-4.512 vs. -4.517 eV/atom). The final internal energy (-4.517 eV/atom) deviates from the perfect single crystal value by less than 0.04%. Although the differences between the pre- and post-anneal structures do not appear significant in energetic terms, the internal hydrostatic stress of the structure has also been significantly reduced during relaxation, dropping from an initial value of 1.87 GPa to < 100 kPa after annealing and equilibration.

It is worth noting that although strain-controlled testing is often implemented in MD simulations, it has not been pursued in this thesis. Tensile studies performed using strain-controlled testing are known to overshoot yielding during loading and deliver anomalous stress-strain profiles [93] which can exhibit a negative work hardening behaviour prior to necking. For examples of strain-controlled testing which illustrate this behaviour, please see Refs. [93, 174]. Testing using a stress-controlled scheme does not suffer from this limitation. Additionally, since deformation processes are stress-driven, a stress-controlled scheme offers a more direct avenue to connect applied loadings with resulting deformation. For these reasons, stress-controlled loading has been used in all MD simulations in this thesis.

It is important to note at this stage of the thesis that the tensile properties measured in MD simulations far exceed the values measured during experiments. For example, MD measurements of yield stress often exceed experimental values by an order of magnitude due to the extremely high applied strain rates \(\approx 10^9/s\). These high strain rates are necessary to observe deformation processes within a simulation window, which is accessible to current computational hardware [78]. Therefore, while nominal MD stress measurements results may be compared to each other, direct comparisons to experiments
3.3. Computational methods

Figure 3.19: Atomic snapshots of an NC MD supercell with a grain size of 10 nm upon initialization (a) and after relaxation (b). The tensile loading direction relative to the supercell is indicated. High magnification images of the grain boundaries between grains showing low angle (c) and high angle (d) boundaries. Atoms coloured in green exist with a perfect FCC coordination and atoms coloured in black are in a defective position. Changes in the lattice orientation are indicated in red stroke. (e) The per-atom ($E_{\text{atom}}$) and potential ($U_{\text{atom}}$) energies of the system during relaxation are plotted on the primary y-axis in blue stroke and the system temperature profile is plotted along the secondary y-axis in red stroke.
should be considered within the context of the high strain rates at which they are collected. Furthermore, it is important that the deformation mechanisms observed in MD simulations are substantiated by experimental evidence, as transitions in the kinetics of deformation are often encountered when crossing multiple orders of magnitude in strain rates.

Figure 3.20a provides the results of a stress-controlled uniaxial tensile test which was performed on the NC MD supercell \((d_{\text{NC}} = 20 \text{ nm})\) shown in Figure 3.13. The stress-strain response of the NC supercell has been plotted in true terms up until its ultimate tensile strength. The MD supercell generated measured \(80 \times 80 \times 2 \text{ nm}\) and was comprised of approximately 1.17 million atoms. The pole of the sacrificial dimension was aligned to a common \(<1\bar{1}0>\) crystal axis, which is shared by all grains simulated in this thesis. This pole was selected such that all dislocation lines are oriented parallel to the sacrificial dimension, eliminating possibility of oblique glide through periodic replicas of the supercell. It should be noted that the supercell does not fracture in the traditional sense during loading in MD simulations. Due to periodic boundary conditions, there are an absence of free surfaces in the simulation, which complicates understanding of failure in MD simulations. In this thesis, the ultimate tensile stress \((\sigma_{\text{UTS}})\) of a MD simulation is determined using Considère’s criterion, which is defined as the point where \(\sigma_t = d\sigma_t/d\varepsilon_t\) [175]. Initial loading of the NC material was found to be largely elastic with a modulus of \(E = 221 \text{ GPa}\). The MD supercell is observed to undergo significant softening at approximately \(\varepsilon_t = 0.05\), which is associated with the NC microstructure entering a regime of comparatively high flow. This transition is characteristic of the yielding phenomenon. However, due to the high rates of loading in MD, the NC sample is observed to yield at strain levels which are much higher than typical in experiments. This disconnect between MD and experimental measurements presents a challenge when defining a yielding criterion. In this regard, the standard 0.2% offset is not accurate as its implementation typically results in underestimates of the yield strength \((\sigma_{\text{YS}})\) which clearly fall in the elastic range of the material.

In order to address this issue, offset criteria ranging from 0.2-3% were examined to define a standardized method for yield stress estimation. Figure 3.20b presents the same stress-strain curve with the estimates for \(\sigma_{\text{YS}}\) overlaid. Additionally, the change in strain \(\Delta\varepsilon_t\) between stress-controlled load increments is also plotted. A clear and distinct change in flow behaviour is observed after a strain level of 5%. Based on these results, a yield criterion of 2% offset was chosen for calculation of \(\sigma_{\text{YS}}\) in all MD simulations. The arrows in the figure indicate the respective stress-strain levels at the 2% offset. This criterion is admittedly arbitrary, but is consistent with the traditional definition in that segments
3.3. Computational methods

Figure 3.20: (a) The uniaxial tensile results of a NC microstructure ($d_{NC} = 20$ nm) subjected to stress-controlled loading. The yield ($\sigma_{YS}$) and ultimate tensile strengths ($\sigma_{UTS}$) of this microstructure are indicated in the figure. See the text for a description of their determination. (b) Estimates for $\sigma_{YS}$ based on various offset methods. The selected 2% offset value is indicated with a black arrow. The stress-strain curve and $\sigma_{YS}$ values are plotted with respect to the primary axis. The change in the measured strain ($\Delta \varepsilon_t$) between each stress-controlled loading increment is plotted on the secondary y-axis. The flow level at a 2% offset yield estimate is indicated with a red arrow.
In order to further verify the proposed yielding criterion, a series of MD tensile studies on purely NC microstructures with average grain sizes ranging from 5 - 25 nm was performed. The purpose of these studies was to assess HP hardening on the yield stress in the NC microstructure as measured by a 2% offset. All microstructures simulated measured 80 x 80 x 2 nm and were comprised of approximately 1.16-1.17 million atoms. Figure 3.21a plots the uniaxial stress-strain curves for each of the NC microstructures considered. The corresponding yield points (2% offset) are provided in Figure 3.21b. Yield strengths for the NC microstructures are measured in the range of 6.3-8.6 GPa. As shown in the figure, an inversion in grain size strengthening is observed at $d_{NC} = 20$ nm. This reversal is associated with the inverse HP effect and is consistent with experimental reports of grain size softening which place a maximum strength in Ni at grain sizes in the range of 10-20 nm [88, 176]. To further illustrate the robustness of the selected yielding criterion, the yield points calculated using a range of offsets (0.2%-3%) are provided in Figure 3.22. From the provided data, it can be seen that the trends in yield stress presented in Figure 3.21b are consistent and only present minor deviations at offsets of less than 1% (e.g. $d_{NC} = 25$ nm).

### 3.3.4 The kinetic Monte Carlo method

The kMC method is a robust approach for the simulation of deterministic behaviours in activated stochastic processes. Provided the energetics of activation are known, the kMC method may be leveraged to investigate the kinetics of activated processes across a wide range of spatial and temporal scales. As a part of this thesis work, a kMC model is developed to predict the competition between thickening and nucleation of deformation twins (see Chapter 8). In this subsection a discussion of the kMC algorithm is presented to provide the reader with background on this method. The kMC method is a variant of the traditional Monte Carlo approach which relies on knowledge of transition rates to generate a stochastic sequence of reactions in a system of interest. Unlike many other Monte Carlo approaches, the selection of states is not purely random, and is rooted in a weighting scheme which encourages the selection of kinetically-favoured state transitions. Thus, the kMC method may be implemented without the occurrence of rejected-states, which can often plague other Monte Carlo approaches, and therefore it serves as an efficient method of evaluation for kinetic processes [177]. Additionally, the computational requirements of the kMC method are not typically high, permitting the concurrent evaluation of reaction pathways with coarser and finer timescales. This flexibility creates the opportunity for
Figure 3.21: (a) Uniaxial stress-strain curves for NC microstructures with average grain sizes in the range of 5-25 nm. (b) The yield stresses as determined using a 2% offset. A reversal in HP strengthening is observed at \( d_{SC} = 20 \) nm, which is associated with the inverse HP effect. The secondary axis in (b) represents the normalized values of MD yield stress measurements.
multi-scale study, whereby the elements of MD simulations may be captured by the kMC method and extended to timescales currently inaccessible to first-principles simulations. A significant drawback of the kMC method, however, is the requirement for \textit{a priori} knowledge of reaction activation energies, which precludes the investigation of unknown reaction phenomena. For an excellent introduction to the kMC method, the reader is directed towards Ref. [178].

The steps involved in the kMC algorithm are outlined below:

1. Set time $t = 0$

2. Form a list of all the possible rates $r_i$ for all the possible state transitions in a system. Each rate is usually defined using a relation that includes the activation energy of the state transition.

3. Calculate the cumulative function $R_i = \sum_{j=1}^{i} r_j$ where $i = 1, \ldots, N$ represents all of the transitions in the system.
4. Generate a random number \( u \in [0, 1] \) from an uniform distribution

5. Perform the transition \( j \) which satisfies \( R_{j-1} < uR_N \leq R_j \)

6. Generate a new random number \( u' \in [0, 1] \)

7. Update the time of the simulation \( t = t + \Delta t \) where: \( \Delta t = -\ln u'/R_N \)

8. Return to step 1.

This procedure is known as the residence-time, n-fold way, or the Bortz-Kalos-Liebowitz algorithm [177]. This process may be envisaged schematically. Consider a binary system of As and Bs, whereby the transition \( A \rightarrow B \) occurs at a rate of 1 and the reverse transition \( B \rightarrow A \) has a rate of 2. The initial configuration of the system is a collection of As. The comparative rates of transition may be graphically compared by plotting the values of \( R_i \) on a line plot, as shown in Figure 3.23a. Consider a random number \( u = 0.25 \), which then forces a transition at site 3. The system configuration evolves to a new collection of states and possesses a new set of comparative rate kinetics, as shown in Figure 3.23b. Examples of applications of the kMC method include atomistic simulations of vacancy diffusion and agglomeration in a porous lattice, and computational modeling of nanocrystalline grain growth during annealing [178]. In these simulations each potential state transition is defined by the individual rates of vacancy diffusion and atom lattice shuffling, respectively. Consequently, these rates are each controlled by the activation energies of the associated state processes. The neighbourhoods of each state

![Figure 3.23](a) A system of As with the comparative kinetics of transition illustrated on a line plot. (b) The updated kinetics and system configuration after a transition \( A \rightarrow B \) at position 3. This figure has been adapted from an example provided in Ref. [178].
particle (i.e., vacancies and interfacial atoms) considered in these simulations can alter the activation energies of these processes and therefore introduce entropic biases in the dynamics of the system, which are captured directly by the kMC algorithm.

3.4 Analytical techniques

Since one of the primary objectives of this thesis is to understand the role of deformation mechanisms in the manifestation of macroscopic mechanical properties, it is relevant to introduce the analytical tools which may be used to evaluate the deformation response of the ML structures. In this regard, the Kocks-Mecking (KM) approach represents one of the most recognized phenomenological work hardening models implemented in the literature. The essential elements of the KM approach are reviewed in detail by Kocks and Mecking [179]. The KM formulation is a single parameter model, which links the hardening behaviours of various deformation mechanisms through the evolution of the stored dislocation density ($\rho$). Under the KM approach, the evolution of the dislocation storage density induced by plastic strain may be described as the competition between storage and annihilation terms [180]:

$$\frac{d\rho}{d\varepsilon} = M \left( \frac{d\rho^+}{d\varepsilon} - \frac{d\rho^-}{d\varepsilon} \right)$$

(3.9)

This relation may be formulated in terms of material parameters as:

$$\frac{d\rho}{d\varepsilon} = M \left( k_1 \sqrt{\rho} - k_2 \rho \right)$$

(3.10)

where $M$ is the Taylor factor, and $k_1$ and $k_2$ are parameters relating to the athermal work hardening limit and dynamic recovery respectfully. The flow stress may then be determined through use of the Taylor relation:

$$\sigma = \alpha MGb \sqrt{\rho}$$

(3.11)

with $G$ representing the shear modulus and $\alpha$ being an efficiency parameter that describes interactions between forest dislocations, which is typically assumed to be $\approx 0.3-0.4$ [181, 182]. In the KM approach, Eq. 3.11 is often expressed in a differential form as:

$$\frac{d\sigma}{d\varepsilon} = \frac{\alpha MGb}{2\sqrt{\rho}} \frac{d\rho}{d\varepsilon}$$

(3.12)
3.4. Analytical techniques

In this manner, the working hardening of a material may be directly calculated from the stress-strain response through determination of the tangent modulus. Under the KM model, the work hardening behaviour of a material is assumed to result in a linear decay of the tangent modulus with respect to flow stress (known as Stage III hardening [179]), which permits a Voce parameterization [183] of the work hardening law in the form:

\[ \frac{d\sigma}{d\varepsilon} = \Theta_o \left(1 - \frac{\sigma}{\sigma_s}\right) \]  

(3.13)

where \( d\sigma/d\varepsilon \) is the tangent modulus (in true stress-strain terms), \( \Theta_o \) is the athermal work hardening limit, and \( \sigma_s \) is the Voce stress. Fitting a set of experimental work hardening data to Eq. 3.13 permits an evaluation of \( \Theta_o \) and \( \sigma_s \), which may then be used to directly calculate \( k_1 \) and \( k_2 \) by substitution into Eqs. 3.10 and 3.12. This set of equations represents the most primitive formulation of the KM phenomenological working hardening model. Alternative approaches to the dislocation evolution law have been developed, which are better able to predict stage IV hardening behaviour [180]. Under the formulation from Bouaziz [180], the competition between dislocation storage and annihilation is assumed to evolve in the following form:

\[ \frac{d\rho}{d\varepsilon} = M [k_1 \sqrt{\rho} \exp(-\xi \sqrt{\rho})] \]  

(3.14)

where \( k_1 \) is defined as before, and \( \xi \) represents capture distance for dynamic recovery. Through substitution of Eq. 3.11 into Eq. 3.12, and coefficient comparison with Eq. 3.14, the strain hardening behaviour under this formulation can be expressed as:

\[ \frac{d\sigma}{d\varepsilon} = \Theta_o \exp \left(-\frac{\sigma}{\sigma_s}\right) \]  

(3.15)

where \( \Theta_o \) and \( \sigma_s \) are now a two parameter function of \( k_1 \) and \( \xi \). Additional extensions to the original KM model have been proposed, which are designed to isolate the effects of grain size as well as the contributions of isotropic and kinematic mechanisms to the overall work hardening behaviour through the use of Bauschinger tests. For examples of these approaches, please see the work of Sinclair et al. [182] and Bouaziz et al. [184]. A particularly notable modification to the KM model is the formulation proposed by Bouaziz et al. to account for the secondary hardening effects of deformation twinning in twinning induced plasticity (TWIP) steels [185]. In this approach, the standard KM dislocation evolution law (Eq. 3.10) is modified to include deformation twins as boundaries to dislocation glide. During deformation, the twinning fraction of the microstructure is
assumed to increase monotonically with the applied strain. The evolution of deformation twins leads to a segmentation of the original microstructure by twin boundaries, effectively reducing the grain size through a so-called “dynamic” HP effect [186, 187]. This dynamic refinement of the microstructure leads to a decrease in the mean free path between dislocations and effectively increases the storage density. In this model, Bouaziz et al. [185] use a mixing law proposed originally by Remy [188] in order to account for the contributions of deformation twinning to overall plastic shear strain accommodation:

\[ d\gamma = (1 - F)d\gamma_g + \gamma_t dF \]  \hspace{1cm} (3.16)

where \( F \) represents the twinning fraction, and \( \gamma_g \) and \( \gamma_t \) are the plastic shear strains due to dislocation glide and deformation twinning as defined in Chapter 2. The shear strain \( \gamma \) may be linked to the overall strain in a uniaxial tension test through Eq. 2.2. Bouaziz et al. [185] assume that dislocation twinning does not contribute to the stored dislocation density and that this parameter may be described solely in relation to the dislocation slip strain. Under this consideration, the dislocation evolution law may be described as:

\[ \frac{d\rho}{d\gamma_g} = \frac{1}{b\bar{\Lambda}_d} - k_2 \rho \]  \hspace{1cm} (3.17)

where \( \bar{\Lambda}_d \) represents the dislocation mean free path and \( k_2 \) is the dynamic recovery term as previously defined. In consideration of several obstacles in the glide of dislocations through a crystal, the dislocation mean free path may be calculated as the combination of a number of microstructure parameters:

\[ \frac{1}{\bar{\Lambda}_d} = \frac{1}{d} + \frac{1}{\bar{\Lambda}} + b k_1 \sqrt{\rho} \]  \hspace{1cm} (3.18)

where \( d \) is the grain size, \( \bar{\Lambda} \) is the average twin spacing, and \( k_1 \) is defined as in the KM model. According to Remy [188], the average spacing between twins may be calculated through knowledge of the average twin thickness (\( \bar{\lambda} \)) and the twinning fraction \( F \) as:

\[ \bar{\Lambda} = 2\lambda \frac{1 - F}{F} \]  \hspace{1cm} (3.19)

This leads to an overall dislocation density law form through combination of Eqs. 3.17, 3.18, and 3.19 :

\[ \frac{d\rho}{d\gamma_g} = \frac{1}{b} \left( \frac{1}{d} + \frac{1}{2\lambda} \frac{F}{1 - F} \right) + k_1 \sqrt{\rho} - k_2 \rho \]  \hspace{1cm} (3.20)
As noted by Bouaziz et al. [185], the twinning fraction evolution may be determined through use of Olson and Cohen’s relation [189]:

\[ F = 1 - \exp(-m\varepsilon) \]  \hspace{1cm} (3.21)

where \( m \) is a coefficient related to the stacking fault energy, and may be left as a free variable for fitting. Application of these equations to experimental data obtained from tensile tests of materials permits a direct determination of the separate contributions of dislocation slip and deformation twinning to overall work hardening.

### 3.5 Chapter summary

This chapter has provided the reader with the relevant background on the relevant multilayer fabrication techniques, as well as the experimental, computational, and analytical tools which are implemented in this thesis. Specifically, a review of the working principles of scanning electron and transmission electron microscopy have been provided along with a description of the associated/related crystallographic (EBSD, TEM diffraction, and XRD) and chemical (EDX) analysis techniques. Mechanical testing protocols such as uniaxial tensile testing, digital image correlation analysis, and nanoindentation have been reviewed. The computational approach to ML microstructure generation, MD tensile testing and mechanical data analysis, as well as the basics of the kinetic Monte Carlo method have also been detailed. Additionally, the framework of a phenomenological work hardening model which is adapted to analyze the deformation behaviour of the ML architecture has been overviewed.
Chapter 4

Characterization of ML architectures and constituent features

Before an in-depth investigation of deformation behaviour may be initiated, it is necessary to characterize the bulk behaviour of the CG and NC features to provide bounds for the expectations of mechanical behaviour in the ML architecture. The purpose of this chapter is to therefore provide the reader with a baseline characterization of the NC and CG constituent layers, as well measurements of the deposited layer thicknesses and chemistries of the ML architectures which are targeted for study in this thesis. Detailed mechanical analysis of deformation behaviour and an investigation of deformation mechanisms in the MLs are reserved for later chapters. Many of the results of this chapter have been previously published [190].

4.1 ML architectures and tensile coupon preparation

Free-standing NiCo plates were fabricated at Integran Technologies Inc. using PED on an inert stainless steel cathode. The pulse profiles of the CG and NC layers were fixed such that the deposited average grain sizes \((d_{CG}, d_{NC})\) remained constant. The thicknesses \((t_{CG}, t_{NC})\) of the constituent CG and NC microstructure features in the MLs were controlled by modifying the recipe duty cycle of the PED process. For further details regarding the PED process, please Section 3.1.1. Figure 4.1 provides the sample matrix which illustrates the different thickness ratios \((t_{\eta})\) in the fabricated ML samples. The thickness ratio is defined here as the ratio of \(t_{NC}\) to ML unit cell thickness (i.e.
4.1. ML architectures and tensile coupon preparation

$t_\eta = t_{NC}/(t_{CG} + t_{NC})$. Bulk CG and NC plates were also fabricated using the appropriate PED recipe to serve as a comparative reference for microstructure characterization and mechanical testing. The design strategy of this sample matrix is to fabricate ML architectures with thickness ratios which span a spectrum of deformation behaviours.

Specifically, it is anticipated that as $t_{CG}$ and $t_{NC}$ increase, the behaviour of the ML architecture approaches an ROM-type response, which is dictated by the independent operation of NC and CG deformation mechanisms. This deformation behaviour is analogous to joining bulk NC and CG specimens in a modulated structure. Conversely, as $t_{CG}$ and $t_{NC}$ decrease, the CG-NC interfacial area fraction increases and deviations from ROM behaviour are expected, stemming from interactions between CG and NC deformation behaviours.

Following PED, the sheets were mechanically stripped from the stainless steel cathode. In order to confirm the presence of the ML architecture, the as-deposited microstructures

Figure 4.1: The sample matrix showing the different nominal thickness ratios in the MLs which were fabricated for this thesis work. Red markers indicate a specific ML which was attempted for manufacture and blue markers denote specific architectures which are studied in this thesis. The shaded gray region defines the processing limits for the PED technique. ML samples with thickness ratios outside of this region did not possess the desired microstructure.
of the NiCo MLs were imaged using SEM and alloy chemistries were measured with EDX analysis using a Hitachi SU 3500 instrument. For SEM imaging, samples were progressively ground to a grit of 1200 and then polished using a 50 nm colloidal silica suspension. Vibratory polishing in a colloidal silica suspension was then performed for 4 hours as the final polishing step. Colloidal silica residue was removed through Ar ion milling at a 6 kV accelerating voltage with a gracing angle of 8° for 10 minutes. It was observed that MLs, with a $t_{NC}$ or $t_{CG} < 1 \, \mu\text{m}$, did not possess the intended layering of microstructure features. Figure 4.2 presents electron micrographs of a ML with a nominal 10 $\mu\text{m}$ NC, 10 $\mu\text{m}$ CG (Figure 4.2a, layering), and 0.1 $\mu\text{m}$ NC, 10 $\mu\text{m}$ CG layer profiles (Figure 4.2b, no layering) as examples. Through extensive electron microscopy analysis, it was determined that the morphology associated with terminal growth in a CG layer is approximately 1 $\mu\text{m}$. Therefore, attempts to deposit NC layers at thicknesses less than 1 $\mu\text{m}$ did not result in clearly defined ML structures. Additionally, the average grain size of the CG layer was measured to be $\approx 1 \, \mu\text{m}$ (see Section 4.2), placing a lower boundary on the thickness of this ML constituent. Consequently, the remainder of the thesis results originate from ML samples within the PED manufacturing window (see Figure 4.1). Specifically, the nominal layer combinations examined in this thesis are: 10 $\mu\text{m}$ CG, 10 $\mu\text{m}$ NC ($t_\eta = 0.50$); 1 $\mu\text{m}$ CG, 1 $\mu\text{m}$ NC ($t_\eta = 0.50$); 3 $\mu\text{m}$ CG, 7 $\mu\text{m}$ NC ($t_\eta = 0.70$); 1 $\mu\text{m}$ CG, 5 $\mu\text{m}$ NC ($t_\eta = 0.83$); and 1 $\mu\text{m}$ CG, 10 $\mu\text{m}$ NC ($t_\eta = 0.91$). Table 4.1 provides a compacted notation which is used to refer to each of these MLs in the subsequent chapters. The MLs produced via PED were all found to have a consistent thickness ratio throughout the sample cross-section. However, during SEM
4.1. ML architectures and tensile coupon preparation

Table 4.1: A comparison of nominal and actual layer thicknesses and ratios for the MLs examined in this thesis. A short-hand notation as well as the measured alloy chemistries are also provided.

<table>
<thead>
<tr>
<th>Short-hand</th>
<th>composition (wt.% Ni)</th>
<th>( t_{CG} ) (μm) nom.</th>
<th>( t_{CG} ) (μm) act.</th>
<th>( t_{NC} ) (μm) nom.</th>
<th>( t_{NC} ) (μm) act.</th>
<th>( t_\eta ) nom.</th>
<th>( t_\eta ) act.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML_{50a}</td>
<td>83</td>
<td>10</td>
<td>7.4 ± 0.2</td>
<td>10</td>
<td>5.8 ± 0.3</td>
<td>0.50</td>
<td>0.44</td>
</tr>
<tr>
<td>ML_{50b}</td>
<td>70</td>
<td>1</td>
<td>0.8 ± 0.0</td>
<td>1</td>
<td>0.7 ± 0.0</td>
<td>0.50</td>
<td>0.46</td>
</tr>
<tr>
<td>ML_{70}</td>
<td>75</td>
<td>3</td>
<td>2.0 ± 0.1</td>
<td>7</td>
<td>3.7 ± 0.1</td>
<td>0.70</td>
<td>0.65</td>
</tr>
<tr>
<td>ML_{83}</td>
<td>66</td>
<td>1</td>
<td>1.2 ± 0.1</td>
<td>5</td>
<td>4.8 ± 0.1</td>
<td>0.83</td>
<td>0.79</td>
</tr>
<tr>
<td>ML_{91}</td>
<td>62</td>
<td>1</td>
<td>1.0 ± 0.0</td>
<td>10</td>
<td>9.8 ± 0.1</td>
<td>0.91</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Imaging of the ML samples it was observed that, while uniform, the as-deposited CG and NC layer thicknesses deviated from the nominal ML architecture. The actual averaged layer thicknesses and corresponding thickness ratios for each of the MLs examined in this thesis are provided in Table 4.1. The composition of all MLs examined in this study was found to be in the range of 62-83 wt.% Ni as measured by EDX analysis. Note that, previous studies of NiCo manufactured by a similar PED procedure report sulphur and carbon concentrations on the order of several hundred ppm [191]. The effects of solid solution hardening due to chemistry variations were found to be minimal and did not significantly affect the comparability of mechanical properties in this thesis work. The composition of each ML studied in this thesis is summarized in Table 4.1.

Tensile coupons with a 100 mm length, 10 mm grip width, 3.5 mm grip fillet radius, and a nominal gauge dimension measuring 33 mm long (\( L_o \)) by 3 mm wide (\( W_o \)) were cut from the bulk PED plates using a waterjet for mechanical testing purposes. The resulting coupons were deburred and ground to at least a grit of 600 with SiC abrasive papers to remove any obvious surface flaws from the gauge length. The coupons all possessed thicknesses (\( t_o \)) ranging from 0.4 – 0.8 mm. All measurements reported in this thesis refer to the caliper dimension. Figure 4.3 illustrates the template used to waterjet cut tensile coupons from the PED plates. The directions defined in this figure represent the laboratory frame and are referred to throughout the experimental portion of this thesis. The figure also relates the microstructural features of the ML to the laboratory frame, which is relevant for proper interpretation of mechanical testing and microscopy results.

During sample preparation, a small taper was observed in the tensile coupon cross-sections due to the waterjetting process, creating a slightly trapezoidal profile and leading to an overestimation of gauge area. Figure 4.4 provides a SEM image of a sectioned tensile coupon which possessed a trapezoidal gauge area. The degree of tapering was found to depend on the waterjet equipment used to cut a particular batch of PED plates and
4.1. ML architectures and tensile coupon preparation

Figure 4.3: (a) A dimensioned schematic of the tensile coupons which were waterjet cut from the bulk PED plate shown in (b). The relation between the laboratory reference frame \((L_0, W_0, t_0)\) and the tensile coupon dimensions is shown. The plating direction of the additive PED process is indicated in (b). (c) A schematic of the ML architecture showing the relation between microstructural features and the laboratory, and plating directions. These orientation relations are important for correct interpretation of microstructural features and mechanical behaviour in the forthcoming chapters of this thesis. The planar directions \(L_0\) and \(W_0\) are ambiguous with respect to microstructural features unless explicitly fixed.

The overall plate dimensions. For a constant coupon width, deviations in the caliper measurements of gauge area due to tapering scale linearly with the coupon thickness. The ratio of the trapezoidal area \(A_{\text{trap}}\) to the caliper area \(A_{\text{cal}}\) was described using the following relation:

\[
\frac{A_{\text{trap}}}{A_{\text{cal}}} = 1 - \frac{t_0}{W_0} \tan(\alpha_{\text{trap}}) \tag{4.1}
\]

where \(\alpha_{\text{trap}}\) is the declination angle of the coupon cross-section, as defined in Figure 4.4. The declination angle was measured to be on average \(\approx 8^\circ\) and the corresponding deviation in stress measurements originating from overestimation of the gauge area was found to be less than 5% for the specimens examined in this thesis. Nonetheless, these discrepancies can prove significant during detailed mechanical analysis and therefore are generally compensated for through application of Eq. 4.1 unless otherwise noted.
4.2 Characterization of the NC and CG microstructures

The grain size of the CG microstructure features were characterized using EBSD mapping with a Hitachi SU 3500 instrument. EBSD maps were collected with a step size of at most 300 nm and an indexing of over 80% was achieved. Due to the high number of interfaces in the PED samples, a conservative interpolation algorithm was utilized to smoothen EBSD results, which had a negligible impact on the orientation distribution of the collected measurements. Figure 4.5 presents EBSD maps collected on the bulk CG sample. As shown in the figure, the grains present as a largely columnar morphology with some smaller equiaxed crystals. The colormap in Figure 4.5a corresponds to the Euler angles of crystal axes relative to the laboratory frame ($L_o$, $W_o$, and $t_o$). In this colouring scheme, the three Euler angles ($\phi_1$, $\Phi$, and $\phi_2$) represent a scaled value ranging from 0 to 255 for the RGB components of a standard 8 bit color-table, respectively. The Euler colormap was chosen as it is the most effective method to plot orientation data within a single micrograph. It should be noted that, due to discontinuities in the colormap, the sharp transitions between colors do not necessarily indicate a large misorientation of the lattice. To illustrate this point, Figure 4.5b plots the intragranular misorientation of...
4.2. Characterization of the NC and CG microstructures

Figure 4.5: (a) EBSD measurements of the bulk CG microstructure. The data is presented here using an Euler angle colormap (see main text for description). The microstructure has been segmented into grains using a misorientation-comparison algorithm. The orientation of the image relative to the laboratory axes is indicated. (b) The intragranular misorientation of the CG microstructure. Several regions of large misorientation are visible in larger crystals, representing independent grains which were not captured by the segmentation algorithm. The colormap represents angular misorientation in degrees. (c) A histogram of the grain size distribution from this EBSD dataset. The scale bars in (a) and (b) represent lengths of 10 μm.
4.2. Characterization of the NC and CG microstructures

the CG microstructure. Intragranular misorientation is defined as the angular deviation of a particular measurement from the mean grain orientation. As shown in this figure, the large colormap transitions observed in Figure 4.5a are not necessarily indicative of a grain boundary (e.g., the blue-green grain in the top left).

The CG microstructure has been segmented into grains using a misorientation-comparison algorithm, whereby adjacent measurements with misorientations greater than a defined threshold are determined to belong to different grains. For this study, a 5° threshold was found to lead to a reasonable microstructure segmentation with an averaged grain size of 0.9 ± 0.1 μm is calculated (Figure 4.5c). The selection of this threshold is supported by a comparison of mechanical properties of the CG sample with existing literature. The yield stress of the CG material is measured to be 352 MPa (see below), which is comparable with measurements of Ni foils with a ≈ 1 μm grain size produced by a similar electrodeposition process [192]. As is evident in Figure 4.5b, intragranular misorientation in the CG microstructure presents as gradual rotations of the lattice. Application of coarser grain boundary thresholds (e.g., 10°) therefore leads to an under-segmentation of the microstructure. Despite best efforts, some of the larger grains are comprised of misoriented regions which appear to be independent grains. However, these occurrences are small in number relative to the overall collected measurements and are not expected to drastically affect the collected grain size statistics.

The grain size of the NC structure was measured using TEM analysis with a Hitachi HF3300 microscope operated at an accelerating voltage of 300 kV. Figure 4.6a,b presents BF and DF planar micrographs of the NC reference microstructure. As shown in the figures, the grains are clearly nano-sized and appear to be relatively equiaxed. Grain size was measured directly from DF images as the average of the major and minor axes of the crystals. 200 measurements in the cross-section orientation were collected to ensure proper statistics for the grain size distribution. An indexed diffraction pattern of the NC reference is also provided in Figure 4.6c. The ratios of the 3rd/1st and 3rd/2nd ring diameters are measured to be 1.63 and 1.42 respectively, which is in excellent agreement with theoretical expectations (1.63 and 1.41) for an FCC lattice. Figure 4.6d plots a histogram of the collected grain size distribution, showing an average of 19.8 ± 0.6 nm. This grain size is typical for NiCo electrodeposits synthesized using comparable plating conditions [191].

The bulk textures of the NC and CG structures were characterized using XRD analysis with a Rigaku MiniFlex 600 Benchtop instrument under Cu–Kα radiation with a wavelength of 0.154 nm. In order to sample the cross-sectional dimension of the NC layer, the XRD spectra were collected to measure texture along the $L_o$ axis. According
4.2. Characterization of the NC and CG microstructures

Figure 4.6: A BF (a) and DF (b) image of the NC reference sample in planar view ($t_o$ axis). (c) An indexed diffraction pattern of the NC reference which confirms the expected FCC lattice of the NC microstructure. (d) A histogram of the collected grain size measurements taken in the cross-section orientation ($L_o$ axis). The scale bars represent lengths of 500 nm.

to XRD analysis (Figure 4.7), the NC reference sample possessed a texture with the (111) peak exhibiting the strongest diffraction condition with the (111) (200) and (220) peaks having relative intensities of 100, 59 and 46, respectively. In comparison to a random texture (Ni powder), which possess relative peak intensities of 100, 42 and 21 for the first three peaks [193], the NC sample exhibited some texturing in the (200) and (220) directions. Using the Scherrer formula, an estimate of a 17 nm average grain size for the NC microstructure was obtained after correction for instrument peak broadening, which is in good agreement with TEM analysis. Additionally, XRD analysis of the CG reference revealed a pronounced (200) peak, with relative intensities of 38, 100 and 35 for the (111)
4.2. Characterization of the NC and CG microstructures

Figure 4.7: XRD spectra of the NC and CG reference samples along. In contrast to the strong (200) texture in the CG sample, a (111) dominated texture was observed in the NC reference. The XRD spectra refer to texture measurements along the $L_o$ axis. The XRD spectra were captured formed Cu–Kα radiation with a wavelength of 0.154 nm. Please note, the background noise of the XRD spectra has been fitted and subtracted from the provided measurements.

(200) and (220) peaks, respectively. The Bragg reflections detected in XRD analysis are indicative of a purely FCC crystal lattice in both the NC and CG microstructures, validating on a bulk-scale the results of the highly localized EBSD and TEM measurements. Additionally, secondary phases were not detected in the XRD spectra of the CG and NC samples, which is consistent with previous studies [191]. Based on the (111) peaks, the lattice parameter was measured to be 0.352 nm for each sample, which is essentially identical to the value for pure Ni [193].
4.2. Characterization of the NC and CG microstructures

Table 4.2: A summary of the mechanical properties of the CG and NC reference samples.

<table>
<thead>
<tr>
<th>PED Sample</th>
<th>$\sigma_{YS}$ (MPa)</th>
<th>$\sigma_{UTS}$ (MPa)</th>
<th>$\varepsilon_f$ (mm/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG</td>
<td>352 ± 3</td>
<td>570 ± 4</td>
<td>0.146 ± 0.008</td>
</tr>
<tr>
<td>NC</td>
<td>1129 ± 20</td>
<td>1689 ± 19</td>
<td>0.048 ± 0.001</td>
</tr>
</tbody>
</table>

Mechanical assessment of the NC and CG reference samples was achieved using tensile testing and instrumented indentation. Room temperature ($\sim 20 ^\circ C$) mechanical measurements were collected via uniaxial tensile testing at a cross-head velocity of 1 mm/min ($5 \times 10^{-4}$/s). In order to avoid errors associated with machine compliance, DIC in combination with a camera system was utilized to provide measurements of the applied strains. All tensile coupons were observed to fail within the gauge length. The camera system was configured to capture photographs at a frequency of 1 Hz, which corresponded to one photograph per $5 \times 10^4$ increment of engineering strain. Nanoindentation of the CG reference was implemented to assess any orientation effects arising from texture on the elastic modulus. Indentation measurements (n=10) were performed at loads of 5, 7.5, 10, 12.5, and 15 mN using the method of Oliver and Pharr [154]. The loading rate was adjusted such that each indent required the same time to perform a load/unload cycle (30 s). Additionally, a 100 s hold time was programmed at peak load to reduce latent plastic effects on modulus measurements. Pile-up effects were estimated to lead to underestimations in $A$ of up to 20% which corresponds to an approximate 10% overestimate of $E$ [194]. Nanoindentation measurements were therefore corrected by 10% to compensate for pile-up error.

Figure 4.8 presents the uniaxial stress-strain response of representative NC and CG reference samples. The overall mechanical behaviour of the reference samples was consistent with expectations. The CG and NC samples possessed average (n=5) yield strengths of 352 ± 3 and 1129 ± 20 MPa, and ultimate tensile strengths of 570 ± 4 and 1689 ± 19 MPa, respectively. Yield was calculated in this thesis using the 0.2% strain offset method. Error in mechanical property measurements are always reported in terms of the 95% confidence interval of a Gaussian distribution. The elongation to failure ($\varepsilon_f$) of the CG and NC samples was measured at 0.146 ± 0.008 and 0.048 ± 0.001, respectively. Table 4.2 summarizes the pertinent mechanical properties of the CG and NC reference samples.

A typical load-displacement ($P-h$) curve for a 10 mN nanoindentation experiment performed on the CG sample is presented in Figure 4.9. In all nanoindentation experiments, the CG sample exhibited the expected elastic-plastic $P-h$ relationship. The contact stiff-
4.2. Characterization of the NC and CG microstructures

\[ \sigma \text{ (MPa)} \]
\[ \varepsilon \text{ (mm/mm)} \]

Figure 4.8: Mechanical response of the CG and NC reference samples loaded under uniaxial tension.

\[ P \text{ (mN)} \]
\[ h \text{ (nm)} \]

Figure 4.9: A typical load-displacement response for the CG sample indented to a load of 10 mN.
ness of indentation $S$ was determined from the unloading curves of each nanoindentation measurement. Taking the contact compliance ($C = 1/S$) as the inverse of contact stiffness, Figure 4.10a provides an iterative fit to Eq. 3.7, with $E_r = 213$ GPa. The values of $A$ have been iteratively solved through consideration of the tip function, which is plotted against $h_c$ in Figure 4.10b. In these nanoindentation experiments the tip function iteratively converged to $A = h_c^2$, which is the ideal relation for a perfect Berkovich tip. Based on these measurements, assumed values of $\nu_{tip} = 0.07$ and $E_{tip} = 1141$ GPa for the indenter tip Poisson’s ratio and elastic modulus, and a Poisson’s ratio of $\nu = 0.3$ for the CG sample, a pile-up corrected elastic modulus of $E = 213$ GPa may be calculated using Eq. 3.6, which is in reasonable agreement with MD measurements and experimental expectations for randomized bulk Ni polycrystals (207 GPa [166]). Texturing in the CG microstructure therefore does not manifest appreciably in the elastic behaviour of the PED sample.

4.3 Chapter summary

The as-deposited microstructures of the NiCo MLs has been characterized and a manufacturing window for the PED process has been established based on SEM imaging of a matrix of fabricated samples. From SEM analysis, ML architectures with NC and CG layers greater than 1 $\mu$m thicknesses were found to possess clearly defined layers. Only samples which possessed clearly defined layers are considered for further study in this thesis. In these samples, layer thicknesses were found to deviate moderately from the nominal target architectures, however, the as-deposited structure was found to be largely uniform, yielding MLs with consistent thickness ratios and layers sizes throughout the sample cross-section. The as-deposited chemistries of the NiCo MLs were found to vary between 62-83 wt.% Ni. The grain size and textures of bulk NC and CG reference samples were measured through a combination of TEM, EBSD, and XRD analysis. Based on EBSD mapping, the crystal size of the CG microstructure was measured to be $0.9 \pm 0.1 \mu$m. DF images of the as-deposited NC microstructure yielded an average grain size measurement of $19.8 \pm 0.6$ nm. XRD analysis resulted in a similar estimate of grain size in the NC microstructure with a measurement of 17 nm based on peak broadening analysis. In comparison to the normalized peak intensities of powder specimens, the collected XRD spectrum for the CG sample showed considerable texturing in the (200) and (220) directions. A purely FCC crystal lattice was detected for both the NC and CG microstructures in all analytical techniques (EBSD, XRD, TEM diffraction). The mechanical responses of the CG and NC reference samples exhibited the anticipated characteristics. The NC
Figure 4.10: (a) The collected compliance measurements and contact areas for nanoindentation of the CG reference. The values for $A$ represent converged values which are iteratively solved through comparison of Eq. 3.7 and the indenter tip function. The dashed line represents the converged fit to Eq. 3.7. The converged reduced modulus $E_r$ was calculated to be 213 GPa. (b) The contact area plotted against indenter contact depth. The line represents a plot of the ideal Berkovich tip function $A = h_c^2$.

The microstructure possessed a high yield and tensile strength but lower elongation to failure, whereas the CG sample exhibited excellent ductility but at a markedly lower flow stress. The elastic properties of the CG microstructure were explicitly examined using nanoindentation to assess texturing effects on the elastic response. Based on nanoindentation measurements, a pile-up corrected elastic modulus of 213 GPa was calculated for the CG sample, which is in good agreement with MD measurements (see Chapter 3) and experimental measurements of a randomized Ni polycrystal agglomerate (207 GPa).
4.3. Chapter summary

[166]).
Chapter 5

Deformation behaviour of a ML with a thick layer architecture

In the current chapter, the deformation behaviour of a ML with relatively thick NC and CG layers is studied. Specifically, this chapter performs a detailed characterization of the ML\textsubscript{50a} architecture which has a nominal 10 μm layer thickness for the NC and CG components. In comparison to the crystal size of each microstructure feature, the layers of the ML are relatively thick and the overall area fraction of CG-NC interface is relatively low. In this regard, the ML may be considered as being comprised of individual bulk CG and NC layers which are adhered together in a modulated assembly, representing a ROM-type baseline for mechanical response. The purpose of this chapter is to identify the multiscale deformation mechanisms by which a the ML undergoes mechanical failure. The results of this chapter are intended to serve as a benchmark for ML performance, and provide context for the ML architectures studied in subsequent sections which possess much higher CG-NC interfacial area fractions. Figure 5.1 shows the ML\textsubscript{50a} architecture from the sample fabrication matrix presented in Chapter 3. Many of the results of this chapter have been previously published [190].

5.1 ML\textsubscript{50a} microstructure characterization

The as-deposited microstructure of the ML\textsubscript{50a} sample was imaged using SEM analysis with a Hitachi SU 3500 instrument. Microscopy samples were prepared in the same manner as described in Chapter 4. At low magnification (Figure 5.2a), it can be seen that the NC and CG layers appeared to have a near equal thickness throughout the full sample cross-section. The orientation of the tensile coupon dimensions relative to the features of the ML are indicated in the figure. At higher magnifications (Figures 5.2b
5.1. $ML_{50a}$ microstructure characterization

Figure 5.1: The sample matrix showing the different thickness ratios in the MLs which were fabricated for this thesis work. Red markers indicate a specific ML which was attempted for manufacture and blue markers denote specific architectures which are studied in this thesis. The $ML_{50a}$ architecture studied in this chapter is indicated.

and 5.2c), a clear interface between NC and CG layers was observed, and the elongated morphology of the CG microstructure became evident. An asymmetric grain morphology associated with the PED growth direction (image down) of the CG layer was visible at high magnification (Figure 1c).

Figure 5.3 presents EBSD maps collected for the $ML_{50a}$ sample using the methodology outlined in Chapter 4. As in the CG reference (Figure 4.5, the morphology of the CG layer microstructure was largely columnar. Figure 5.3a,b presents the sample texture in the $t_o$ (growth orientation) and $L_o$ directions and the corresponding orientation distribution functions of the collected EBSD data are provided in Figure 5.3c,d, respectively. The microstructure is coloured in Figure 5.3a,b based on the standard FCC inverse pole figure colormap. According to the EBSD texture data, the CG layer possess a strong $<100>$ fiber texture along the growth orientation (Figure 5.3c), which is common in PED materials [195] and was reported in NiFe MLs [122]. Given this orientation restriction, the EBSD pole figures along the loading axis ($L_o$) show a preferred $<0kl>$ orientation...
5.2 Tensile properties and fractography

Figure 5.2: Low (a), intermediate (b), and high (c) magnification micrographs of the as-deposited ML\textsubscript{50a} sample revealed through backscatter SEM imaging. The ML lacked any observable porosity, and possessed a periodic spacing of NC and CG layers. The orientation of tensile coupon dimensions relative to the SEM image is indicated in (a). The scale bars represent lengths of 100 (a), 20 (b), and 5 \( \mu \text{m} \) (c). The growth direction of the ML\textsubscript{50a} sample from PED is indicated in (a).

(Figure 5.3d). This result is also in good agreement with the XRD data presented in Figure 4.7.

5.2 Tensile properties and fractography

Figure 5.4 presents the engineering stress-strain curves (\( \sigma, \varepsilon \)) of representative CG, ML\textsubscript{50a} and NC samples. Tensile testing was conducted using the methodology described in Chapter 4, except an extensometer was used to obtain engineering strain measurements. DIC analysis was used explicitly for strain localization analysis. The average \((n=3)\) \( \sigma_{\text{YS}} \) and \( \sigma_{\text{UTS}} \) of the CG, ML\textsubscript{50a} and NC samples were measured to be 365 ± 48, 664 ± 15 and 1017 ± 30 MPa and 557 ± 11, 1112 ± 24 and 1622 ± 39 MPa, respectively. In terms of elongation to failure, the CG and NC reference samples exhibited the expected elastic-plastic material responses, with evidence of necking occurring in both specimens. Due to the limited dislocation storage capacity of the NC microstructure, the ductility of the NC sample was substantially less than the CG reference. The post-yielding elongation of the PED samples may be divided into two categories, with elongation occurring prior to and after peak load \( \sigma_{\text{UTS}} \), representing the uniform (\( \varepsilon_u \)) and non-uniform
5.2. Tensile properties and fractography

Figure 5.3: EBSD maps collected showing the CG texture along the growth orientation (a) and loading axis (b), which fall along the \( t_o \) and \( L_o \) directions, respectively. The CG microstructure appeared to have a columnar morphology. (c,d) The respective orientation distribution functions calculated for the EBSD patterns in (a,b) indicated a strong \(<100>\) fiber texture along the growth direction (a) and a \(<0kl>\) texture along the loading direction (b). The colormap in (c) corresponds to the inverse pole figure of the EBSD data in (a,b). The scale bars represent lengths of 5 \( \mu m \).

\( (\varepsilon_{nu}) \) deformation of the sample [196]. Based on this classification, \( \varepsilon_u \) and \( \varepsilon_{nu} \) values of 0.113 \( \pm \) 0.007 and 0.049 \( \pm \) 0.009 (CG), 0.042 \( \pm \) 0.003 and 0.027 \( \pm \) 0.015 (ML\(_{50a}\)), and 0.037 \( \pm \) 0.004 and 0.020 \( \pm \) 0.006 (NC) were measured for the PED samples, respectively. As expected, the CG reference possessed the highest uniform elongation. Additionally, the ML\(_{50a}\) sample possessed only marginally higher uniform elongation when compared against the NC reference, highlighting the role of the NC layer in the initiation of necking. It should be noted that the mechanical results reported in this chapter were not corrected using Eq. 4.1, as the gauge area distortions due to waterjetting were not found to be significant to the reported trends. Additionally, the CG and NC reference samples
5.2. Tensile properties and fractography

![Stress-strain curve](image)

**Figure 5.4:** Uniaxial tensile response of the PED samples. In terms of yield and ultimate strengths, the ML_{50a} sample appeared to follow a rule of mixtures behavior. The elongation to failure of the ML_{50a} sample was also higher with respect to the NC reference. Notably, non-uniform elongation appeared to be improved with respect to the NC specimen, which indicated a better developed and stable neck. The callouts on the stress-strain curve correspond to loading stages in the DIC analysis presented in Figure 5.9. It should be noted that the CG and NC references presented here are from an initial manufacturing run and are not the same samples presented in the other chapters of this thesis.

The mechanical properties in this chapter are collected and presented in an internally self-consistent manner but the nominal data is standalone with respect to the rest of this thesis.

Measured here were obtained from an initial manufacturing batch. The CG and NC results presented in other chapters are from later manufacturing runs. The stress-strain responses of the CG and NC references are therefore not the same samples plotted in other chapters and are only directly comparable when corrected for gauge area distortion. The mechanical properties in this chapter are collected and presented in an internally self-consistent manner but the nominal data is standalone with respect to the rest of this thesis.

Although measurements indicated the ML_{50a} sample possessed superior non-uniform deformation characteristics, when compared to the NC reference, it is difficult to draw strong conclusions from these values due to the inherently large error in end-of-life mea-
5.2. Tensile properties and fractography

Figure 5.5: SEM micrographs of the CG (a), NC (b), and ML\textsubscript{50a} (c) fracture surfaces which were captured from the perspective of the loading axis. The scale bars all represent lengths of 1 mm.

measurements of elongation. Therefore, planar images of fracture surfaces were collected and the reduction in area ratios ($R_a$) for the tested specimens were compared. $R_a$ is defined here as the ratio of original area before deformation to final fracture area as projected onto the plane formed by $W_o$ and $t_o$. Figure 5.5 presents representative fracture surfaces of the PED samples. Comparatively, the CG sample exhibited the largest degree of necking, whereas the NC reference did not appear to have a significant neck. The ML\textsubscript{50a} sample showed an intermediary fracture behavior, with the development of a neck visible in the SEM image. Based on image analysis, the CG, ML\textsubscript{50a} and NC samples were found to have area reductions of $12.2 \pm 1.1$, $2.0 \pm 0.2$ and $1.5 \pm 0.2$, respectively. From these calculations, the ML\textsubscript{50a} sample was found to possess a statistically significant ($p \leq 0.05$) larger reduction ratio than the NC reference. Furthermore, the effects of cross-sectional dimensions on the ability of the coupon to form a well-developed neck cannot explain the relative increase in $R_a$ for the ML\textsubscript{50a} sample [197]. On the other hand, the $R_a$ of the
ML\textsubscript{50a} structure was still considerably lower (\sim 6 times) than the CG sample, which suggested that the fracture behavior of the ML was influenced significantly by the presence of the NC layer. Careful inspection of the ML\textsubscript{50a} fracture surface (Figure 5.5c) revealed a periodic stacking of microscopic features which transcended the relief cross-section. A high magnification SEM image of the ML\textsubscript{50a} fracture surface (Figure 5.6) revealed a sequence of coarse and fine dimpled structures which corresponded to microvoid coalescence failure modes in the CG and NC layers respectively. A recent study of hard-soft Cr/Cu MLs has also reported similar microscopic features along the fracture surface, with the protrusions being identified as the ductile Cu layers \cite{119}.

A summary of the collected mechanical properties of the PED samples is provided in Table 5.1 and Figure 5.7. The measured values of $\sigma_{\text{YS}}$ and $\sigma_{\text{UTS}}$ were in reasonable agreement with ROM predictions of 652 and 1026 MPa, respectively. ROM calculations are based off the measured thickness ratio ($t_\eta = 0.44$). From a strengthening perspective, these results confirm the notion that the stress-response of the ML can be judged as the aggregate behaviour of independent deformation in the CG and NC constituents. In this
regard, layering at these thicknesses does not lead to a measurable synergy of deformation mechanisms. While elongation was somewhat improved in the ML\textsubscript{50a} sample, it fell short of ROM behavior. Tensile failure is a complicated process which is driven by the evolution of the stress-state from a global-uniaxial to a localized-multiaxial condition, and therefore a simple ROM behavior for elongation of the ML cannot be assumed. A detailed investigation of the development of strain localization and plastic interaction between constituents is required in order to understand deformation behavior in the ML architecture.

**Table 5.1:** A summary of the mechanical measurements extracted from tensile testing of the PED samples.

<table>
<thead>
<tr>
<th>PED Sample</th>
<th>$\sigma_{YS}$ (MPa)</th>
<th>$\sigma_{UTS}$ (MPa)</th>
<th>$\varepsilon_u$</th>
<th>$\varepsilon_{nu}$</th>
<th>$R_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG</td>
<td>365 ± 48</td>
<td>557 ± 11</td>
<td>0.113 ± 0.007</td>
<td>0.049 ± 0.009</td>
<td>12.2 ± 1.1</td>
</tr>
<tr>
<td>NC</td>
<td>1017 ± 30</td>
<td>1622 ± 39</td>
<td>0.037 ± 0.004</td>
<td>0.020 ± 0.006</td>
<td>1.5 ± 0.2</td>
</tr>
<tr>
<td>ML\textsubscript{50a}</td>
<td>664 ± 15</td>
<td>1112 ± 24</td>
<td>0.042 ± 0.003</td>
<td>0.027 ± 0.015</td>
<td>2.0 ± 0.2</td>
</tr>
</tbody>
</table>
5.3 Uniform deformation hardening behavior and strain localization during necking

In order to understand uniform deformation behavior during tensile loading, the hardening response of the PED samples was examined. As shown in Figure 5.8, the tangent moduli of the ML\textsubscript{50a} and NC samples decayed in a linear manner, conforming to Stage III work hardening, whereas the CG sample exhibited both linear Stage III and near-asymptotic Stage IV behavior [179]. The tangent modulus (\(\Theta\)) is presented here as the ratio of differential true stress and true strain and the data in the figure is plotted until the point of peak load in each sample respectively. The absence of Stage IV in the ML\textsubscript{50a} tensile data suggested that NC layer work hardening mechanisms were dominant during uniform elongation and that contributions from the CG layer were negligible prior to necking. Considering the microstructure architecture of the ML and the weakest-link nature of tensile loading, this behavior was expected and is a consequence of the uniaxial stress-state prior to neck formation.

The non-uniform deformation behavior during necking was captured using DIC analysis. An image of a representative tensile coupon speckled for DIC analysis is presented in Figure 5.9a and Figure 5.9b provides line-scans of the strain profile along the normalized gauge length for each of the PED samples. The relative positions of the strain stages in each of the line-scans are indicated in the stress-strain curves of Figure 5.4. The selected line-scans present the strain localization during the following deformation stages: post-yield uniform elongation; at peak load; after strain localization within the tensile neck; and immediately prior to coupon failure. In general, the progression of deformation in the PED samples was consistent. In each of the DIC tensile tests, the coupon failed within the gauge dimension of the sample. As anticipated from tensile data, each sample experienced a period of uniform elongation which transitioned to high strain localization just prior to failure. In the CG reference, fracture proceeded through strain development within a local neck. At strain stage 2, there were several local maximums along the gauge length. The largest of which developed into the localized neck. This behavior is well-known for materials with high strain hardening capabilities [198], where potential necks may stabilize during mechanical loading. In contrast to the CG reference, the NC and ML\textsubscript{50a} samples appeared to experience a mixed mode of deformation behavior, with diffuse and local necks evident in the strain maps. In order to examine the relative size of macroscale deformation features, a methodology that tracks changes in the strain profiles during loading was proposed. The size of the diffuse (\(L_{dn}\)) and local necks (\(L_{ln}\)) were quantified by considering the spatial and temporal derivatives.
5.3. Uniform deformation and strain localization

![Graph showing hardening data for PED samples up until the peak load.](graph.png)

**Figure 5.8:** Hardening data for the PED samples up until the peak load. All samples exhibited a linear decay in the tangent modulus, which was consistent with Stage III hardening. The CG sample also showed asymptotic Stage IV hardening. This behavior was absent in the ML\textsubscript{50a} sample, which indicated that the CG layer did not contribute significantly to deformation behavior before necking.

of the DIC line-scans. Excluding the shoulder, the diffuse neck represented the length of the tensile coupon where the tangent of the strain profile deviated from zero (i.e. $|d\varepsilon/dx| > 0$). Similarly, the local neck was identified near the point of fracture when the temporal derivative of strain increased significantly from zero (i.e. $d\varepsilon/dt > 0$). The degree of strain localization ($\varepsilon_{ln}$) was then calculated as the difference from the peak strain to the baseline at the incidence of the local neck. The definition of these measurements is illustrated in Figure 5.9c and the corresponding derivatives were calculated for each of the PED sample line-scans presented in Figure 5.9b. The calculated quantities of $L_{dn}$ and $L_{ln}$ were normalized against $W_o$ and these measurements, along with $\varepsilon_{ln}$, are provided in Table 5.2. From this analysis, the CG sample possessed the highest degree of strain localization. Notably, the strain localization in the ML\textsubscript{50a} sample was much larger than the NC reference, indicating a significant contribution from the CG layers to deformation.
5.3. Uniform deformation and strain localization

Figure 5.9: (a) A photograph of a tensile coupon speckled for DIC measurements. The normalized length \((x/L)\) was defined as indicated in the image. (b) The strain profiles along the gauge length of the PED samples at various stages: 1) during uniform elongation; 2) at peak load; 3) at the initiation of localized necking; and 4) immediately prior to fracture. The relative positions of these stages are indicated on the stress-strain curves provided in Figure 5.4. (c) Measurements of the diffuse \((L_{dn})\) and local necks \((L_{ln})\) were defined by considering the spatial and temporal derivatives of the strain profiles in (a) for the ML\textsubscript{50a} sample. The strain localization in the local neck \((\varepsilon_{ln})\) was defined as the peak strain subtracted from the baseline of the local neck length. The scale bar in (a) is 5 mm.
behavior within the tensile neck. It should be noted that a distinction between the local and diffuse necks could not be established for the CG sample. The CG measurements are therefore considered as localized neck values.

In order to compare the local necks in the PED samples, DIC strain maps were collected just prior to fracture (Figure 5.10). The colormap is normalized with respect to maximum engineering strain within each of the PED samples and the final dimensions of each tensile coupon are scaled to fit the image frame. As anticipated from tensile stress-strain data, the CG sample appeared to fail by conventional necking mechanisms. Conversely, strain localization in the ML\textsubscript{50a} and NC samples was confined to a band rotated 55\textdegree to the loading axis. Macroscopic shear banding at this angle is a commonly reported fracture mechanism in bulk nanocrystalline metals [199–201] and is a result of the collapse of dislocation storage capacity within nanoscale microstructures [202, 203]. It is interesting to note that although the ML\textsubscript{50a} sample appeared to fail macroscopically by NC dominated shear banding, the extent of strain localization within the band was substantially higher than the NC reference, indicating a significant contribution to material plasticity from the CG layers (Figure 5.9b).

### 5.4 Multiscale deformation mechanism within the tensile neck

In order to gain insight into the interplay between fracture morphology and microscale plasticity within the tensile neck of the ML\textsubscript{50a} samples, SEM images captured perpendicular to the loading axis of the coupon are provided in Figure 5.11. The low magnification images presented in Figures 5.11a and 5.11b are mating fracture surfaces and examination of the images revealed a number of interesting features. As in DIC analysis of the planar dimensions, the fracture plane also appeared inclined at 55\textdegree to the loading axis through the coupon cross-section. The shear band is therefore inclined at compound angles of 55\textdegree to the loading axis in both the planar and cross-section views, forming a fracture plane...
which sectioned the waist of the tensile coupon along an oblique path (Figure 5.11b). Consequently, although the fracture plane initiated at the thinnest cross-section, fracture did not propagate directly through the waist. This phenomenon was a factor responsible for the large reduction in $R_a$ relative to the CG reference. It is interesting to note that in the cross-section view the fracture plane appeared to fall along planes oriented $\pm 55^\circ$ to the loading axis. Conversely, observations from DIC testing showed a single fracture path in the planar view. This behavior was not observed in the NC sample (Figure 5.5c) and was unique to the ML$_{50a}$ coupons. It is possible that the laminate layering of CG microstructure through the sample cross-section disrupted the formation of a singular shear band orientation, permitting a mixed fracture plane. On the microscopic scale, the flow of NC and CG layers into the multiaxial stress field of the localized neck is clearly visible in Figure 5.11b. A higher magnification micrograph (Figure 5.11c) images the interfacial boundary between layers in the tensile neck. The pronounced refinement and distortion of the CG layer microstructure near the ML interface was likely the result of interfacial

![Figure 5.10](image-url)
5.4. Multiscale deformation mechanism within the tensile neck

Figure 5.11: (a) A low magnification SEM image of the fractured ML$_{50a}$ sample. The sample appears to have fractured through a shear band oriented at ± 55° to the loading axis. The orientation of the nominal tensile coupon dimensions relative to the image plane is provided. (b) An SEM image of the mating fracture surface to (a) after polishing. The flow of CG and NC layers into the neck is evident. The fracture path initiated at the thinnest region of the coupon waist and propagated along an oblique path, following the observed shear band. (c) A high magnification SEM micrograph of the CG and NC layers within the diffuse neck. Arrows highlight distortion in the CG microstructure along the interface between layers, suggesting dislocation activity that contributed to the improved necking stability in the ML. The scale bars are 200 in (a) and (b), and 2 μm in (c).
dislocation activity which was caused by the multiaxial stress-state resulting from macroscopic strain localization in both the diffuse and local necks. From a macromechanical perspective, this deformation accommodation in the interfacial structures was believed to contribute to the comparatively increased tensile strain measured within the necking region of the ML (Figure 5.9b).

As observed in reduction area measurements (Figure 5.5c), the fracture surface shown in Figure 5.11a is populated by a landscape of dimpled CG and NC features. In order to gain insight into the relative topography of these features, focussed ion beam (FIB) milling was implemented to cut a trench within the fracture plane and image the cross-section of the dimpled features. Figure 5.12a presents a low magnification SEM image which provides perspective for the higher magnification images. The FIB was positioned such that the trench was aligned approximately parallel to the loading axis. The resulting milled surface is imaged in Figure 5.12b. The axes provided in the figure may be referenced with respect to Figure 5.12a. Despite the large deformation near the fracture surface, backscatter SEM imaging (Figure 5.12c) of the trench cross-section revealed a faint channeling contrast in the underlying microstructure of the fracture surface. From these microstructure features, it can be seen that the large dimples correspond to failure in the CG layer whereas the finer dimples represent fracture in the NC layer. Note that, the bright layer visible in the image is a surface-conforming protective layer of tungsten which was deposited to prevent damage to the underlying material during ion milling and also assisted in visualizing the topographical landscape of the fracture surface. Further examination of the trenched cross-section showed that the CG layers have a saw-toothed shape that protruded approximately 2-3 μm above the fracture plane. The outline of these features was measured to be approximately 45° from the loading axis. Considering the <100> texture measured in the EBSD data (Figure 5.3), and the proximity of the observed CG layer fracture angle relative to the localized neck (55° to the loading axis), this fracture orientation likely corresponds to activation of the <110>//{111} slip system, which has been previously reported as a possible deformation mechanism in NiFe MLs [122].

The deformation behavior of the NiCo ML is an inherently multiscale phenomenon in which the modulation of grain size on the microscale translates into the macroscopically observed fracture geometry. Figure 5.13 presents a schematic representation of this multiscale deformation mechanism. In each test, tensile failure initiated from the surface of the coupon, which was consistent with observations in other mechanical studies of PED materials [204]. Due to the relatively low strain hardening capability of the NC layer, a macroscopic shear band formed, which developed into a localized neck. The change from
Figure 5.12: (a) An SEM micrograph of the ML_{50a} fracture surface taken from a perspective orientation. (b) An image of the trench which was cut using FIB milling. The trench is aligned approximately to the loading axis of the coupon. The orientation of the nominal tensile coupon dimensions relative to the image plane is provided in (a) and (b). (c) A backscatter SEM image of a trench milled into the fracture surface. The protruding structures appear to have a saw-tooth geometry which were inclined at approximately 45° to the loading axis. The scale bars are 1 mm (a), 50 μm (b), and 5 μm (c).
a uniaxial to a multiaxial stress-state caused plastic interaction between the constituent layers and led to the formation of a shear band, which activated the \( <110>/\{111 \} \) slip system in the CG layer and permitted the development of a significant neck. Continued elongation resulted in fracturing of both the NC and CG layers by microvoid coalescence. Macroscopically, the fracture plane initiated at the thinnest region of the loaded cross-section and propagated along the shear band. This behavior caused the waist of the tensile coupon to be cut along an oblique angle oriented at 55\(^\circ\) from the loading axis along the width and thickness of the sample. In comparison to the CG sample, the oblique orientation of the fracture path relative to the loading axis was also likely the cause of the drastically reduced \( R_a \). The relatively small area reduction due to uniform elongation.
is not represented in the schematic. On the microscopic scale, the dimpled fracture surface was populated by periodic saw-toothed protrusions which revealed the topographical landscape of the CG layer. It is expected that the orientation of CG protrusions in the fracture surface is highly texture dependent. A more randomized texture may lead to a less uniform saw-toothed fracture feature, but is not expected to significantly alter the interacting deformation mechanisms observed in the ML architecture.

5.5 Chapter summary

The deformation behavior of a ML with a comparatively thick layering of CG and NC features was examined. Uniaxial testing showed a rule of mixtures yield and tensile strength in the ML$_{50a}$ sample relative to CG and NC references, confirming expectations that the ML$_{50a}$ architecture may be considered as an aggregate of bulk CG and NC mechanical behaviours. In this regard, a synergy of deformation mechanisms is not appreciable in MLs with comparatively thick layers. Digital image correlation analysis and examination of the ML$_{50a}$ fracture surface offered important insight into the micro- and macroscale deformation mechanisms leading to ultimate material failure. Fracture was preceded by the development of a diffuse and local neck within the ML$_{50a}$ sample. Inside the local neck, a shear band was observed to form. The shear band was oriented at $55^\circ$ to the loading axis along both the coupon width and thickness. Upon the formation of a shear band, the resulting multiaxial stress state induced deformation in the CG layer, improving the neck stability in the ML. Further elongation of the sample resulted in ultimate failure with fracture initiating at the thinnest point of the neck cross-section and propagating along the shear band, which sectioned the coupon waist at an oblique angle relative to the loading axis. High magnification SEM micrographs indicated dislocation activity in the CG-NC interfacial region. Failure of the ML resulted in the pullout of CG layers which protruded from the fracture surface. The saw-toothed topography of the resulting fracture relief was created by activation of the $<110>/\{111\}$ slip system in the ML, which was a consequence of the texture of the CG layer as well as the orientation of a shear band during tensile loading. Based on these observations, a multiscale mechanism was proposed to describe the deformation behavior in MLs with modulated NC and CG layers. Study of MLs with higher CG-NC interfacial fractions are therefore warranted to further investigate the role of interfacial interactions in determining overall deformation behaviour.
Chapter 6

Deformation behaviour of MLs where $t_{CG}$ approaches $d_{CG}$

The current chapter examines the deformation behaviour of ML architectures where the thickness of the CG layer approaches its grain size. For a constant thickness ratio, the relative fraction of CG-NC interfacial area increases at lower $t_{CG}$. In the limiting case, where $t_{CG} \approx d_{CG}$, single CG grains are confined within a NC matrix. The deformation mechanisms arising at the CG-NC interface in this configuration are of particular interest. The purpose of this chapter is to investigate the limits of applicability of ROM behaviour to the ML architecture. The ROM assumption is based off the concept of a weighted aggregate treatment of the independent CG and NC mechanical responses, however, it ignores deformation mechanisms which may arise due to an increase in CG-NC interfacial area fraction. It is anticipated that the increase in CG-NC interfacial area fraction encourages an interplay between CG and NC microstructures, which leads to a nonintuitive mechanical response. Specifically, it is expected that the mechanical properties of these ML architectures cannot be predicted by a simple ROM calculation. Figure 6.1 shows the ML architectures which are studied in this chapter from the sample fabrication matrix presented in Chapter 3. Please refer to Table 4.1 for a comparison of nominal and actual measurements of the ML architecture layer thicknesses and thickness ratios.

6.1 Microstructures of the ML architectures

The as-deposited microstructures of the selected ML architectures were imaged using SEM inside a Hitachi SU 8230 microscope. All microscopy samples were prepared using standard metallography techniques, as outlined in Chapter 4. Channeling contrast
6.1. Microstructures of the ML architectures

Figure 6.1: The sample matrix showing the different thickness ratios in the MLs which were fabricated for this thesis work. Red markers indicate a specific ML which was attempted for manufacture and blue markers denote specific architectures which are studied in this thesis. The specific ML architectures studied in this chapter are indicated along with their shorthand designations.

Electron micrographs of the ML50b and ML91 architectures are provided in Figures 6.2 and 6.3 respectively. The relevant laboratory axes are provided and the growth direction from PED is image down. Both architectures were manufactured with a nominal 1 µm CG layer but possessed different thicknesses of NC material (1 µm, ML50b; 10 µm ML91), representing the extremities of the PED manufacturing window for architectures where $t_{\text{CG}} \rightarrow d_{\text{CG}}$. As shown in the figures, a clear and regular layering of NC and CG features can be observed in the as-deposited ML microstructure. High magnification images of the CG layers in both architectures illustrate the confinement of single CG grains within a NC matrix. Additionally, high magnification imaging of the ML50b architecture (Figure 6.2) indicates the presence of a small number of growth twins which are formed during the PED process. The formation of growth twins during PED is not unexpected due to favourable kinetics associated with the low stacking fault energy of the NiCo chemistry [145–147]. Growth twins have been previously observed in the electrodeposition NiCo foils [205] as well as other low stacking fault energy materials (e.g. Cu [206]). It is in-
6.1. Microstructures of the ML architectures

Figure 6.2: (a) A low magnification electron micrograph of the ML$_{50b}$ architecture. A clear and regular layering of CG and NC features is readily visible in the micrograph. (b) A higher magnification image of the CG layer, showing single CG grains confined within a NC matrix. A number of growth twins are also visible in the microstructure and are indicated by the white arrows. The laboratory axes are provided and the scale bars represent lengths of 5 μm (a) and 500 nm (b).
6.1. Microstructures of the ML architectures

Figure 6.3: (a) A low magnification electron micrograph of the ML₉₁ architecture. A clear and regular layering of CG and NC features is readily visible in the micrograph. (b) A higher magnification image of the CG layer, showing single CG grains confined within a NC matrix. Growth twins were not readily visible in this architecture. The laboratory axes are provided and the scale bars represent lengths of 10 μm (a) and 1 μm (b).
6.2 Mechanical behaviour of the ML architectures

The mechanical properties of the ML architectures were studied using uniaxial tensile testing. The methodology for this testing protocol is described in Chapter 4. It should be noted that all uniaxial tensile results presented in this chapter have been corrected using Eq. 4.1 and the representative CG and NC reference curves are the same as those presented in Chapter 4. The discussion of the mechanical properties of the ML architectures studied in this chapter begins with a review of the behaviour of the ML$_{50a}$ structure (see Chapter 5). Figure 6.4 plots the stress strain response of the ML$_{50a}$ architecture along with the representative CG and NC reference curves. The ROM expectations of mechanical response based on the measured $t_\eta$ of 0.44 for the ML$_{50a}$ architecture is plotted in blue stroke for comparison. The ROM response was calculated by taking the ROM-weighted average of the representative CG and NC responses up until the point of necking instability (i.e. $\sigma_{UTS}$) in the NC reference and is plotted using a solid line. The dashed-dotted line represents an extrapolation of mechanical behaviour which is determined using a fit of Ludwik’s equation to the plastic components of the ROM curve: $\sigma = \sigma_{YS} + C\varepsilon^{n_h}$, where $C$ is the strength coefficient and $n_h$ is the work hardening exponent [207]. As shown in the figure, the mechanical response of the ML$_{50a}$ architecture is well predicted by ROM calculations. These findings again indicate that the CG and NC layers in the ML$_{50a}$ architecture operate as independent bulk structures without significant interactions between deformation mechanisms.

Figure 6.5 provides the stress-strain responses for all of the ML architectures considered in this chapter along with their expected ROM curves. In contrast to the ML$_{50a}$ architecture, all of the ML structures exhibit significant deviations from ROM behaviour. While it is possible that there are small differences between the CG grain size distributions in each of the ML samples, the gains in yield strength cannot be rationalized purely based on differences in HP hardening. Based solely on HP strengthening effects, a CG layer that would deliver an equivalent yield strength possesses an average grain size of $d \approx 100$ nm [192], which is not consistent with SEM observations. On average, ROM predictions were found to underestimate the responses of the ML architectures by approx-
6.2. Mechanical behaviour of the ML architectures

Figure 6.4: Stress-strain behaviour of the ML$_{50a}$ architecture plotted with the ROM-weighted ($t_\eta = 0.44$) expected response. The CG and NC bulk references are plotted for comparison.

approximately 4, 10, 19, and 30% for the ML$_{91}$, ML$_{83}$, ML$_{70}$, and ML$_{50b}$ samples, respectively (based on comparison of $\sigma_{YS}$, see Table 6.1). In this regard, the deviations from ROM expectations are observed to grow as the thickness ratios decrease and the relative fraction of CG material increases, suggesting that ROM predictions underestimate the underlying mechanical response of the CG layer. This finding is explicitly clear for the ML$_{50b}$, ML$_{83}$, and ML$_{91}$ architectures which all possess nominally the same thickness of CG material ($\approx 1$ $\mu$m thick CG layers), but varying thicknesses of NC layers. In consideration of the mechanical response of the ML$_{50a}$ architecture, these results are counterintuitive and indicate that the fundamental assumption underpinning ROM is invalid at the current length-scale (i.e. as $t_{CG} \to d_{CG}$). Specifically, the notion of an independent operation of CG and NC deformation mechanisms which then manifests as ROM mechanical behaviour is invalid in these specific ML architectures. This finding suggests an unknown interaction of CG and NC deformation mechanisms in the CG-NC interfacial area and motivates a deeper investigation of the underlying deformation behaviour.

Before an in-depth investigation of deformation behaviour is initiated, it is prudent
to first assess the reliability and repeatability of these findings. Figure 6.6 provides replicas (n=5) of the stress-strain responses of each ML architecture considered in this study along with the NC and CG reference samples. Yield strengths were found to range from 1012 (ML\textsubscript{50b}) to 1121 MPa (ML\textsubscript{91}) and tensile strengths were measured in the range of 1527 (ML\textsubscript{50b}) to 1723 MPa (ML\textsubscript{91}). Interestingly, the strength of the ML\textsubscript{91} architecture was found to be comparable to the NC reference (σ\textsubscript{UTS} = 1736 ± 19 MPa), despite the presence of clearly defined CG layers. The elongation to failure for each sample was measured to range from 0.048 (ML\textsubscript{50b}) to 0.059 (ML\textsubscript{70}), which was largely comparable to the average of the NC reference (ε\textsubscript{f} = 0.048 ± 0.001). As shown in Figure 6.6, the mechanical responses of the ML architectures and reference samples are highly

Figure 6.5: Mechanical behaviour of the ML architectures deformed under uniaxial tension. ROM expectations for each of the structures are provided in blue stroke. Each of the ML structures examined here showed significant deviations from ROM behaviour, indicating that unexpected deformation mechanisms are dominant in the mechanical behaviour of these architectures. The CG and NC bulk reference responses are plotted for comparison.
Figure 6.6: Stress-strain curves for the NC and CG references and ML architectures. Five replications of each structure are plotted in each graph, showing excellent repeatability. The consistency of the mechanical behaviour provides further confidence for the observations of ROM behaviour deviations in each ML architecture.
reproducible, providing further confidence in the reported ROM deviations. Specifically, the yield and ultimate tensile strengths for each of the presented structures exhibit excellent consistency. All tensile curves exhibited the characteristics of ductile fracture (i.e., stress-strain responses associated with failure by necking). However, variations in the elongation to failure of some tensile specimens are notable. Since the tensile coupons were waterjet cut, it is likely that residual roughness which was not smoothened during specimen preparation is responsible for the scatter in the total elongation to failure. The relevant averaged mechanical properties ($\sigma_{YS}$, $\sigma_{UTS}$, and $\varepsilon_f$) are provided graphically in Figure 6.7 and numerically in Table 6.1 along with the averaged ROM predictions for each structure. As discussed in Chapter 5, under a uniaxial loading condition the NC layer limits the extension of uniform elongation, therefore ROM calculations of the elongation to failure are not applicable to the current analysis.

In addition to unanticipated deformation mechanisms, it is conceivable that the enhanced yield and tensile strengths measured in ML architectures are the result of a stronger NC layer in the ML with respect to the NC reference sample. To confirm that
Table 6.1: The averaged mechanical properties (n=5) for the ML architectures studied in this chapter. ROM predictions are provided along with the experimental averages.

<table>
<thead>
<tr>
<th>Architecture</th>
<th>( \sigma_{YS} ) (MPa)</th>
<th>( \sigma_{UTS} ) (MPa)</th>
<th>( \varepsilon_f ) (mm/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROM exp. dev. (%)</td>
<td>ROM exp. dev. (%)</td>
<td>ROM exp. dev. (%)</td>
<td></td>
</tr>
<tr>
<td>ML (_{50b})</td>
<td>713±10</td>
<td>1012±10</td>
<td>30</td>
</tr>
<tr>
<td>ML (_{70})</td>
<td>860±7</td>
<td>1065±7</td>
<td>19</td>
</tr>
<tr>
<td>ML (_{83})</td>
<td>970±25</td>
<td>1077±25</td>
<td>10</td>
</tr>
<tr>
<td>ML (_{91})</td>
<td>1077±15</td>
<td>1121±15</td>
<td>4</td>
</tr>
</tbody>
</table>

the NC material deposited in the ML is comparable in mechanical properties to the NC reference, nanoindentation experiments were conducted to selectively probe the hardness of the NC layer material. Nanoindentation hardness measurements were performed on the NC layers within the ML\(_{91}\) architecture and the bulk NC reference sample at peak loads of 5 and 10 mN. The methodology described in Chapter 4 was used to collect all nanoindentation measurements except that the peak hold time was reduced to 10 s. The ML\(_{91}\) architecture was selected for nanoindentation as it possessed the thickest NC layers (\( \approx 10 \) \( \mu \)m), facilitating a targeted study of the NC material. Additionally, microindentation of the ML was performed at 100 and 500 g loads using a Vickers tip geometry. The goal of this measurement was to probe the entire ML microstructure for further assessment of ROM deviations and validation of tensile results. Microindentations were performed using the same peak hold time (10 s) as the nanoindentation experiments. In order to provide a consistent measurement of hardness, the indentation area was measured using atomic force microscopy (AFM). Indentation hardness is reported using the Vickers hardness number (HV) and was calculated as the ratio of peak load to the projected indentation area of contact. In order to validate the AFM as an accurate tool for measurement of indentation area, AFM measurements of the residual depth of indentation (\( h_p \)) were compared against values collected from nanoindentation \( P - h \) curves. Figure 6.8a provides a schematic of an indentation impression and defines \( h_p \) as the distance between the depth of a indentation impression and the undisturbed surface. As shown in Figure 6.8b, the measurements collected directly from the nanoindentation equipment (solid bars) and the AFM (hatched bars) are consistent, validating the implementation and calibration of the AFM. Figure 6.9 presents AFM images of nano- and microindentation impressions in the ML\(_{91}\) architecture. The nanoindentation impressions (Figure 6.9a,b) appear to be well-positioned in the NC layer, whereas the microindentations have clearly engaged a number of CG layers (Figure 6.9c,d). A summary of the averaged nanoindentation and microindentation hardness measurements is
6.2. Mechanical behaviour of the ML architectures

Figure 6.8: (a) A cross-section schematic of a residual indentation impression. $h_p$ is defined as the difference between the depth of the indentation impression and the undisturbed surface. (b) A comparison of $h_p$ values collected directly from the $P-h$ curves (solid bars) and from AFM measurements (hatched bars) showing excellent agreement for the ML$_{91}$ and NC samples which were nanoindented at loads of 5 and 10 mN.

provided in Figure 6.9e. The ML$_{91}$ architecture was found to have nanoindentation hardnesses of $564 \pm 7$ and $556 \pm 5$ HV for measurements ($n=5$) collected at peak loads of 5 and 10 mN, respectively. These values were comparable to measurements of the NC reference which were found to be $560 \pm 7$ (5 mN) and $554 \pm 1$ HV (10 mN). Therefore the NC material deposited in the ML is verified to have comparable mechanical properties to the NC reference and can be excluded as a cause of undue strengthening in the ML architectures presented here. Interestingly, microindentation experiments, which effectively probed a representative volume of the ML microstructure, showed similar deviations in ROM behavior as was measured during uniaxial tensile testing. Microindentation hardnesses of $545 \pm 1$ and $545 \pm 3$ HV were measured for indentations performed at 100 and
6.2. Mechanical behaviour of the ML architectures

Figure 6.9: AFM amplitude signal images of nanoindentation impressions at $5 \text{ mN}$ (a) and $10 \text{ mN}$ (b) loads in the NC layer of the ML$_{91}$ architecture. The white arrows indicate the positions of the CG layers. AFM deflection signal images of microindentations at $100 \text{ g}$ (c) and $500 \text{ g}$ (d) loads. (a) and (b) were collected using the dynamic tapping mode, and (c) and (d) were imaged using the static deflection mode. The scale bars represent lengths of $5 \mu m$ (a)-(b), $10 \mu m$ (c), and $20 \mu m$ (d). (e) A summary of the averaged hardness measurements ($n=5$) for the ML$_{91}$ architecture as well as the CG and NC reference samples. The solid and hatched bars represent measurements collected at 5 and 10 mN (nano), and 100 and 500 g (micro) loads, respectively. The dashed lines represent ROM predictions.
Deformation mechanisms in ML architectures

Table 6.2: The averaged indentation hardnesses (HV) for the CG, NC, and ML₀₉₁ samples (n=5). ROM predictions and deviations for microindentation tests are also provided.

<table>
<thead>
<tr>
<th>Sample</th>
<th>HVnano</th>
<th>HVµ</th>
<th>100 g exp.</th>
<th>ROM</th>
<th>dev. (%)</th>
<th>500 g exp.</th>
<th>ROM</th>
<th>dev. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 mN</td>
<td>10 mN</td>
<td>100 g</td>
<td>500 g</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CG</td>
<td>-</td>
<td>-</td>
<td>221 ± 6</td>
<td>-</td>
<td>-</td>
<td>211 ± 3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NC</td>
<td>560 ± 7</td>
<td>554 ± 1</td>
<td>552 ± 1</td>
<td>-</td>
<td>-</td>
<td>557 ± 1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ML₀₉₁</td>
<td>564 ± 7</td>
<td>556 ± 5</td>
<td>545 ± 1</td>
<td>521</td>
<td>4</td>
<td>545 ± 3</td>
<td>525</td>
<td>4</td>
</tr>
</tbody>
</table>

500 g load, respectively. The CG and NC reference samples possessed microindentation hardnesses of 221 ± 6 and 211 ± 3 HV (CG), and 552 ± 1 and 557 ± 1 HV (NC) for the 100 and 500 g load tests. These measurements provide ROM estimates of microindentation hardnesses of 521 (100 g) and 525 (500 g) HV, which differ from experimental measurements by ≈ 4%, in good agreement with ROM deviations reported for the ML₀₉₁ architecture under tensile loading. A summary of the nano- and microindentation properties are provided in Table 6.2. Considering the agreement between the combined sets of indentation and tensile data, these findings prove that the measured ROM deviations are indeed robust and provide strong evidence for a mechanism-based explanation for this counterintuitive deformation behaviour. Future mechanical investigations of the ML architecture using different loading configurations such as three point bending or deep drawing are recommended to identify other loading scenarios which lead to deviations from ROM behaviour.

6.3 Deformation mechanisms in ML architectures

High magnification electron micrographs were collected of ML samples which have been indented at high loads (500 g) in order to image deformation structures which have been created due to mechanical loadings. Electron channeling contrast images were collected in a high-resolution SEM using a modification of the technique pioneered by Gutierrez-Urrutia et al. [208], which is known to provide high contrast images of dislocation cell structures and deformation twins [209, 210]. Indentation was selected as the deformation medium for this experiment as the localized strains are high compared to the failure strains of the ML architectures under uniaxial tension (∇ ≈ 0.05), which should assist in visualizing deformation structures. Figure 6.10a illustrates the positioning of the Vickers indenter relative to the underlying microstructure and also shows the area where high magnification images are collected. Figure 6.10b presents a low magnification image
6.3. Deformation mechanisms in ML architectures

Figure 6.10: (a) The configuration of the Vickers indentations relative to the microstructure features in the ML$_{91}$ architecture. The region of interest in Figures 6.11 and 6.12b is indicated by the red box. (b) A low magnification SEM image of the ML$_{91}$ sample after indentation. The indentation impression appears to be distorted due to misalignment of the sample and SEM pole piece during imaging. The scale bar in (b) represents a length of 10 μm.
of the indenter impression. The indenter apex is observed to pass through the middle of a CG layer. It should be noted that the Vickers indenter is a true square-based pyramid (see the AFM image in Figure 6.9) and that the distorted indentation impression is due to sample misalignment with the SEM pole piece during imaging. Furthermore, the debris visible within the indentation impression was observed on every indentation and is believed to be caused by defects in the Vickers tip profile. Figure 6.11 provides a high magnification electron channeling contrast image of a CG layer inside the indentation impression. The dark line running horizontal across the image represents the impression of a pyramidal edge on the Vickers indenter. As shown in the figure a number of twins are visible in the image, whereas the presence of a significant dislocation cell structure in the CG layer is not evident. It is believed that these twins are deformation twins that have been formed to accommodate the indentation deformation. This distinction between deformation and growth twins in the ML\textsubscript{91} architecture is based on qualitative observations of the CG layer pre and post-indentation. In the former condition (see Fig-
6.3. Deformation mechanisms in ML architectures

Figure 6.12: (a) A low magnification image of the indentation in the CG reference sample. The distortion in the indent impression is due to misalignment of the sample with the SEM pole piece. (b) A high magnification electron channeling contrast image of the indentation. A dislocation cell structure is visible as regions of mottled contrast within the CG grains. The dark line across the microstructure is the impression formed by the pyramidal-edge of the Vickers indenter. The scale bars represent lengths of 10 μm (a) and 1 μm (b), respectively.
ure 6.3b), twins were not observed, whereas after indentation, twins were observed only in CG layers within the indented region. A complete quantitative analysis of twin density evolution as it relates to indentation testing is recommended for future investigation to assess the degree of deformation twinning in this architecture. In order to highlight these findings, a similar experiment was performed on a CG reference sample. Low and high magnification images of the indentation impression are displayed in Figure 6.12. In contrast to the ML architecture, the CG reference sample exhibits strong evidence of dislocation slip as seen through dislocation cell structure formation, which is visible as regions of mottled contrast in the SEM image. Twins are not readily visible in the micrograph.

The implications of these findings are compelling. Without the presence of NC layering, the microstructure of the CG reference is observed to accommodate deformation through dislocation slip. Conversely, the ML architecture, which is comprised of the same CG features, shows evidence of deformation twinning. In this regard, the effect of confinement of the CG microstructure has led to the observation of a different deformation mechanism. The emergence of twinning as an active deformation mechanisms is significant due to its implications on the flow stress. Deformation twinning is known to lead to a dynamic refinement of microstructure during mechanical loading, introducing new boundaries which can significantly strengthen a material in a manner analogous to Hall-Petch hardening. Indeed, deformation twinning has been intentionally encouraged through alloy and microstructure design in many materials and is responsible for the mechanical property improvements in many engineered structures. For example, deformation twinning is the dominant strengthening mechanism in the deformation of nano-twinned Cu [211] and Mg alloys [212], as well as in twinning-induced plasticity steels [213]. It is still not clear, from the current results, the exact mechanism by which deformation twins may grow in the CG layer. The observation of twins in a confined microstructure suggests a role of the CG-NC interface, however, the current methodology lacks the spatial and temporal resolution sufficient to capture deformation twin evolution. Further investigation is required to understand potential growth pathways for deformation twins in the CG layer.

6.4 Chapter summary

In this chapter the deformation behaviour of ML architectures where \( t_{\text{CG}} \) approaches \( d_{\text{CG}} \) was examined. Through uniaxial tensile testing and indentation experiments significant deviations from ROM behaviour were observed. The degree of deviation was found
to correlate inversely with the thickness ratio, indicating that the mechanical behaviour of the CG layer was significantly different from the bulk CG response. In this regard, ROM calculations, which are based off a weighted aggregate of the NC and CG references responses, are inaccurate in predicting ML behaviour. It was further confirmed that the anomalous strengthening in the ML architecture was not the result of differences in mechanical properties between the NC layers within a ML structure and the NC reference sample. It is assumed that the anomalous hardening measured in these ML architectures is a consequence of unknown deformation mechanisms which are active at the CG-NC interface. High resolution electron channeling microscopy analysis implicated deformation twinning as an active deformation mechanism in the ML architectures examined here. By comparison, evidence of deformation twinning was not observed in the CG reference sample. These results suggest an interface-mediated deformation twinning mechanism, however, further investigation is required to understand the emergence of this deformation behaviour and its connection to the specific material architecture of the ML.
Chapter 7

MD simulation of deformation in ML architectures

At this stage in the thesis body, it is helpful to briefly summarize the results of the experimental testing. The results of the previous chapters have led to the following conclusions regarding the deformation behaviour of the ML architecture:

1. ROM calculations, taken as the weighted aggregate of independent NC and CG mechanical responses, accurately predicts ML behaviour for structures with thick CG layers.

2. ROM calculations underpredict ML behaviour when the $t_{CG}$ approaches $d_{CG}$, and these underestimations becomes larger at lower thickness ratios.

3. These deviations are related to the observation of deformation twinning, which has been observed in CG layers for the ML$_{91}$ architecture, but not in the CG reference sample. This implicates a CG-NC interface-mediated deformation twinning mechanism.

The previous experiments, however, have not provided a direct observation of deformation twinning. Furthermore, the implication of an interface-mediated mechanism raises other issues which require clarification. Specifically, if deformation twinning is interface-mediated, why is this mechanism not observed in the CG reference structure or in the ML architecture with thicker CG layers (see Chapter 5, ML$_{50a}$ sample)? This dearth of mechanistic insight motivates the current chapter, which examines the deformation behaviour of the ML architecture using MD simulations. The purpose of this study is to provide atomistic insights into the emergence of deformation mechanisms in the ML...
architecture. The high resolution of MD simulations may be leveraged to directly investigate the inherent deformation modes of the ML structure at length and timescales inaccessible to experiments. For these purposes, MD tensile simulations are performed on supercells which are representative of the non-ROM conforming ML architectures (i.e., where $t_{CG}$ approaches $d_{CG}$). Specific attention is given to interfacial deformation mechanisms in order to rationalize the trends observed in experimental measurements.

The results of this chapter provide a framework for understanding deformation twinning within ML architectures and provide a mechanism-based description of deformation which complements the laboratory measurements collected in the experimental chapters. Furthermore, MD simulations may be used as a platform to parametrically investigate design variables such the NC grain size.

### 7.1 Representation of ML architectures in MD supercells

As described in Chapter 3, the limitations of current computational hardware place restrictions on the number of atoms which may be simulated using the MD method. Under these restrictions, a complete representation of the ML architecture, which contains CG features on the order of 1 μm in scale ($\approx 10^{12}$ atoms) is not accessible with the current hardware and presents a non-trivial supercell design challenge. In order to address this computational resource issue, the principle of quasi-3D supercell design with a sacrificial dimension is utilized in this chapter. This methodology has been previously implemented in large-scale MD simulations [174]. Please see the Section 3.3 for a detailed description of quasi-3D supercell construction. In order to achieve a reasonable representation of ML features (i.e., NC and CG features), the Voronoi-based NC microstructure generation algorithm presented in Chapter 3 has been modified to incorporate a large single crystal slab within the MD supercell. In this context, the slab is representative of the CG features in a ML and this supercell design targets the non-ROM conforming ML architectures where a single CG grain is embedded in a NC matrix (i.e., where $t_{CG}$ approaches $d_{CG}$). Figure 7.1 presents a schematic of the slab insertion scheme. As shown in the figure, the NC microstructure (see Figure 3.10b) is segmented along a transecting pathway of the grain boundary network and a large Voronoi cell is inserted. The cell is then populated with atoms which are textured to match the common pole figure of the quasi-3D supercell. Using this procedure, the atom-filling algorithm accurately enforces periodic boundary conditions within the inserted slab. As shown in the figure, the
Figure 7.1: The strategy used to design a MD supercell representative of the ML architecture. The progression of steps in formation of the supercell is indicated by the arrow. The quasi-3D NC architecture from Figure 3.10b is segmented along a transecting path in the grain boundary network. A large Voronoi cell is inserted which is representative of the CG features in the non-ROM conforming MLs (i.e., where a single CG grain is confined in a NC matrix). The Voronoi cell is then populated with atoms which are textured to the common pole of the quasi-3D microstructure. Atoms in green are in a perfect FCC coordination and atoms in black are in a defective state. The slab dimension in this supercell is 100 nm.

ML architecture space is not perfectly partitioned by the Voronoi algorithm and there exists overlaps between the inserted slab and the resident NC microstructure, presenting a problem with respect to the atom-filling algorithm. Two different schemes were considered to prevent the overlap of grains in the MD supercell. In the first approach, the overlapping atoms in the inserted slab were deleted and atoms in the resident NC microstructure were kept in the final MD supercell. This scheme created slabs with an ‘expanded’ boundary that conformed to the shape of the resident NC microstructure, which is presented in Figure 7.1. Conversely, in the second approach the overlapping atoms in the NC microstructure were deleted, leading to slabs with ‘truncated’ boundaries. Figure 7.2 presents a comparison of the two filling strategies. Uniaxial tensile testing was performed to assess differences in the mechanical response arising from the selected slab filling scheme. Other than structural changes caused by the slab filling scheme, the two supercells are identical (i.e., same texture, chemistry). All MD tensile tests presented in this chapter were performed using the methodology described in Chapter 3. As shown in Figure 7.2b, both samples exhibited very similar mechanical responses.
In lieu of a distinct difference in mechanical response, the expanded scheme was selected for implementation in the remainder of this thesis. The rationale behind this decision is that the truncated scheme artificially alters the grain size of the NC microstructure and exposes new NC grains to NC-slab interfacial region. These alterations to the NC grain size statistics may prove problematic when performing parametric MD tensile studies of
The slabs generated for MD simulation in this thesis are pristine crystals without any prior existing defects or dislocation sources, other than the grain boundary structures at the NC-slab interface. This slab design therefore permits a targeted assessment of interfacial deformation, independent from other convoluting deformation processes. The slab dimension is an additional design parameter which must be considered prior to initiation of MD tensile studies of the ML architecture. Despite the comparatively large planar supercell dimensions which may be accessed by implementation of a quasi-3D supercell design, slab dimensions on the order of 1 μm are not feasible. However, the nature of the current MD testing does not necessarily require access to μm-level dimensions. The goal of this thesis study on heterogeneous microstructures is targeted towards understanding deformation behaviour when extremely small NC crystals share interfaces with comparatively large CG microstructure features. The slab dimension constructed in the MD supercell must, therefore, only be sufficiently large such that it does not behave as a NC grain. The strategy pursued in this chapter with respect to slab dimension selection follows this principle. In this context, the slab dimension is designed to be as large as allowable, given current computational limitations. The viability of the selected slab is then assessed through parametric variation of the slab dimension.

Figure 7.3a presents the uniaxial tensile response of MD supercells with slab dimensions ranging from 20 - 100 nm. The tested MD supercells were exactly identical except for the dimension of the slab. The overall mechanical properties of the MLs are found to decrease with increasing slab width, and plateau at a slab dimension of 80 nm. The yield stresses (2% offset) are measured to be in the range of 6.92 - 7.41 GPa. As shown in the figure, the post-yield hardening behaviour ($\varepsilon_t > 5\%$) of the 80 and 100 nm slab samples is nearly identical. It is therefore concluded that at widths above 80 nm, the dimension of the slab does not have a significant impact on the deformation behaviour of the ML and a 100 nm slab dimension is selected as being representative of the CG features in the ML architecture for the remainder of MD tensile simulations presented in this thesis. MD supercells with slabs larger than 100 nm were found to be too expensive in terms of computational time and file storage requirements to be feasible for parametric analysis. It should be noted that the inclusion of larger slabs is not expected to lead to further softening of the overall ML structure due to the pristine condition of the slab prior to testing. Tested independently from the ML architecture, the slab behaves as a pristine structure with a theoretical strength of $G/2\pi \approx 12$ GPa [214]. It is the introduction of boundaries at the CG-NC interface which weaken the structure. At dimensions above 80 nm, the slab serves as an extremely large medium to accommodate deformation arising
7.1. Representation of ML architectures in MD supercells

Figure 7.3: (a) Uniaxial tensile results for MD simulation of ML architectures with varying slab dimension. The post-yield ($\varepsilon_t \approx 5\%$) hardening behaviour of the 80 and 100 nm slab samples is nearly identical. (b) The yield stress (2% offset) which are calculated from the data in (a). A plateau in ML softening is observed at slab dimensions above 80 nm.

from the NC-slab interface. Below 80 nm, size effects become appreciable in the slab and the mechanical behaviour begins to exhibit HP hardening. Conversely, while slab dimensions greater than 80 nm do not significantly influence the strength of the supercell, excessively large slab dimensions could introduce texturing into the elastic properties of the ML. Biasing of the elastic modulus due to the slab dimension was not measured to
be significant in the ML samples prepared for MD simulation in this thesis.

7.2 Tensile simulation of the ML architecture

The investigation of deformation behaviour may be most logically initiated with a basic characterization of the tensile response of a representative ML architecture. Using the structural assumptions detailed in the above discussion and based on experimental measurements of the NC microstructure, a ML architecture was created with an averaged NC grain size of \( d_{NC} = 20 \text{ nm} \). The chemistry of the NiCo ML supercell was set to a composition of 70 at.% Ni and 30 at.% Co, which is consistent with EDX measurements. Figure 7.4 provides atomic snapshots of the MD supercell upon initialization and after structural relaxation. During relaxation of the MD supercell, a number of grain boundary features have been annealed. Specifically, needle-like grains have been rounded and high connectivity nodes have been reorganized due to the annealing algorithm. In order to replicate experimental conditions, uniaxial loadings are applied to the horizontal dimension of the supercell. As noted previously (see Chapter 3) the pole figure of the sacrificial dimension in all NC grains as well as the slab is aligned to the \(<1\bar{1}0>\) crystal direction. The loading axis of the slab is chosen to be aligned to the \(<110>\) vector, such that the Schmid factors of the (111) and (11\bar{1}) slip planes are equivalent. This definition of system geometry additionally maximizes the number of slip systems which are available for activation. This selection of slab orientation is also consistent with experimental EBSD and XRD measurements presented in Chapters 4 and 5. The generated MD supercell had dimensions measuring 80 x 180 x 2 nm and possessed 2.63 million atoms.

Figure 7.5 presents the MD tensile stress-strain curve for the ML architecture. The elastic modulus of the ML was measured to be 220 GPa, which is consistent with measurements reported for a fully NC microstructure with \( d_{NC} = 20 \text{ nm} \) (221 GPa) and experimental expectations (207 GPa [166]). As shown in the figure, the ML exhibited the expected elastic-plastic transition during high stress loading. Figure 7.6a illustrates the same stress strain data but is annotated to accompany the atomic snapshots of deformation stages which are provided as subfigures. Both dislocation-slip and deformation twinning are observed during mechanical loading. As shown in Figure 7.6b, deformation accommodation begins at low strain values (\( \varepsilon_t = 1.9\% \)) with dislocation glide originating from the NC-slab interface being observed. The glissile dislocation emitted from the NC grain boundary is indicated with an arrow in Figure 7.6d. As strain increases, deformation twin embryos are nucleated from the NC-slab interfacial region. A grain-boundary nucleated deformation twin is indicated in Figure 7.6e with an arrow. All deformation
twins were of the $\Sigma 3$-type and all associated Shockley partial dislocations were observed to be of a 90° edge character and possessed Burgers line vectors which were parallel to the sacrificial dimension of the MD supercell. The corresponding stress-states of dislocation-slip and deformation twinning initiation are indicated on the stress-strain curve shown in Figure 7.6a. Notably, inflection points in the stress-strain response are coincident with the activation of these deformation mechanisms. Figure 7.6f presents a snapshot of the MD supercell at the yield point. As shown in the figure, a number of planar faults structures which are associated with the formation of deformation twins are visible in the slab region. Each of these fault structures has been nucleated from the NC-slab interface. Therefore the deformation mechanisms in these MD simulations may be explicitly classified as boundary-driven processes, which excludes intragranular phenomena such as a pole-based deformation twinning mechanism [39]. It should be noted that the comparative competition between deformation twinning and dislocation-slip cannot be explicitly evaluated due to the lack of defective debris left from the glide of perfect dislocations.
across the slab.

The emergence of deformation twinning in MD simulations reinforces experimental observations from Chapter 6. Furthermore, the nucleation of twins specifically at the NC-slab interface highlights the role of this structure in mediating deformation. A similar boundary-mediated deformation twinning nucleation mechanism has been reported in the work of Van Swygenhoven et al. [158]. To the author’s knowledge this is the first observation of this phenomenon in MD studies of modulated microstructures, although this behaviour can be largely extrapolated from previous MD studies on interfaces in nanocrystalline materials. For examples please see Refs. [158, 215]. While these observations rationalize an interface-mediated mechanism, they do not directly explain the absence of deformation twinning in purely CG microstructures, motivating a more detailed analysis.

In order to understand the role of deformation twinning in the plastic accommodation, a high resolution study of the atomic strain-state during leading Shockley partial nucleation was undertaken. Figure 7.7 provides snapshots of an NC-slab interface during partial dislocation nucleation and emission. During the process of Shockley emission, atoms along the NC-slab interface were observed to reorganize to facilitate dislocation nucleation. This process of atomic shuffling permits strain relaxation within the NC grain.
Figure 7.6: (a) The uniaxial stress-strain response for the ML architecture. The annotations in this curve highlight the stress-strain state of the atomic snapshots in subsequent subfigures. (b) The ML architecture after structural relaxation. The annotations in this image correspond to the spatial location of deformation events in (c),(d), and (e). Dislocation-slip is observed to occur at low angle grain boundaries along the NC-slab interface. (c),(d) High magnification snapshots of the NC-slab interface prior to and just after dislocation emission into the slab. The arrow indicates the position of a glissile extended dislocation. (e) A high resolution image of deformation twin formation along the NC-slab interface. (f) The overall structure of the ML architecture at yielding. Several planar faults are visible within the slab. Atoms coloured in green exist in a perfect FCC coordination whereas black atoms are in a defective position. Please note, the atomic snapshots provided here are not at the same scale.
Figure 7.7: Atomic snapshots of the NC-slab interface just prior to (a) and after (b) Shockley partial dislocation nucleation. The change in atomic configurations between (a) and (b) are quantified by the strain relaxation map in (c). The nucleation of the Shockley partial dislocation serves to relax the NC-slab interfacial region and effectively provides a pathway for strain relief within the NC microstructure. The dashed line denotes the NC-slab interface and the arrow indicates regions of the NC microstructure which experience strain relief. Strain relaxation is defined here as the change in local shear strain between configurations. Atoms colored in green exist in a perfect FCC coordination whereas black atoms are in a defective position in (a) and (b).

(Figure 7.7c). Strain relaxation is defined here as the change in localized shear strain pre- and post-dislocation emission. Therefore, deformation twinning in the slab serves to facilitate strain relief within the NC microstructure. In this regard, the slab acts as a sink for the storage of dislocations, whose emission relaxes the accumulated strain of the NC grain.

The observation of interface-mediated deformation twinning is now discussed in the
context of other deformation mechanisms. As discussed in Chapter 2, intragranular Frank-Read sources are a common deformation pathway observed in FCC materials. The stresses required to activate these sources depends on a number of parameters, but are typically in the range of $\approx 100$ MPa [216]. In comparison to the activation of Frank-Read sources, the emission of deformation twin embryos from grain boundaries in FCC lattices is a high-stress process. The nominal stresses required depend on a number of factors including the shear modulus, stacking fault energy, the grain size, and the Burgers vector of the nucleated Shockley partial dislocations. Estimates based on Ogata et. al [217] place nucleation stresses at above 1 GPa. Stress-assists, in the form of grain boundary regions with high free volume, or existing grain boundary dislocations can lower this nucleation threshold significantly. However, the stresses required to nucleate Shockley partials from grain boundary dislocations are reported to be in the range of 200-1100 MPa for FCC materials with a 20 nm grain size [218]. Using the relations in Ref. [218], estimates for NiCo place this stress at $\approx 620$ MPa. This observation is critical to the observed dichotomy of deformation twinning in the CG structures of this thesis. Deformation twinning does not occur at boundaries in the CG microstructure as lower-stress Frank-Read mechanisms are preferentially activated. In this manner, yielding and ultimate failure of the CG microstructure occurs before sufficient stress is available to activate deformation twinning. The high-stresses required to nucleate deformation twins are only accessible to NC microstructures. Therefore, deformation twinning is only achievable at the CG-NC interface and the emergence of this mechanism is a direct result of the heterogeneous design of the ML architecture. Figure 7.8 provides a schematic of this interpretation of deformation behaviour. The overall deformation behaviour of the ML architecture is broken into stages which are consistent with the discussion in the above text.

In terms of work hardening, the stacking faults and twin boundaries associated with deformation twinning serve to segment the slab microstructure and dynamically refine its grain size during mechanical loading, introducing new boundaries into the material. Under continued loading, this deformation phenomenon provides a mechanistic pathway to create a high density of barriers which impede dislocation glide and harden the microstructure. In order to quantify the degree of microstructure refinement, an examination of the stored dislocation density and dislocation mean free path during deformation was performed. The post-yield behaviour of the ML architecture is characterized by a significant increase in the stored dislocation density as well as a rapid decrease in the dislocation mean free path within ML architecture due to deformation twinning-driven segmentation of the slab. The aggregate effect of this deformation behaviour leads to
7.2. Tensile simulation of the ML architecture

Figure 7.8: The progression of deformation stages in the ML architecture. At low stresses, elastic loading occurs in both the NC and CG layers. As the stress rise above $\approx 100$ MPa, Frank-Read sources lead to intragranular deformation in the CG layer. Deformation in the NC features remains elastic. At higher stresses, deformation twins are nucleated at the CG-NC interface to relax strain accumulation in the NC layer.

Figure 7.9 provides the stored dislocation density of the ML architecture during deformation. As shown in the figure, the evolution behaviour of the stored dislocation density is separated into distinct regimes which are separated by the yielding point. Whereas, in the elastic regime the stored dislocation density remains relatively constant, there is a clear increase in $\rho$ just after yielding. The post-yield storage behaviour is observed to increase proportionally with the plastic strain ($\varepsilon_p$), reaching a value of $\approx 7 \times 10^{16}$ at the Considère point (Figure 7.9b). $\varepsilon_p$ defined here as the post-yield strain in true terms. Based on the Kocks-Mecking work hardening model, the evolution of the dislocation storage term is known to rely on the competition between twin spacing, forest hardening, and dynamic recovery (see Eqs. 3.17 and 3.18). In this relation, forest hardening and dynamic recovery lead to non-linearities in the evolution law. A linear evolution behaviour
7.2. Tensile simulation of the ML architecture

Figure 7.9: (a) The stored dislocation density as a function of the measured strain in the MD supercell. $\rho$ is observed to increase dramatically after yielding of the ML architecture. (b) The post-yield evolution of the stored dislocation density. A linear increase in dislocation density is observed in the post-yielding deformation behaviour. (c) The dislocation mean free path as a function of applied true strain. A relatively constant $\bar{\Lambda}_d$ is measured after yielding of the ML. The dislocation density has been calculated using the Dislocation Extraction Algorithm developed by Stukowski et al. [219].
therefore implicate the development of a deformation structure with a relatively constant dislocation mean free path. Figure 7.9c provides the evolution of the dislocation mean free path during MD tensile simulations. In this context, the dislocation mean free path may be considered as the average distance traveled by a dislocation before it encounters a boundary. \( \Lambda_d \) considers grain boundaries, twin boundaries and stacking faults in its determination. It may also be considered as an approximation of the average cell size of deformation structures bounded by planar faults within the slab. As shown in the figure, the evolution of the mean free path remains relatively constant after yielding, varying between 15 to 10 nm at the yield and ultimate tensile strains, respectively, with the majority of mean free path refinement occurring just prior to yielding.

Figure 7.10 provides atomic snapshots of the ML architecture at the ultimate tensile strain. A number of voids have formed in the intergranular region of the NC microstructure as denoted by blue arrows. Black arrows in the figure indicate extended glissile dislocations. These dislocations are typically observed to freely glide until intercept with the deformation twin structure of the ML (e.g., pink arrow), supporting the proposed boundary-driven hardening model. In general, both leading Shockley partial and extended dislocations were observed to interact with twin boundaries in the MD supercell. Furthermore, after pile-up along a twin boundary, these dislocations were observed to often cross-slip at higher applied stresses onto the conjugate twin boundary plane and resume glide. This reaction was observed to thicken the existing deformation twin in a manner consistent with the twin interaction mechanism described by Zhu et al. [51]. These type of boundary-dislocation interactions comprised the vast majority of all deformation behaviours observed during MD simulations. Indeed, only a few occurrences of dislocation-dislocation interactions were observed. Figure 7.10b illustrates a stair-rod dislocation which has been formed from the interaction of two Shockley partial dislocations. Also visible in this image are a number of leading Shockley partial dislocations which are gliding towards an existing deformation twin. Subsequent cross-slip of these partials leads to the thickening mechanism described above.

The implications of interface-driven deformation twinning are compelling when considered within the context of the experimental results. These MD observations provide a mechanistic explanation for the ROM and non-ROM conforming ML architectures observed in experiments. In the former structures, the thickness of the CG layer is large relative to the grain size and the overall fraction of CG-NC interfaces is consequently low. Therefore, the overall mechanical behaviour of the ML architecture is dictated by the weighted bulk mechanical responses of the individual CG and NC microstructures, which manifests in the ROM measurements that were experimentally collected. In this regard,
7.2. Tensile simulation of the ML architecture

Figure 7.10: (a) Atomic snapshot of the ML architecture at the ultimate tensile strain. Black arrows indicate glissile extended dislocations. The pink arrow indicates a sessile dislocation which has piled-up at a twin boundary. Dislocation-boundary interactions are identified to be the predominant deformation mechanism in MD simulations of the ML architecture. Blue arrows highlight intergranular regions of the NC microstructure that have begun to form voids. Atoms coloured in green here are in a perfect FCC coordination and atoms in black are in a defective position. (b) A high magnification image of the area indicated in (a). A stair-rod dislocation has been formed here due to the reaction of leading Shockley partial dislocations. Shockley partial dislocations are also observed in this image. Cross-slip of these Shockley partials onto the conjugate twin boundary plane represented a common deformation pathway observed during MD simulations. This cross-slip mechanism is consistent with the twin-thickening process described by Zhu et al. [51]. Atoms coloured in pink and white in this figure represent atoms with a local hexagonal close-packed or non-crystalline coordinations.

definition twinning and the subsequent dynamic grain size refinement and hardening of the microstructure is not a dominant deformation mechanism. In the latter structures, single CG grains are confined within a NC matrix and the fraction of CG-NC interface is comparatively high. Deformation twinning arising from plastic accommodation of the NC microstructure and plays a significant role in the overall strengthening of the microstructure. Therefore, the expectation of ROM behaviour represents a naive assumption of deformation behaviour which does not properly account for CG-NC interfacial deformation processes. Figure 7.11 summarizes the deformation processes which underpin the ROM and non-ROM behaviours. Under ROM behaviour, Frank-Read (F-R) type intragranular dislocation-sources lead to conventional dislocation pile-up at grain boundaries in the CG features and grain boundary-mediated deformation mechanisms dominate the deformation behaviour of NC crystals. Conversely, for ML architectures where $t_{CG}$ approaches $d_{CG}$ grain boundary-mediated deformation twinning at the CG-NC
interface leads to a dynamic refinement of the CG grain size through a reduction of the dislocation mean free path, which is responsible for the anomalous hardening measured in experiments. This phenomenon is similar to the deformation behaviour encountered in TWIP steels [210]. Most notably, the emergence of this deformation twinning mechanism is a direct consequence of the heterogeneous microstructure of the ML architecture. Indeed, deformation twinning is not directly observed in a fully CG microstructures due to the high stresses required for Shockley partial nucleation. The grain boundary-mediated deformation twinning mechanism observed here is therefore not accessible to homogeneous CG microstructures and it is the modulation of crystal features in a heterogeneous microstructure design which has explicitly enabled the activation of this deformation process. Caution must be exercised when comparing MD results directly to experiments.
significance, the exact quantities of the measured parameters (e.g., strengths, dislocation mean free path lengths) are not directly comparable due to the length and timescale limitations of MD simulations. It should be noted that the MD simulations analyzed in this section were based on ML architectures which were generated with slabs that possessed a pristine grain interior. It is of considerable interest to investigate ML architectures where the slab feature possesses pre-existing Frank-Read style intragranular dislocation sources in order to qualify the competition between intragranular and boundary-mediated deformation. Similarly, it is recommended that future work examine slab structures which possess growth twins. With consideration of the growth twins experimentally observed in the ML structures, it is relevant to understand the evolution of twin densities based on the interactions between these growth twins and the deformation twins which form during mechanical loading.

7.3 Parametric studies of the ML architecture

In order to explore the influence of ML design parameters on deformation behaviour, parametric studies were performed using MD simulations on the grain size of the NC phase. Figure 7.12a provides the uniaxial stress-strain responses of ML architectures which possessed NC microstructures with grain sizes measuring between 5 and 25 nm. The uniaxial tensile studies were performed using the same methodology as previous simulations. All MD supercells measured 80 x 180 x 2 nm and possessed between 2.62 and 2.63 million atoms. The texture and size of the embedded slab was the same as shown in Figure 7.4 for all supercells. As shown in the figure, each ML exhibited the expected stress-strain characteristics. Yield stresses were measured in the range of 6.6-7.2 GPa (Figure 7.12b).

In contrast to the NC reference structures tested in Chapter 3, the mechanical behaviour of these MLs was much more uniform, with smaller overall differences being measured in yield strengths. With the exception of the 25 nm structure, the MLs were found to have lower yield stresses relative to their NC references. This result is generally expected and can be predicted from consideration of the HP hardening observed during MD simulations of MLs with reduced slab sizes (see Figure 7.3). Interestingly, when examined against comparable NC reference samples (Figure 3.21), a shift in the maximum peak stress from 20 nm to 10 nm is observed. It should be noted that the reference NC microstructures and the NC features embedded in the ML are exactly identical, except for the presence of the slab.

In order to provide a physical rationale for this transition in the maximum yield
Figure 7.12: (a) The uniaxial stress-strain curves for the ML architectures with NC grain sizes in the range of 5-25 nm. (b) The yield stresses of the MLs, based on the mechanical responses in (a). These results have been overlaid with the reference NC microstructures which were tested in Chapter 3. A shift in the maximum strength from 20 nm to 10 nm is observed due to the presence of the slab in the ML architecture.
strength, analysis of the stored dislocation density and deformation twin structure was performed. Figure 7.13 presents the evolution of stored dislocation densities in each of the ML architectures. Dislocation densities are plotted here up to the point of plastic instability as defined by the Considère criterion. As shown in the figure, the 20 nm sample actually possessed the lowest dislocation density, which indicates that strength may not be naively correlated in a monotonic sense with the storage of plastic carriers. This finding can be considered in part as a consequence of the inverse HP effect. Specifically, while the 5 nm ML is expected to have a high dislocation density due to the high number of grain boundaries dislocations required to form the structure, the 5 nm NC reference sample has been measured to be intrinsically weaker than structures with lower numbers of grain boundary dislocations. Given the significant role that deformation twinning plays in the overall plastic response of the ML, the evolution of deformation twin density ($n_{TB}$) has been measured for the 10 and 20 nm MLs as well as their NC references (Figure 7.14). In this context, the twin density refers to the number of twin boundaries intercepted by a random line draw across the supercell in specific terms. It is calculated using the method of Underwood [220], where the total length of the boundaries are measured in

Figure 7.13: The evolution of the stored dislocation density with respect to plastic strain for each of the MLs examined in this section. The stored density is plotted up to the point of plastic instability as defined by the Considère criterion.
7.3. Parametric studies of the ML architecture

In order to calculate $n_{TB}$, the twin boundary density with respect to applied strain for the 10 and 20 nm ML and NC reference structures. The red and blue arrows indicate the densities at yielding for the 10 and 20 nm ML architectures respectively.

Figure 7.14: The evolution of the twin boundary density with respect to applied strain for the 10 and 20 nm ML and NC reference structures. The red and blue arrows indicate the densities at yielding for the 10 and 20 nm ML architectures respectively.

order to calculate $n_{TB}$. In this determination, both twin boundaries and stacking fault structures are considered. As shown in the figure, the twin densities are measured to monotonically increase for all samples during mechanical loading. A distinct increase in the twin boundary density is measured around the yield points of the structures which are indicated by the red and blue arrows for the 10 and 20 nm ML architectures, respectively. In general, the 20 nm NC reference possessed the lowest twin densities, whereas the 10 nm NC sample exhibited the largest values. Interestingly, a cross-over between twin densities is observed for the 10 and 20 nm ML samples around their yielding points. At high strains, the 10 nm ML structure is measured to have comparatively higher twin densities than the 20 nm ML architecture.

Further consideration of the twin density evolution provides some insight into the relationship between deformation structures and yield strength. Specifically, it is observed that the MD supercells with the highest yield strengths possessed the lowest twin densities. For example, the 20 nm NC reference sample exhibited the lowest twin densities during uniaxial tensile loading, and was measured to have the highest yield strength of all structures considered. This trend may be rationalized under the following considerations. As discussed above, deformation twinning was observed to play a large role in the
deformation accommodation of the ML architecture, specifically during yielding. Therefore, structures which resist the formation of deformation twins (i.e., possess lower twin densities) are able to suppress plastic flow and extend the elastic range of their mechanical response, effectively increasing the yield strength. A caveat regarding the results of this section should be noted at this point. The qualitative relation of deformation twin suppression to yield strength cannot be directly extended to experimental results due to the incompatibility of timescales.

The physical mechanism underpinning this shift in yield strengths between ML samples can be rationalized from a geometric perspective. The radius of curvature of the 10 nm grains is comparatively smaller, which increases the ledge density required to close the microstructure feature. This increase in ledge density manifests itself in the increased dislocation densities measured at smaller grain sizes (see Figure 7.13). To highlight this effect, Figure 7.15 provides a scaled schematic of a boundary ledge structure in grains of 10 and 50 nm. The ledge structure is formed by stacking \{111\}-type slip planes (gray boxes) along the crystal directions noted. The slip planes are scaled such that they contain an integral number of atoms positioned along the close-packed \(<10\bar{1}>\) crystal direction. The curvature of each grain is outlined in red stroke. As shown in the figure, the ledges created by stacking 5 \{111\} planes are dispersed over a larger arc length in the grain boundary of the 50 nm grain, which leads to an overall lower density of ledges in the grain boundary.

An increase in ledge density is significant in this context as ledges are known to serve as nucleation points for Shockley partial dislocations [156, 158], therefore leading to a higher dislocation source density for the emission of partials into the slab region. This observation is significant as it provides an explanation for the higher yield stresses measured in the 10 nm ML samples. The elastic fields created by arrays of Shockley partial dislocations with the same Burgers vector require additional applied loadings in order to overcome their interaction stresses. Therefore, the increase in source density, which is geometrically necessary to form smaller grain sizes, is then responsible for the suppression

![Figure 7.15: A scaled schematic illustrating the changes in ledge density along the grain boundary for grains of 10 and 50 nm. The \{111\} slip planes (gray boxes) are scaled to fit appropriately within each grain boundary (red stroke). The planes are scaled such that an integral number of close-packed atoms are contained within each layer.](image)
7.3. Parametric studies of the ML architecture

Figure 7.16: An in-plane shear stress map showing the elastic field generated by an interacting dislocation array. The stress-field of the central dislocation (arrow) has not been included to clearly illustrate the cumulative effect of the array. The values of shear stress were calculated using a Volterra solution for an array of 90° Shockley partial dislocations [2]. The blanked areas in the map correspond to the dislocation cores, for which the Volterra solution is not applicable. The shear stresses in the colormap have been normalized against the maximum values in the elastic field.

of twin nucleation and subsequently higher yield stresses. Figure 7.16 presents the elastic field of a parallel array of 90° Shockley partials with the same Burgers vector. The elastic fields of each Shockley partial have been calculated using the classic Volterra solutions for the in-plane shear stress [2] (see Chapter 8 for further details on this calculation). The stress field of the central dislocation has not been included in order to clearly illustrate the cumulative effects of the array. The blank areas in the surface plot correspond to the dislocation cores where a direct analytical solution is not tractable using the Volterra method. As shown in the figure, the cumulative effects of the dislocation array create a compressive shear stress field in the glide path of the dislocation indicated with the arrow. This effect is amplified as the dislocation array density is increased, requiring larger applied stresses to escape the dislocation stress field. The color map represents the normalized magnitude of the shear stress. Shear stress values have been normalized
7.3. Parametric studies of the ML architecture

Figure 7.17: (a) The ledge structure of a 10 nm NC grain along the NC-slab interface after structural relaxation of the MD supercell. (b) After mechanical loading, a number of Shockley partial dislocations have been nucleated, forming an array of ISFs. Free glide of these Shockley partials is restricted due to the combined elastic effects of the dislocation array. Atoms coloured in green are in a perfect FCC coordination whereas atoms in black are in a defective position.

The most notable observation of this parametric evaluation of NC grain size is that the inherent weaknesses in the 10 nm microstructure, when compared to the 20 nm NC reference, are offset by the increase in dislocation source density at the slab boundary. This increase in density suppresses plastic flow within the slab region of the ML. In order to further illustrate this concept, Figure 7.17 presents an example of a 10 nm grain along the NC-slab interface in the ML architecture. As shown in the figure, there are a number of ledges associated with this interfacial structure. Upon mechanical loading, a number of Shockley partial dislocations are nucleated from the ledges to form ISFs. However, due to summation of stress fields from the leading Shockley partials, these dislocations are not able to freely glide and require higher stresses to escape the combined elastic field of the dislocation array. The aggregate effect of these stress field interactions along other
NC-slab interfaces in the microstructure suppresses yielding of the ML architecture.

One of the most attractive aspects of MD simulations is the flexibility they offer in scientific investigations. Therefore, future parametric studies of the influences of texture are planned in order to assess the effects of crystallography on the measured mechanical properties. It is also recommended that the codes and algorithms, which have been designed to examine FCC crystal structures, be expanded to include other crystal lattices such as hexagonal close-packed and body-centered cubic structures, such that the deformation behaviour of these heterogeneous microstructures may also be explored.

### 7.4 Chapter summary

Experimental observations do not possess the necessary resolution to provide a direct observation of deformation twinning in the ML architecture. Therefore, the current chapter leverages the capabilities of MD simulations to investigate the deformation behaviour of the ML structure. The goal of this study was to provide a mechanism-based interpretation of deformation behaviour which can reconcile experimental observations. Specifically, it is of great interest to connect deformation twinning with the anomalous hardening measured in ML architectures where $t_{CG}$ approaches $d_{CG}$. Furthermore, a rationale is required which can explain the observation of deformation twinning in CG layers, but not in the CG reference sample. For this purpose, uniaxial tensile simulations were conducted on MD supercells which were designed to be representative of the non-ROM conforming ML architectures. Based on MD simulations, a boundary-mediated deformation twinning mechanism was uncovered. From MD simulations, it was observed that deformation twins nucleated readily from the NC-slab interfaces in the generated MD supercells. The nucleation of these deformation twins served as a mechanism for strain relaxation within the NC microstructure. Most importantly, this mechanism is only possible at the NC-slab interface, where stresses are sufficiently high to permit the nucleation of Shockley partial dislocations from interfacial ledges. The high stresses required for Shockley partial nucleation preclude the dominance of this deformation twinning mechanism in the CG reference and ROM-conforming ML structures, where the fraction of CG-NC interfaces is insignificant. In MD simulations, the propagation of deformation twins within the slab was observed to rapidly increase the twin density and served to significantly decrease the dislocation mean free path, which has significant implications on the work hardening of the ML architecture. Within the context of experimental results, the segmentation of the CG microstructure by deformation twins leads to a dynamic refinement of the grain size and effectively hardens the
microstructure through the introduction of a high density of dislocation barriers. It is critical to note that the observed deformation mechanisms and mechanical behaviour only arise due to the heterogeneous features of the ML architecture. Parametric analysis of the ML architecture showed that the inherent softening of NC microstructures with grain sizes in the inverse HP regime may be offset through implementation of the ML architecture.
Chapter 8

Development of tools for analytical modeling

As shown in previous chapters, a weighted aggregate ROM-based assumption to describe the mechanical behaviour of ML architectures does not provide accurate results for structures where $t_{CG}$ approaches $d_{CG}$. These deviations in the expected mechanical properties are a result of the activation of a deformation twinning-based mechanism at the CG-NC interface. Due to discrepancies between timescales, MD simulations cannot be directly used to predict stress-strain behaviour at experimentally relevant loading rates.

Dynamic grain refinement, which is a consequence of deformation twinning, provides additional high strength barriers for dislocation glide, effectively increasing the flow strength of a twinning material. The influence of deformation twinning on work hardening behaviour has been incorporated into a number of notable phenomenological laws, where the effects of dynamic grain refinement are considered in tandem with dislocation interaction mechanisms. For example, the Kocks-Mecking-based (KM) phenomenological model developed in several papers by Bouaziz and colleagues (see Refs. [184–186, 221] and Chapter 3) has been successfully implemented in the prediction of the flow stress evolution in a number of TWIP steels. Within the mathematical framework of these models, the deformation twin is considered as an impassible barrier with static dimensions, which occupies an overall volume defined by the evolution of the twinned material fraction. Increases to the twinned material fraction are treated explicitly as the nucleation of new deformation twins with the same assumed average thicknesses. Mathematically, this assumption is captured in current models by a static treatment of the average twin thickness, $\bar{\lambda}$, in Eq. 3.19. The simplicity of this assumption belies the nature of deformation twinning, whereby both nucleation events and thickening of existing
twins are possible kinetic outcomes in response to increments in the deformation twin-accommodated plastic strain. This shortcoming in existing models raises an interesting question: under which conditions do separate deformation twins nucleate or existing deformation twins thicken in response to plastic deformation? Nucleation-based deformation twinning implies a rapid segmentation of a microstructure and significant grain refinement, whereas deformation by twin thickening leads to a unit-step decrease in the effective grain size, as defined by the interplanar spacing of \{111\} slip planes. An intrinsic material tendency towards one behaviour has significant implications on the magnitude of dynamic grain refinement, and consequently, on overall hardening behaviour. Furthermore, under the current model, estimates for the average twin spacing are delivered based on the minimization of fitting residuals and are not tethered to physical principles. An independent estimation of the average twin spacing is therefore required to guide the fitting of parameters in the KM model.

The purpose of this current section is to investigate the competition between nucleation and thickening in the deformation twinning of FCC materials in order to provide an analytical framework for assessing its influence on grain refinement. The relative occurrence of these events is considered through kinetic Monte Carlo simulations, using the GPFEs of common FCC materials as predictors of nucleation and thickening. The results of this study serve to complement the deformation mechanism roadmap conceived by Tadmor and Hai [32], by providing a first-principles-based method to assess the influence of deformation twinning in various FCC materials on dynamic grain refinement. Additionally, the forthcoming kMC model is implemented in a work hardening analysis to predict the high flow stresses of non-ROM conforming ML architectures (see Chapter 9). In the second section of this chapter, an analytical relation is developed which uses the kMC results to accurately describe the evolution of the average spacing between deformation twins during straining. This analytical relation is shown to provide a more accurate estimate of the average twin spacing than the formulation provided by Remy [188]. Taken together, the kMC model and analytical formula provide an independent estimate for \bar{\Lambda} which may be used to guide fitting procedures in the KM work hardening model.

8.1 Kinetic Monte Carlo simulations

Two-dimensional kMC simulations of deformation twinning were performed using the residence-time algorithm of Bortz et al. [177] on five common FCC materials (Ag, Al, Cu, Ni, and Pb), covering a wide range of GPFEs. This wide range of materials was
selected in order to generate sufficient results for verification and comparison with literature. Although materials such as Al do not normally undergo deformation twinning under conventional processing conditions, they were selected in order to observe the extremes of deformation twinning behaviours. Figure 8.1a provides a schematic of the simulation cell. A square-shaped single crystal grain was assumed for all kMC simulations with $x$ and $y$ axes directed along the $<11\bar{2}>$ and $<111>$ directions, respectively. Each cell measured $500b$ by $500d_{111}$, where $b$ is the magnitude of the $<11\bar{2}>$-type partial dislocation and $d_{111}$ is the spacing between $\{111\}$-type slip planes. Deformation twins were assumed to form through the nucleation and glide of leading $90^\circ$ edge-type Shockley partial dislocations across the simulation cell, forming an intrinsic stacking fault. Progressive nucleation and glide of Shockley partials on adjacent $\{111\}$ slip planes leads to the formation of a two-layer extrinsic stacking fault (esf), and subsequently, a multi-layer twin fault (tf) which is bordered by coherent twin boundaries. In this regard, deformation twins are assumed to originate from grain boundary-mediated nucleation mechanisms, as is common in observations of deformation twinning of nanocrystalline materials [55] and was observed in the MD simulations presented in Chapter 7. This mechanism may be distinguished from intragranular pole-based deformation twin formation mechanisms (e.g., Ref. [36]). In order to obtain a pure assessment of the competition between twin nucleation and thickening, dislocation-slip processes, including the emission of trailing partials, dislocation cross-slip, and dislocation constrictions are not considered. Deformation therefore proceeds exclusively through the glide of leading partials across the simulated grain. In the current model, the kinetics of deformation twinning are examined through consideration of the relevant GPFEs.

Figure 8.1b illustrates a typical fault energy ($\gamma$) curve, with the relevant energies indicated. The activation barrier for the nucleation ($E_1$) and thickening ($E_2$, $E_3$, $\ldots$, $E_\infty$) of a fault structure is defined here as the difference between the energy of the existing fault and the peak fault energy of the subsequent defect along the deformation twin reaction pathway. Using the common nomenclature for the GPFEs, the peak energies $\gamma_{usf}^1$ and $\gamma_{usf}^2$ refer to the unstable stacking fault energies of an isf and esf, and $\gamma_{utf}^3$ $\cdots$ $\gamma_{utf}^\infty$ indicate the unstable twin fault energies of an embryonic and thickened deformation twin, respectively. For each unstable energy, the superscript refers to the number of partial dislocations required to create the fault structure under activation. In FCC materials, the GPFEs are known to stabilize after formation of an esf [217], which may be considered as a twin embryo with two twin boundaries separated by a single $\{111\}$ slip plane. Therefore, the activation barrier for the formation of the twin embryo is calculated as: $E_3 = \gamma_{utf}^3 - \gamma_{esf} \approx \gamma_{asf}^2 - \gamma_{esf}$ and the energy of the stable embryo is $\approx 2\gamma_{tf}$, where $\gamma_{tf}$
8.1. Kinetic Monte Carlo simulations

Figure 8.1: (a) A schematic of the single crystal grain used in all kMC simulations. $E_1$ represents the activation barrier against dislocation nucleation from available sites along the cell boundary. The barriers associated with the isf ($E_2$), esf ($E_3$), and tf ($E_\infty$) deformation structures are indicated next to the appropriate faults, which are bounded by partial dislocations. Barriers associated with dislocation glide ($\sigma_{PN}$) are also marked. The configuration of the applied external loading ($\sigma_a$) is denoted by red arrows. (b) The GPFE curve associated with the deformation twin pathway.

is the energy of an isolated twin boundary. The activation barrier for deformation twin thickening (i.e., growth beyond three layers) is assumed to be defined by $E_\infty$, which has almost the same magnitude as $E_3$ for all materials considered in this section.

Within the context of the kMC model, the rates ($R_i$) of nucleation and glide events along the $i^{th}$ slip plane in the simulation cell are assumed to follow Boltzmann statistics
8.1. Kinetic Monte Carlo simulations

and are described by the following relation:

\[ R_i = R_o \exp \left\{ \frac{-(\sigma_i - \sigma_i^*) V}{k_b T} \right\} \]  
\[(8.1)\]

where \( R_o \) is the Debye frequency, \( T \) is the temperature (set at 300 K for all simulations), \( k_b \) is the Boltzmann constant, \( V \) is the activation volume (taken as \( 10b^3 \)), and \( \sigma_i \) and \( \sigma_i^* \) are the elastic shear and activation stresses operative at the deformation site on the \( i^{th} \) slip plane, respectively. At each step in the kMC model, \( \sigma_i^* \) is calculated based upon consideration of the deformation history. If a partial dislocation is not present on the \( i^{th} \) slip plane, then \( \sigma_i^* \) defines the barrier to dislocation nucleation. This barrier is calculated based on the existence and type of fault on adjacent slip planes and, in this manner, captures the competition between nucleation and thickening of deformation twins (see Figure 8.1). However, in the case that a dislocation is present, \( \sigma_i^* \) describes the barrier to dislocation glide (i.e., the Peierls-Nabarro stress, \( \sigma_{PN} \)). According to the analysis of Ogata et al. [217], the relevant segments of the GPFE curve represent a Peierls potential which can be used directly to determine activation barrier \( \sigma_i^* \) of partial dislocation nucleation. By contrast, if glide is operative, then \( \sigma_i^* \) is determined from standard solutions to the Peierls-Nabarro problem for a partial edge dislocation (e.g., Ref. [222]). These considerations lead to a conditional definition of \( \sigma_i^* \) which follows as:

\[ \sigma_i^* = \begin{cases} 
\pi E_i b, & \text{twin nucleation/thickening} \\
\frac{2G}{3(1-\nu)} \exp \left\{ \frac{-4\pi \zeta}{3b} \right\}, & \text{glide}
\end{cases} \]  
\[(8.2)\]

where \( E_i \) is the activation barrier of the corresponding fault structure in the deformation twin pathway, \( G \) is the shear modulus, \( \nu \) is Poisson's ratio, and \( \zeta = \frac{Gb^2}{4\pi^2(1-\nu)E_i} \) is the half-width of the dislocation core. The shear stress, \( \sigma_i \), is calculated as the additive sum of elastic field interactions (\( \sigma_{xy} \)) from dislocations which are existent in the simulation cell and the constant applied external loading, \( \sigma_a \) (Figure 8.1a). The shear stress applied on a dislocation located on plane \( i \) is thus given by the classic solution to a Volterra
8.1. Kinetic Monte Carlo simulations

treatment of $J$ edge partial dislocations at distances of $(\Delta x, \Delta y)$ [2]:

$$\sigma_i = \sigma_a + \sum_{j=1}^{J} \sigma_{xy}(\Delta x_j, \Delta y_j)$$ (8.3a)

$$\sigma_{xy}(\Delta x, \Delta y) = \frac{Gb}{2\pi (1-\nu)} \left[ \frac{\Delta x (\Delta x^2 - \Delta y^2)}{(\Delta x^2 + \Delta y^2)^2} \right]$$ (8.3b)

The external loadings applied are required to ensure dislocation glide within a reasonable timescale and represent the stress needed to stabilize twin embryos formed from $90^\circ$ Shockley partial dislocations [223]. Once dislocations have reached the opposing simulation cell wall, they are assumed to be absorbed at the grain boundary and do not contribute to the overall stress. This assumption simplifies the overall analysis as it eliminates the need for hardening behaviour to be considered in the application of external loadings. A contour plot showing the elastic shear stress field created by a partial dislocation in Pb under an applied external load is provided in Figure 8.2.

Implementation of Eqs. 8.1-8.3b with the kMC method for each active site in the simulation cell enables a kinetically weighted observation of deformation twinning progression. Table 8.1 provides the input parameters for all kMC simulations performed in this section. The simulation supercells were initialized with no dislocations or twinned material present and simulations were terminated once the deformation twinning fraction ($F$) reached 0.3. At each timestep, $F$ is measured from the linear section of the simulation cell midpoint, and the number of twins ($N_T$) across this section is recorded. One hundred replications of each material condition are simulated to collect statistics of parameter measurements. Although isfs and esfs are not explicitly fully developed deformation twins, they are also included in parameter measurements as they also represent structures which segment the simulation cell and lead to dynamic grain refinement. Stacking fault structures and twins were permitted to merge during deformation through the nucleation and glide of an appropriate 90 partial on a plane of shared adjacency. Furthermore, dislocations were not permitted to nucleate on planes within $3d_{111}$ of the $<111>$ simulation edges, as the GPFEs in close proximity to grain boundaries are not well known, and this deformation pathway is assumed to be kinetically unfavourable.

Figure 8.3 presents typical snapshots of the kMC simulation cell at different stages of deformation twinning in Pb. The coloured regions represent areas which have undergone twinning. Snapshots of deformation twinning in the other materials studied are provided in Figure 8.4. As shown in Figure 8.3, deformation twinning proceeds, as expected, with the nucleation and thickening of twins via the glide of partial dislocations across the
 simulated grain. Individual partial dislocations (marked by blue arrows) are visible as step edges at the twin boundaries. Additionally, merging of deformation twin structures occurs between snapshots at $F = 0.1$ and $F = 0.2$. The evolution of the average number of deformation twins with respect to the twinned material fraction is plotted in Figure 8.5a for each material examined in this section. A monotonic increase in the number of twins is observed, with Ag and Ni/Al showing the largest and smallest values of $\bar{N}_T$ respectively. It should be noted that due to the nature of statistical averaging, non-integer values

**Figure 8.2:** (a) The $\sigma_{xy}$ field of an isolated $90^\circ$ Shockley partial dislocation in Pb. (b) A higher magnification view of the inset region in (a). The region at the center of the dislocation where the contour is not tractable represents the dislocation core.
Table 8.1: Material parameters, Debye frequencies, applied shear stresses\(^a\), and GPFEs\(^b\) (mJ/m\(^2\)), used in kMC simulations.

| Material | \(b\) (nm) | \(d_{111}\) (nm) | \(G\) (GPa)\(^c\) | \(\nu\) | \(R_0\) (10\(^{13}\)/s) | \(\sigma_a\) (MPa) | \(\gamma^{1}_{usf}\) | \(\gamma^{2}_{usf}\) | \(\gamma^{\infty}_{utf}\) | \(\gamma^{isf}_{isf}\) | \(\gamma^{esf}_{esf}\) | \(\gamma^{tf}_{tf}\) |
|----------|-------------|-----------------|------------------|-----|-----------------|--------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Ag       | 0.167       | 0.236           | 29.9             | 0.37| 3.94            | 65           | 91             | 100            | 93             | 16             | 12             | 8              |
| Al       | 0.165       | 0.234           | 26.0             | 0.35| 9.66            | 220          | 140            | 196            | 135            | 112            | 112            | 50             |
| Cu       | 0.148       | 0.209           | 45.7             | 0.34| 7.98            | 120          | 158            | 179            | 161            | 36             | 40             | 18             |
| Ni       | 0.147       | 0.208           | 75.8             | 0.31| 9.88            | 250          | 258            | 323            | 251            | 133            | 138            | 65             |
| Pb       | 0.202       | 0.286           | 5.6              | 0.44| 2.70            | 40           | 55             | 79             | 53             | 48             | 48             | 23             |

\(^a\)Ref. [223]  
\(^b\)Ref. [169]  
\(^c\)Shear modulus calculated along <11\(^{-2}\)>

Figure 8.3: Typical snapshots of grain segmentation during deformation twinning in Pb at twinned fractions \((F)\) of 0.1 (a), 0.2 (b), and 0.3 (c). Twinned regions are shaded in purple and partial dislocations are marked by blue arrows.

of \(\tilde{N}_T\) are possible. The integral nature of the \(N_T\) is thus more apparent for materials which were observed to deform by twin thickening such as Ni and Al. The average twin thickness (\(\bar{\lambda}\)) may be determined directly from \(N_T\) using the following relation:

\[
\bar{\lambda} = \frac{FN}{N_T} \quad (8.4)
\]

where \(N\) is the number of \{111\} slip planes in the simulation cell. Figure 8.5b shows the change in average twin thickness during deformation twinning for each material, as determined by Eq. 8.4. As shown in Figure 8.5b, the trends in \(\bar{\lambda}\) show an inverse correlation with the difference between activation barriers for nucleation and twin thickening (e.g., \(E_d = E_1 - E_\infty\)). For example, Ni and Al have the highest values of \(E_d\) (72 and 55 mJ/m\(^2\), respectively) and formed the thickest deformation twins, whereas Ag \((E_d = 6\) mJ/m\(^2\)) and Cu \((E_d = 15\) mJ/m\(^2\)) possessed the smallest \(\bar{\lambda}\). This trend is qualitatively
Figure 8.4: Grain segmentation during deformation twinning in Ag, Al, Cu, and Ni at twinned fractions ($F$) of 0.1, 0.2, and 0.3. Twinned regions are represented by the shaded areas of the simulation cell.
consistent with existing literature \[224\]. The relative magnitude of activation energies, \(E_d\), therefore defines an intrinsic material parameter which determines the competition between nucleation and thickening of deformation twins. In addition to GPFE parameters, the energies and structure of grain boundaries are contributing factors to the values of \(N_T\) and \(\bar{\lambda}\). These parameters are both electronic and structure-dependent, and represent a layer of configurational complexity which is not captured by the current kMC simulations. Nonetheless, the current results are consistent with several experimental observations. For example, deformation twins with thicknesses on the order of 2-3\(d_{111}\) have been observed in nanocrystalline Cu \[225\]. Conversely, the formation of thick deformation twins via grain boundary-mediated partial dislocation nucleation has been reported for nanocrystalline Al \[226\].

The competition between nucleation and thickening of deformation twins may be analytically examined through consideration of the kinetics for the formation of new twins. The rate of change in the number of deformation twins in the simulation with respect to the change in the twinned material fraction \(\left(\frac{dN_T}{df}\right)\) is related to the probability of twin nucleation \(P_N\) by:

\[
\frac{dN_T}{df} = N P_N \quad (8.5)
\]

In this context, \(P_N\) is defined as the ratio of twin nucleation rates \(R_N\) to the total rates of all dislocation nucleation events (i.e., the sum of twin nucleation and twin thickening \(R_G\) rates). From Eqs. 8.1, 8.3b:

\[
P_N = \frac{R_N}{R_N + R_G} \quad (8.6a)
\]

\[
= \frac{\sum_{i=1}^{N-FN-2N_T} \exp \left\{ -\frac{V}{k_bT} \left( \frac{\pi E_1}{b} - \sigma_i \right) \right\}^{N-FN-2N_T}}{\sum_{i=1}^{N-FN-2N_T} \exp \left\{ -\frac{V}{k_bT} \left( \frac{\pi E_1}{b} - \sigma_i \right) \right\} + \sum_{j=1}^{2N_T} \exp \left\{ -\frac{V}{k_bT} \left( \frac{\pi E_i}{b} - \sigma_i \right) \right\}} \quad (8.6b)
\]

where the terms \(N - FN - 2N_T\) and \(2N_T\) represent the remaining slip planes available for twin nucleation and thickening at a fraction of \(F\), respectively. Here, \(2N_T\) represents the upper bound for thickening sites as there are a number of twin configurations where thickening sites are shared between adjacent twins. Since dislocations were generally observed to glide a significant distance from the simulation cell boundary before a subsequent nucleation event and the applied stress \(\sigma_a\) is much lower than the dislocation nucleation stress (e.g., 40 MPa vs. \(\approx\) 467 MPa for Pb, see Table 8.1 and Eq. 8.1), it is assumed that elastic stresses may be ignored. Furthermore, given that nominal activation
Figure 8.5: (a) The evolution of $N_T$ during deformation twinning for each material in this section. Each data point represents the statistical average of 100 simulation replications. (b) The average twin thickness as a function of twinned material fraction. Analytical predictions based on Eqs. 8.4, 8.7 are overlaid with the kMC simulation results in the dashed-dotted lines. The average twin thickness is plotted here as multiples of the $d_{111}$ spacing.
8.2 Analytical relation for average twin spacing

barriers for fault thickening events (i.e., $E_2$, $E_3$, ..., $E_\infty$) are approximately equal, thickening of deformation twins is assumed to be reasonably represented by the $E_\infty$ barrier. Application of these assumptions to Eq. 8.6b enables the formulation of the non-linear differential equation:

$$\frac{dN_T}{dF} - N \left\{ \frac{(N - FN - 2N_T) \exp \{-A\}}{(N - FN - 2N_T) \exp \{-A\} + 2N_T \exp \{-B\}} \right\} = 0 \quad (8.7)$$

where $A = \frac{V\pi E_1}{k_b T_b}$ and $B = \frac{V\pi E_\infty}{k_b T_b}$. Eq. 8.7 is not tractable using normal analytical solution methods, however, it may be readily solved using numerical approaches. A 4th-order Runge-Kutta solution to Eq. 8.7 for $N_T$ along with the corresponding values for $\bar{\lambda}$ (via Eq. 8.4) is plotted for each material system in Figure 8.5, showing excellent agreement. This analysis therefore provides a first-principles-based methodology for determining the competition between nucleation and thickening in the deformation twinning of FCC materials. In the broader context of phenomenological models (e.g., Refs. [182, 184, 186, 188]) this theoretical framework enables an avenue for estimating the evolution of microstructure refinement based on intrinsic material properties, which has significant implications for dynamic grain refinement and subsequent material hardening. It should be noted, that many of the assumptions undertaken in the kMC simulations may be easily modified without loss of compatibility with the analytical framework developed in this section. Minor discrepancies between the analytical predictions and kMC results are associated with a combination of the formative assumptions of the analytical model and the effect of twin merging, which is not explicitly accounted for in this analysis. The exact mechanism of deformation twin merging is still an open question in the literature, although it has been observed during MD simulations performed for this thesis. Furthermore, a significant limitation of the current model is that it assumes homogeneous nucleation of deformation twins. In this regard, all potential nucleation sites are initially treated as being kinetically equivalent, which ignores the several structural inhomogeneities and stress concentrations at grain boundaries that can lead to heterogeneous deformation twin nucleation. Future work coupling the kMC approach developed here with MD simulations is recommended in order to extend the model to consider heterogeneous nucleation.

8.2 Analytical relation for average twin spacing

The evolution of the average twin spacing ($\bar{\Lambda}$) is a critical parameter in the work hardening model developed by Bouaziz and colleagues [184–186, 221]. As shown in Eq. 3.18, it is one of the parameters which influences the overall dislocation mean path, and
consequently plays a major role in determining the dislocation storage evolution. In the current model, the average twin spacing may be calculated directly from the average twin thickness ($\bar{\lambda}$) using the following equation (same as Eq. 3.19):

$$\bar{\Lambda} = 2\bar{\lambda}(1 - F) \frac{F}{F}$$

(8.8)

where $F$ is the twin fraction, as previously defined. This equation first appears in this form in a work from Remy [188] and it is derived from the stereological analysis of Fullman for a randomized dispersion of circular disks within a volume [227]. It has been used in a number of studies of work hardening [184–186, 221]. However, its implementation is problematic because Fullman’s definition of the mean free path between particles is inconsistent with the concept of average twin spacing. Specifically, the value for $\bar{\Lambda}$ obtained using Eq. 8.8 provides an estimate for the average intercept distance of a randomly drawn line between disks embedded in a body. With respect to deformation twinning, however, the most meaningful definition of $\bar{\Lambda}$ is the average perpendicular distance between parallel deformation twins, as measured from a perspective axes within the $<111>$ zone. This is the statistic normally reported in the literature (e.g., Refs. [174, 228, 229]). Therefore, before the deformation twinning contributions to the work hardening behaviour of MLs can be modeled, an appropriate analytical relation for $\bar{\Lambda}$, which properly calculates the perpendicular distance between parallel deformation twins, is required. In this section, a first-principles analytical relation is developed to calculate the average twin spacing. The results of this section are used in conjunction with the results of Section 8.1 and the work hardening analysis approach presented in Chapter 3, to model the mechanical response of the ML architecture (see Chapter 9).

Figure 8.6 provides a schematic of a single grain which is populated by a number of twinned regions ($F=0.3$). The relevant structural features considered in this section are indicated in the figure. Twinned regions are indicated by hatched areas within the cell, which has an overall dimension of $d$ (i.e., the grain size) along the $<111>$ crystal direction. The cell is draw from the perspective of a $<1\bar{1}0>$ zone axis. The average twin spacing, $\bar{\Lambda}$, is defined as the perpendicular intercept between twins along the $<111>$ axis, which is consistent with the literature definition. The average twin thickness, $\bar{\lambda}$ is considered as the mean caliper dimension of the hatched region. The total length of twinned material measured along $<111>$ in the grain is $Fd$, which is partitioned into $N_T$ twins of mean thickness $\bar{\lambda}$. $N_T$ may be calculated directly as:

$$N_T = \frac{Fd}{\bar{\lambda}}.$$  

(8.9)
8.2. Analytical relation for average twin spacing

Similarly, the length of pristine material is \((1 - F)d\) in the cell. Assuming twins do not lie directly adjacent to the boundary, the cell is then partitioned by the twins into \(N_T + 1\) regions. \(\bar{\Lambda}\) may therefore be directly calculated as the ratio of the length of pristine material to the number of cell partitions:

\[
\bar{\Lambda} = \frac{(1 - F)d}{Fd} \hspace{1cm} (8.10)
\]

A comparison of Eqs. 8.8 and 8.10 shows that these estimators of \(\bar{\Lambda}\) deviate by a factor of \(2 \left(1 + \frac{1}{N_T}\right)\). It should be noted that the current model accurately returns an average twin spacing of \(d\) as \(F \rightarrow 0\), whereas the equation from Remy approaches a singularity. In order to evaluate the accuracy of each equation, a numerical simulation was coded using MATLAB for a grain with a dimension of \(d = 100d_{111}\), which has been randomly partitioned into \(N_T\) twins with a variable average thickness and the results of
Figure 8.7: Analytical predictions of average twin spacing evolution using Eq. 8.10 and the relation from Remy [188]. The proposed relation reproduces the simulation result with excellent accuracy. These calculations were performed on a cell measuring $100d_{111}$ and possessing an average twin thickness of $\bar{\lambda}=5d_{111}$.

Eqs. 8.8 and 8.10 have been calculated and compared. Figure 8.7 provides the analytical predictions along with simulation results for a cell which has been partitioned at twinning fractions ranging from $F=0.05$ to $F=0.5$ with an average twin thickness of $\bar{\lambda} = 5d_{111}$. As shown in the figure, the evolution of the average twin spacing proceeds as expected and $\bar{\Lambda}$ decays in a non-linear manner at increased $F$. The current model reproduces the simulation results with excellent accuracy, whereas the relation from Remy [188] significantly overestimates the average twin spacing. Therefore the current analysis has led to the development of an accurate relation for $\bar{\Lambda}$ which may be implemented along with kMC predictions for the evolution of $\bar{\lambda}$, with the work hardening model presented in Chapter 3. Figure 8.8 illustrates the predictions of Eq. 8.10 for a number of different average twin thicknesses. As shown in the figure, the analytical model again recreates the simulation data, providing further confidence in its robustness and applicability.
8.3 Chapter summary

In the current chapter a number of analytical tools have been created to improve the KM work hardening model such that it may be applied to the experimental data for the ML architectures. In this first section, a kMC model was developed to assess the kinetics of competition between deformation twin nucleation and thickening. The results of this section provide insight into the evolution of the average twin thickness during deformation which has a significant impact on the contributions of deformation twinning to work hardening. In the second section of this chapter, an analytical expression was developed to calculate the evolution of the average twin spacing as a function of twinning density. It was shown that this relation is more accurate than the existing expression developed by Remy [188], which is currently implemented in the work hardening model. The analytical tools from this chapter provide a physically-based estimate of the average twin spacing evolution. This estimate can be used in conjunction with the existing KM model developed by Bouaziz and colleagues [184–186, 221] to provide predictions of work hardening.

Figure 8.8: The results of numerical simulations for a number of average twin thicknesses are overlaid with analytical predictions based on Eq. 8.10, showing excellent agreement.
hardening behaviour in the ML architecture.
Chapter 9

A model for work hardening in the ML architecture

In this chapter, the analytical tools developed in Chapter 8 are implemented in conjunction with the KM-based phenomenological model of Bouaziz and colleagues [184–186, 221] to examine the work hardening behaviour of the ML architecture. The purpose of this approach is to provide a mechanism-based model for work hardening which can accurately predict mechanical behaviour in the non-ROM conforming MLs. In this regard, the results of this chapter connect mechanistic observations from MD studies with experimental measurements of ML mechanical properties to provide a holistic description deformation behaviour and a complete understanding of the structure-property relationship.

9.1 Implementation of the phenomenological model

In order to provide an estimate for dynamic grain refinement due to deformation twinning in the NiCo ML, a kMC simulation was performed using the method described in Section 8.1. Due to a lack of any direct measurements of the relevant GPFES in the literature, a ROM assumption was made to calculate the energetic barriers resisting deformation twinning in a NiCo alloy composed of 30 at.% Co. The calculated values were based off a linear interpolation of GSFE measurements collected from DFT simulations of deformation twinning in pure Ni [169] and a NiCo alloy comprised of 33 at.% Ni. [230]. The remainder of the required kMC parameters (e.g., $G$, $d_{111}$, etc.) were assumed to be the same as pure Ni, which is consistent with experimental results. Table 9.1 provides the GSFE energies as well as the other parameters assumed for the NiCo alloy. Figure 9.1 illustrates the kMC predictions for the evolution of the average twin thickness during
9.1. Implementation of the phenomenological model

Table 9.1: The kMC parameters and GSFEs (mJ/m²) for a NiCo₃₀at.% alloy.

<table>
<thead>
<tr>
<th></th>
<th>b (nm)</th>
<th>d₁₁₁ (nm)</th>
<th>G (GPa)</th>
<th>ν</th>
<th>R₀</th>
<th>σₐ</th>
<th>γ₁₅₈₃</th>
<th>γ₁₅₈₄</th>
<th>γ₂₅₈₄</th>
<th>γ₅₈₄</th>
<th>γ₈₅₈</th>
<th>γ₈₅₈</th>
<th>γ₈₅₈</th>
<th>γ₈₅₈</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.147</td>
<td>0.208</td>
<td>75.8</td>
<td>0.31</td>
<td>9.33</td>
<td>250</td>
<td>0.234</td>
<td>0.275</td>
<td>0.235</td>
<td>0.082</td>
<td>0.085</td>
<td>0.040</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 9.1: The evolution of the average twin thicknesses for an NiCo₃₀at.% alloy. The average twin thickness is plotted here as multiples of the d₁₁₁ interplanar spacing and represents data collected from 100 kMC simulations. The bounded region is equivalent to 1 standard deviation from the mean result.

dehesion twinning. The kMC simulation results were averaged over 100 replications from a supercell measuring 500 b x 500 d₁₁₁. A shown in the figure, deformation twin thicknesses monotonically increase and reach value of approximately 17d₁₁₁ at a twinning fraction of F = 0.3. Compared to pure Ni (see Figure 8.5), the NiCo alloy exhibits a significant preference for deformation twin nucleation as opposed to twin thickening, which is facilitated by the comparatively lower activation barriers for twin nucleation.

Despite the failure of the weighted aggregate ROM assumption, the overall mechanical response of all ML architectures may, nevertheless, be broken down into its CG and NC components. Since the mechanical behaviour of the NC structure has been experimentally shown to be identical in both the ML and bulk samples, it is the CG feature which is implicated in causing non-ROM behaviour. In this regard, all anomalous strengthening effects in the ML architectures are assumed to be caused by hardening in the CG layer.
This implication is supported by the MD simulations of Chapter 7 which highlight the role of deformation twinning in the overall mechanical behaviour of a single CG grain confined within a NC matrix. It is therefore interesting to determine if there is a common CG behaviour in the non-ROM conforming ML architectures. Figure 9.2 plots the mechanical responses of the CG features (CG*) which are required, under a weighted aggregate assumption, to have produced the measured ML responses. Specifically, CG* is calculated here as:

\[
CG^* = \frac{ML - t\eta NC}{1 - t\eta}
\]  

(9.1)

where \(t\eta\) is the thickness ratio as previously defined, and the acronyms ML and NC represent the sets of stress data for their respective structures. This calculation was performed only for the ML architectures with \(t_{CG} \approx d_{CG}\) (i.e., ML\(_{50b}\), ML\(_{83}\), and ML\(_{91}\)) and is plotted in true terms up until the point of plastic instability in the NC reference material. As shown in the figure, all the MLs exhibited a comparable response for CG*.

The small discrepancies of within each sample are related to statistical error as well as

**Figure 9.2:** The required stress-strain behaviour of the CG features in the ML architectures where \(t_{CG} \approx d_{CG}\). CG* is calculated based on Eq. 9.1 for the ML\(_{50b}\), ML\(_{83}\), and ML\(_{91}\) samples.
the differences in layer thicknesses, which may have had a small impact on the grain size
distribution in each of the respective CG features (see Table 4.1). It should be noted that
the gains in yield strength for CG* relative to the CG reference cannot be rationalized as
unforeseen differences between grain size distributions. Based solely on HP strengthening
effects, a CG layer that would deliver an equivalent yield to CG* possesses an average
grain size of \( d \approx 100 \text{ nm} \) [192], which is not consistent with SEM observations (see Chapter
6). The mechanical responses of CG*\text{50b}, CG*\text{83}, and CG*\text{91} are therefore all assumed to be
caued by identical hardening phenomena. Within the context of work hardening, the
CG*\text{50b} is selected as being representative of CG* deformation behaviour and is used for
fitting of the KM-based phenomenological model outlined in Chapter 3. This model is
appropriate as it quantifies the effects of dislocation-dislocation and dislocation boundary
influences on strengthening, which is consistent with mechanisms observed in the MD
simulations. Although qualitatively critical in their mechanistic insight, the evolution of
parameters (e.g., twin boundary density, dislocation mean free path, etc.) as determined
by MD simulation cannot be directly compared to the forthcoming results of the current
model due to disparities in length and timescales. The relevant equations for the KM
model are given in Chapter 3, but are also repeated, as required, in this section.

Under the KM model, all hardening is assumed to be caused by dislocation-dislocation
or dislocation-boundary interactions, and all dislocations involved in hardening are of the
\(<1\bar{1}0>-\text{type. The dislocation storage term is described by the following relation:}

\[
\frac{d\rho}{d\gamma_g} = \frac{1}{b\bar{\Lambda}_d} - k_2\rho
\]

where \( \rho \) is the stored dislocation density, \( \gamma_g \) is the shear strain due to dislocation-slip,
\( \bar{\Lambda}_d \) is the dislocation mean free path, and \( k_2 \) is the responsible for work softening due to
dynamic recovery (i.e., dislocation annihilation during loading). The dislocation mean
free path may be further broken down into dislocation-dislocation interactions, which are
represented by forest hardening and the dislocation-boundary interactions, respectively,
in the relation:

\[
\frac{1}{\bar{\Lambda}_d} = \frac{1}{d} + \frac{1}{\bar{\Lambda}} + bk_1\sqrt{\rho}
\]

where \( d \) is the grain size, \( \bar{\Lambda} \) is the average twin spacing, and \( k_1 \) is the forest hardening
coefficient. In this form, this equation is not tractable as \( \bar{\Lambda} \) is not constant during
deformation (see Chapter 8). Therefore, Eq. 9.3 has been simplified into the form:

\[
\frac{d\rho}{d\gamma_g} = \frac{1}{b\bar{\Lambda}_{\text{eff}}} + k_1\sqrt{\rho} - k_2\rho
\]
where $\bar{\Lambda}_{\text{eff}}$ is an effective boundary spacing which is averaged over the entire deformation history of the sample. The incremental crystallographic shear strain due to dislocation-slip may be isolated from overall shear strain using the following equation:

$$d\gamma = (1 - F) \gamma_g + \gamma_t dF$$

(9.5)

where $\gamma$ is the overall crystallographic shear strain and $\gamma_t$ is the shear strain accommodated by the glide of $<11\bar{2}>$-type Shockley partial dislocations during deformation twin formation. The evolution of the deformation twinning fraction is described by the Olson and Cohen relation as [189]:

$$F = 1 - \exp(-m\varepsilon_t)$$

(9.6)

where $m$ is a coefficient which is left free for fitting purposes. The overall flow stress is related to the dislocation storage density through:

$$\sigma = \alpha MGb\sqrt{\rho}$$

(9.7)

and in differential form by:

$$\frac{d\sigma}{d\varepsilon_g} = \frac{\alpha MGb d\rho}{2\sqrt{\rho} d\varepsilon_g}$$

(9.8)

where $\alpha$ is a dislocation efficiency parameter, $M$ is the Taylor factor, and $\varepsilon_g$ is the extensional applied strain during mechanical loading. The overall extensional strains are related to the crystallographic strains through Eq. 2.2 (i.e. $\gamma = M\varepsilon$). Eq. 9.8 defines the work hardening rate of the material. Through combination of Eqs. 2.2, 9.7, and 9.8, the work hardening data collected from experiments may be fit to obtain estimates for $k_1$, $k_2$, and $\bar{\Lambda}_{\text{eff}}$ for CG$_{50b}^*$. The nature of this fitting procedure is highly sensitive to the evolution of the twinning fraction, which determines the partitioning of overall strain into dislocation-slip ($\gamma_g$) and deformation twinning contributions ($\gamma_t$). The growth of $F$ is dependent on the selection of the twin evolution constant, $m$, which introduces another element into the KM fitting procedure. With the introduction of this parameter, the KM fitting procedure is underconstrained, requiring additional considerations for its implementation. In this regard, the kMC predictions for $\bar{\lambda}$ may be used in conjunction with Eq. 8.10 to provide an independent estimate of $\bar{\Lambda}_{\text{eff}}$. The deviations between $\bar{\Lambda}_{\text{eff}}$ determined from kMC simulations ($\bar{\Lambda}_{\text{kMC}}$) and KM fitting ($\bar{\Lambda}_{\text{KM}}$) may be considered as a residual ($R_1$) which steers the fitting to find a error-minimized solution for $m$. In this section, $R_1$ is calculated as the normalized difference between $\bar{\Lambda}_{\text{kMC}}$ and $\bar{\Lambda}_{\text{KM}}$.

Figure 9.3a presents the values of $\bar{\Lambda}_{\text{eff}}$ which have been determined using each method
9.1. Implementation of the phenomenological model

Figure 9.3: (a) The values for $\bar{\Lambda}_{\text{eff}}$ as determined through KM fitting and kMC simulation. The kMC estimate remained constant at $\approx 20$ nm for all values of $m$ due to the assumption of homogeneous deformation twin nucleation. (b) A comparison of the two normalized residuals defined in this section with respect to the twin evolution constant. A minimum for the equal-weighted sum of the residuals exists at $m = 4.31$. This value of $m$ corresponds to a $\bar{\Lambda}_{\text{eff}}$ of 159 nm.

over a range of twin evolution constants, $m = 4 \ldots 4.47$. At values of $m < 4$, the value of $\bar{\Lambda}_{\text{KM}}$ was found to be larger than the CG grain size ($d_{\text{CG}} = 1 \mu$m) and above $m = 4.47$, $\gamma_g$ was observed to approach 0, which created an instability in the work hardening data. As
shown in the figure, the kMC estimate of $\bar{\Lambda}_{\text{eff}}$ remains relatively constant at $\bar{\Lambda}_{\text{eff}} \approx 20$ nm for all values of $m$, which suggests that the kMC model is largely insensitive to changes in $F$. Conversely, the estimate from KM fitting shows a non-linear decrease, which is more typical of the expected behaviour. The KM estimate approaches the $\bar{\Lambda}_{\text{kMC}}$ value at of $m \approx 4.45$, which is near the extremes of validity for the twin evolution constant, and represents a point of a minimized $R_1$. It is unlikely that this is the true measure for $\bar{\Lambda}_{\text{eff}}$. The large discrepancy in these results and the relatively insensitivity of $\bar{\Lambda}_{\text{kMC}}$ to $m$ is a result of the limitations of the kMC simulation, which utilize a homogeneous treatment of deformation twin nucleation sites. Under this restriction, the nucleation of new deformation twins is preferred to twin thickening when compared against a heterogeneous treatment of nucleation. This causes a rapid segmentation of the microstructure and precludes deformation twin thickening, which is required to observe a clear monotonic decrease in $\bar{\Lambda}_{\text{eff}}$ with $m$. Future work is recommended to combine MD simulations with the developed kMC approach to provide a model for heterogeneous twin nucleation which can better emulate the expected profile of $\bar{\Lambda}_{\text{eff}}$.

Due to the limitations of the current kMC model, an additional residual was defined in order to estimate $m$. It was observed during KM fitting that the error in KM predictions for CG$^*_50b$ increased monotonically with $m$, and were maximized near the extreme value, $m = 4.47$. Therefore, a second residual ($R_2$) was defined as the cumulative absolute difference between the KM fitting (CG$^*_{\text{KM}}$) and experimental measurements for CG$^*_50b$: $R_2 = \sum \text{abs}(\text{CG}^*_{\text{KM}} - \text{CG}^*_50b)$. Figure 9.3b provides a normalized plot of the two residuals against the twin evolution constant. As shown in the figure, the two residuals exhibit opposing relationships with $m$, and the equal-weighted sum of $R_1$ and $R_2$ reaches a minimum at $m = 4.31$. This value of $m$ corresponds to a $\bar{\Lambda}_{\text{eff}}$ of 159 nm (Figure 9.3a), which is in much better agreement with estimates of the effective grain size based purely on HP effects ($d_{\text{CG}} \approx 100$ nm [192]). Future work involving experimental measurement of $\bar{\Lambda}_{\text{eff}}$ through TEM analysis is recommended. However, an accurate assessment of the average twin spacing over all the deformation history would require an exhaustive study at many stages of mechanical strain. Figure 9.4a plots the post-yield predictions of CG$^*_{\text{KM}}$ against experimental measurements for $m = 4.31$. The bounding cases of $m = 4$ and 4.47 are also provided for comparison. The input parameters used in KM fitting as well as the estimates of $k_1$, $k_2$ and $\bar{\Lambda}_{\text{eff}}$ are provided in Table 9.2. The experimental data is plotted up until the point of plastic instability for the NC reference sample, which is the boundary restriction for KM analysis. As shown in the figure, the flow stress curve generated by CG$^*_{\text{KM}}$ for $m = 4.31$ is in good agreement with the experimental data. Predictions of the mechanical response for the bounding cases of the twin
Figure 9.4: (a) The results of KM analysis on the CG$_{50b}^*$ data. Flow stress predictions from the KM model for $m = 4.31$ are in good agreement with the experimental data. Results for the bounding cases of the twin evolution constant at $m = 4$ and 4.47 are provided for comparison. (b) The dislocation-dislocation ($\sigma_{k_1} + \sigma_{k_2}$) and dislocation-boundary ($\sigma_A$) contributions to the overall flow stress in the CG$_{KM}^*$ predictions are plotted separately here.
Table 9.2: The input parameters and fitted values from the KM model based on a twin evolution constant of $m = 4.31$.

<table>
<thead>
<tr>
<th>Input parameter</th>
<th>Fitted parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0.3</td>
</tr>
<tr>
<td>$b$ (nm)</td>
<td>0.147</td>
</tr>
<tr>
<td>$G$ (GPa)</td>
<td>76</td>
</tr>
<tr>
<td>$M$</td>
<td>3.06</td>
</tr>
<tr>
<td>$k_1$ (m$^{-1}$)</td>
<td>4.2 x 10$^{10}$</td>
</tr>
<tr>
<td>$k_2$</td>
<td>1.5 x 10$^3$</td>
</tr>
<tr>
<td>$\Lambda_{\text{eff}}$ (nm)</td>
<td>159</td>
</tr>
</tbody>
</table>

Evolution constant are also provided for comparison. Figure 9.4b provides the individual contributions of dislocation-dislocation interactions in the forms of forest hardening ($\sigma_{k_1}$), dynamic recovery ($\sigma_{k_2}$), and dislocation-boundary interactions ($\sigma_{\Lambda}$), respectively. In the initial stages of deformation, forest hardening dominates the dislocation-dislocation interactions, whereas at higher strains dynamic recovery leads to softening. Conversely, hardening from dislocation-boundary interactions is observed to increase monotonically with strain. It should be noted that the distinction between dislocation-dislocation and dislocation-boundary effects, as captured by the mathematical terms of the KM model, is somewhat arbitrary. Secondary hardening effects due to boundaries, such as kinematic hardening from dislocation pile-up, are encompassed by the dislocation-dislocation terms in this model but could conceivably be considered as boundary driven phenomena. Further breakdown of the particular contributing elements to work hardening are possible through the KM model but require measurement of the Bauschinger effect in order to isolate kinematic and isotropic hardening effects. For examples of this procedure, see Refs. [182, 184].

Based on KM analysis, a mechanism-based phenomenological model has been applied to provide an estimate for $CG_{50b}^*$. Using the fitting terms, $k_1$, $k_2$, and $\Lambda_{\text{eff}}$, similar predictions can be made for the $CG^*$ of other MLs. The comparison of these estimates with the experimental data serves to evaluate the self-consistency of the current approach. Additionally, this approach may be generalized to predict the mechanical properties for the ROM ML architecture (ML$_{50a}$) as well as the intermediary structure (ML$_{70}$). In order to achieve this generalization, an additional mixing rule is required to describe the evolution of the fraction of the CG microstructure which undergoes deformation twinning-based hardening. For the ML$_{50a}$ the contributions of deformation twinning to overall hardening are expected to be minor, however, it is expected that the fraction of CG material ($G$) undergoing deformation twinning for the other ML structures is much higher due to the higher overall fraction of CG-NC interface.

$G$ should not be confused with $F$. $G$ defines the amount of twinned material at the microstructure level whereas $F$ refers to the fraction of deformation twinning within a
9.1. Implementation of the phenomenological model

Figure 9.5: The evolution of the twinned grain fraction in each of the ML architectures studied in this thesis.

For this purpose, a mixing rule similar to that used in Eq. 9.6 was assumed. Figure 9.5 shows the predicted evolution of deformation twinning in the overall CG microstructure during post-yield mechanical loading. As shown in the figure, \( G \) evolves as expected for the ML architectures, with values of \( G \approx 1 \) being predicted for the MLs with \( t_{CG} \approx d_{CG} \) and extremely low values for the ML50a architecture. The ML50b sample is the reference case and therefore is inherently represented by \( G = 1 \).

The ML70 sample exhibits an intermediate response, with \( G \) increasing from \( \approx 0.85 \) to 0.95 during deformation. The overall prediction of CG*, for each of the ML samples, can then be calculated using a linear combination of \( CG_{KM}^* \) and CG such that \( CG^* = GCG_{KM}^* + (1 - G)CG \) and the overall properties of the ML architectures may be predicted through rearrangement of Eq. 9.1. Figure 9.6 presents the predictions of mechanical properties for each of the ML structures studied in this thesis using the KM estimates for CG* and the relevant values of \( G \) for each sample. As shown in the figure, an excellent agreement is achieved between the experimental dataset and the predictions of the analytical model. This is significant, as the model provides a general framework
9.1. Implementation of the phenomenological model

Figure 9.6: The experimental data for each ML architecture examined in this thesis plotted up until the point of plastic instability in the NC reference. The ROM and analytical predictions based on the KM analysis performed in this section are overlaid for reference. The current model is in excellent agreement with the experimental data, providing a generalized framework for a description of ML work hardening in both ROM and non-ROM conforming architectures.

to describe the overall behaviour of the ML architecture for both ROM and non-ROM structures. In this regard, the model captures aspects of bulk CG and NC behaviour, as well as CG-NC interfacial contributions to overall work hardening. With reference to the interfacial mechanism described by MD simulations, this model complements atomistic observations of deformation behaviour by providing the final link which can tether the structure-property relationship of the ML architecture. Figure 9.7 provides a summa-
9.2 Chapter summary

In the current chapter, the analytical tools from Chapter 8 have been implemented with the KM-based deformation twinning work hardening model developed by Bouaziz and colleagues [184–186, 221] to provide a phenomenological description of work hardening behaviour in the ML architecture. Based on KM analysis, the stress-strain results of both ROM and non-ROM conforming ML architectures were predicted with excellent accuracy. The adapted model is therefore successful in providing a generalized frame-
work for the prediction of flow stress in the ML architectures. These results bridge the experimental measurements of mechanical properties with the deformation mechanisms provided by MD simulations. In this regard, a holistic understanding of the structure-property relationship has been achieved in MLs with modulated microstructures.
Chapter 10

Conclusions and future work

10.1 Thesis summary and concluding remarks

The current thesis investigates the deformation behaviour of heterogeneous material architectures in the form of metallic multilayers with modulated microstructures. The goal of this investigation is to study the emergence of novel deformation mechanisms, which result from the introduction of abrupt structural homogeneities in a material architecture. Formed from a periodic layering of alternating CG and NC features, the ML is the ideal architecture to assess transitions in deformation behaviour arising from changes in the organization of structural components. The independent deformation behaviours of CG and NC microstructures have been well studied, which is advantageous to this work as it facilitates the isolation of new deformation behaviours arising from layering in the ML architecture. Indeed, it remains an open question as to how these deformation mechanisms may interact in a heterogeneous structure, and what influence these interactions have on the prevailing deformation behaviour and measured mechanical properties.

For the purposes of this thesis, a wide range of ML architectures were fabricated using an additive pulsed electrodeposition process developed by Integran Technologies Inc. The as-deposited thicknesses of NC and CG layers were determined to be highly uniform, permitting the design of ML architectures with excellent control over layer fractions. Since interactions between CG and NC deformation mechanisms were believed to be interface-mediated, a large test matrix of multilayers with a wide variety of CG-NC interfacial fractions were fabricated for experimental testing purposes. ML architectures with NC and CG layer thickness in the range of 1 - 10 μm were created for study. The average grain sizes of the CG and NC features were measured to be 0.9 ± 0.1 μm and 19.8 ± 0.6 nm, respectively. Based on experimental measurements, the mechanical properties of the ML architectures were found to diverge significantly in samples where $t_{CG}$
10.1. Thesis summary and concluding remarks

approached $d_{CG}$, which was indicative of a strong influence from interfacial deformation mechanisms. ROM predictions, which were based on a weighted aggregate treatment of bulk CG and NC reference properties, were found to deviate from experimental measurements of yield and tensile strengths by up to 30%. Conversely, ROM predictions were found to be accurate for MLs with comparatively thick CG layers, which defined the operative length-scale for a transition to bulk mechanical behaviour, and a diminished influence from interfacial effects. This dichotomy in mechanical response underscores the naivety of the ROM assumption, which essentially simplifies the complexities of deformation behaviour by partitioning a material architecture into regions of non-interacting mechanistic regimes.

An indentation survey of the ML architecture provided further insight into the origins of strengthening due to structural modulation in the ML architectures. Through a combination of nano and microindentation, the NC features in the ML ($HV = 556-564$) were found to behave almost identically to the bulk reference ($HV = 554-560$), implicating the CG layers as the source of added strength. Indeed, evidence of deformation twinning was observed in post-mortem electron microscopy examinations of the indented CG layers in a ML, but not in the bulk CG reference sample. These findings motivated a deeper investigation into deformation mechanisms in the CG layers. The deformation behaviour of the ML architecture was directly examined through targeted molecular dynamics tensile simulations. Representative microstructures possessing both NC and CG features were fabricated for MD simulation. During uniaxial tensile simulation, deformation twins were observed to nucleate and propagate from interfaces between CG-NC features, which complements post-mortem experimental imaging efforts. The nucleation of deformation twins was observed to facilitate strain relaxation within the NC grains. This mechanism is not prevalent in coarse-grained microstructures of materials with comparable GPFEs due to the prohibitively high stresses required to nucleate Shockley partial dislocations, and is typically only accessible within the inherently high stresses of NC microstructures. The emergence of deformation twinning within the CG microstructure highlights the interactions between deformation mechanisms which are achievable in heterogeneous material architectures. The nucleation of deformation twins served to significantly reduce the dislocation mean free path in MD simulations by introducing a high density of dislocation barriers into the microstructure. This process of dynamic grain refinement is therefore implicated as the source of anomalous hardening in ML architectures with high interfacial CG-NC fractions. Parametric evaluation of the NC microstructure delivered interesting predictions for the effect of NC grain size on overall ML properties. Through MD simulations, it was observed that smaller NC grain sizes (e.g., $d_{CG} = 10$ nm) increased the
twin densities in the ML architecture. This presents the potential for improved work hardening in the CG layer, which can offset the softening of NC features at smaller grain sizes.

In order to connect the experimental measurements of improved strength in the non-ROM conforming MLs with MD observations of interface-mediated deformation twinning, a phenomenological work hardening model was designed and implemented. Based on Kocks-Mecking analysis, the effects of deformation twinning and subsequent dynamic grain refinement were captured mathematically within the work hardening model. A kinetic Monte Carlo-based simulation was developed in combination with an analytical relation to describe the evolution of the average twin spacing, providing an independent estimate of dynamic grain refinement. The results of this simulation were used to guide the fitting procedure of the Kocks-Mecking model. Using this combined approach, a generalized mechanism-based work hardening model was developed which accurately predicted the mechanical properties of both ROM and non-ROM conforming ML architectures. In this regard, this model connects the mechanistic observations of molecular dynamics simulations with the experimental measurements of ML properties to provide a holistic description of deformation behaviour of the ML architecture.

With consideration of the objectives of this thesis work discussed in the introduction chapter, the major conclusions of this research are as follows:

1. The mechanical behaviour of the ML architecture is adequately described by an ROM assumption for structures where the thickness of the CG layer is significantly larger than its grain size. At this scale, the overall mechanical properties of the ML reflect a weighted aggregate of the bulk properties of the underlying CG and NC features.

2. ROM predictions degrade as the thickness of the CG layer approaches its grain size. This is due to an increase in the overall CG-NC interfacial fraction, and subsequently, an increased influence of interface-mediated deformation twinning mechanisms.

3. The mechanical behaviour of all ML architectures can be predicted by a generalized phenomenological model which accounts for both bulk and interfacial deformation mechanisms.

4. Reduction of the grain size of the NC layer has been shown in MD simulations to increase the twin density within CG features due to an increased dislocation source density at the CG-NC interface. The increase of twin density within CG features
may provide a means to offset softening in the NC microstructure and shift the peak of the HP curve to smaller grain sizes.

10.2 Recommended future work

Based on the findings of this thesis, a number of avenues for future work are recommended:

1. A detailed study on the density of growth twins in the as-deposited ML architectures is recommended in order to isolate the contributions of deformation twins to the overall twin density in the structure. This investigation requires extensive electron microscopy imaging and structural measurements.

2. A mechanical survey of the ML architecture under three point bending and deep drawing conditions is recommended to ascertain the effects of multi-axial loadings on deformation behaviour. It is particularly interesting to determine if the measured deviations in ROM behaviour are preserved in other loading configurations.

3. The MD simulations of this thesis have only considered pristine CG features. In a realistic structure, CG grains are populated by a distribution of defects which can play a significant role in the deformation behaviour. Specifically, targeted MD simulations are recommended on ML architectures with pre-existing growth twins and Frank-Read type intragranular dislocation source embedded in the CG features.

4. One of the attractive aspects of computational simulations is the flexibility they offer in parametric studies. It is therefore recommended that the current MATLAB code be extended to permit MD simulations of ML architectures constructed from non-FCC lattices such as the body-centered cubic and hexagonal close-packed crystal structures.

5. Although highly novel, the kMC model which has been developed assumes a homogeneous treatment of deformation twin nucleation sites. This assumption is appropriate for nanoscale single crystal structures such as nanowires, but has limited applicability in polycrystalline agglomerates, where the heterogeneities of grain boundaries bias the deformation twinning kinetics. It is therefore recommended that the kMC model be combined with molecular dynamics simulations to develop a generalized deformation twinning model which can predict the comparative kinetics of nucleation and thickening while accounting for heterogeneous effects.
References


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Appendices
Appendix A

LAMMPS input files

The following LAMMPS input files were used to perform MD uniaxial tensile simulations for this thesis. The code is found in two files. The first file performs an equilibration of the MD supercells which are generated using a custom-built MATLAB code. The second file performs stress-controlled uniaxial tensile simulations on the equilibrated microstructures. Results derived from these input files are presented in Chapters 3 and 7.

#Matthew Daly, 2016
#Equilibration for NiCo ML samples

#Basic Settings
units metal
atom_style atomic
boundary p p p
dimension 3
read_data 10nm.atoms

#Specify inter-atomic potential
pair_style eam/alloy
pair_coeff * NiCo2013.eam.alloy Ni Co
neighbor 2.0 bin
neigh_modify every 1 delay 10 check yes
delete_atoms overlap 1.2 all all

#Energy minimization

#compute cnaatom all cna/atom 3.0
#variable test atom "c_cna!=1"
#group relevant dynamic all var test every 500
#compute energ all pe/atom
compute central all centro/atom fcc

#compute stress all stress/atom NULL

thermo 500

thermo_style custom step atoms temp pe ke etotal pxx pyy pzz
  pxy lx ly lz

thermo_modify lost error norm no flush yes

fix 1 all box/relax iso 0.0 vmax 0.0001

dump 1 all cfm 10000 dump_10nm/min.*.cfg mass type
  xs ys zs id c_cent type

min_style cg

minimize 1e-5 1e-5 10000 10000

undump min

unfix 1

# Heating

reset timestep 0

timestep 0.001

fix 1 all npt temp 10 773 0.1 x 0.0 0.0 1 y 0.0 0.0 1 z
  0.0 0.0 1

thermo 500

thermo_style custom step atoms temp pe ke etotal pxx pyy pzz
  pxy lx ly lz

thermo_modify lost error norm no flush yes

dump relax all cfm 10000 dump_10nm/heating.*.cfg mass
  type xs ys zs id c_cent type

run 20000

undump relax

unfix 1

# Annealing

reset timestep 0

timestep 0.001

fix 1 all npt temp 773 773 0.1 x 0.0 0.0 1 y 0.0 0.0 1 z
  0.0 0.0 1 drag 1.0

thermo 500

thermo_style custom step atoms temp pe ke etotal pxx pyy pzz
  pxy lx ly lz

thermo_modify lost error norm no flush yes

dump relax all cfm 10000 dump_10nm/anneal.*.cfg mass
  type xs ys zs id c_cent type

run 200000

undump relax

unfix 1

# Cooling
reset_timestep 0
fix 1 all npt temp 773 1 0.1 x 0.0 0.0 1 y 0.0 0.0 1 z 0.0 0.0 1
thermo 500
thermo_style custom step atoms temp pe ke etot pxx pyy pzz pxy lx ly lz
thermo_modify lost error norm no flush yes
dump relax all cfg 10000 dump_10nm/cool.*.cfg mass
type xs ys zs id c_cent type
run 20000
undump relax
unfix 1

#Equilibriate
reset_timestep 0
fix 1 all npt temp 1 1 0.1 x 0.0 0.0 1 y 0.0 0.0 1 z 0.0 0.0 1 drag 1.0
thermo 500
thermo_style custom step atoms temp pe ke etot pxx pyy pzz pxy lx ly lz
thermo_modify lost error norm no flush yes
dump relax all cfg 10000 dump_10nm/equil.*.cfg mass
type xs ys zs id c_cent type
run 50000
undump relax
unfix 1

write_restart restart_10nm/10nm.restart
#Matthew Daly, 2016

#uniaxial tensile testing of NiCo MLs using load−control

read_restart ../../../relax/restart_10nm/10nm.restart

neighbor 2.0 bin
neigh_modify every 1 delay 10 check yes

pair_style eam/alloy
pair_coeff * * NiCo2013.eam.alloy Ni Co

timestep 0.001

variable loadint equal 500
variable loadint2 equal 500
variable relaxint equal 500
variable relaxint2 equal 500
variable load equal 1000
variable relax equal 10000
variable sstep equal step
variable aatoms equal atoms
variable ttemp equal temp
variable ppe equal pe
variable kke equal ke
variable eetotal equal etotal
variable llx equal lx
variable lly equal ly
variable llz equal lz
variable ppyy equal pyy
variable ppzz equal pzz
variable ppxy equal pxy
variable ppress equal press
variable time loop 100
variable llx equal lx
variable lxx equal $xllx$
variable pressx equal "−pxx/10000"
variable initpress equal 1000
variable aveengstrain equal "(favelength−v_lx0)/v_lx0"
variable aveengstrain2 equal "(favelength2−v_lx0)/v_lx0"
variable vavex equal f_avex
variable vavex2 equal f_avex2
variable loadtime equal v_tottime−v_load
variable relaxtime equal v_tottime−v_relax

compute cnaatom all cna/atom 3.0
variable test atom "c.cnaatom!=1"
group relevant dynamic all var test every ${relaxint}
compute ccent all centro/atom fcc
#compute totstr all stress/atom NULL
#shell ./process_first.sh
label loop
print "Loop\_iteration\_${time}"
reset timestep 0
variable start equal "+1*(v.time-1)*v.initpress"
variable stop equal "+1*v.time*v.initpress"
variable tottime equal (v.time-1)*v.load+(v.time-1)*v.relax+
step
#fix atomstressx all ave/atom 2 50 ${loadint}
c_totstr[1]
fix avelength all ave/time 2 250 ${loadint2} v.llx
fix avex all ave/time 2 250 ${loadint2} v.pressx
fix 1 all npt temp 1 1 0.1 x ${start} ${stop} 1 y 0.0 0.0 0.0 0.0 1
thermo ${loadint2}
thermo_style custom step v.tottime atoms temp pe ke etotal lx
   ly lz pxx ppy pzz pxy ppress v.aveengstrain v.pressx f_avex
thermo_modify lost warn norm no flush yes
dump deform_tot_load all custom ${loadint} dump10nm/
tot_load.${tottime}.lammps.* type xs ys zs c_ccent c_cnaatom
#f_atomstressx
dump_modify deform_tot_load element Ni Co
dump deform_load relevant cfg ${loadint2} dump10nm/
deform_load.${tottime}.cfg.* mass type xs ys zs c_cnaatom
dump_modify deform_load element Ni Co
fix 2 all print ${loadint2} "$${tottime}$$s{step}$$s{l1}$$s{l2}$$s{l3}$$s{aveengstrain}$$s{pressx}$$s{vavex}" append 10nm.
dat screen no title "blah"
run ${load}
unfix 1
unfix 2

#unfix atomstressx
unfix avelength

undump deform_tot_load
undump deform_load

#shell dump_10nm/process_load.sh ${loadtime}

reset_timestep 0

variable tottime equal (v_time)*v_load+(v_time-1)*v_relax+
step

#fix atomstressx2 all ave/atom 2 50 ${relaxint}
c_totstr [1]
fix avelength2 all ave/time 2 250 ${relaxint} v_llx
fix avex2 all ave/time 2 250 ${relaxint} v_pressx
fix 1 all npt temp 1 1 0.1 x {stop} {stop} 1 y 0.0 0.0
1 z 0.0 0.0 1

thermo ${relaxint}
thermo_style custom step v_tottime atoms temp pe ke etotal lx
ly lz pxx pxy pzz pxy press v_aveengstrain2 v_pressx f_avex2
thermo_modify lost warn norm no flush yes
dump deform_tot all custom ${relaxint} dump_10nm/tot.
${tottime}.lammps.* type xs ys zs c_ccent c_cnaatom #
atomstressx2
dump_modify deform_tot element Ni Co
dump deform relevant cfg ${relaxint} dump_10nm/deform.${tottime}.cfg.* mass type xs ys zs c_cnaatom
dump_modify deform element Ni Co
dump

fix 2 all print ${relaxint} "$tottime"${sstep}"${llx}"${llly}"${lllz}"aveengstrain2"${pressx}"vavex2" append 10nm.dat screen no title "blah"
run ${relax}

unfix 1
unfix 2
#unfix atomstressx2
unfix avelength2

undump deform_tot
undump deform

#shell cd dump_10nm
#shell ./process_relax.sh ${relaxtime}
#shell ./process_test.sh
#shell cd ..

write_restart restart_10nm/10nm_tensile.${tottime}.restart

if "${time} > 99" then "jump SELF break"
next time
jump SELF loop
label break

#shell ./dat_process.sh
print "ALL DONE"