Abstract

A combination of atomistic simulations and experiments is used to study the microscopic deformation mechanisms of materials. Atomic scale simulation tools include molecular dynamics and density functional theory. The experiments involve uniaxial tension and compression tests on: (a) single crystals of low stacking fault energy Co-33%Ni alloys, (b) polycrystalline nano-twinned Ni-x%Co alloys (x = 1, 1.62, 2.9 and 5.6), and (c) equiatomic NiTi shape memory alloys. The reason these materials are chosen as candidates for study is that these materials have very distinct microstructure and mechanical properties.

The single crystals of Co-33%Ni alloys demonstrated a competition between slip and twinning based deformations. Depending on the single crystal orientation and loading direction (tension/compression), either mode is activated. A Schmid factor analysis demonstrated that slip or twinning is triggered when the resolved shear stress on the respective systems is the maximum. In other words, the critical resolved shear stress (CRSS) for slip and twinning are found to be around 15 MPa and 38 MPa respectively. To rationalize the experimental observations, the fault energy surfaces (generalized stacking/planar fault energies) are computed. Using a Peierls-Nabarro based modeling framework, the CRSS levels for slip and twinning are predicted on a physical ground. On the whole, the results indicate the inherent material propensity to select either mode of plasticity originates from the underlying fault energetics.

Using the fault energy considerations, the anomalous composition dependence of Ni-x%Co alloys (x = 1, 1.62, 2.9 and 5.6) is clarified. The experimental stress-strain curves demonstrated a non-uniform strengthening attributes with respect to the composition. This effect is traced back to the atomic level fault energy surface as a direct consequence of alloying. The existence of competing mechanisms (solid solution hardening versus Suzuki segregation) was discovered. The presence of nano-sized twins in the microstructure (as unveiled by electron backscatter diffraction and transmission electron microscopy) serve to enhance the atomic scale energetics in the form of slip characteristics. Using molecular dynamics simulations, various slip transfer mechanisms at the coherent twin boundary is categorized. The extrinsic levels of the energy barriers to the dislocation slip for individual mechanisms are computed. The corresponding frictional stresses are extracted to eventually arrive at CRSS values. These CRSS values for each alloys represents those for the nano-twinned microstructure. A reasonably good agreement between the experiments and theory lends credence to the modeling approach.

Using similar atomistic simulations, we resolve the mechanistic origin of the NiTi superelasticity. Using a newly developed pair potential, the compressive load/unload behavior of austenitic NiTi (consisting of B2 lattice) is examined. The material is demonstrated to undergo full strain recover upon 5% of straining. The origin of such deformation recoverability is traced
back to the existence of a reversible phase transformation between the austenite and martensite crystals. The existence of a tension-compression asymmetry is observed in general agreement with the earlier experimental trends in the literature. Such behavior is attributed to the uni-directional nature of phase transformation phenomena (which is found to be governed by deformation twinning of the martensite phase).

Inspired by the model output on the pristine (i.e. defect-free) NiTi, we set out to examine the similar attributes in terms of stress-strain response as well as the crystallographic mechanisms in presence of a precipitate. A nano-sized precipitate of rhombohedral lattice type is constructed with a lenticular geometry. Such shape is assumed on the basis of literature electron microscopy observations. Then, the precipitate is embedded in an austenite B2 lattice and then the composite system is energetically minimized. Upon the energetic relaxation, an elastic disturbance field is observed to generate as a direct consequence of the local atomic misfit at the precipitate-matrix periphery. The observed disturbance is quantified in terms of the stress profile along a line. The profile is found to be in good experiment agreement with high resolution electron microscopy measurements as reported earlier in the literature, however, in disagreement with Eshelby based continuum predictions. Subsequently, simulations of compressive deformation reveals that the presence of precipitate reduces the transformation stress, strain and the overall hysteresis of the load-unload hysteresis curve.
To my parents
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Chapter 1 Introduction

1.1 Background

In today’s major industries (such as transportation, structural, petrochemical), computer simulations are playing a vital role in assessing component performance prior to their induction into laboratory tests or services. These models are reducing costs and human efforts by massively enhancing design efficiency. The governing principles of these simulations are based on the phenomenological elastic/plastic laws of materials behaviors. Central to these models are the materials properties which are pre-defined and incorporated into the continuum formulations. It is noted that the deformation mechanism at the discrete lattice scale is not considered therein, rather approximated using these constants. With the advent of computational materials science tools, now we are in a position to make strides towards capturing discrete lattice level mechanisms. Particularly noteworthy are the advances in the molecular dynamics and density functional theory modeling endeavors. Revelation of important metrics at the microscopic scale holds potential for future breakthrough in the form of incorporation into a broader simulation scheme for use in industry and academia alike (Figure 1.1).
The consideration of physical lengthscale is of paramount importance in modeling materials. For instance, at higher lengthscale, component-oriented simulations at the continuum scale are performed using phenomenological plasticity laws within finite element framework. On the other hand, simulations of the micromechanism of deformation (e.g. twinning, slip) would require proper input from the crystallographic level. At the smallest lengthscale, the material building blocks are essentially discrete in nature (i.e. consisting of atoms). The governing laws of atoms are drastically different than that employed for the bulk. Nonetheless, there are effects originating from this very atomistic stage that influence mechanical behavior across the lengthscale. It is a critical challenge to transition from atomic scales to meso- and even higher length scales. The challenges are that at the atomic scale the deformation of a pristine crystal is considered, and the representative volumes are relatively small. At the mesoscale, there would be material interfaces being intercepted by other propagating defects (twin and/or slip) and the misorientations among them that dictate the global mechanical response. Evidently, it is imperative that bridging the atomic scale phenomena to the continuum scale should be substantiated with rigorous and careful experimental characterizations. However, the scope of the experimental resolution is currently limited to capture the discrete lattice phenomena either spatially or temporally.

Over the last decade, our understanding of materials has significantly benefited from powerful simulation capabilities ranging from atomistic to continuum. The atomistic simulations are addressing phenomenon that cannot be gleaned from experiments because of spatial and temporal resolution issues. The first issue of spatial resolution deals with the imaging conditions. For example, phenomenon at elasto-plastic transition could be particularly challenging to capture given the fact that they occur over several atomic layers and with minute displacements. For example, dislocation transmission, lock formation, dislocation incorporation to boundaries and dislocation multiplication at the matrix-grain boundary interfaces cover some of the most significant reactions that can physically occur. The importance of these strain transfer mechanisms is reflected in the form dictating the global mechanical response. These reactions can be both qualitatively and quantitatively evaluated by means of the lattice level fault
simulations as we will show in parts of this thesis. The local changes (such as twin nucleation and ensuing migration) can be detectable with experiments performed at the correct length scale.

To develop an appreciation of the length scales, modern experimental characterization tools could be utilized judiciously. For example, techniques such as advanced digital image correlation (DIC), electron backscatter diffraction (EBSD) mapping could provide the accurate mechanisms of deformation (e.g. twins being impeded by other twins and associated strain gradients). Figure 2 demonstrates such a strategy aimed at developing a hierarchical methodology for materials modeling utilizing the current experimental and atomistic tools.

Figure 1.2 – Addressing multiple lengthscale physics with appropriate experimental and theoretical methods.

We envisage the prospects of a similar sequential, multi-scale design methodology for even more complex alloy systems with confirmation of the model validity at the corresponding
length scale. Further refinement of such methodology will accelerate the design of advanced materials by avoiding the large test matrix approach and optimization trials. It is important to identify the specific role of the solutes in terms of the energy barriers. Unlike available phenomenological models, we will achieve this without the adjustable parameters at any length scale.

1.2 Methods

1.2.1 Material Preparation and Monotonic Experiments

Single crystal specimens of Co-33%Ni were fabricated using the Bridgman technique in an inert Helium atmosphere. Room temperature tension and compression experiments were conducted using 1.5mm x 3 mm x 10 mm (dog-bone) and 4 mm x 4 mm x 10 mm specimens (thickness x width x gage-length), respectively, at a strain-rate of 5 x 10^{-5} s^{-1}. Prior to the tests, all the specimens were solutionized at a constant temperature of 900 °C for one hour and then quenched by room temperature water. The loading axes for the tension samples were aligned along ⟨123⟩ and ⟨111⟩ crystallographic directions, and the compression samples along ⟨001⟩ and ⟨111⟩. These orientations were verified by electron backscatter diffraction (EBSD) analyses. Each set of loading (compressive or tensile) and crystal orientation case was investigated with multiple companion experiments (up to four tests per each case) to ensure the repeatability of the stress-strain trends, and hence statistically reduce the experimental error levels. The samples were loaded in a servo-hydraulic load frame where strain levels were measured using a miniature extensometer and stress levels with a load cell. Post-deformation microstructure is then studied ex-situ with transmission electron microscopy (TEM).

1.2.2 Digital Image Correlation (DIC)

DIC is an experimental visualization method that utilizes the distinction between a reference and a modified speckle pattern pre-deposited on the specimen surface in question. The surfaces of the specimens were polished to a mirror finish for DIC analysis. An adherent layer of black paint was airbrushed onto the polished surfaces to create a fine speckle pattern thereon. An IMI model IMB-202FT CCD digital camera (1600 pixel x 1200 pixel) was used to capture high
resolution images for the reference state and deformed state of the surface under study. In-situ DIC measurement was utilized to identify the strain localization contour plots in real time at various levels of macroscale deformation. In addition, higher resolution ex-situ DIC was performed in order to identify the number of active plastic systems as well as distinguish between various local strain bands (slip- and twinning-induced).

1.2.3 Density Functional Theory (DFT)

The DFT is a quantum mechanical simulation method based on the Schrodinger’s equation, where the interatomic bonding forces are determined by the valence electrons. Two primary assumptions of the DFT based modeling of the deformation are that: (a) the plastic deformation is equivalent to the permanent movement of atomic nuclei, which are bonded together by sharing electronic clouds (also known as the Born-Oppenheimer approximation), and (b) inter-nuclei forces are solved in terms of the electronic densities (instead of direct solutions of wave functions) to achieve numerical feasibility. For example, the slip of material creates a permanent atomic displacement equal to the Burgers vector. Using DFT methods, one can solve for the associated free energy differential (i.e. the energy cost to create such displacement). Hence, the GSFE and GPFE curves were constructed by computing the energy differential between the bulk \( E_{\text{bulk}} \) and sheared \( E_{\text{sheared}} \) crystal normalized by the shear area \( A \) as in Equation (1) after Vitek [1].

\[
\gamma = \frac{E_{\text{sheared}} - E_{\text{bulk}}}{A}
\]  

(1)

The convergence of the \( \gamma \) energy levels was ensured with respect to the simulation supercell size (i.e. number of layers in x, y and z directions). Three dimensional periodic boundary conditions were enforced on the supercell eliminates the effects of free surface energy, thereby simulating a system of bulk material. Shear displacement is applied along the x direction (corresponding to the <112> crystallographic direction) on the y plane (i.e. \{111\} slip plane), which generated corresponding shear forces. It was ensured the no traction existed except for the
designated shears. For the post-processing of simulation data, the atomic configuration viewer, VMD (Visual Molecular Dynamics) [2] was used.

For the current DFT calculations, we used the commercial quantum simulation software - Vienna Ab initio Simulation Package (VASP) [3] to create the solid solution of Co-33%Ni. Upon constructing the Co-Ni fcc crystal structure, the conjugate gradient method was used to iteratively minimize the total energy of the overall crystal structure, and the atomic positions are updated accordingly. During the iteration, an acceptance criterion adjusts the new atomic positions, conjugate to the previous ones that follow the direction of the steepest descent on the inter-atomic energy profile (which is established by solving for the valence electron densities). Inherent in DFT assumptions are the charged nature of the atomic nuclei (positively charged) and the surrounding electronic cloud (negatively charged). To model the electrostatic interactions among the nuclei and electrons, the projector augmented wave method was used. During deformation, electron movements are “correlated” due to their mutual Coulombic interactions (the so-called correlation effects); to make each electronic energy state unique (as dictated by the Pauli’s exclusion principle), the densities of two electrons have to be antisymmetric upon switching positions (the so-called exchange effects). The exchange-correlation energies were computed using the generalized gradient approximation [4]. The DFT based electronic solutions are conducted in reciprocal space by creating a meshed Brillouin zone. In the current work, the Brillouin zone is constructed as a 12 x 12 x 12 mesh size (using Monkhorst Pack k-point with an energy cut-off of 300 eV). Spin polarized conditions were enforced on the electrons, which ensures the ferromagnetism of the elemental Co and Ni. For a fundamental discussion of the quantum modeling of materials, the readers are also referred to [5].

1.3 Thesis organization
In this thesis, we present applications of modern atomistic tools and experimental characterization techniques to study select materials with a variety of microstructural features as well as constitutive attributes. We aim to seek physical rationales for the observed behaviors. Our specific goals are as follows:

(i) First part of the thesis deals with low stacking fault energy Co-33%Ni alloys. We use single crystals to perform tension/compression tests for various orientations. Using digital image correlation (DIC), electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM), the deformation mechanism for the individual loading cases will be investigated thoroughly. Based on the microstructure characterizations from the foregoing techniques, we would be able to construct a physical model with appropriate atomistic input. Particularly, we investigate the transition of elastic-plastic deformation by experimentally determining the critical resolved shear stress (CRSS) and predicting it based atomistic calculations. Our ultimate goal is to study the competition between deformation twinning and slip in Co-33%Ni and rationalize such behavior with atomic level energy considerations. In doing so, we will develop methodology to predict CRSS levels for slip or twin nucleation and twin-slip interaction.

(ii) The second part of the thesis consists of studying a very special type of material (Ni-Co alloys with Co content ranging from 1% to 5.6%) which already has annealing (i.e. pre-existent) twins in the microstructure as a result of electrodeposition process. The existence of the annealing twins is ensured by TEM analysis on the specimens prior to any deformation tests. Uniaxial tension tests are performed on NiCo specimens to reveal their stress-strain behaviors. Then, we will use molecular dynamics modeling of the role of twin boundaries in inhibiting slip under various local stress situations. The associated energetics and the frictional stresses would be quantified. The overall objective is to predict the experimentally determined CRSS levels for all composition of NiCo alloys.
(iii) In the third part of this thesis, we turn our attention to a completely new class of materials, namely, NiTi shape memory alloys. The superelastic behaviors of these materials are studied using a newly developed pair-potential function to be used in molecular dynamics simulations. We also study the role of nano-sized rhombohedral precipitate embedded in an austenitic matrix. In this part of the thesis, we explore the mechanism of reversible phase transformation between B2 lattice and B19' under loading/unloading simulations. In doing so, we establish a mechanistic understanding of the superelastic mechanical attributes.
Chapter 2 Mechanical Response of Low Stacking Fault Energy Co-Ni Alloys – Continuum, mesoscopic and atomic level treatments

2.1 Abstract

Low stacking fault energy fcc alloys deform via either mechanical twinning or dislocation slip. A single crystal poses an excellent avenue to studying inherent material preference for plastic flow mechanism. This chapter examines the physical process underlying the flow behavior of Co-33%Ni single crystals at continuum, mesoscale and atomic levels. Digital image correlation, electron backscatter diffraction and transmission electron microscopy permitted an in-depth analysis of the deformed microstructure. Emphasis is placed on rationalizing the experimentally discovered competing modes of plasticity from an atomistic perspective. Experimentally, predisposition for slip or twinning is observed to be specific to a given crystal orientation and loading direction (tension/compression). Particularly, flow in \( \langle 111 \rangle_{tension} \) and \( \langle 100 \rangle_{compression} \) proceeds with a single twinning system and ensuing twin-slip interactions. By contrast, dislocation slip nucleation followed by multi-system forest hardening prevails in the post-yield behavior of \( \langle 123 \rangle_{tension} \) and \( \langle 111 \rangle_{compression} \) cases. The stress-strain curves reveal that the twinning-mediated flow induces superior hardening characterized by pronouncedly serrated flow behavior. A first principle based mechanics model is proffered to account for the relative material propensity for either slip or twinning on the basis of atomic level generalized stacking/planar fault energies. The model considers the energy balance between the applied work and the total energy expenses as contributed by both continuum and atomistic effects. Upon establishing the \( \gamma \) surfaces from density functional theory, critical stresses for the initiation of slip, twin and post-yield twin-slip interactions are computed within a Peierls-Nabarro modeling framework. Predicted critical stress levels demonstrate reasonably good agreement with the experimentally determined critical resolved shear stresses. Concurrence of
the theoretical inferences with the experimental observations is discussed in the context of the related literature.

2.2 Background

Alloying of metals has long been exploited in custom-tailoring desired mechanical properties dating as far back as to the Bronze Age [6]. In modern applications, extreme operating conditions for engineering service components warrant superior properties such as high strength and creep resistance. Cobalt/nickel base alloys constitute the bulk of this specialized class of materials suited for a broad thermo-mechanical loading spectrum [7, 8]. These materials employed in aerospace, nuclear and petrochemical industries are manufactured by adding various alloying elements to different extents so as to impart unique macro-scale characteristics. In essence, the addition of these elements invokes considerable modification to the deformation micromechanics of the respective base metals. From a solid state physics standpoint, the solute elements embedded in the matrix material contribute to the hardening effects due primarily to an atomic volume mismatch with their host lattice atoms [9, 10]. For the case of a binary Co-Ni alloy, the solid solution strengthening attributes would be negligible owing to the elemental volumetric ratio between Co and Ni being very close to unity. Nonetheless, the substitutional solute atoms integrated to the base metal lattice alters the fault energy landscape [5] in the alloy crystal. The adjusted electronic structure of the metallic lattice drastically affects the relative propensity of competing crystal deformation mechanisms, which occur in the form of various defect evolution (such as dislocations, stacking faults and twin boundaries). The modification in quantum bonding at the atomic substructure subtends the macroscopic operative flow mechanisms in the form of slip, twinning, twin-slip and slip-slip interaction. The gradual evolution and mutual interplays among slip and/or twinning processes in turn constitute the mechanistic origin of macroscale hardening behavior of the alloy. In view of the foregoing rationale, in the current undertaking, we are particularly interested in elucidating the relative material predilection towards slip versus twinning. In classical phenomenological considerations [11-14], the stacking fault energy (SFE) has been regarded as the most crucial material parameter in interpreting the competition between slip and twinning-dominated flow. However, recent theoretical advances [15-18] indicate that the entire \( \gamma \) energy surfaces (i.e. the generalized
stacking/planar fault energies abbreviated as GSFE/GPFE first conceptualized by Vitek [1] of the metallic solid solution dictate the favored plastic flow mechanism, rather than the SFE itself. The physical interpretation of GSFE/GPFE represents the energy expenditure (per unit area) to be overcome during various degrees of rigid shear displacements between two crystals (later to be explained in more details in sections 4.2 and 4.4). These $\gamma$ energy landscapes are reported to be strong functions of the material electronic structure [19], which can be resolved by quantum mechanical methods [20]. In the last decade, significant advancement in computational material science has prompted major strides in understanding the non-continuum effects of slip/twinning processes, establishing the physical rationale behind observed plastic mechanism [21-23]. Evidently, these important discoveries entail a revisit to the classical modeling endeavors, and, thereby, incorporation of the most contemporary knowledge of the underlying atomistics into deformation theory. The present research is aimed at addressing the long-standing question of theorizing the preferred mode of plastic deformation via slip or mechanical twinning on a physical basis, principally noting their respective atomic level fault energetics. We build on the foundation laid by classical and modern plasticity theories, and forward a model accompanied by extensive experimental analyses. We study the experimental stress-strain behavior and the associated deformation features of a representative low stacking fault energy material at the microstructure level.

Within the current scope, we have selected single crystals made from a Co-33\%Ni alloy. Early literature [24-26] reports that the polycrystalline Co-33\%Ni alloy possess a considerably low stacking fault energy ($\approx 20 \text{ mJ/m}^2$), and a face centered cubic (fcc) crystal structure. Single crystals offer a superior understanding of the metallic deformation mechanics by circumventing the effects of grain boundaries and texture associated with polycrystalline materials [27, 28]. The choice of this particular binary composition of Co-Ni is especially advantageous, in that this material is reportedly predisposed to plastic deformation via mechanical twinning at room temperature [29]. Moreover, we note that a judicious selection of the Co-33\%Ni single crystal orientation and loading direction (tension or compression) culminates in the plasticity proceeding preferentially via either dislocation slip or mechanical twinning. Consequently, it facilitates characterizing the governing variables pertaining to the preferred deformation mode both on
experimental and theoretical grounds as noted in the literature of low SFE materials [30-32]. The current analysis of the Co-33%Ni alloy serves to be representative of low SFE fcc alloys, and hence can pave the way for extending the inferences reached in this work to similar classes of materials.

In early literature [11-14, 33], lowering of the SFE in fcc metals and alloys has been correlated with an increased inclination to deformation by a mix of planar/wavy slip and deformation twinning. The strain hardening response would be pronouncedly altered subjected to the activation of slip or twinning upon yielding. Typically, twinning-dominated strain hardening is manifested in the form of a serrated stress-strain curve [33, 34]. Experimental observations suggest that the preferred plastic mechanism would be a strong function of the loading direction and crystallographic orientation [35], provided the respective critical stresses (which are material properties) are similar. Depending on compressive or tensile load along a certain crystallographic orientation, different levels of shear stresses would be resolved on various slip and twinning systems as per the Schmid law. On account of the maximum Schmid factor, a specific loading configuration would trigger either slip or twin nucleation accordingly. In the slip-mediated plasticity, low stacking fault energy would promote splitting of full dislocations into Shockley partials bound by stacking fault. Early literature notes that the mechanistic process of deformation twin nucleation and migration processes is fundamentally founded on the collective glide pattern of Shockley partial dislocations [34, 36-41]. The successive passage of Shockley partials on consecutive slip planes amounts to the mechanical twinning phenomenon. Therefore, in classical modeling undertakings, twin nucleation and migration processes are generally treated by considering the elastic interaction effects among the twinning partial dislocations [34, 42]. A more comprehensive account of the classical twinning models is discussed in Section 5.2 of this chapter. In summary, the previous models in the literature are mostly empirical (requiring fitting parameters), and hence cannot predict the critical stress magnitudes of various flow mechanisms from physical considerations (e.g. twin or slip nucleation, twin-slip interaction etc.). Most importantly, the evolution of fault energetics related with the shearing of the discrete crystal lattice [1, 17] accompanying slip/twinning processes has not been utilized in quantifying the macro-scale flow stresses. Essentially, the non-continuum nature of the metallic crystal at the atomic level necessitates overcoming periodic resistance forces, i.e. the so-called Peierls barrier
during the slip or twinning process. The periodic energy-displacement correlation associated with slip- and twinning-induced shearing at the atomic level can be correctly outlined by the so-called \( \gamma \) surfaces i.e. generalized stacking fault energy (GSFE) and generalized planar fault energy (GPFE) profiles. However, these \( \gamma \) surfaces can only be quantified theoretically with the knowledge of the underlying electronic nature of the specific metal or alloy system. With the advent of modern quantum mechanical simulation tools such as density functional theory (DFT)\[^{20}\], one can precisely account for the electron bonding effects from first principles, thereby permitting accurate computation of the GSFE/GPFE levels. These \( \gamma \) surfaces provide an ab-initio energetic perspective into the material predilection for the operative plasticity. Furthermore, they constitute essential ingredients in the recipe of predicting critical stresses for slip and twin nucleation within a Peierls-Nabarro modeling framework.

Figure 2.1 illustrates an overview of the scale and structure of the current methodology directed at addressing the deformation mechanisms of Co-33%Ni. We adopt a bottom-up approach comprising electronic properties at the atomic lengthscale, the onset of defect dynamics at the mesoscale, and continuum level critical flow stresses. At the continuum scale, uniaxial tension and compression experiments are conducted on single crystals loaded along \( \langle 111 \rangle \), \( \langle 123 \rangle \) and \( \langle 001 \rangle \) directions. The loading orientations were selected on the basis of prompting the material to deform via twinning or slip. Critical resolved shear stresses for dislocation slip and mechanical twin nucleation is extracted from the stress-strain curves with the aid of Schmid law. In-situ digital image correlations (DIC) analysis is used to study the nature of the active plastic systems providing a measure of the strain localization levels. In addition, ex-situ electron backscatter diffraction (EBSD) scans are performed so as to reveal local misorientations associated with twinning. Extensive transmission electron microscopy (TEM) conducted ex-situ in and around the localized strain bands permits a detailed insight into the flow mechanism for
Figure 2.1 – A schematic illustrating the lengthscale of the current study. Tension/compression experimental data are analyzed via DIC and EBSD methods at continuum level. Mesoscale considerations include extensive microstructure study via TEM and SAD accompanied by modeling efforts. At atomic level, GSFE/GPFE curves are computed from the electronic structure of Co-Ni alloys using DFT.

the individual loading cases. Complementary selected area diffraction (SAD) patterns in conjunction with the TEM images confirm the presence of local material reorientation (i.e. twinning-induced) by revealing twin diffraction spots. At the mesoscale, we model critical resolved shear stresses for slip and twinning (i.e. demarcating the onset of plasticity) as well as the critical stress level indicating the onset of twin-slip interaction (i.e. second stage of hardening following the initial plasticity). We utilize a Peierls-Nabarro modeling framework, which accounts for continuum elastic theory of dislocation interaction and non-continuum $\gamma$ surfaces. The central premise of the Peierls-Nabarro model requires generalized stacking fault energy
(GSFE) and generalized planar fault energy (GPFE) landscapes, to be considered as essential constituents. To that end, density functional theory (DFT) simulations are employed to compute the ab-initio \( \gamma \) surfaces based on the electronic structure of the Co-33\%Ni fcc solid solution.

The current study, based on the behavior of Co-33\%Ni as a representative material, can be deemed as a necessary revisit to the fundamental deformation theory related to the low SFE fcc alloys. Reinforced with sufficient experimental evidence, we propose to accommodate the quantum mechanical contributions of material deformation to the classical continuum context addressed in recent literature [43, 44]. As a result, we derive the critical flow stress predictions free of empirical constants.

2.3 Experimental Results

2.3.1 Stress-strain Behavior

Figure 2.2(a) – Shear stress-strain for \( \langle 1\overline{1}1 \rangle \) and \( \langle 123 \rangle \) tension cases resolved onto \( \langle 1\overline{1}1 \rangle[121] \) and \( \langle \overline{1}11 \rangle[211] \). The error bars represent multiple experiments. The arrow pointing to the right indicates that experiments were continued at higher strains.
Figure 2.2(b) - Shear stress-strain for \( \langle 100 \rangle \) and \( \langle 111 \rangle \) compression cases resolved onto \( \{11 \overline{1} \}[\overline{1}21] \) and \( \{1 \overline{1}1\}[121] \) twin and slip system respectively.

Figures 2.2(a) and 2.2(b) report the experimental resolved stress-strain levels of Co-33\%Ni single crystals loaded along four different crystallographic directions.Resolved shear stresses (nominal) on the activated systems for respective curves have been plotted against the resolved shear strains. Depending upon the operative mode of plasticity, the global stress-strain levels are resolved on the maximum Schmid factor slip or twinning systems. These plots illustrate the differences in single crystal plastic flow response as a function of the crystal orientation as well as the loading direction. A careful examination of the post-deformation microstructure (with the aid of extensive TEM and EBSD analyses, to be discussed in Section 2.3.2) suggests the existence of different plastic flow mechanisms for the individual cases. For \( \langle 111 \rangle \) tension and \( \langle 100 \rangle \) compression, flow mechanism has been found to be dominated by deformation twinning. On the other hand, \( \langle 123 \rangle \) tension and \( \langle 111 \rangle \) compression deform plastically due primarily to dislocation slip.
In Figure 2.2(a), the stress-strain response in \(\langle 111 \rangle\) tension is characterized by highly serrated flow. By contrast, the flow stress under \(\langle 123 \rangle\) tension appears rather uniform. The serrated plastic stress-strain for the \(\langle 111 \rangle\) tension and \(\langle 001 \rangle\) compression indicates twinning-based hardening behavior. On the other hand, the \(\langle 123 \rangle\) tension and \(\langle 111 \rangle\) compression curve is noticeably indicative of dislocation slip-induced flow mechanism. The tensile yield stresses for \(\langle 111 \rangle\) and \(\langle 123 \rangle\) tension (0.1% offset) have been found to be \(27 \pm 5\) MPa and \(15 \pm 1.5\) MPa respectively. These yield stresses denote the critical resolved shear stresses \(\tau_{\text{CRSS}}\) for twin or slip nucleation for the Co-33%Ni alloy. The \(\tau_{\text{CRSS}}\) is considered a material property independent of loading direction and orientation. Under compression as in Figure 2.2(b), the \(\langle 001 \rangle\) single crystal shows a yield stress level of \(26 \pm 3\) MPa whereas that of \(\langle 111 \rangle\) case is determined to be \(16 \pm 1.2\) MPa. These stress values represent the critical resolved shear stresses for twin and slip nucleation respectively, which are consistent with the tension results. We note that multiple experiments are conducted to ensure the repeatability of the stress-strain trends as indicated by the error bars in Figures 2.2(a) and 2.2(b). Therefore, the critical resolved shear stresses extracted from these stress-strain curves represent the statistical average values over multiple measurements. The horizontal arrows adjacent to each curve on the right hand side indicate that the experiments were continued to higher strain levels (than shown). We note that the rest of the stress-strain response in Figures 2.2(a) and 2.2(b) are mere continuation of the trend as currently presented. It is our objective in this work to study the very initial stage of the plasticity (i.e. the phenomena such as onset of slip, twinning, twin-slip interaction etc. The subsequent modeling is directed at predicting the foregoing critical stresses to initiate various plasticity mechanisms.

A summary of the foregoing findings is presented in Table 2.1. In addition, critical resolved stress for the activated plastic flow mechanism in polycrystalline Co-33%Ni has been studied (discussed in the Appendix A).
Table 2.1 – Summary of Schmid factor analysis and experimental determination of critical resolved shear stress (CRSS)

<table>
<thead>
<tr>
<th>Cases</th>
<th>Maximum Schmid factor</th>
<th>Observed system(s) activated</th>
<th>Observed flow mechanism</th>
<th>Experimental $\tau_{\text{CRSS}}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slip</td>
<td>Twin</td>
<td>Partials</td>
<td>Leading</td>
</tr>
<tr>
<td>(111) tension</td>
<td>0.27</td>
<td>0.31</td>
<td>0.31</td>
<td>0.16</td>
</tr>
<tr>
<td>(123) tension</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
<td>0.34</td>
</tr>
<tr>
<td>(111) compression</td>
<td>0.28</td>
<td>0.16</td>
<td>0.16</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(100) compression</td>
<td>0.41</td>
<td>0.47</td>
<td>0.47</td>
<td>0.24</td>
</tr>
</tbody>
</table>
2.3.2 Microstructure

\( \langle 111 \rangle \) tension

Figure 2.3(a) - Ex-situ DIC local strain contour on the \( \{101\} \) surface of a single crystal sample loaded along \( \langle 111 \rangle \) in tension.

Figure 2.3(b) - EBSD data for \( \langle 111 \rangle \) tension are presented in the form of inverse pole figures (upper row) and pole figures showing the distributions of \( \langle 100 \rangle \) and \( \langle 110 \rangle \) crystallographic directions.
Figure 2.3(c) - Another presentation of EBSD data from the \{101\} surface of the specimen in tension along \{1 1 1\} direction. The presence of a 60° misorientation between the matrix material and strain bands substantiates the occurrence of deformation twinning.

Figure 2.3(a) illustrates the in-situ DIC local strain contour on the \{101\} surface of a single crystal sample loaded along \{1 1 1\} in tension. The plot shows the residual local strain (normal and not shear) after deformation. The localization of strain in bands is associated with the activation of a particular slip/twin system. To accurately identify these strain bands observed in this case (whether caused by either slip or twinning), EBSD scans on the same deformed surface were conducted as presented in Figure 2.3(b) and 3(c). Inverse pole figures in Figure 2.3(b) indicate significant crystal misorientations in the deformed crystal. The presence of more than one orientation is also noticeable in the distribution of \{100\} and \{110\} poles. In Figure 2.3(c), an EBSD map of the \{101\} surface identifies the DIC-observed shear bands as induced by local crystal misorientation. Based on the maximum Schmid factor, this twinning system has been identified as \{111\}[121]. The misorientation of the twin with respect to the matrix material has been determined to be approximately 60° from the EBSD data. TEM micrographs sampled from the bulk of the crystal in Figure 2.4(a) through 2.4(e) further attest to the fact that the shear bands are caused by deformation twinning.
Figure 2.4 – (a) TEM and SAD for $\langle 111 \rangle$ tension demonstrating the deformation twins, (b) a magnified view of twins with the corresponding SAD spots, (c) further evidence of twinning in $\langle 111 \rangle$ tension along with the presence of stacking faults., (d) an example of a propagating mechanical twin interacting with a dislocation arrangement and (e) evidence of twin-stacking fault intersections.

The TEM image in Figure 2.4(a) shows the prevalence of nano-scale parallel mechanical twins. The SAD patterns in the inset further testify to the presence of twins in the sampled material. Another magnified view of the deformed area is presented in Figure 2.4(b). Parallel deformation twins are distinctly visible in the micrograph. The corresponding SAD pattern confirms the twin reflections. Figure 2.4(c) illustrates a number of fine twins advancing through a forest of stacking faults (binding partial dislocations at both ends). An example of a propagating mechanical twin interacting with a dislocation arrangement is presented in Figure 2.4(d). A deformation twin appears to have created a kink upon interacting with a pre-existent...
local dislocation arrangement. Further evidence of twin-slip interactions can be noted in Figure 2.4(e). A representative deformed microstructure in the close proximity of twinning bands is shown in Figure 2.4(e).

The analyses of these micrographs indicate that the flow behavior of the single crystals deformed in \(<111>\) tension is characterized by mechanical twinning as the primary deformation mode. Secondary strain hardening effects can be attributed to the interaction between the propagating mechanical twin and the local dislocation arrangements as well as classical forest hardening among dislocations themselves. However, no evidence of twin-twin interaction has been found from the DIC and TEM investigations. Upon straining the material to a level as high as 7%, the deformed surface morphology indicates no major variation in the observed plastic flow mechanism. The preferred deformation mode through a broad range of strain has been found to be consistently dominated by parallel non-interacting deformation twin nucleation followed by twin migration, which is influenced by twin-slip interaction.

\(<123>\text{tension}\)

Figure 2.5 – EBSD scan of \(<101>\) surface of a Co-33%Ni single crystal sample loaded along \(<123>\) in tension to a strain level of 60%.
Figure 2.5 illustrates an EBSD scan of \{101\} surface of a Co-33%Ni single crystal sample loaded along \{123\} in tension to a strain level of 60%. It follows from the EBSD that a uniform orientation exists throughout the deformed surface (as opposed to the \{111\} case in Figure 2.3(c), where twinning causes considerable local misorientation in the form of bands). The EBSD result demonstrates no presence of local misorientation with respect to the matrix material (which confirms the nonexistence of twinning for \{123\} tension). Furthermore, the TEM evidences as

![Figure 2.5](image1.png)

Figure 2.6 – (a) Microscopic slip band (MSB) formation due to dislocation slip on parallel planes along a single slip system, (b) a magnified view of Figure 2.6(a) demonstrates dislocation entanglement in the vicinity of the microscopic strain band, (c) further evidence of entangled dislocations, (d) formation of stacking faults as a result of splitting of full dislocations, and (e) fine stacking faults are observed.
presented in Figure 2.6(a) through 2.6(e) reveal extensive slip activities (with no twinning). These images support the EBSD results concluding that deformation is slip-mediated for the single crystal in $\langle 123 \rangle$ tension. We note that the slip predominantly occurs as $\alpha_6\langle 112 \rangle$ type.

The micrograph in Figure 2.6(a) illustrates an instance of microscopic slip band (MSB) formation due to dislocation slip on parallel planes along a single slip system. Entanglement of dislocations interacting with the slip band can be noticed in the inter-band regions. In Figure 2.6(b), a magnified view of the deformation morphology near the band shows the entanglement of dislocations in the neighborhood of the band structure. Figure 2.6(c) shows further evidence of entangled dislocations. These entangled dislocations dissociated into partial dislocations bound by stacking faults, the evidence of which is shown in Figure 2.6(d) and 2.6(e). Splitting of full dislocation arrangements into partials, thereby creating co-planar stacking faults, can be seen in Figure 2.6(d). Additionally, parallel fine stacking faults at low applied strain level are visible in Figure 2.6(e).

$\langle 111 \rangle$ compression

Figure 2.7(a) – In-situ DIC local strain distribution on the $\{101\}$ surface under $\langle 111 \rangle$ compression demonstrating two systems of intersecting strain bands.
Figure 2.7(b) – EBSD scan of the \{10\overline{1}\} surface showing the existence of a uniform crystal orientation upon 3\% global strain.

Figure 2.7(a) illustrates the in-situ DIC local strain distribution on the \{10\overline{1}\} surface of Co-33\%Ni single crystal compressed along the \{1\overline{1}\overline{1}\} crystallographic orientation. Two systems of intersecting strain bands can be observed. To understand whether these strain bands are due to slip or twinning, we have conducted EBSD scans on the same surface as presented in Figure 2.7(b). The EBSD result reveals no local crystal misorientation (as opposed to the 60\textdegree misorientation bands visible in the \{1\overline{1}\overline{1}\} tension case). This observation dismisses any occurrence of twinning associated with the strain bands identified via DIC. On the basis of the maximum Schmid factor, these two systems are identified as the \{(1\overline{1}1)[1\overline{2}1]\} and \{(1\overline{1}1)[\overline{1}\overline{2}1]\} slip systems. The TEM micrographs in Figure 2.8(a) through 2.8(e) provide more in-depth views into the operative plastic flow mechanism.
Figure 2.8 – (a) Intersecting stacking faults from two different systems can be seen close to a dislocation band formed along a third slip system, (b) a magnified view of Figure 2.8(a), providing a clear depiction of the faults interlocked with each other, (c) parallel stacking faults as a consequence of splitting of full dislocations into Shockley partials, (d) presence of stacking faults is visible and (e) further evidence of stacking faults.

In Figure 2.8(a), intersecting stacking faults from two different systems are visible near a macroscopic dislocation band formed along a third system. Figure 2.8(b) shows a magnified view of the same area, providing a clear visualization of the faults interlocked with each other. Another deformed area is reported in Figure 2.8(c), depicting the presence of parallel stacking faults as a consequence of splitting of full dislocations into Shockley partials. Figure 2.8(d) and 2.8(e) demonstrates further evidence of the prevalence of stacking faults. These TEM findings confirm the widespread participation of extended dislocations as the material continues to deform plastically to higher strain levels.
(100) compression

Figure 2.9(a) – In-situ DIC strain contour on the \{001\} surface is presented at a global strain level of 6\% for (100) compression.

Figure 2.9(b) – EBSD data on the \{001\} surface of the deformed specimen confirm the existence of a 60° (approximately) misorientation between the matrix and the strain band as illustrated with the rotated cubes (\{100\} compression).
For the $\{001\}$ compression samples, in-situ DIC strain contour on the $\{001\}$ surface is presented in Figure 2.9(a) at an applied (global) strain level of about 6%. Parallel non interacting strain bands are distinctly visible. These bands are identified as the $(1 \overline{1} \bar{1})[ar{1}21]$ slip system (corresponding to the maximum Schmid factor). Figure 2.9(b) presents the EBSD analysis of the $\{001\}$ surface of the deformed specimen. The EBSD data confirm that there exists a $60^\circ$

![Image](image.png)

Figure 2.10 – (a) Note the presence of mechanical twins along with stacking faults also supported by twin diffraction spots in the inset SAD pattern, (b) evidence of twins, stacking faults and grouped dislocations, (c) presence of fine twins can be seen as supported by the corresponding SAD patterns, (d) notice an advancing though grouped dislocations and (e) further evidence of twin propagation through dislocation forest is clearly visible.

(approximately) misorientation between the matrix and the strain band (i.e. twins) as illustrated with the rotated cube. This observation attests to the occurrence of twining associated with the strain localizations seen in the DIC image. In Figure 2.10(a) through Figure 2.10(e), the TEM
micrographs provide further evidence of twinning in the deformation of Co-33%Ni single crystals in $\langle 001 \rangle$ compression.

Figure 2.10(a) reports the presence of mechanical twins in the deformed single crystal. Some stacking faults are also visible in the close neighborhood of the twin. The inset SAD patterns show the twin diffraction spots as a result of deformation-induced crystal reorientation, thereby confirming the presence of twinning in the probed area. Another part of the deformed crystal as in Figure 2.10(b) showed twins, stacking faults and grouped dislocation. Figure 2.10(c) reveals fine twins as demonstrated by the corresponding SAD pattern in the inset. In Figure 2.10(d), a mechanical twin propagating through what appears to be an entanglement of grouped dislocations is clearly visible. Finally, Figure 2.10(e) illustrates an instance of twin advancement through a forest of dislocation entanglements.

2.4. Theoretical Results

2.4.1 DFT Simulation of Co-33%Ni solid solution

Figure 2.11 shows the potential energy per atom as a function of lattice constant, $a_{\text{Co-Ni}}$, of the Co-33%Ni solid solution as calculated from density functional theory (DFT) simulations. The lattice constant of the alloy is determined by considering the magnitude of $a_{\text{Co-Ni}}$ corresponding to the minimum per-atom energy as highlighted with a solid circle in Figure 2.11. The basis of the crystal lattice is considered fcc-structured. The lattice constant $a_{\text{Co-Ni}}$ for Co-33%Ni alloy has been determined to be 3.521 Å with the per-atom energy level of -5.4438 eV (electron volt). The current value of the lattice constant is in good agreement with the experimental value of 3.52 Å of the same composition [45]. The inset illustrates the primitive unit cell of the Co-Ni alloy. In view of the fact that Co-Ni is a disordered alloy i.e. with no long or short range atomic order, the solute atoms (Ni) are distributed randomly in the Co-Ni substitutional solid solution matrix. Upon establishing the lattice constant of the binary alloy, we simulate rigid shear of two crystal blocks consisting of discrete atoms in order to construct the associated planar fault energy profile.
Figure 2.11 – The curve showing the per-atomic potential energy versus various levels of the lattice constant, $a_{\text{Co-Ni}}$, of the Co-33%Ni calculated from density functional theory (DFT). The magnitude of $a_{\text{Co-Ni}}$ corresponding to the minimum per-atom energy is considered the stable one (as highlighted with a solid circle).

Figure 2.12(a) – A planar cutaway view of the close-packed (111) slip plane in Co-33%Ni fcc lattice. Two crystal blocks with adjoining interface on the (111) slip (in green and gray) were rigidly displaced along the [121] direction in the DFT simulations to compute GSFE/GPFE landscapes.
Figure 2.12(a) shows a planar cutaway view of the close-packed (111) slip plane in Co-33%Ni alloy. Slip or twinning phenomenon causes permanent shear displacement of atomic lattice on the slip/twinning plane and slip/twinning direction as denoted by the associated Burgers vectors, $\mathbf{b}$. For a fcc lattice, partial dislocation slip as well as deformation twinning occur on the \{111\} family of planes along any of the \{112\} family of crystallographic directions. Hence, to profile the shear-induced energy-displacement landscape for a specific slip/twin system, two crystal blocks with adjoining interface on the (111) slip (highlighted in green and gray) were rigidly displaced along the [121] direction in the DFT simulations. Figure 2.12(b) illustrates an example of the resultant structure as a consequence of shearing of the two blocks by a displacement of $|\mathbf{b}|$ along the vector, $\mathbf{u}_{ab} = \mathbf{b} = a_{\text{Co-Ni}}/6[112]$. The lattice structure represents a

Figure 2.12(b) – An example of the resultant structure from shearing of the two blocks in Figure 2.12(a) by a displacement of $|\mathbf{b}|$ along the vector, $\mathbf{u}_{ab} = \mathbf{b} = a_{\text{Co-Ni}}/6[112]$. 

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discontinuation from the regular fcc stacking i.e. a stacking fault in the fcc lattice (as highlighted with the dark gray area and yellow line). GSFE and GPFE plots were constructed by computing the entire energy profile in course of rigid shearing as a function of the displacement as presented in Figures 2.13 and 2.15 respectively.

Figure 2.13 – DFT-computed generalized stacking fault energy (GSFE) profile of the Co-33%Ni solid solution.

### 2.4.2 Generalized Stacking Fault Energy (GSFE)

Figure 2.13 reports the DFT-computed GSFE of the Co-33%Ni solid solution. The inset diagrams illustrate the atomic configurations corresponding to the various energy levels on the curve. Starting with an initial perfect fcc stacking, shear displacement along the [121] direction (\( a \rightarrow b \)) by \( \mathbf{u}_{ab} = \frac{b}{2} \) results in a stacking fault configuration. The energy barrier to create the
stacking fault (i.e. the unstable stacking fault energy, $\gamma_{\text{us}}$) has been found to be about 205 mJ/m$^2$. The intrinsic stacking fault energy, $\gamma_{\text{isf}}$, is calculated to be 20 mJ/m$^2$, which is in agreement with the experimentally determined value [24-26]. The lattice with the stacking fault, upon shearing by an equal displacement along the $\langle 112 \rangle$ direction ($b \rightarrow c$), reverts back to the perfect fcc lattice. The thus-generated $\gamma$ surface represents the atomic level periodic energy profile associated with an extended dislocation, i.e. two partials bound by a stacking fault in-between. The $\gamma$ energy consideration is used as an important constituent in calculating the corresponding Peierls stress, $\tau_{\text{CRSS}}$.

2.4.3 Critical Resolved Shear Stress for Slip Nucleation

The Peierls–Nabarro model provides the theoretical framework for predicting crystal impedance to slip. According to the Peierls-Nabarro theory, the introduction of a dislocation in a perfect crystal requires overcoming two different types of energy expenses – elastic (long-ranged) and misfit (short-ranged) energies [46].

The elastic energy expense originates from the resistance to the stretching of atomic bonds surrounding the dislocation core. The elastic displacements of the atoms are represented by the so-called disregistry function, $f(x)$, upon insertion of an extra half-plane of atoms creating the dislocation [46]. On the other hand, the aforementioned misfit energy cost arises from the dislocation glide on a particular slip plane along a slip direction. The GSFE serves to capture the atomistic energy expenditure in the slip-induced shear of the discrete lattice. The misfit energy can be obtained by calculating the area underneath the GSFE curve (hence, we denote it as the “$E_{\text{GSFE}}$” in the following discussion). In order to compute the Peierls stress i.e. lattice frictional resistance, one needs to quantify both the disregistry and the misfit contributions.

Figure 2.14 illustrates the physical significance of the disregistry function, $f(x)$, for the case of a full dislocation (i.e. no partials). The function $f(x)$ captures the horizontal displacement differential of the atoms (before and after the occurrence of slip) across the slip plane. The
analytical solution of $f(x)$ is obtained by balancing the total elastic force with the periodic restoring force of the lattice.

Figure 2.14 – The physical significance of the disregistry function, $f(x)$ for the case of a full dislocation. The function $f(x)$ captures the horizontal displacement differential of the atoms (before and after the occurrence of slip) across the glide plane at a distance, $x$, from the dislocation core.

For any extended dislocation with a partial separation distance, $d$, the disregistry function $f(x-d)$ is given by Equation (2) [47, 48].

$$f(x-d) = b + \frac{b}{\pi} \left[ \tan^{-1} \left( \frac{x}{\zeta} \right) + \tan^{-1} \left( \frac{x-d}{\zeta} \right) \right]$$

Where, $x$ indicates any position on the slip plane along slip direction measured from the dislocation core; $b = |\vec{b}| = a_{Co-Ni}/\sqrt{6}$ is the magnitude of the partial dislocation's Burgers vector; $\zeta$ the core half-width of the individual partial ($\zeta_{screw} = a_{Co-Ni}/2\sqrt{3}$ and $\zeta_{edge} = a_{Co-Ni}/2\sqrt{3}(1 - \nu)$; $\nu$ is Poisson’s ratio, $\nu = -\frac{s_{12}}{s_{11}}$) [49] (where, compliance elements $s_{11}$ and $s_{12}$ are determined from the stiffness constants, $C_{11}$, $C_{12}$ and $C_{44}$ are 238.7, 155.3 and 131.5 GPa, respectively [50]).
By representing GSFE as a function of the disregistry function, \( f(x - d) \) from Equation (2), one can express the total energy requirement, \( E_{GSFE} \) to create dislocation slip in a pristine crystal as in Equation (3) [46, 47, 51].

\[
E_{GSFE} = \sum_{x=-\infty}^{\infty} \gamma \left[ f(x - d) \right] a'
\]  

(3)

Where, \( a' \) is the lattice periodicity i.e. shortest distance between two equivalent atomic rows in the Burgers vector direction (\( a' = 2b = 2a_{Co-Ni}/\sqrt{6} \)). In other words, the parameter \( a' \) is the total span of the GSFE curve (i.e. between two the fault energy values equal to zero). The quantity \( E_{GSFE} \) is computed numerically by fitting Frenkel type trigonometric expressions by disintegrating the total span of the GSFE (i.e. \( a' = 2b \)) into symmetric segments as in Equation (4). For the ease of numerical procedure, \( x \) can be written in terms of dislocation position, \( u \) as \( x = ma' - u \); where, \( m \) is an integer ranging from \(-\infty\) to \(+\infty\). Since the range of GSFE or misfit energy is very short, the consideration of the infinite magnitude of \( m \) can be restricted to a large number instead during the calculation (i.e. ensuring the entire span of the GSFE i.e. for \( a' = 2b \)).

\[
E_{GSFE} = 2 \sum_{m=-\infty}^{m=\infty} \left[ \frac{\gamma_{us} \sin \frac{\pi f}{b}}{2} b + 2 \sum_{m=-\infty}^{m=\infty} \left[ \frac{\gamma_{us} + \gamma_{af}}{2} - \frac{\gamma_{us} - \gamma_{af}}{2} \sin \frac{\pi f}{b} \right] b \right]
\]  

(4)

The \( E_{GSFE} \) is evaluated numerically from Equation (4). The combined treatment of the GSFE and dislocation disregistry allows for predicting the theoretical critical resolved shear stress for slip nucleation (the Peierls stress), \( \tau_{CRSS}^{slip} \) from Equation (5) [46, 47, 51].

\[
\tau_{CRSS}^{slip} = \left( \frac{1}{b} \frac{dE_{GSFE}}{du} \right)_{max}
\]  

(5)

The thus-computed \( \tau_{CRSS}^{slip} \) for Co-33%Ni alloy has been found to be 14 MPa. This value conforms to the experimentally determined \( \tau_{CRSS} \) magnitude for the single crystals under \( \langle 123 \rangle \) tension (15 ± 1.5 MPa), \( \langle 111 \rangle \) compression (16 ± 1.2 MPa) and polycrystalline material in
tension (16 ± 1MPa). The comparison is summarized in Figure 2.19. As elaborated in Section 3.2, these loading orientations have been found to be particularly conducive to slip nucleation. The reported error levels in the experimental values are attributed to the statistical average obtained from multiple experiments.

2.4.4 Generalized Planar Fault Energy (GPFE)

Figure 2.15 – DFT-calculated generalized planar fault energy (GPFE) curve of the Co-33%Ni solid solution. It represents the twin energy pathway.

Figure 2.15 reports the DFT-calculated GPFE curve of the Co-33%Ni solid solution. As illustrated with the inset schematics, the perfect fcc lattice results in a stacking fault upon shearing along $[121](a \rightarrow b)$ by one Burgers vector. The associated $\gamma$ energy profile corresponds to the first half portion of the GSFE curve from Figure 2.13. However, the GPFE is generated via continued shear along the same crystallographic direction on consecutive parallel (111) planes. The adjoining atoms one layer above the stacking faults, upon displaced by 1b
(resulting in a total displacement of $2b$ with respect to the initial perfect fcc configuration) creates a two-layer fault. The corresponding energy barrier i.e. the unstable twin fault energy, $\gamma_{ut}$, is found to be 216 mJ/m$^2$, and the coherent twin boundary energy, $\gamma_{tsf}$, is 10 mJ/m$^2$ (which is equal to $\gamma_{isf}/2$). Translation by another Burgers vector on the adjacent atomic layer above the two-layer fault (i.e. $3b$ total displacement) generates a twin nucleus. Further displacement on successive layers above the twin nucleus culminates in the onset of the twin migration process, i.e. a layer-by-layer growth of the twin. In the following sections, we demonstrate that the consideration of the twinning energy pathway (i.e. the GPFE) is crucial in predicting the critical resolved shear stress for twin nucleation, $\tau_{CRSS}^{\text{twin}}$ as well as twin-slip interaction, $\tau_{CRSS}^{\text{twin-slip}}$.

2.4.5 Critical Resolved Shear Stress for Twin Nucleation

Deformation twinning induces the shearing of discrete lattice at the atomic level. The GPFE landscape delineates the corresponding atomistic energy aspect. The physical process of mechanical twin nucleation is associated with successive passages of Shockley partial dislocations on consecutive glide planes \[36, 37\]. Figure 2.16 illustrates the mechanism of atomistic shearing of the crystal due to the sequential gliding of twinning partials of three parallel (111) planes. It is, therefore, imperative that, in addition to the atomic level energetics, the mutual elastic interaction and long-range disregistry effects of these twinning dislocations be considered to accurately predict the critical resolved shear stress for twin nucleation, $\tau_{CRSS}^{\text{twin}}$. The applied shear stress to nucleate a twin ought to work against the elastic interaction effects as well as the periodic lattice resistance to atomic shear displacements. In the current model, we balance the total applied work with the energy expenditure to be overcome (i.e. total elastic interaction energy and shear-induced GPFE contributions) as follows in Equation (6).
Figure 2.16 – The mechanism of twin nucleation via atomistic shearing of the crystal due to the sequential gliding of twinning partials on three parallel (111) planes.

\[ \text{twin} \times \text{CRSS}_\text{applied work} = E_{\text{interaction}} + E_{\text{GPFE-nucleation}} \]

\[ = \mu_{\{111\}} b_{\text{twin}}^2 \left( \frac{D}{d_{1-2}} + \frac{D}{d_{2-3}} + \frac{D}{d_{1-3}} \right) + \sum_{x=1}^{x=\infty} \gamma f_{\text{twin}}(x,d_{1-2},d_{2-3},d_{1-3}) \times 3b \]

Where, the twin thickness \( t = 3 a_{\text{Co-Ni}}/\sqrt{3} \) (corresponding to the height of three (111)-type atomic layers); the width of the twin \( w \approx 10t \) upon minimization of the total energy with respect to \( w \) and \( t \) (which is consistent with the \( w/t \) ratio reported in earlier literature) \([52, 53]\); the twinning-induced eigenstrain \( \varepsilon_{\text{twin}} = 1/\sqrt{2} \); the magnitude of the twinning dislocation Burgers vector \( b_{\text{twin}} = a_{\text{Co-Ni}}/6 \langle 112 \rangle \); the dimension of the single crystal containing the twin \( D \approx 2000 \)
microns; the shear modulus $\mu_{(111)} = \frac{3C_{44}(C_{11} - C_{12})}{4C_{44} + C_{11} + C_{12}}$, where $C_{11}$, $C_{12}$ and $C_{44}$ are 238.7, 155.3 and 131.5 GPa, respectively [50]; the spacings among the twinning dislocations $d_{i-3} = \frac{\mu b_{\text{twin}}^2}{2\pi\gamma_{\text{slf}}}$, $d_{2-3} = 0.732d_{i-3}$ and $d_{i-2} = d_{i-3} - d_{2-3}$ as derived upon balancing the acting elastic forces [54]; and the total disregistry of the three-layered twin $f_{\text{twin}}(x, d_{i-2}, d_{2-3}, d_{i-3}) = f(x - d_{i-2}) + f(x - d_{2-3}) + f(x - d_{i-3})$ from Equation (2). The disregistry associated with the deformation twin is obtained by assuming linear superposition of the pairwise disregistries of the twinning partials, as though they are on the same glide plane. We note that a singular twinning dislocation induces long range elastic distortion, and the thickness of the nucleus is rather small compared to the elastic range of the disregistry. Therefore, the refinement of twinning disregistry distribution over three adjoining atomic planes (separated by $a_{\text{co-Ni}}/\sqrt{3}$) would not significantly differ from the current assumption. The line energy contribution of individual dislocations is found to be insignificant compared to the rest energy terms; hence, not considered in the above formulation. The energy quantity, $E_{\text{GPFE-nucleation}}$, in Equation (6) is computed numerically by fitting the GPFE curve from Figure 2.15 with multiple-segmented trigonometric functions (of the form: $\gamma_{\text{max}} \sin \frac{\pi f}{b}$, where $\gamma_{\text{max}}$ refers to the respective peak for each segment) in the same manner as in Equation (4).

From Equation (5), the theoretical critical twin nucleation stress, $\tau_{\text{CRSS}}^{\text{twin}}$, has been determined to be about 26 MPa. This magnitude agrees well with the experimentally determined resolved yield stress (0.1% offset) for the single crystals oriented along $\langle 111 \rangle$ in tension (27 ± 5 MPa) and $\langle 001 \rangle$ in compression (26 ± 3 MPa). The comparison is presented in Figure 2.19. It follows that the theoretical value is in good agreement with the experimental critical resolved shear stress for twinning. The reported error levels are due to the statistical average considered from a number of experiments.
2.4.6 Critical Resolved Shear Stress for Onset of Twin-Slip Interaction

![Diagram of Deformation Twin and Dislocation Arrangement](image)

Figure 2.17 – A three-layer deformation twin (consisting of twinning partial dislocations) about to intercept a dislocation dipole arrangement.

In order to model the critical shear stress for the onset of twin-slip interaction, we suppose an approaching three-layer deformation twin (consisting of twinning partial dislocations) about to intercept a dislocation arrangement as shown schematically in Figure 2.17. We address this problem on the basis of classical continuum theory of applied work overcoming dislocation interaction energy complemented with the additional contribution from the GPFE considerations.
Figure 2.17 illustrates the arrangement of the twin-slip interaction to be modeled. The twinning partials are designated with \( i = 1, 2 \) and \( 3 \). The obstacle dislocations are arranged in a columnar Taylor lattice configuration i.e. dislocation dipoles (i.e. a pair of dislocations with of opposite signs placed at 45 degrees with a spacing of \( h \)) aligned vertically. The effect of increasing \( h \) magnitudes (i.e. the horizontal and vertical dipole spacing) has been determined to reach a saturation level with respect to the model output; therefore, we assume the corresponding magnitudes of \( h \) (on the order of tens of Burgers vectors) for the current calculations. In the following equations, we designate the vertical dipole arrangement as the “wall”. The vertical dislocations are labelled as \( j = 1, 2, 3, \ldots N_{dipole} \) (odd numbers denoting the dislocations of one sign and the even the opposite). The consideration of dipole array is rationalized due to the energetically stable configuration as reported earlier in the literature [55]. Nevertheless, other array configurations (e.g. non-dipole vertical arrangement) do not invoke significant deviation from the current prediction levels. The mechanics of the twin-slip interaction is described as follows.

In order for the oncoming twin to intercept the dislocation wall, the applied work \( (W_{\text{applied}}) \) ought to equal/surpass the combination of the total energy expense due to the interaction among the wall and the twinning dislocations (designated as \( E_{\text{twin-wall interaction}} \)) and the discrete lattice energy to be overcome (\( E_{\text{GPFE-migration}} \)). The \( E_{\text{twin-wall interaction}} \) originates from the attractive or repulsive depending on the sign of the dislocation within each dipole [46]. The \( E_{\text{GPFE-migration}} \) is equivalent to the total energy related to the one-layer migration portion of the GPFE curve. The work-energy balance can be written as follows in Equation (7).

\[
W_{\text{applied}} = E_{\text{twin-wall interaction}} + E_{\text{GPFE-migration}}
\]  

(7)

The term \( W_{\text{applied}} \) for twin of thickness \( t \), situated at a distance \( d \) from the dislocation wall with a twinning shear of \( \tau_{\text{CRSS}}^{\text{twin-slip}} \) is straightforward to establish as in Equation (8).

\[
W_{\text{applied}} = td\varepsilon_{\text{twin}} \tau_{\text{CRSS}}^{\text{twin-slip}}
\]  

(8)
For the term $E_{\text{twin-wall interaction}}$, let us consider the most simple hypothetical case of one twinning dislocation (with the Burgers vector magnitude $b_{\text{twin}}$) and one wall dislocation ($b_{\text{wall}}$), the elastic interaction among whose is given by the classical expression of $\frac{\mu b_{\text{twin}} b_{\text{wall}}}{4 \pi (1 - \nu)} \left( \ln \frac{D}{d} \right)$ (where, $D$ is the single crystal size) [46]. Now, for an approaching twin nucleus (with three twinning dislocations i.e. $N_{\text{twin}} = 3$) and a dislocation wall with a number of ($N_{\text{wall}}$) dislocations, one has consider the summation of individual twin-wall pair interactions. Now, since the assumed wall consists of dislocation dipoles, the wall dislocation of the same sign with the twinning dislocation will repulse, and the of the opposite sign will attract the twinning partials. Hence, there will be attraction/repulsion energy contribution. Considering all the foregoing factors, the total interaction energy between the oncoming twin and the dislocation wall, $E_{\text{twin-wall interaction}}$ can be written as follows in Equation (9).

$$E_{\text{twin-wall interaction}} = \frac{\mu b_{\text{twin}} b_{\text{wall}}}{4 \pi (1 - \nu)} \sum_{i=1}^{N_{\text{twin}}} \sum_{j=1}^{N_{\text{wall}}} (-1)^{i-j} \left( \ln \frac{D}{d_{i-j}} \right)$$

(9)

Where, $d_{i-j}$ the distance between the $i$-th twinning dislocation and $j$-th wall dislocation (which incorporates the horizontal/vertical dipole spacing, $h$).

Now, for the energy expense originating from shear the discrete lattice during the twinning-slip interaction, we consider the portion of the GPFE curve given within the range $3 < u/b \leq 4$ as given in Equation (10).

$$E_{\text{GPFE-migration}} = \sum_{x=-\infty}^{x=+\infty} \gamma \left[ f_{\text{twin}}(x, d_{1-2}, d_{2-3}, d_{3-1}) \right] b$$

(10)
Hence, combining Equations (8), (9) and (10), we obtain the Equation (11) wherefrom the critical resolved shear stress for the onset of twin-slip arrangement interaction stress, $\tau_{\text{CRSS}}^{\text{twin-slip}}$, can be evaluated.

$$
\tau_{\text{CRSS}}^{\text{twin-slip}} = \frac{\mu b_{\text{twin}} b_{\text{wall}}}{4\pi(1-\nu)} \sum_{i=1}^{N_{\text{twin}}} \sum_{j=1}^{N_{\text{wall}}} (-1)^i \left( \ln \frac{D}{d_{i-j}} \right) + \sum_{x=-\infty}^{x=+\infty} \gamma f_{\text{twin}} \left( x, d_{1-2}, d_{2-3}, d_{1-3} \right) a' \quad \text{(11)}
$$

Following Equation (11), (when the impinging mechanical twin is very close to the dislocation arrangement i.e. $d$ in the range of 1 to 4 nanometers), the maximum magnitude of $\tau_{\text{CRSS}}^{\text{twin-slip}}$ is determined to be 38 MPa. This value is compared with the corresponding experimental flow stress (39 ± 10 MPa as indicated with solid red circle) in Figure 2.19. It is important to note that experimentally it is rather challenging to pinpoint the exact flow stress for the onset of the twin-slip interaction from the stress-strain plots alone. We have considered the inflection point on the stress-strain curve (i.e. an abrupt change of the slope) following the initial yield as indicative of the interaction. We establish the CRSS value from the combination of the shear stress-strain curves and the ex-situ TEM images at low deformation level. We have conducted a number of low strain tension/compression experiments with corresponding TEM images at various strain levels. Upon inspecting the TEM images for the low strain cases (<1%), we have established that the <111> tension and the <001> compression cases give rise to yielding by twinning and subsequent twin-slip interactions. We note the critical resolved shear stress levels for the onset of twin-slip interactions for each set of experiments for <111> tension and <001> compression. In this manner, we measure the CRSS levels for the twin-slip interactions from a range of experiments to be 39 ±10 MPa. By studying the flow behavior from a number of experiments, the error level in the experimental $\tau_{\text{CRSS}}^{\text{twin-slip}}$ magnitudes is established as shown (solid red circles) in Figure 2.19.

It is important to take into account the parametric sensitivity of the geometric considerations on the model output, $\tau_{\text{CRSS}}^{\text{twin-slip}}$. From elasticity theory standpoint, one may select from several combinations of the dislocation geometries (i.e. edge/screw or full/partial) as well
as the array alignment/orientation (i.e. perpendicular or angled to the approaching twinning direction). In the current model, the selection of the twinning dislocations as \( a/\sqrt{112} \) type Shockley partials and the obstacle dislocation arrangement as a vertical array of (screw/edge) dislocation dipoles provides the most reasonable agreement with the experimental observations. We note that consideration of other combination of geometric consideration (e.g. non-dipole vertical array of edge/screw/partial dislocations) does not pose any fundamental modification to the proposed theory. The levels of theoretical \( \tau_{\text{twin-slip}} \) obtained using various sets of geometric input are well within the range of experimental \( \tau_{\text{twin-slip}} \) values as indicated by the error bars in Figure 2.19. Hence, we adhere to reporting only one consistent level of theoretical \( \tau_{\text{twin-slip}} \) corresponding to a fixed set of input constants, thereby facilitating comparison with the statistically averaged (over a number of tests) experimental results.

### 2.4.7 Critical Resolved Shear Stress for Forest Hardening

For the case of slip-mediated plasticity (in \( \{123\}_{\text{tension}} \) and \( \{111\}_{\text{compression}} \), dislocations upon nucleation continues to glide on one slip system until applied stress is sufficiently large to initiate secondary non-parallel systems. With increase in deformation, dislocations from either system cut through the other, giving rise to the initiation of the so-called forest hardening effects. That is to say, in order for the forest hardening to start influencing the global stress-strain response, a considerable extent of forest dislocation density is required. One may argue that the critical stress level for slip-slip interaction could be modeled as a problem of elastic dislocation interactions following the same approach as the previous case of twin-slip interaction. However, unlike the twin-slip interaction case, the degree of forest hardening stress level would be considerably affected by the mean dislocation spacing (as in Figure 2.18) i.e. the dislocation density. Therefore, we deem it appropriate to resort to the classical treatment of the forest hardening as a direct function of the dislocation density [56] as given in Equation (12). Figure 2.18 illustrates an example of glissile slip from one system cutting through (vertically arrayed) dislocations on another non-parallel slip system.
Figure 2.18 – The mechanism of forest hardening when a series of dislocation on one glide plane proceed to intercept dislocations on another slip system.

$$\tau_{\text{CRSS, forest}} = \frac{\alpha \mu_{\{111\}} b}{\lambda}$$

$$= \alpha' \mu_{\{111\}} b \sqrt{\rho}$$

(12)

Where, $\alpha$ and $\alpha'$ are constants specific to the material; $\rho$ the dislocation density; $\lambda$ the mean free path of gliding dislocations (considered along the dislocation motion direction).

We note that it is rather challenging to precisely establish the dislocation density from TEM study alone due to the limited portion of the material that the TEM images represent. Therefore, we adopt an ad hoc methodology on the basis of the current TEM analysis and the literature reported values of the dislocation density for the typical pre-deformation density. As pointed out earlier, we have conducted a number of experiments, and TEM images are taken at various global strain levels ex-situ. Upon inspecting the TEMs (which indicated massive slip-slip entanglement), we have pinpointed the initiation of the forest hardening following the nucleation of slip. Upon studying the slip morphology of the deformed microstructure for the slip-based hardening cases (i.e. for $\{123\}$ tension and $\{111\}$ compression) from the TEM analyses, we make
an educated assumption of the dislocation density to be on the order of $10^{14}$/m$^2$ at the initiation of the forest interactions on an ad hoc basis.

Figure 2.19 – Comparison of experimentally determined $\tau_{\text{slip CRSS}}$, $\tau_{\text{forest CRSS}}$, $\tau_{\text{twin CRSS}}$ and $\tau_{\text{twin-slip CRSS}}$ with the predicted values.

Using Equation (12), the critical shear stress for the forest hardening initiation is determined to be about 24 MPa. The comparison with the experimental magnitudes (which is determined to be $25 \pm 4$ MPa from multiples experiments in $\langle 123 \rangle$ tension and $\langle 111 \rangle$ compression and polycrystalline tension) is provided in Figure 2.19. We note the error level in the experimentally determined values, which arises owing to the difficulties in pinpointing the exact location on the stress-strain curve. We consider the sharp change of the strain-strain slope following the yielding to indicate the onset of the forest interaction mechanism.
Table 2.2 – Summary of the experimentally extracted CRSS levels and the theoretical results (also, presented in Figure 19).

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Equations</th>
<th>Input parameters</th>
<th>Theoretical $\tau_{\text{CRSS}}$ (MPa)</th>
<th>Experimental $\tau_{\text{CRSS}}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slip nucleation</td>
<td>$\tau_{\text{CRSS}} = \frac{1}{b} \frac{\partial E_{\text{GSFE}} (\gamma_{\text{us}}, \gamma_{\text{us}})}{\partial u} \max$</td>
<td>$\gamma_{\text{us}} = 205 \text{ mJ/m}^2$, $\gamma_{\text{isl}} = 20 \text{ mJ/m}^2$, $b = a_{\text{Co-Ni}}/\sqrt{6}$, $a_{\text{Co-Ni}} = 3.521 \text{ Å}$</td>
<td>14</td>
<td>15</td>
</tr>
<tr>
<td>Twin nucleation</td>
<td>$\tau_{\text{CRSS}} = \frac{E_{\text{interaction}} + E_{\text{GPFE-nucleation}} (\gamma_{\text{us}}, \gamma_{\text{ut}})}{t \varepsilon_{\text{twin}}}$</td>
<td>$\gamma_{\text{ut}} = 216 \text{ mJ/m}^2$, $\gamma_{\text{isl}} = 10 \text{ mJ/m}^2$, $t = 3 a_{\text{Co-Ni}}/\sqrt{3}$, $w = 10t$, $\varepsilon_{\text{twin}} = 1/\sqrt{2}$</td>
<td>26</td>
<td>27</td>
</tr>
<tr>
<td>Onset of twin-slip interaction</td>
<td>$\tau_{\text{CRSS}} = \frac{E_{\text{twin-wall interaction}} + E_{\text{GPFE-migration}} (\gamma_{\text{isl}}, \gamma_{\text{ut}})}{td \varepsilon_{\text{twin}}}$</td>
<td>$\gamma_{\text{ut}} = 216 \text{ mJ/m}^2$, $\gamma_{\text{isl}} = 10 \text{ mJ/m}^2$, $d = 3 \text{ nm}$, $\varepsilon_{\text{twin}} = 1/\sqrt{2}$</td>
<td>38</td>
<td>39</td>
</tr>
<tr>
<td>Onset of slip-slip interaction</td>
<td>$\tau_{\text{CRSS}} = \alpha' \mu_{(111)} b \sqrt{\rho}$</td>
<td>$\alpha' = 0.2$, $\rho = 10^{14} \text{ /m}^2$, $\mu_{(111)} = 35 \text{ GPa}$</td>
<td>24</td>
<td>25</td>
</tr>
</tbody>
</table>
(which is also supported by the TEM images taken at low global strain level). The modeling results are summarized in Table 2.2.

2.5 Discussion

2.5.1 Flow Behavior and Microstructure Evolution

In early literature, the plastic stress-strain behavior of fcc single crystals has been demarcated into three mechanistically distinct hardening regimes referred to as stage I, II and III [57-59]. Upon yielding, the initial plasticity in the form of either slip or twin nucleation, precede the more complex defect interplays of the ensuing hardening stages. Typically, stage I, II and III type strengthening behaviors originate from (i) easy dislocation glide restricted to few systems, (ii) multi-system poly-slip and (iii) dynamic recovery processes. The extent of all individual stages is reported to be a function of factors such as temperature, crystal purity, pre-existent dislocation density and crystallographic orientation. Most recently, Kalidindi et al. [60, 61] conducted extensive experimental and theoretical study on characterizing the different hardening regimes of polycrystalline low SFE Co-Ni alloy deformed to large strain levels. The hardening stages of the present material Co-33%Ni are observed to be a strong function of the crystallographic orientation and the loading direction [59]. In the current study, from the TEM studies of the post-deformation microstructure, the strain hardening of the Co-33%Ni single crystals in $\{123\}_{\text{tension}}$ and $\{111\}_{\text{compression}}$ occurs via extensive dislocation activities (with no twinning). From the stress-strain analysis, the initial $\{123\}_{\text{tension}}$ flow stress is found to be mostly non-hardening (i.e. having a low hardening coefficient $\partial \varepsilon / \partial \gamma$) which complies with stage I type behavior. This observation is also consistent with the Schmid factor argument which, under $\{123\}_{\text{tension}}$ condition, predicts activation of only one slip system. The commencement of a distinct stage II hardening in this loading case occurs at higher strain levels (> 10%). At this stage, the strengthening effects underlie glissile dislocations cutting through the pre-existent slip entanglements as revealed from the transmission electron micrographs. Classically, such a strengthening process is described by the so-called forest hardening [56, 62] considerations, which dictate an empirical proportionality of flow stress to the square root of forest dislocation
density. On the other hand, the material under $\langle 111 \rangle_{\text{compression}}$ loading activates six slip systems in accordance with the Schmid law, immediately following the onset of yielding. The observed higher hardening rate in the $\langle 111 \rangle_{\text{compression}}$ case can be attributed to extensive interactions among the multiple slip systems, conforming to the stage II type mechanism. In the early literature, Gerold and Karnthaler [63] reported the presence of wavy slip patterns in Co-Ni alloys. In the present study, we observe that the deformed microstructures under $\langle 123 \rangle_{\text{tension}}$ and $\langle 111 \rangle_{\text{compression}}$ demonstrate a considerable extent of stacking fault presence. Prevalence of stacking faults testifies to the existence of widespread dissociation of full dislocations into partials. In earlier experimental literature, the occurrence of partials is reported to be typical of low stacking fault energy materials. On the other hand, no evidence of deformation twinning is found for $\langle 123 \rangle_{\text{tension}}$ and $\langle 111 \rangle_{\text{compression}}$ although pervasive partial dislocation activities are known to be a prerequisite for twin nucleation.

Previous experimental literature [33, 34, 64] reports fluctuating flow behavior in low stacking fault energy fcc metals and alloys. In the current investigation, Co-33\%Ni under $\langle 111 \rangle_{\text{tension}}$ and $\langle 100 \rangle_{\text{compression}}$ exhibits somewhat serrated flow behavior, albeit with no significantly large drop. Based on the microstructural observation (via DIC, EBSD and TEM), the mechanistic origin of the flow fluctuation can be interpreted in terms of a dynamic process of twin nucleation and interaction with the existing dislocation arrangement. The macroscopic stress level undergoes a sudden attenuation as a consequence of accommodating local shear strains induced by twin nucleation. The follow-up stress upsurge occurs as the newly generated twin advances through sporadic pre-existent dislocation arrangements. Therefore, multiple nucleation events throughout the bulk of the material followed by interactions with slip cause the apparent raggedness to the flow curves under $\langle 111 \rangle_{\text{tension}}$ and $\langle 100 \rangle_{\text{compression}}$. It is worth noting that twinning induces a greater flow level than the slip based deformation. The present study (both theory and experiment) demonstrates a higher level of critical stress required to initiate twin-slip interactions (39 MPa) in Co-33\%Ni, compared to mere twin nucleation (27 MPa) and slip nucleation (15 MPa) (values are approximate as indicated with error bars in Figure 2.19). It is
It follows from the experimental stress-strain curves that twinning-dominated flow levels are considerably greater than the slip-induced plasticity. The TEM images have suggested that some extent of slip activities always accompany the observed twinning phenomena (especially, in the inter-twinning bands regions). Upon studying the behavior of polycrystalline Co-33%Ni Remy [29] attributed the twinning-induced augmented hardening effects to the obstruction of slip motion due to an abundance of newly-generated coherent twin boundaries. Remy argued that extensive twinning sub-divides a particular grain in multiple segments restricting the mobility of slip in the vicinity (either pre-existent or nucleated in concurrence with twinning), therefore, giving rise to Hall-Petch type strengthening effects. It is important to note that the current theory considers the case of an advancing twin front (modeled by a multi-layered arrangement of twinning partial dislocations), which approaches a dislocation array. The whole twin-slip intersection configuration has been treated as a problem of elastic interactions among continuum dislocations. In other words, the current model captures the elevated critical twin-slip interaction stress (as presented in Figure 2.19) with fundamental elasticity theorems supplemented by atomic level shear contribution. One may argue that the problem could also be addressed via an analysis of dislocation slip impinging on migrating twin boundaries (resulting in elevated critical stress level). This type of investigation would essentially differ in details as reported in the earlier literature [34]. The analysis of slip intercepting a twin boundary is compounded by different reaction outcomes, which are a strong function of local stress state and the nature of residual dislocations on the interface. There exists considerable number of literature addressing the problem of slip intercepting a coherent twin boundary. We note that such approach would
essentially yield similar conclusions as from the current method i.e. the resultant elevation of the critical stress level, which is addressed by the authors in their earlier publication [65-67]. Therefore, the present treatment of twin-slip intersection based on basic elasticity assumptions is particularly advantageous, in that it provides a simple intuitive theory in good agreement with the experiments, circumventing the aforementioned complications (related with slip-intercepting-twin case).

Early literature notes that single crystals of conventional fcc metals undergo deformation twinning only at very high stress. For instance, pure Ni single crystals are reported to have twinning only preceding the ultimate fracture [68]. However, the present material, Co-33%Ni manifests a twinning stress level that is on the same order of magnitude with that of slip as observed experimentally. From the classical twinnability criterion [12-14], the stacking fault energy (SFE or $\gamma_{isf}$) has been correlated as being proportional to the critical twinning stress (adjusted with some fitting constants). To illustrate this empirical trend, one may compare pure Ni (with a SFE of 127 mJ/m$^2$ [19, 25, 26]) with the current material Co-33%Ni (SFE being 20 mJ/m$^2$). Intuitively, the critical resolved shear stress for twinning in Co-33%Ni would be considerably lower (as currently determined to be about 27 MPa from Table 2.1) than that of pure Ni (predicted to be 250 MPa in earlier literature [52]). However, It is quite intriguing to note that the critical resolved shear stress for slip in Co-33%Ni (about 16 MPa from current measurement from Table 2.1) is not significantly altered from that of pure Ni (about 9 MPa, from literature [69, 70]). This is an important observation that clearly demonstrates the insufficiency of the stacking fault energy, $\gamma_{isf}$, as the sole parameter to dictate both the slip and the twinning tendency simultaneously. While the classical SFE-based approach can qualitatively indicate the twinnability, it cannot provide a quantitative basis to compare the competition between slip and twinning. Moreover, the twinning-assisted flow is observed to demonstrate a superior hardening behavior compared to slip that apparently cannot be modeled solely based on the phenomenological parameter $\gamma_{isf}$. We address this dilemma by additionally incorporating the atomistic energy barriers $\gamma_{us}$ (unstable stacking fault energy) and $\gamma_{ut}$ (unstable twinning fault energy) into a Peierls-Nabarro based theory to quantify the critical slip/twin nucleation stresses.

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Upon a careful review of the relevant literature, we note that the theoretical aspects of slip and twinning are not mutually exclusive. That is to say, the physical process of twin nucleation can be disintegrated into a problem of collective behaviors of twinning dislocations. Therefore, we consider a uniform Peierls-Nabarro modeling framework accompanied by necessary atomistic ingredients to rationalize the aforementioned quandary.

2.5.2 Prediction of Slip, Twin, Twin-Slip Interaction

Theoretical quantification of slip nucleation stress in a pristine crystal has been treated universally by the Peierls-Nabarro model [46, 47, 51, 71-73]. The basic premise thereof states that a dislocation in a metallic crystal is assumed to be embedded in a continuous elastic medium except for the slip plane (whereupon non-continuum discreteness is imposed). The continuum assumption of the metallic matrix serves to provide the solution of the disregistry function, f(x), owing to the elastic distortion of the crystal as in Equation (2) (illustrated in Figure 2.14). The atomistic discreteness of the lattice is assumedly smeared upon the glide plane in the form of periodic energy topography. The early models [46, 72, 73] considered sinusoidal energy profile on an ad hoc basis until recent advances [48, 74] establish the generalized stacking fault energy (GSFE) profile as the most appropriate energetic representation of the lattice periodicity. As per the original Peierls-Nabarro proposition, the required critical stress to create dislocation slip amounts to the applied shear stress level to move the dislocation core and disregistry assembly through the periodic energy-displacement landscape. Therefore, it is imperative that both the elastic effects and the atomistic fault energy profile be considered simultaneously in quantifying the Peierls stress. In the current undertaking, we achieve that objective by numerically reconstructing the atomistically-computed GSFE as a function of the disregistry, f(x), in the form of a Fourier-type trigonometric series (as in Equation (4)). Given the complexity of the mathematical expression, it is deemed necessary to seek a numerical solution for the Peierls stress (from Equation (5)), rather than establishing a closed form analytical expression. The present numerical scheme is particularly advantageous, in that it does not incur exponential dependence of the Peierls stress on the dislocation core width as reported in earlier literature [51]. The reasonable agreement with the theoretical Peierls stress and the experimentally determined critical resolved shear stress (presented in Figure 2.19) attests to the accuracy of the
current method. Furthermore, we proceed to prove that the Peierls-Nabarro foundation can also be effectively utilized in modeling the critical twin nucleation stress.

Venables [14] first hypothesized the critical stress to nucleate a mechanical twin on the basis of overcoming the frictional resistance to create a plane with an intrinsic stacking fault. Subsequently, Pirouz [13] improved the original Venables’ assumption by incorporating the mobility differential between a leading and a trailing partial dislocation that tether the stacking fault end-to-end. Moreover, Miura, Takamura and Narita [12] considered the formation of an extrinsic stacking fault (i.e. a two-layer fault) as a precursor to the twin nucleation. Karaman et al. [75] extended this idea to incorporate solute drag effects. Meyers et al. [11] conducted an Eshelby type analysis to incorporate deformation kinetics considerations (i.e. strain-rate, temperature etc.). All these theories are essentially phenomenological, in that they consider only the intrinsic stacking fault energy (SFE or $\gamma_{\text{isf}}$) as the material input parameter. From a thermodynamic perspective, Fischer et al. [76] approached the problem by balancing the total interaction energy among a vertical arrangement of dislocations and mechanical work necessary to create a twinned region represented by its eigenstrain. Tadmor et al. [15, 16] first proposed the necessity of assessing twinnability in fcc materials with a combined treatment of three fault energy parameters, i.e. $\gamma_{\text{isf}}$, $\gamma_{\text{us}}$ (unstable stacking fault energy) and $\gamma_{\text{ut}}$ (unstable twin fault energy) from first principles. They argued that it is equally vital to consider the unstable energies ($\gamma_{\text{us}}$ and $\gamma_{\text{ut}}$), in conjunction with more traditionally used $\gamma_{\text{isf}}$ to establish a comprehensive twinning criterion. However, it is important to note that prediction of the critical stress level, according to these models, is contingent upon the presence of a sufficiently high local stress concentration source (e.g. dislocation pile-up [14], Lomer-Cottrell barrier [13, 75], grain boundary [12], dislocation wall [76], micro-crack [15] etc.) that can trigger the nucleation process. However, in a single crystal with the absence of the aforementioned sources, a deformation twin is more likely to nucleate near surface imperfection or bulk inhomogeneity. In such case, it can be initiated from pre-existent dislocation conglomerates that are prone to dissociate into multi-layered stacking faults [36]. In experimental literature, it is indicated through high resolution electron microscopy that some extent of slip activities precedes the mechanical twinning [34]. It is now well-established that the mechanism of deformation
twinning is analogous to a succession of Shockley partials on adjoining glide planes (as illustrated in Figure 2.16). Consecutive shearing induced by each dislocation leads to the evolution of a twin nucleus via the creation of an intrinsic stacking fault followed by an extrinsic stacking fault. In the present work, we incorporate the combined disregistries of the participant twinning partials and the entire atomistic energy landscape, i.e. the GPFE, within a Peierls-Nabarro framework. This approach inherently allows for the inclusion of slip, intrinsic/extrinsic stacking fault generation as a precursor to the twin nucleation as classical theories dictate. As per the current experimental observation, the twin nucleus grows in thickness (also known as the twin migration) and advances to intercept a pre-existent dislocation arrangement. We model the critical stress to initiate twin-slip interaction by considering the underlying energy cost for the atomistic migration process as well as continuum interaction effects.

Elastic properties of dislocation walls (consisting of edge or screw type dislocations) and their interaction with approaching dislocations (edge or screw) have been discussed extensively by Li et al. [77-79]. We approach the process of a twin intercepting a dislocation arrangement principally as a similar elastic problem with the addition of a migration-induced atomic shear contribution. The partial dislocations at the front of the advancing twin nucleus would experience attractive/repulsive forces from the dislocation wall arrangement. In the current model, we have considered a vertical dipole arrangement consisting of straight dislocations (as shown in Figure 2.17). As suggested by Neumann [55], a dipole wall will be energetically favorable upon minimizing the total elastic energy of the configuration under external shear stress. We note that a particular choice of wall anatomy (i.e. edge versus screw or full versus dissociated or single versus double column) does not alter the fundamental aspect of the current model, invoking only a slight sensitivity on the predicted critical stress levels (< 8%). Moreover, given the effective range of the elastic influences, one can optimize the spacing between the impinging twin and the slip wall to rectify the predictions so as to reach an acceptably converged level. Thus, we adhere to the assumptions that produce the most reasonable agreement with the experimental critical resolved shear stress magnitudes (as compared in Figure 2.19).

The most important contribution of the current model can be deemed as establishing a theoretical framework to incorporate the GSFE and GPFE profiles into quantifying the
aforementioned critical stresses. Thus, we essentially account for the underlying electronic effects of the alloy crystal to rationalize the slip and twinning phenomena both in a qualitative and quantitative manner.

2.5.3 Role of Electronic Structure and $\gamma$ Surfaces on Deformation Behavior

From the phase diagram of Co-Ni alloy system, the current composition (67% Co) of the binary Co-Ni alloy possess a fcc crystal structure [45], while elemental Co and Ni are hcp and fcc crystals, respectively, at room temperature. It is well established in the earlier literature [24-26] that the stacking fault energy, $\gamma_{st}$ of Co-Ni alloys gradually decreases with the addition of Co starting from the pure Ni level. The Co-Ni alloys possess neither long-range nor short-range ordering. These observations are consistent with the fact that both nickel and cobalt have similar physical, chemical and electronic properties. In particular, the near identical atomic volumes of elemental Ni and Co [10] induce negligible elastic distortion upon mixing. Hence, the observed reduction in stacking fault energy from pure Ni level (127 mJ/m$^2$) to Co-33%Ni (20 mJ/m$^2$) can be elucidated in terms of the underlying solid state bonding effects.

Metallic bonding is characterized by a de-localized electron cloud shared by many atoms in the crystal lattice [80]. From a quantum mechanical perspective, metallic deformation amounts to the collective translation of atomic nuclei embedded in such an electronic environment within the Born-Oppenheimer approximation [5]. The electronic structure of the transition metals (Co and Ni) is especially dictated by their respective valence electron configuration. In particular, the state of complete or partial electron fulfilment of the d-orbitals critically influences the lattice bonding landscape, and hence governs the defect formation tendency. From a solid state physics standpoint, the origin of GSFE and GPFE profiles can be traced back to local variations in atomic bond strength as the gradual crystal shearing process creates various types of stable/unstable lattice structures [19]. That is to say, it is the electronic bonding strength among the nearest neighboring atoms in and around these faults that dictate $\gamma$ surface levels in different metals and alloys. For instance, an intrinsic stacking fault in an otherwise perfect fcc lattice creates a local hcp structure. Thus, the apparent incongruity in the local atomic coordination
would incur a considerable difference in bond lengths (and hence electron cloud density) among the fcc and hcp nearest neighbors surrounding the faulty lattice. The entire $\gamma$ energy profile therefore quantifies the free energy differences to be overcome by external driving forces (e.g. applied stress) in order to nucleate a certain type of defect (e.g. intrinsic or extrinsic stacking faults, dislocation, twin boundary etc.). The so-called intrinsic stacking fault energy (SFE or $\gamma_{ist}$) in fact measures up to the differential of the hcp and fcc free energy density (per unit area). Intuitively, the free energy of a stacking fault in a solid solution would be a strong function of the solute atom concentration in the vicinity.

Early literature [24] reports that the gradual addition of Co to the pure nickel matrix reduces the SFE (from pure Ni level) to naught (corresponding to a composition demarcating the fcc-to-hcp transition, i.e. around 70% Co [45]). Suzuki [81] observed that when the energy of the stacking fault in a crystal becomes negative, the fcc structure is no longer stable and hence tends to transform to a hcp lattice. In the current calculations, we observe that the abundance of Co also drastically reduces the $\gamma_{us}$ (unstable stacking fault energy) and $\gamma_{ut}$ (unstable twinning fault energy). Apostol and Mishin [82] demonstrated, in DFT simulations, that the distribution of the solute atoms relative to the fault substantially modifies the entire GSFE level. They revealed that if the solute atoms are located close to the fault, the corresponding fault energy reaches its minimum (which is known as the so-called Suzuki segregation). In the present quantum simulations, we distributed the solute atoms randomly throughout the base metal lattice on an iterative basis until the minimum energy configuration is obtained. Thus, we computed the minimum possible GSFE/GPFE levels that would be the most favorable energy pathway for the atomistic shearing of the material during slip/twinning. We emphasize that it is imperative to consider the entire GSFE and GPFE levels to glean a more complete comprehension of the observed slip characteristics and twinning propensity.

Swygenhoven et al. [17] demonstrated the insufficiency of the classical approach of using the SFE as the only parameter to reconcile twinning and/or partial dislocation prevalence in a material. They proposed full consideration of the surface in the form of the ratio $\gamma_{ist}/\gamma_{us}$ as the deciding parameter to justify the prevalence of full versus extended dislocations (especially when
material predominantly deforms by slip). They argued that a lowered $\gamma_{\text{ist}}/\gamma_{\text{us}}$ ratio would indicate a greater propensity towards dissociation into partials (with increasing splitting distance between the partials). Separated partials are connected by a plane with a stacking fault with an fault energy density equal to the $\gamma_{\text{ist}}$. Upon the nucleation of leading partial (by overcoming the energy barrier $\gamma_{\text{us}}$), the trailing partial ought to exceed a quantity equivalent to $(\gamma_{\text{us}} - \gamma_{\text{ist}})$. That is to say, a large difference between $\gamma_{\text{ist}}$ and $\gamma_{\text{us}}$ promotes splitting of full dislocations into partials. In the current TEM studies, a considerable amount of extended dislocation activities has been observed. Such a trend can be understood consulting the nature of the computed GSFE in terms of the $\gamma_{\text{ist}}/\gamma_{\text{us}}$ level (which is computed to be 0.097 for Co-33%Ni). On the basis of a similar argument, experimentally equal propensity of twinning relative to the slip is also reflected in the GPFE landscape as the $\gamma_{\text{ist}}/\gamma_{\text{us}}$ ratio tends to unity (calculated to be 1.0455) for Co-33%Ni. This result suggests that the current material uniquely possess nearly identical energy barriers for slip and twin nucleation. This is an important observation, in that experimentally only the Schmid factor has been found to dictate the initiation of either slip or twinning (indicating the existence of similar material resistance towards these two competing modes of plasticity).

2.5.4 Impact of Current Work and Future Challenges

The principal objective of the current undertaking is to address the inherent material preference for initiating plastic deformation by slip or twinning from the first principle. The present work provides quantitative evidence that the preferred plastic mechanism is governed by the quantum level fault energetics. The current emphasis is on predicting the critical stresses for initiating plastic flow via slip, twinning and twin-slip interactions. We chose to model the nucleation of slip and twinning at small strains (<1%). It is well established that the initiation of the macroscopic yielding (following the elastic deformation) is equivalent to overcoming the respective critical resolved shear stresses (CRSS) (for slip or twinning) at the microscale. However, the latter stage of plasticity involves multiple mechanisms contributing to the flow resistance at the mesoscale (sub-micron). On the other hand, the onset of plasticity is primarily
governed by the atomistic lattice shear resistance (in the form of GSFE/GPFE energetics) originating at the sub-nanometer atomic lengthscale. At the elastic-plastic transition, the applied forces are spent in overcoming the lattice resistance for the slip/twin nucleation. Hence, it is rational to directly use the GSFE/GPFE levels to predict the mesoscopic critical resolved shear stresses (CRSS) within the Peierls-Nabarro framework. The reasonable agreement between the predicted and the experimental values of the CRSS lends sufficient credence to the current assumptions. The current research could be deemed as a step forward in understanding the inherent materials deformation propensity using ab initio techniques.

However, the deformation scenario becomes gradually more complicated for the post-yield stages as the extent of plasticity continues to evolve. For such case, the mesoscopic deformation process would be characterized by extensive defect interactions, whose nature will play critical roles in the flow behavior. The current TEM, DIC and EBSD results serve to reveal the existence of competing plastic mechanisms (i.e. slip versus twinning) at higher strain levels (>6%) in the current Co-Ni alloys. As clarified earlier, the present work from a theoretical perspective) focuses on modeling the critical stresses to initiate plasticity, not the evolution thereof. However, the microstructure analyses via the optical techniques suggest the need of a comprehensive modeling framework for a complete understanding of the entire spectrum of stress-strain response. For example, the mesoscale plastic processes at large strains (at >6%) involves massive degrees of defect dynamics, the volume fraction evolution (of slipped and/or twinned regions) and the complex interlocking mechanisms (as observed by the TEM micrographs). The flow resistance at this stage is contributed by a number of plastic mechanisms. To that end, the Peierls-Nabarro formalism alone is insufficient, and cannot directly relate the atomistic GSFE/GPFE level with the continuum level flow behavior (without considering the extensive mesoscopic defect dynamics). The sub-nanometer quantum effects and the continuum mechanical behavior need to be bridged via extensive mesoscale defect modeling. Therefore, it is evident that not all processes can be fully covered at the present stage. As follows, we discuss the possible extension of the current model.

The current model can be extended by coupling the quantum contributions with: (a) the dislocation dynamics corresponding to large strain plasticity, and (b) the consideration of rate-
and temperature-dependent flow behavior. To address the large deformation problem, the most significant extension of the current model can be conducted in the form of incorporating the dislocation dynamics simulations at the mesoscale [83, 84]. The slip and twinning phenomena can be modeled separately through a statistically representative model of crystal plasticity [85]. Through dislocation dynamics, the multiple contributions to the flow resistance at the larger strain regimes could be quantified from extensive defect interactions at the mesoscale (as also informed by the underlying quantum effects from the nanoscale, which the present work particularly brings into light for the initial plasticity). It would be of great interest to develop such a combined quantum mechanics-dislocation dynamics model, which would generate new knowledge on designing novel alloys with superior deformation properties.

For the present Co-Ni alloys, the Peierls-Nabarro based theory provides accurate predictions of the slip versus twinning CRSS levels independent of any temperature and strain-rate input. In the literature, there are evidences that the competition between the dislocation glide and the twinning in some low stacking fault fcc alloys can also be influenced thermally and/or by the deformation rate [86]. In order to develop a generic model, the current theory could be incorporated with the principles of the deformation kinetics [87]. The rate/temperature-dependent flow mechanisms obey the Arrhenius type laws, which dictate an exponential dependence on an “energy barrier”. In that regard, the current calculations provide evidence of the unstable stacking fault energy, \( \gamma_{us} \), being the most deciding energy barrier parameter to quantify the resistance to plastic flow. These implications pave the way for the scientific community to further explore the materials microstructure-property correlation.

### 2.6. Conclusion

The current research documents the deformation behavior of single crystal Co-33%Ni alloy. The major contributions can be synopsized as follows:

1) Experimental monotonic strain hardening behaviors of the Co-33%Ni single crystals under tensile and compressive loading have been studied extensively. Two different modes of plasticity (slip and twinning) were observed as a function of crystallographic orientation and loading direction, triggered by the maximum Schmid factor on the
respective systems. The crystals stressed in tension along \( \langle 111 \rangle \) and \( \langle 100 \rangle \) orientations undergo twinning, while compression induces extensive partial dislocation-mediated plasticity in \( \langle 123 \rangle \) and \( \langle 111 \rangle \)-oriented samples. Twinning-induced plasticity demonstrates superior hardening behavior compared to that of dislocation slip. Critical resolved shear stresses corresponding to the initiation of twinning, twin-slip interaction, slip and forest hardening (slip-slip interaction) are measured from the experimental stress-strain curves as 27 MPa, 39 MPa, 15 MPa and 24 MPa respectively, also to be compared with theoretical predictions.

2) An assortment of experimental visualization techniques (DIC, EBSD and TEM) were employed to pinpoint the exact plastic flow mechanism in the individual loading cases. These methods assist in garnering an in-depth understanding of the macroscale flow behavior with the microscopic defect evolution mechanism (e.g. slip and twin nucleation, forest hardening, twin-slip interaction). These experimental observations unearthing the microscale defect dynamics help lay the foundation of a comprehensive theoretical framework to rationalize the observed trends in plasticity from an ab-initio perspective.

3) A physical theory is forwarded to account for the material predilection for slip and twinning in a both qualitative and quantitative manner. In particular, GSFE and GPFE landscapes were computed for a Co-33%Ni solid solution. A Peierls-Nabarro framework accompanied by requisite continuum considerations was employed to predict critical slip, twin and twin-slip interaction initiation stresses. A reasonable agreement of these theoretical stresses levels with the experimentally-determined CRSS levels attests to the validity of the modeling assumptions. The theoretical aspects of the current study in particular serve to incorporate the first principle based material parameter (e.g. \( \gamma_{us} \), \( \gamma_{ut} \)) into the classical continuum context of slip and twinning.
Chapter 3 Strength Prediction in NiCo Alloys - The Role of Composition and Nanotwins

3.1 Abstract

Experimentally, hardening behaviors of nano-twinned Ni-Co alloys in tension demonstrate strong composition dependence. The strengthening characteristics improve substantially with increasing Co content (up to 2.9%Co), however, accompanied by an abrupt decline (at 5.52%Co), suggesting the existence of a critical composition. On theoretical grounds, atomistic modeling is performed to rationalize the experimental observations. First, the origin of Co content effects is traced back to an atomic level competition between solid solution hardening and Suzuki segregation processes, resulting in a non-uniform $\gamma$ surface variation. Secondly, the different slip transfer mechanisms across a coherent twin boundary are found to experience altered degrees of unstable fault energies ($\gamma_{us}$) owing to various residual dislocations. With evolving incident/residual slip, the $\gamma_{us}$ values first increase, and then attain saturated levels. Thus-computed $\gamma_{us}$ magnitudes are converted into corresponding frictional stresses within a Peierls-Nabarro modeling framework. Then, critical resolved shear stresses (CRSS) are predicted for different Ni-Co alloys. In conclusion, the apparently puzzling trends in the Ni-Co macroscopic strengths can be both qualitatively and quantitatively theorized by considering the combined effects of: (a) the twin influenced slip activities at the mesoscale and (b) the alloying induced fault energetics at the quantum scale.

3.2 Introduction

The microstructure-property correlation in metals and alloys has remained an important topic of research endeavors throughout the last century. Significant progresses were made in the 1950s through the early 1980s establishing important phenomenological laws [56, 62, 88-90]. With the advent of major innovations in materials processing and testing, the last decade in particular has witnessed considerable developments in the knowledge of microplasticity that shape our modern understanding of microstructural influences on deformation response [23, 91-
For the current generation of scientists and researchers, advancement of novel alloys essentially requires delving deeper into an atomic level understanding of the structure-property relationship devoid of empiricism. Given the vast improvements in computational materials science tools [5, 20, 96], we deem it timely and necessary to make major strides in establishing material laws informed by underlying atomic physics, free of empirical constants from a new perspective. To that end, we build on the foundation laid by the most contemporary knowledge of microplasticity at various lengthscales of relevant operative flow mechanisms [5, 97-104]. The current research emphasizes on a synergistic modeling approach, which bridges atomistic and mesoscale theories with experimental hardening behavior, considering a case study of electrodeposited nano-twinned Ni-Co alloys of different compositions. The consideration of nano-twinned alloy as the candidate material for this study is rooted upon the recently growing research interests therein [105-107] due to the prospect of drastic improvement of mechanical properties. The current undertaking begins with the documentation of experimental stress-strain responses of electrodeposited nano-structured NiCo alloys along with extensive analyses on pre- and post-deformation microstructures. On modeling grounds, firstly we isolate the effects of alloy composition in terms of material fault energetics from first principles. Subsequently, the role of coherent twin boundaries on mesoscale slip characteristics has been extensively investigated using molecular dynamics simulations. A unified theory combining atomic level solute effects and mesoscale strain transfer mechanisms is offered to rationalize the continuum hardening behaviors as observed experimentally.
Early literature notes that the significant improvement in polycrystalline strengthening attributes can be accomplished via grain refinement strategies [108, 109]. The correlation between the grain size and the hardening behavior is described phenomenologically by the classical Hall-Petch type formulations [110, 111]. The genesis of the Hall-Petch effects has been ascribed to an amplified degree of dislocation slip obstruction [97, 112, 113] as a consequence of an increased volume fraction of slip-obstacles (i.e. grain boundaries). However, improved strength due to reduced grain size in conventional coarse-grained materials occurs at the significant expense of ductility. On the other hand, metallic microstructure rife with thermally stable nano-sized annealing twins reportedly demonstrate high strengthening attributes with the retention of substantial ductility [114]. Recent literature suggested that widespread distribution of annealing twins serves to divide the host grains into multiple sub-grain type segments (Figure 3.1). As a result, the sheer presence of additional interfacial obstacles (i.e. the coherent twin boundaries) contributes to the macroscopic strength, to the same effect as the grain refinement [115]. However, the preceding argument does not hold when it comes to explaining the retention
of relatively high ductility upon introducing nano-sized twins in the microstructure. In order to elucidate the beneficial attributes of nano-twinned microstructure, a number of theoretical studies ventured into the mechanistic origin of combined high strength and ductility on the basis of various slip twin boundary interaction mechanisms [116-123]. It has been suggested that a coherent twin boundary can uniquely provide complete or partial or no transfer whatsoever of the impinging slip, depending on the local stress situation and geometric considerations. Moreover, unlike most commonly encountered grain interface types, a pristine twin boundary can allow for significant degree of glissile motion on the interface, leading to a twin migration process to which the origin of superior ductility has been attributed by some researchers [124]. In the earlier literature, the conditions for the outcome of slip intercepting a generic grain boundary has been experimentally established [125] as follows – (a) maximization of local resolved shear stress, (b) minimization of angle between incoming and outgoing slip plane and (c) minimization of residual Burgers vector. The slip transfer mechanisms are also expected to vary from grain to grain abiding by the foregoing rules, due to differences in grain orientations (Figure 3.1).

From a non-continuum perspective, widespread introduction of nano-sized annealing twins in the material microstructure would be manifested as a considerable variation in the overall Peierls energy barrier landscape. In a nano-twinned material, owing to an abundance of the coherent twin boundaries, the average Peierls energy barrier for each grain would be considerably greater than that of conventional coarse-grained counterparts. As a result, a higher magnitude of external forces would be required to sustain adequate dislocation activities during plastic deformation. Intuitively, the magnitude of critical resolved shear stress, \( \tau_{\text{CRSS}} \) in the presence of an increased number of slip-barriers would be considerably augmented. In the Peierls-Nabarro formalisms, the theoretical value of \( \tau_{\text{CRSS}} \) is a direct function of the so-called unstable stacking fault energy, \( \gamma_{us} \) [46, 72-74]. The \( \gamma_{us} \) is defined as the maximum value on the energy-displacement curve during rigid shear of two crystal blocks, known as the generalized stacking fault energy (GSFE) or \( \gamma \) surface [126, 127]. The intrinsic magnitude of the \( \gamma_{us} \) represents the energy barrier for free dislocation glide. Conventionally, the \( \gamma_{us} \) can only be determined from first principle or molecular statics energy minimization procedure. Moreover,
the extrinsic levels of the $\gamma_{us}$ for glide under the influence of a residual dislocation, $\vec{b}_r = \vec{b}_{\text{incoming}} - \vec{b}_{\text{transferred}}$, can be computed using molecular dynamics simulations during the actual motion of a dislocation [67, 128, 129]. The $\vec{b}_r$ is created upon the twin boundary when an incoming dislocation from the matrix material, $\vec{b}_{\text{incoming}}$, intercepts the interface, and transfers slip inside the twin, $\vec{b}_{\text{transferred}}$. Utilizing the foregoing concepts, we propose a comprehensive theory to answer the long-standing question of microstructure-property correlation in nano-twinned binary Ni-Co alloys.

Figure 3.2 – Summary of the current research addressing continuum, mesoscale and quantum lengthscale considerations.

We conduct uniaxial tension experiments on Ni-Co alloys, and critical resolved shear stresses are determined. Ex-situ electron backscatter diffraction (EBSD) scans establish the grain orientation map, giving insight into the surface texture. Transmission electron microscopy
(TEM) is used to reveal the prevalence of nano-scale annealing twins, and the widespread twin boundary-slip interception during plastic deformation. Extensive molecular dynamics simulations are conducted to investigate various slip-twin boundary interaction mechanisms, and the associated evolution of the energy parameter, $\gamma_{us}$. Using density functional theory (DFT) simulations, we capture the alloying-induced $\gamma$ surface. Combining quantum calculations and the molecular dynamics simulations, the critical resolved shear stresses are predicted within the Peierls-Nabarro modeling framework. The proposed theory is used to rationalize the experimentally observed deformation behavior of the nano-structured Ni-Co alloys in question. The current approach is schematically summarized in Figure 3.2.

![Figure 3.3](image)

Figure 3.3 – Stress-strain response of the electrodeposited Ni-Co alloys - Ni–1.0% Co, Ni–1.62% Co, Ni–2.9%Co, and Ni–5.52% Co (Sangid et al., 2011).

### 3.3 Experimental Results – Stress-strain Response and Microstructure

Figure 3.3 demonstrates the stress–strain responses for the electrodeposited Ni–Co alloys. All these materials possess nearly similar elastic slopes i.e. the Young’s moduli. However, their
plastic hardening characteristics differ to a considerable extent from alloy to alloy. The alloy with 1% Co content has the lowest 0.2% offset yield strength (522 MPa) and hardening rate with the maximum extent of ductility (5.6% elongation). The Ni-1.62%Co alloy with a yield strength of 631 MPa has a reduced degree of elongation (4.2%). Further strength enhancement is demonstrated for the Ni-2.9%Co material, with pre-rupture elongation as high as 1.9%. Most interestingly, addition of Co beyond 2.9% results in an apparently opposing trend. Using a Taylor factor of 3.06, critical resolved shear stresses for the alloys are. A summary of tension experiment results is presented in Table 3.1.

Table 3.1 – Experimentally determined mechanical properties of the current Ni-Co alloys.

<table>
<thead>
<tr>
<th></th>
<th>Young’s Modulus, E (GPa)</th>
<th>Yield strength (0.2% offset), $\sigma_y$ (MPa)</th>
<th>Critical resolved shear stress, $\tau_{CRSS} = \frac{\sigma_y}{3.06}$ (MPa)</th>
<th>Ultimate strength, $\sigma_{UTS}$ (MPa)</th>
<th>Elongation (%) (until rupture)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-1%Co</td>
<td>180</td>
<td>522</td>
<td>170.6</td>
<td>689</td>
<td>5.6</td>
</tr>
<tr>
<td>Ni-1.62%Co</td>
<td>159</td>
<td>631</td>
<td>206.2</td>
<td>961</td>
<td>4.2</td>
</tr>
<tr>
<td>Ni-2.9%Co</td>
<td>163</td>
<td>1304</td>
<td>426.2</td>
<td>1487</td>
<td>2.6</td>
</tr>
<tr>
<td>Ni-5.52%Co</td>
<td>165</td>
<td>1020</td>
<td>333.3</td>
<td>1332</td>
<td>1.9</td>
</tr>
</tbody>
</table>
Figure 3.4(a) – The grain orientation map of Ni-1%Co alloy from EBSD [130].

Figure 3.4(b) – Distribution of grain orientation superimposed on the stereographic triangle for Ni-1%Co.

The EBSD scans in Figures 3.4(a) and 3.4(b) indicates that the Ni-1%Co alloy has a mild [011] texture. However, the Taylor factor is determined to be 3.06, a value indicative of a wide range of grain distribution [130]. Similar grain distribution is observed for other Ni-Co alloys (not shown) from EBSD.
Figure 3.5 – TEM images demonstrating the widespread presence of nano-scale annealing twins. Notice the lack and the presence of dislocations at the twin boundaries before and after plastic deformation.

Figure 3.5 shows the nano-twinned microstructure of Ni-Co alloys. The deformed material demonstrates a considerable degree of slip obstruction at the twin boundaries. Quite interestingly, although the alloys have very similar microstructure, their macroscopic mechanical response differs significantly. In order to rationalize the foregoing experimental findings, atomistic modeling is performed.
3.4 Theoretical Results

3.4.1 Ni-Co fault energy Surface from First Principles

Figure 3.6 shows the $\gamma$ surface for the Ni-2.9% alloy calculated via density functional theory (using the method described in Appendix D). The unstable stacking fault energy $\gamma_{us}$ for $\langle 110 \rangle$ and $\langle 112 \rangle$ slip directions are found to be 360 mJ/m$^2$ and 305 mJ/m$^2$ respectively, and the intrinsic stacking fault energy $\gamma_{isf}$ to be 150 mJ/m$^2$. The peak energy to further shear the crustal along the same $\langle 112 \rangle$ direction is very high (about 720 mJ/m$^2$). This indicates that the slip would occur predominantly along the $\langle 112 \rangle$ family of directions (i.e. forming partial dislocations separated by stacking fault plane). The parameters $\gamma_{isf}$ and $\gamma_{us}$ for Ni-1%Co, Ni-1.62%Co, Ni-2.9%Co and Ni-5.52%Co are provided Table 3.2. In Figure 3.7(a), the current $\gamma_{isf}$ data are compared with literature DFT [131] and experimental values [24] as well as those computed using EAM potentials.

![Figure 3.6 – The $\gamma$ surface of the Ni-2.9%Co alloy.](image)
Figure 3.7(a) shows that there exists a non-uniform $\gamma_{\text{isf}}$ variation for <10% Co concentration. With increasing Co content, the $\gamma_{\text{isf}}$ initially rises to a maximum value of 153 mJ/m$^2$ and then continues to drop. The same trend is also observed for $\gamma_{\text{us}}$ values which are provided in Table 3.3. The rise portion is found to be caused by solid solution effects (i.e. the solute atoms providing additional resistance to the rigid shearing of the two blocks). By contrast, the gradually increasing presence of Co solutes triggers a solute segregation process in the vicinity of the fault. These two competing mechanisms give rise to the apparent the $\gamma_{\text{isf}}$ non-uniformity for low Co concentration. This phenomena is schematically illustrated in Figure 3.7(b).

![Figure 3.7(a)](image)

Figure 3.7(a) – Comparison of the intrinsic stacking fault energy ($\gamma_{\text{isf}}$) from various sources.
Figure 3.7(b) – The mechanistic origin of the non-uniform variation in the $\gamma_{\text{isf}}$ and $\gamma_{\text{us}}$ values at low Co content regime.

Table 3.2 – First principles fault energy parameters (thus-computed unstable stacking fault energy represents the bulk value i.e. the $\gamma_{\text{bulk}}^{\text{us}}$).

<table>
<thead>
<tr>
<th></th>
<th>Intrinsic stacking fault energy, $\gamma_{\text{isf}}$ (mJ/m$^2$)</th>
<th>Unstable stacking fault energy, $\gamma_{\text{us}}$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Ni</td>
<td>128</td>
<td>254</td>
</tr>
<tr>
<td>Ni-1%Co</td>
<td>139</td>
<td>275</td>
</tr>
<tr>
<td>Ni-1.62%Co</td>
<td>143</td>
<td>287</td>
</tr>
<tr>
<td>Ni-2.9%Co</td>
<td>153</td>
<td>305</td>
</tr>
<tr>
<td>Ni-5.52%Co</td>
<td>149</td>
<td>297</td>
</tr>
</tbody>
</table>
In the next step, we perform MD simulations to establish various slip transfer mechanisms in Ni-2.9%Co as the representative alloy.

3.4.2 Molecular Dynamics Slip-twin boundary Interactions

Figure 3.8(a) shows a single grain with an annealing twin constructed for conducting molecular dynamics (MD) simulations using Ni2.9%Co as the representative Ni-Co alloy. A dislocation source (a void) is placed in the vicinity of the nano-twin in the matrix so as to facilitate nucleation and subsequent incidence of dislocation on the neighboring coherent twin boundary. The dislocation geometries are observed to be of extended type (i.e. a pair of leading and trailing Shockley partials of type $\frac{a}{6}\langle 112 \rangle$ connected by a plane of the stacking fault). Depending on the orientation of the single grain, various degrees of Schmid factor would be operative on the leading/trailing partials as in Figure 3.8(b).
Figure 3.8(b) – Variation of Schmid factor on leading/trailing dislocations depending on the crystal orientation.

As far-field load, $\sigma_{ij}$ is applied to the twinned grain, dislocations nucleate in accordance with the Schmid law on the $\{111\}$ family of planes. For the activated slip systems, the resolved shear stress, $\tau_{RSS}$ under the farfield applied stress, $\sigma_{ij}$ is calculated, using Equation (13).

$$\tau_{RSS} = \sigma_{ij} n_i s_j$$  \hspace{1cm} (13)

In Equation (13), $\sigma_{ij}$ is the farfield stress tensor, $n_i$ the slip plane normal vector, and $s_i$ the vector representing the slip direction. The Schmid factor, $m$ is defined as the ratio between the resolved shear stress, $\tau_{RSS}$ and the Tresca stress, $\sigma_{Tresca}$ (i.e. maximum differential between the principal stresses) given in Equation (14). For example, $\tau_{xy}$ type pure shear applied loading leads to, $\sigma_{Tresca} = 2\tau_{xy}$, and for $\sigma_{yy}$ type pure uniaxial tension, $\sigma_{Tresca} = \sigma_{yy}$.

$$m = \frac{\tau_{RSS}}{\sigma_{Tresca}}$$  \hspace{1cm} (14)
Table 3.3 – Summary of slip-twin boundary interactions, the applied stress states and the Schmid factors, m on the partial dislocation of type $a/6\{1\overline{1}2\}$.

<table>
<thead>
<tr>
<th>Stress state</th>
<th>Incorporation</th>
<th>Transmission</th>
<th>Multiplication</th>
<th>Transmission-Incorporation</th>
<th>Blockage by Lomer lock</th>
</tr>
</thead>
<tbody>
<tr>
<td>[0 $\sigma_{xy}$ 0] [$\sigma_{yx}$ 0 0] [0 0 0] [0 0 $\sigma_{xz}$] [0 0 0]</td>
<td>Screw</td>
<td>Edge</td>
<td>Mixed</td>
<td>Mixed</td>
<td>Mixed</td>
</tr>
<tr>
<td>Incident dislocation (full) type</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m_{\text{incident}}$</td>
<td>0.39</td>
<td>0.41</td>
<td>0.34</td>
<td>0.46</td>
<td>0.31</td>
</tr>
<tr>
<td>$m_{\text{boundary}}$</td>
<td>0.5</td>
<td>0.00</td>
<td>0.22</td>
<td>0.5</td>
<td>0.00</td>
</tr>
<tr>
<td>$m_{\text{outgoing}}$</td>
<td>-</td>
<td>0.41</td>
<td>0.34</td>
<td>0.46</td>
<td>0.16</td>
</tr>
</tbody>
</table>
Figure 3.9 (a) incorporation of slip on twin boundary, (b) slip transmission across the interface, (c) nucleation of new dislocation (i.e. multiplication), (d) simultaneous transmission and incorporation (e) Formation of Lomer lock and stair rod dislocation.
We observe that different reactions occur depending on various combinations of the Schmid factors on the incident, twin boundary and the outgoing slip systems (Table 3.3). In the next sections, we describe the reactions case-by-case with atomic configurations and a double Thompson tetrahedron representing the matrix and twin.

(a) Incorporation

On intercepting the twin boundary, the leading partial \( \frac{a}{6}[\overline{2}1\overline{1}] \) creates a twinning dislocation \( \frac{a}{6}[\overline{1}2\overline{1}] \) and a sessile stair rod dislocation. When the trailing Shockley partial \( \frac{a}{6}[\overline{1}2\overline{1}] \) interact with the sessile stair rod dislocation, and creates another twinning partial \( \frac{a}{6}[211] \). The overall reaction is summarized by Equation (15) and by the double tetrahedron in Figure 3.15(a).

$$\frac{a}{6}[21\overline{1}] + \frac{a}{6}[\overline{1}2\overline{1}] \rightarrow \frac{a}{6}[\overline{1}2\overline{1}] + \frac{a}{6}[211]$$  \hspace{1cm} (15)

By incorporation, the approaching dislocation cross-slips onto the interface. The twinning partials (the residual dislocations, \( b_r \)) continue to glide in opposite directions, resulting in twin migration (i.e. growth/shrinkage of a twin). These initial \( b_r \) provides additional resistance to new oncoming dislocations.

(b) Transmission

In Figure 3.15(b), an oncoming pair of partial dislocations \( (\frac{a}{6}[2\overline{1}1] \) and \( \frac{a}{6}[112]) \) intercepts the twin boundary and transmits inside the twin. A sessile Frank partial type residual dislocation is left behind on the interface. Equation (16) summarized the interaction.

$$\frac{a}{6}[21\overline{1}] + \frac{a}{6}[112] \rightarrow \frac{a}{3}[\overline{1}1\overline{1}]_r + \frac{a}{6}[21\overline{1}]_r + \frac{a}{6}[112]_r$$  \hspace{1cm} (16)
The newly approaching dislocations interact with the Frank partial and further slip nucleation at the reaction site ensues.

(c) Multiplication

Figure 3.15(c) illustrates the nucleation of new dislocations i.e. the multiplication process. An extended dislocation intercepts the twin, and constricts into a full dislocation on the twin boundary. With favorable Schmid factors the interface, incident and outgoing slip systems (Table 3.3), the constricted dislocation disintegrates into two more extended dislocations - one inside the twin (\(\frac{a}{6}[2\overline{1}1]_r\) and \(\frac{a}{6}[112]_r\)) and one re-emitting to the matrix (\(\frac{a}{6}[121]\) and \(\frac{a}{6}[\overline{1}12]\)) as in Equation (17).

\[
\frac{a}{6}[2\overline{1}1] + \frac{a}{6}[112] \rightarrow \frac{2a}{9}[\overline{1}11]_r + \frac{a}{6}[2\overline{1}1]_r + \frac{a}{6}[112]_r + \frac{a}{6}[121] + \frac{a}{6}[\overline{1}12] \\
\text{Leading (Matrix)} \quad \text{Frank partial} \quad \text{Trailing (Matrix)} \quad \text{Trailing (Twin)} \quad \text{Leading (Twin)} \quad \text{Re-emitted (Matrix)}
\]

(d) Transmission and Incorporation

In Figure 3.15(d), when the oncoming leading partial \(\frac{a}{6}[2\overline{1}1]\) impinges on the matrix-twin interface, a Shockley partial \(\frac{a}{6}[1\overline{1}2]_r\) is emitted inside the twin along with a twinning partial \(\frac{a}{6}[121]\). Once the trailing partial \(\frac{a}{6}[12\overline{1}]\) catches up, another twinning partial \(\frac{a}{6}[\overline{1}12]\) and Shockley partial \(\frac{a}{6}[2\overline{1}1]_r\) (inside the twin) is generated. The interaction is summarized in Equation (18).

\[
\frac{a}{6}[2\overline{1}1] + \frac{a}{6}[12\overline{1}] \rightarrow \frac{a}{6}[\overline{1}12] + \frac{a}{6}[1\overline{1}2] + \frac{a}{6}[\overline{1}21] + \frac{a}{6}[\overline{1}12]_r
\\
\text{Leading (Matrix)} \quad \text{Trailing (Twin)} \quad \text{Twinning (Twin)} \quad \text{Trailing (Twin)} \quad \text{Leading (Twin)}
\]

(e) Blockage by Lomer Lock Formation
In Figure 3.15(e), when the leading Shockley partial $\frac{a}{\sqrt{2} \{21 \bar{1}\}}$ impinges on the boundary, it creates a Lomer dislocation $\frac{a}{2} \{101\}$. As the trailing partial catches up, a sessile stair rod dislocation $\frac{a}{3} \{100\}$ is generated in the vicinity of the Lomer lock. The overall reaction can be summarized as follows in Equation (19).

\[
\frac{a}{6} \{21 \bar{1}\} + \frac{a}{6} \{\bar{1}21\} \rightarrow \frac{a}{2} \{101\} + \frac{a}{3} \{100\}
\]  

Unlike incorporation, the Lomer lock-induced blockage precludes any glissile activity on the twin boundary. Further slip incidence generates sufficiently high local stress to cause disintegration of the sessile dislocations.

### 3.4.3 Fault Energetics of Slip-boundary Interactions

Due to different magnitudes of residual dislocation $\vec{b}_r = \vec{b}_{\text{incoming}} - \vec{b}_{\text{transferred}}$ various degrees of local stress concentration is imposed on the twin boundary (Figure 3.10). The magnitude of the residual dislocation is

\[
b_r = \sqrt{b_1^2 + b_2^2 + b_3^2}
\]

when, $b_1 = \hat{x} + b_2 \hat{y} + b_3 \hat{z}$, and $b_1$, $b_2$ and $b_3$ are vector component values and $\hat{x}$, $\hat{y}$, $\hat{z}$ are orthonormal unit vectors in the crystallographic directions.

Using the method described in Appendix C, we compute the values of $\gamma_{us}$ for different interactions as a function of the number of impinging dislocations, $N$, and the magnitude of residual slip, $b_r$ (Figure 3.11). To illustrate the cause-and-effect relationship among the parameters - $\gamma_{us}$, $b_r$ and $N$, the data from Figure 3.11 are presented separately in Figures 3.12(a) and 3.12(b). It can be noted from Figure 3.12(a) that the magnitude of the residual Burgers vector, $b_r$, eventually leads to saturated levels (denoted by $b^\text{sat}_r$), regardless of the reaction type with increasing number of oncoming dislocations.
3.4.4 Evolution of $\gamma_{us}$ during slip-boundary interactions

Figure 3.10 - Stress concentrations on the twin boundary for various residual dislocations.

Figure 3.11 – Evolution of the unstable stacking fault energy ($\gamma_{us}$) from the bulk magnitude to the higher values at the site of the slip-interaction reactions.
Figure 3.12(a) - Variation in the magnitude of the total residual dislocation at the interface with increasing incidence events.

Figure 3.12(b) – The linear correlation between the $\gamma_{us}$ and the residual Burgers vector, $b_r$. 
The apparent saturation occurs due to the dissociation of the $b_r$ with increased slip impingement. The dissociated $b_r$ shifts from the original reaction site, thereby offering no stress concentration to the newly approaching slip. One can recall that the stress concentrations associated with a $b_r$ is extremely localized. Hence, the dissociation/relocation of the $b_r$ precludes any stress contribution towards increasing the $\gamma_{us}$ value for the approaching slip. The details differ for individual reaction cases. However, the fundamental mechanistic process is essentially similar.

The maximum (at saturation) elevation in the $\gamma_{us}$ due to Lomer lock formation is as high as 1957.2 mJ/m$^2$ (denoted by $\gamma_{us}^{sat}$). The saturated energy barrier for incorporation, $\gamma_{us}^{sat}$ is calculated to be the lowest of all the reactions in the current study (474 mJ/m$^2$). We note that the fault energy barrier associated with incorporation process is traditionally designated as “unstable twinning energy barrier” ($\gamma_{ut}$) [19] as incorporated glide is essentially equivalent to a twin migration process. However, for the sake of simplicity, we treat the peak $\gamma$ energy barrier during the glide of the twinning partial (i.e. the incorporated Shockley partial) as the $\gamma_{us}$ in the present study.

### 3.4.5 Prediction of Critical Flow Stresses

#### 3.4.5.1 Free glide strength

We employ Peierls-Nabarro (PN) model [72, 73] to convert the $\gamma_{us}$ energies into frictional stresses. The total energy expenditure during dislocation glide (also known as the misfit energy, $E_{\text{mismatch}}$) is a function of $\gamma_{us}$ and the disregistry function $f_{\text{disregistry}}$. Using the bulk energy barrier $\gamma_{us}^{bulk}$, the free glide strength $\tau_{\text{free glide}}$ for a dislocation can be computed from Equation (20) [46, 47, 51].

$$\tau_{\text{free glide}} = \max \left\{ \frac{1}{b} \frac{\partial E_{\text{mismatch}}}{\partial u} \left( f_{\text{disregistry}} \gamma_{us}^{bulk} \right) \right\}$$

(20)
where, \( u \) is the dislocation location and the Burgers vector magnitude, \( b = |\mathbf{b}| = a/\sqrt{6} \).

![Figure 3.13(a) - The model configuration for calculating the slip-twin interaction strength, \( \tau_{\text{slip-twin}} \) in the presence of the net residual slip \((\mathbf{b}_1)_\text{net} = (\mathbf{b}_1) + (\mathbf{b}_2)\).

The \( f_{\text{disregistry}} \) represents the horizontal displacement differential of the atoms (before and after the occurrence of slip) across the slip plane, and hence captures the elastic distortion surrounding the dislocation core \([47, 51]\). The disregistry function, \( f_{\text{disregistry}} \) for an extended dislocation with partial splitting distance, \( d_{\text{split}} \), is given by Equation (21) in the literature \([47, 48]\).

\[
f_{\text{disregistry}} = b + b \left[ \frac{1}{\pi} \tan^{-1} \left( \frac{ma' - u}{\zeta} \right) + \tan^{-1} \left( \frac{ma' - u - d_{\text{split}}}{\zeta} \right) \right]
\]  

(21)

where, \( m \) is an integer ranging from \(-\infty\) to \(+\infty\), which accounts for the long range of \( f_{\text{disregistry}} \) (for numerical calculation, \( m \) is assumed to be a large number); \( a' \) is the lattice periodicity i.e. shortest distance between two equivalent atomic rows in the Burgers vector direction i.e. \( a' = 2b = 2a/\sqrt{6} \); \( \zeta \) the core half-width of the individual partial (\( \zeta_{\text{screw}} = a/2\sqrt{3} \) and \( \zeta_{\text{edge}} = a/2\sqrt{3}(1 - \nu) \); \( \nu \) is Poisson’s ratio).
The $E_{\text{misfit}}$ denotes the area underneath the $\gamma$ surface, and can be written as a Frenkel type expression [46, 47, 51]:

$$E_{\text{GSFE}} = \sum \gamma \left( f_{\text{disregistry}}, \gamma_{us} \right)$$

as in Equation (22).

Equation (22) represents a generic expression, wherein any magnitude of $\gamma_{us}$ (e.g. for the free glide and/or the obstructed glide) can be inserted to obtain the corresponding misfit energy level.

### 3.4.5.2 Slip-twin Boundary Interaction Strength

![Diagram of Twin Boundary Interaction](image)

Figure 3.13(b) – The model configuration for calculating the slip-twin interaction strength, $\tau_{\text{slip-twin}}$, in the presence of the net residual slip $(\vec{b}_r)_{\text{net}} = (\vec{b}_r)_1 + (\vec{b}_r)_2$.

Figure 3.13(b) illustrates the current approach of computing the $\tau_{\text{slip-twin}}$. The presence of accumulating $\vec{b}_r$ leads to two distinct forms of energy expenditure for the newly approaching
slip to overcome - (a) the aforementioned misfit energy, $E_{\text{mismatch}} = E_{\text{mismatch}}(\gamma_{us})$, and (b) the $\mathbf{b}$-induced elastic energy, $E_{\text{residual}} = E_{\text{residual}}(\mathbf{b})$. The applied stress $\tau_{\text{slip-twin}}$ required to move the oncoming dislocation towards the boundary by a distance of $\partial d$ can be derived from the work-energy balance as in Equation (23). 

$$b_{\text{incident}} \tau_{\text{slip-twin}} \frac{\partial d}{\text{work done}} = \partial E_{\text{mismatch}}(f_{\text{interface}}, \gamma_{us}) + \partial E_{\text{residual}}(\mathbf{b})$$ (23)

Due to high local stress (on the twin boundary) as a result of accumulation, individual $\mathbf{b}$'s are located at different positions from the initial site. Figure 3.13(b) considers the case of the net $\mathbf{b}$ comprising, for example, two component residual dislocations - $(\mathbf{b}_1)$ and $(\mathbf{b}_2)$ located at $r_1$ and $r_2$ distances away from the original interception site as indicated. Based on the work-energy balance in Equation (23), we propose the generic expression of the $\tau_{\text{slip-twin}}$ for any number of component residual dislocation $(\mathbf{b}_i)$ located at $r_i$ ($i = 1, 2, 3...$) as in Equation (24).

$$\tau_{\text{slip-twin}} = \max \left\{ \frac{1}{b_{\text{incident}}} \frac{\partial E_{\text{mismatch}}(f_{\text{interface}}, \gamma_{us})}{\partial \mathbf{u}} \right\} + \frac{1}{db_{\text{incident}}} \sum_i \frac{\mu (\mathbf{b}_i)^2}{4\pi} \ln \left( \frac{R}{r_i} \right)$$ (24)

where, $R$ is the size of the grain containing the twin and $\mu$ the shear modulus. The $\frac{R}{r_i}$ ratios are assumed to be constant at a magnitude of 1/500, considering the fact that such a value amounts to the summation of the classical strain energy expressions of the residual dislocations i.e. $

\sum_i \frac{\mu (\mathbf{b}_i)^2}{2}$ [46].

For the current calculations, we deem it reasonable to assume the magnitudes of “d” to be on the order of tens of nanometers (from 10 to 20 nanometers). Clearly, this parameter in reality will be decided by the twin spacing as well as the dislocation source density. It is rather challenging to establish this parameter experimentally. Hence, to assume realistic values (in
accordance with the TEM observations), we adhere to the magnitudes which correspond to the nano-dimensions of the twins in the TEM pictures as well as predicts a reasonable $\tau_{\text{slip-twin}}$ level. It is important to note that the assumption of “d” values does not necessarily alter the fundamental aspect of the modeling.

Equation (24) can be used to predict the slip transfer strength, $\tau_{\text{slip-twin}}$ corresponding to any particular mechanisms by inserting the saturated values of $b_r$ (i.e. the $b_{r,\text{sat}}$), and the unstable stacking fault energy value i.e. $\gamma_{\text{us}}$. The calculated values are presented in Table 3.4.

Table 3.4 - Strength of slip transfer mechanisms past a twin boundary $\tau_{\text{slip-twin}}$ and free glide strength (i.e. Peierls stress) $\tau_{\text{free glide}}$ in different Ni-Co alloys.

<table>
<thead>
<tr>
<th></th>
<th>$\tau_{\text{free glide}}$ (MPa)</th>
<th>$\tau_{\text{slip-twin}}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Free glide</td>
<td>Incorporation</td>
</tr>
<tr>
<td>Ni-1%Co</td>
<td>33</td>
<td>153</td>
</tr>
<tr>
<td>Ni-1.62%Co</td>
<td>48</td>
<td>161</td>
</tr>
<tr>
<td>Ni-2.9%Co</td>
<td>60</td>
<td>175</td>
</tr>
<tr>
<td>Ni-5.52Co</td>
<td>55</td>
<td>166</td>
</tr>
</tbody>
</table>
3.4.5.3 Prediction of CRSS for Different Ni-Co Alloys

First, we propose a suitable extrapolation strategy to obtain various $\tau_{\text{slip-twin}}$ levels for all Ni-Co alloys. Based on simulating Ni-2.9%Co as the representative material, the $\gamma_{\text{us}}$ is found to be a linear function of the $b_r$. It is quite reasonable to assume that the other Ni-Co alloys would undergo similar reaction mechanisms, and hence essentially yield similar $\gamma_{\text{us}} - b_r$ correlation. Therefore, we propose a simple linear relation in the form of Equation (25) to predict the energy barrier levels in various alloys. In doing so, each alloy differ in terms of the composition-dependent bulk $\gamma_{\text{us}}^{\text{bulk}}$ values computed from first principles (Table 3.2). Such an approach is particularly advantageous, in that it circumvents repeating the same set of MD reaction simulations on each alloy (which is clearly a superfluous measure).

$$\gamma_{\text{us}} = \frac{M_{\text{reaction}}}{M_{\text{from MD}}} \frac{b_r}{a} + \frac{\gamma_{\text{us}}^{\text{bulk}}}{M_{\text{from DFT}}}$$

(25)

where, $M_{\text{reaction}}$ is the slope of $\gamma_{\text{us}}$ versus br curves in Figure 3.19(b) for each reaction: $M_{\text{incorp}} = 352.05 \text{ mJ/m}^2$, $M_{\text{trans}} = 457.55 \text{ mJ/m}^2$, $M_{\text{Multi}} = 598.53 \text{ mJ/m}^2$, $M_{\text{trans-incorp}} = 774.47 \text{ mJ/m}^2$, $M_{\text{Lomer}} = 985.31 \text{ mJ/m}^2$. Now, by inserting the $\gamma_{\text{us}}^{\text{bulk}}$ from Table 3.2 and the appropriate $M_{\text{reaction}}$ and $b_r^{\text{sat}}$ for a particular reaction mechanisms in Equation (25), we extrapolate the corresponding $\gamma_{\text{us}}^{\text{sat}}$ values for all Ni-Co alloys. These new $\gamma_{\text{us}}^{\text{sat}}$ magnitudes in turn are input into Equation (24) to predict the corresponding $\tau_{\text{slip-twin}}$ levels (Table 3.4).

To predict the $\tau_{\text{CRSS}}$ for the current nano-twinned alloys, we consider three major microscopic flow contributions – (a) the free glide stress $\tau_{\text{free glide}}$, (b) slip-twin boundary interaction stress, $\tau_{\text{slip-twin}}$, and (c) the forest hardening stress (at a pre-deformation dislocation density) $\tau_{\text{forest}} = \alpha \mu b \sqrt{\rho}$ [56, 132]; where $\alpha$ is a material constant (from 0.5 to 1) and $\rho$ the forest dislocation density (assumed to be $10^{14}$ /m$^2$ which is the typical pre-deformation literature
value). The $\tau_{\text{slip-twin}}$ is observed to be the most dominating. Using Equation (26), we calculate the $\tau_{\text{CRSS}}$ levels for different Ni-Co alloys based on iso-strain type mixing formulations.

$$\tau_{\text{CRSS}} = (1 - V_f) \tau_{\text{free glide}} + \sum_{\text{reaction}} V_{f}^{\text{reaction}} \tau_{\text{slip-twin}} + (1 - V_f) \tau_{\text{forest}}$$  \hspace{1cm} (26)

where, $V_f$ is the total volume fraction of the material region hosting the aggregate slip-twin reactions; $V_{f}^{\text{reaction}}$ is the assigned volume fraction for a specific reaction i.e. $V_f = \sum_{\text{reaction}} V_{f}^{\text{reaction}}$. The $V_{f}^{\text{reaction}}$ value to a particular reaction is assigned on the basis of the fact that the EBSD results demonstrated only an mild texture (almost close to random distribution of grains).

![Graph showing comparison between predicted and experimentally determined $\tau_{\text{CRSS}}$ levels for different Ni-Co alloys.](image)

Figure 3.14 – Comparison between the predicted and experimentally determined $\tau_{\text{CRSS}}$ levels for different Ni-Co alloys.
in Figures 3.4(a) and 3.4(b). From the EBSD analyses, the grain orientation distribution in the four Ni-Co alloys is found to be very slight texture. Hence, we assume that the MD-observed stain transfer mechanisms would occur with equal frequency/probability. Therefore, for the modeling purpose, an equal volumetric contribution of the all five categories of the slip transfer mechanisms is considered in Equation (26). The values of the $\tau_{\text{CRSS}}$ for the current Ni-Co alloys are predicted and compared with experimentally determined $\tau_{\text{CRSS}}$ in Figure 3.14.

3.5 Discussion

3.5.1 Role of Composition

The role of the Ni-Co composition has been identified as particularly influencing the fault energetics at the atomic scale. Early literature [24-26] note that the intrinsic stacking fault energy $\gamma_{\text{isf}}$ values of Ni-Co alloys undergo a gradual reduction with increasing Co content from the pure Ni level. Through quantum mechanical calculations, we report the presence of a non-uniform trend at low Co concentration. Recent theoretical literature also report similar findings on the Ni-Co $\gamma_{\text{isf}}$ levels [131, 133]. We trace the origin of such trend to an atomic level competition between the solid solution hardening effects and the solute segregation (known as the so-called Suzuki segregation). Suzuki first reported the experimental evidence of the role of solute segregation on reducing the fault energetics [81]. Starting from pure Ni up to a Co content of 2.9% (by weight), the gradual rise in the fault energy levels (both $\gamma_{\text{us}}$ and $\gamma_{\text{isf}}$) is observed to be dominated by solid solution hardening. Throughout the rising portion of the curve, the Co solutes continue to create enhanced resistance for lattice shearing. On reaching the peak magnitude (at 2.9%Co), the solute drag effects are eventually overwhelmed by the Suzuki segregation effects, leading to the dip of the curve. The evidence of a decrease in the fault energies due to the solute segregation is also reported in the recent literature [82, 134].

Now, questions may arise regarding whether the observed trend in the Co-influenced $\gamma$ surface are indeed representative of the inherent material properties [135]. Specifically, one must
check the sensitivity of: (a) the energy relaxation procedure, (b) the positioning of solutes, and (c) the simulation supercell size.

We have investigated the role of different relaxation methods [135] – (i) the full relaxation (when atomic positions are allowed to adjust in all directions), (ii) “the vertical relaxation” (when atoms adjust positions only vertical to the fault plane), and (iii) no relaxation whatsoever. In doing so, the maximum variation was limited to ± 4 mJ/m² both in the levels of $\gamma_{isf}$ and $\gamma_{us}$, assuring the accuracy of our results. Secondly, various positioning of the solute atoms results only in a variation of ± 3 mJ/m². The physical origin of such insensitivity can be attributed to the strong similarity between the Co and Ni atoms discussed as follows.

Typically in metallic alloys, the addition of the substitutional solute atoms of different elements to the base metal matrix results in the lattice distortion and the change in bonding landscape. The lattice distortion depends on the volumetric mismatch among the constituent elements while bonding landscape is decided by the electronic configurations. Other important factors are the chemical potential and the magnetic properties of each element. All these variables would essentially factor in the nature and magnitudes of the alloy $\gamma$ surface. For instance, the mixing of two elements, which are very dissimilar in terms of the atomic volumes, would result in a large lattice distortion and hence higher sensitivity to the solute positioning with respect to the fault. Likewise, the magnetism of the constituent atoms (which is in fact dictated by the nature of electronic spin at the outermost shells in individual atoms) would impart a profound influence on the fault energetics. However, for the Ni-Co binary alloys, both Ni and Co are transitional metals, which possess very similar physical attributes in terms of the atomic volumes (the respective radii being 0.124 and 0.125 nm), the electronic configurations (Ni = [Ar] 3d⁸ 4s² and Co = [Ar] 3d⁷ 4s²) and the magnetism (both being ferromagnetic). In other words, during alloying the Co solute atoms can substitute Ni atoms without creating a considerable disturbance in the base metal properties. Therefore, when the quantity of the Co solutes in the Ni matrix is only very minute, no significant change in the neighborhood of the Co solute atoms is noticed by the material. As a result, the role of Co solutes as the point defects
would be negligible except for altering the electronic structure in the vicinity, thereby eliminating the aforementioned simulation artifacts.

In summary, the compositional dependence of the Ni-Co $\gamma$ surface is demonstrably tuned with the trends in the experimental yield strengths. Given fact that the $\gamma$ surface governs the inherent slip characteristics, the overall tendency towards slip glide resistance at the mesoscale would differ considerably among the various Ni-Co alloys. Particularly, the presence of the nano-sized annealing twins would significantly enhance the composition-dependent slip characteristics within individual grains, thereby deciding the macroscopic hardening behavior.

### 3.5.2 Role of Nano-twins

At the mesoscale, the coherent twin boundaries play the role of increasing the impedances to dislocation motion. Hence, the magnitudes of the critical resolved shear stress $\tau_{\text{CRSS}}$ of the Ni-Co alloys are decided by the presence of annealing twins. Particularly, we demonstrate the importance of considering different slip-twin boundary reactions in imparting various degrees of glide resistances. Hence, in the proposed theory, we have examined multiple types of reaction mechanisms to predict the relative $\tau_{\text{slip-twin}}$ levels for the respective mechanisms.

These reactions are triggered on the basis of: (a) the local stress state i.e. the relative Schmid factors on the twin boundary, incident, and outgoing slip systems, and (b) the geometry of the intercepting slip i.e. edge/screw/mixed [125]. For a polycrystalline material, different local stress states at twin boundaries would arise from grain to grain. We note that the current reactions occur under the unique local stress state and the geometry of the incident slip (as summarized in Table 3.3). Further investigation of modifying either of these two variables, and the associated change in the mechanism would be one interesting future research. Earlier literature have addressed the details of individual reactions both theoretically and experimentally: (a) incorporation [116, 136, 137], (b) transmission [123, 124], (c) multiplication [138], (d) transmission and incorporation [119, 139, 140], and (e) blockage by a Lomer lock formation [141, 142]. The relative preference for these reactions bears important implications regarding the macroscopic strength and ductility. For example, the incorporation process can be
deemed as a special case of slip blockage mechanism, which still permits straining along twin boundaries. Early literature [124] note that the origin of considerable ductility in nano-twinned materials can be attributed to the pervasive incorporation process. On the other hand, a large number of grains favorably oriented for Lomer lock formation would contribute to increased strengthening attributes. Similarly, multiplication and transmission-incorporation processes would play roles in both hardening and ductility to some extent. The currently predicted resistance stresses $\tau_{\text{slip-twin}}$ for various mechanisms hold considerable promise for the use in modeling further material properties such as damage tolerance [66].

We note that a detailed exploration of further combinations of applied stresses (e.g. shear, tension etc.) on the nano-twinned grain (in the molecular dynamics simulations) would essentially differ only in terms of the local stress state. This, in turn, may culminate in other reactions types (or the currently reports ones with slight modifications depending again on the combination of the Schmid factors on incident/boundary/outgoing slip planes). That is why it is more convenient to categorize the slip-twin boundary reaction mechanisms in light of the Schmid factor scenario. It is because, for example, even apparently different global stress states may yield the same local resolved shear stresses on the respective systems, leading to the same slip transfer mechanisms. Hence, we resort to categorizing five different types which are also experimentally verified in earlier literature.

Now, the question may arise regarding what volume fraction of individual reactions prevails during the deformation. Intuitively, if a material is very strongly textured, the majority of grains will have the same orientations, and hence a predominant local stress state, which in turn will result in the prevalence of a particular reaction. On the other hand, a material with random/mild texture, which is the current case, is most likely to have an equal distribution of various slip transfer mechanisms. We note that it is rather challenging to experimentally establish the exact nature of slip transfer processes at twin boundaries in individual grains in-situ. For example, TEM methods can only probe sub-micron area. On the other hand, EBSD cannot reveal any interaction mechanisms on a grain by grain basis. Now, for the current Ni-Co alloys, even though the EBSD map indicates a mild texture, the Taylor factor for this material is computed to
be 3.06 [130], which in fact suggests the presence of a wide range of grain distribution. Therefore, it is quite reasonable to assume that the current set of reactions is likely to prevail with nearly equal probability.

3.6 Summary and Conclusion

The major contributions of the present research are summarized below.

1) Constitutive responses of polycrystalline Ni-Co alloys are investigated via uniaxial tension experiments. Critical resolved shear stresses for Ni-1%Co, Ni-1.62%Co, Ni-2.9%Co and Ni-5.52%Co alloys are determined to be 170.6 MPa, 206.2 MPa, 426.2 MPa and 333.3 MPa respectively. The observations suggest the existence of a critical composition to achieve the maximum strength. TEM micrographs reveal a prevalence of nano-sized annealing twins in the alloys. On deformation, a substantial increase in dislocation density at the twin boundaries is evidenced, suggesting widespread slip-twin interactions contributing to macroscale strengths.

2) First principles calculations reveal that the compositional dependence is related with an atomic-scale competition between solid solution hardening and solute segregation. The $\gamma$ surface values undergo a rise (controlled by solid solution hardening), and subsequently a fall (governed by solute segregation) with increasing Co content. The overall compositional trend in the alloy $\gamma$ surface (i.e. $\gamma_{us}$ and $\gamma_{isf}$ values) is found to follow the same experimental trend as the alloy strengths.

3) Various strain transfer mechanisms past a coherent twin boundary have been studied using molecular dynamics simulations. Different residual dislocations are found to influence the extrinsic levels of the $\gamma_{us}$. A Peierls-Nabarro framework was employed to convert the extrinsic $\gamma_{us}$ levels into the twin boundary penetration strengths for the corresponding strain transfer mechanisms. The computed boundary strengths are subsequently extrapolated for different alloy compositions. Critical resolved shear stresses ($\tau_{crss}$) are predicted for the Ni-Co alloys in question.
4) Overall, the present theory suggests that the experimental differences in hardening behaviors originate from alloying-induced quantum level differences in the \( \gamma \) surfaces. Alterations in the fault energetics (owing to adding even minuscule amounts of substitutional Co atoms) can be considerably amplified at the mesoscale defect interaction level. As a result, the frictional stresses required for widespread dislocation interactions with twin boundaries would undergo augmented effects from one composition to another. Therefore, these discrete lattice level effects manifest themselves in the form of considerable differences in the macroscopic strengthening behaviors.
Chapter 4 NiTi Superelasticity via Atomistic Simulations

4.1 Abstract

The NiTi shape memory alloys (SMAs) are promising candidates for the next-generation multifunctional materials. These materials are superelastic i.e. they can fully recover their original shape even after fairly large inelastic deformations once the mechanical forces are removed. The superelasticity reportedly stems from atomic scale crystal transformations. However, very few computer simulations have emerged, elucidating the transformation mechanisms at the discrete lattice level, which underlie the extraordinary strain recoverability. Here we conduct breakthrough molecular dynamics modeling on the superelastic behavior of the NiTi single crystals, and unravel the atomistic genesis thereof. The deformation recovery is clearly traced to the reversible transformation between austenite and martensite crystals through simulations. We examine the mechanistic origin of the tension-compression asymmetries and the effects of pressure/temperature/strain-rate variation isolatedly. Hence, this work essentially brings a new dimension to probing the NiTi performance based on the mesoscale physics under more complicated thermo-mechanical loading scenarios.

4.2 Background

Since the discovery in 1960s [143], NiTi SMAs have found widespread commercial usage in biomedical, aerospace and automotive industries today [144, 145]. There have been a considerable number of experimental [146, 147] and theoretical undertakings ever since to rationalize the unique pseudoelastic attributes therein on physical basis (Figure 4.1). On theoretical grounds, the last decade has witnessed significant progresses in terms of advancing from phenomenological continuum modeling [148-150] into the atomic-scale approaches [151, 152]. Atomistically, two distinct classes of theories can be noted, namely, the quantum mechanical predictions of lattice properties (e.g. the elastic moduli, the transformation energy pathways), and mesoscale deformation simulations. While very informative, the \textit{ab initio} methods are confined to only tens of atoms (due to a rather rigorous requirement of computational capability [153, 154]). By contrast, molecular dynamics (MD) simulations can address mesoscale crystals (consisting of millions of atoms) by utilizing pair-potential based
descriptions. This letter documents such predictions of phase transformations and accurate constitutive response with the aid of a newly developed potential.

Figure 4.1 – A schematic illustration of some select applications of the NiTi based SMAs, and the study of the associated physics spanning various lengthscales.
MD studies using previously developed potentials on NiTi SMAs [155-158] have been able to predict various interesting aspects of NiTi behaviors at the lattice scale. For instance, Farkas et al. [155] predicted the B2 lattice cohesive energy. Subsequently, Lai and Liu theorized the melting behavior thereof using a new potential. Most recently, Zhu and co-workers [157, 159] further modified Lai’s potential to study martensitic phase transformation. Independently, Mutter and Nielaba [158, 160] improved Lai’s original potential to model temperature/composition dependent transformation. In view of the literature findings, we note that the central features of NiTi SMAs to be modeled are essentially threefold: (a) the correct shape and magnitudes of stress-strain hysteresis loops (i.e. comparable to experimental ones), (b) the reversibility of martensitic phase transformation (i.e. B2 ↔ B19’), and (c) the stability of individual phases subjected to stress and temperature variations. As experimental literature noted, NiTi SMAs possess distinctive mechanical traits such as strong tension-compression asymmetry, dependence of hydrostatic stress and temperature, the origin of which merits rigorous atomistic rationalizations. While the previous models were successful in capturing various crystal level responses, there still exists a need for predicting the full spectrum of the NiTi constitutive attributes using a single potential. Utilizing the literature knowledge, we adopt several improvement strategies in the form of fine-tuning the cut-off sensitivity and accurately fitting the cross-interaction energy terms to better describe the material potential energy landscape (see appendix D). As a result, we set out to address the inherently complex NiTi constitutive behaviors under various thermo-mechanical conditions, using extensive MD simulations [161].

4.3 Model description

The austenitic NiTi single crystals of CsCl type unit cells were constructed using the basis: \( \text{Ni} = (0 \ 0 \ 0) \) and \( \text{Ti} = (0.5 \ 0.5 \ 0.5) \). The size of the cubic crystal (with each side being 30 nanometers) is selected based on the convergence of physical observables (e.g. temperature, pressure, kinetic and potential energy) to the system size independence. The crystals represent bulk material (i.e. without any free surface or dangling bonds) as ascertained by enforcing
periodic boundary condition on the crystal facets [67]. The number of atoms in a typical simulation supercell was about $3 \times 10^5$, which is sufficiently large to avoid any size- and/or periodicity-induced artifacts. The stress-strain responses reported in this letter are computed based on the concept of virial stress (which is the atomistically equivalent quantity of the conventional Cauchy stress).

Figure 4.2(a) – Single crystal NiTi at the austenite phase (B2) prior to any deformation (i.e. at 0% strain). The unit cell structure is of CsCl type.

Figure 4.2(b) – The NiTi martensite (B19' crystal) at 5% strain (notice the internally twinned structure). The B19' unit cell structure is monoclinic with one angle of the unit cell being non-right angled.
Energetically minimized defect-free bulk B2 crystal structure is characterized by its distinctive CsCl type unit cell with a lattice constant, \( a_{B2} = 3.021 \, \text{Å} \) in Figure 4.2(a). We have selected the \( \langle 011 \rangle_{B2} \) crystallographic orientation along which to apply loads. Choosing one particular orientation is important for consistency due to the strong orientation dependence of the NiTi superelastic response [162].

On deforming to 5% strain, the B2 phase fully transforms into a martensitic material (i.e. B19’ phase) as shown in Figure 4.2(b). The primitive unit cell of the B19' crystal is of monoclinic type with the lattice variables: \( a_{B19'} = 4.606 \, \text{Å} \), \( b_{B19'} = 4.386 \, \text{Å} \), \( c_{B19'} = 2.699 \, \text{Å} \) and \( \alpha_{B19'} = \gamma_{B19'} = 90^\circ \), \( \beta_{B19'} = 96.7^\circ \). During the deformation simulations, the austenite and the martensite phases are identified by their distinctive unit cells.

### 4.4 Results and Discussion

First, we examine the superelastic load-unload behaviors under compression and tension. Figures 4.3(a) and 4.3(b) present the respective stress-strain curves (at 300K temperature), and illustrate the governing atomistic mechanism step by step. In the following discussion, we describe the compression case in full details. Then we analyze the mechanistic foundation of the observed tension and compression asymmetries. In Figure 4.3(a), the austenitic NiTi deforms elastically along the linearly rising stress-strain curve (from 0% strain up to 1.8%). During this period, the crystal phase remains the same as the initial B2 structure. On reaching a critical stress level of 830 MPa (i.e. the “transformation stress”, the experimental value of which is about 800 MPa [162]), the B2 austenite starts to transform into B19’ martensite in various regions of the parent crystal. At this stage, three simultaneous atomistic processes are observed to be happening. Firstly, the atoms, that constitute the original CsCl type B2 lattice, start rearranging into the monoclinic B19' lattice. Secondly, the atoms, part of the newly transformed martensite...
Figure 4.3(a) – Superelasticity of NiTi under \( \langle 011 \rangle_{b2} \) compression and at 300K. Notice the reversible austenite (B2) ↔ martensite (B19') transformation.

lattice, undergo ordering among themselves to create multiple mirrored strips (a phenomenon known as the “internal twinning” of the martensite). Such twinning process is designated as the “compound type” prevailing on the \( \{001\} \) family of planes. And thirdly, further loading continues to produce the deformation twins on the \( \{001\} \) systems, extending to high strains. The single crystal becomes fully martensitic at 4% strain. This behavior is consistent with early experiments [162]. Continuation of applied force results in the elastic distortion of the twinned martensite, corresponding to the rise of stress-strain curve (from 4% up to 5% strain). No significant structural modification is discerned due to the elastic straining of martensite. The final atomic structure at the end of loading (at 5% strain) is characterized by multiple internal twins (made of monoclinic unit cells).
On full unloading, the deformed crystal completely reverts back to its initial undeformed state (i.e. the B2 austenite at 0% strain) as in Figure 4.3(a). Mechanistically, the martensite first undergoes elastic recovery (from 5% to 4% strain). Then, the reverse transformation process is initiated i.e. the martensite starts returning to austenite, marked by the beginning of the lower stress plateau. The phenomenon implies that the internally twinned B19' structure is stable only under high stress, and hence the removal of stress triggers the reverse B19'-to-B2 transformation. The volume fraction of the martensitic B19' phase continuously decreases along the stress plateau. After complete unloading, the material retains no residual martensite and hence no residual strain/stress. The transformation strain i.e. the total strain (5%) minus the elastic strain (about 1%) is calculated to be about 4% (which is experimentally reported to be around 5% [163]). As noted in the early literature, higher transformation strain can result if one variant growth is occurring in the expense of others i.e. detwinning [164]. By contrast, crystals with

![Figure 4.3(b) – Tensile strain behavior at 300K for \(\{011\}_{B2}\) loading orientation.](image)
multiple twins promote reduced transformation strain. In the current case, the presence of multiple variants (i.e. internally twinned structure) is strongly believed to be the reason for the slightly lower predictions than the experiments.

The tensile behavior is superelastic, however, with reduced hysteresis area as shown in Figure 4.3(b). The corresponding transformation stress is determined to be about 720 MPa (matching with early experiments [162, 163]). The asymmetric deformation behavior in tension/compression can be clarified upon carefully examining the deformed atomistic structures under various loading modes. The observed stress-strain asymmetries can be interpreted as the natural outcome of the very “uni-directional” nature of the deformation twinning. The process of twinning occurs on a very specific set of crystallographic planes as well as along a unidirectionally preferred sense [34] (also known as the “transformation direction”). That is to say, if the resolved shear stress along a certain transformation direction triggers twinning, the 180°-opposite transformation direction is unfavorable for such process as schematically illustrated in Figure 4.3(c). Therefore, under the compression and tension, phase transformation occurs on a different set of plane and direction in Figures 4.3(a) and 4.3(b) insets. As a result, the apparent asymmetries in the transformation stresses and in the overall constitutive hysteresis arise for different loading senses.

Most interestingly, regardless of high strain-rates (inherent in all MD simulations), the predicted transformation stresses are found remarkably close to the typical experimental values [162, 163]. This finding has very important mechanistic implications. Experimentally, high strain rates cause increased hysteresis and eventually loss of superelasticity due to: (a) nucleation of dislocation slip in the austenitic phase [165], and (b) preclusion of deformation-generated heat flow [166]. However, the current molecular dynamics deformation proceeds only via twinning of the B19' lattice with no slip activities whatsoever. Reportedly, pure twinning has very low rate-dependence as opposed to the slip activities [11]. Moreover, the heat flow rate is in synchronization with the deformation rates in the simulations, thereby producing no adiabatic side-effect. In other words, the simulated deformation scenario is mechanistically equivalent to the experimental low-rate constitutive response governed solely by deformation twinning. Therefore, the present transformation stress levels as well as the hysteresis loops are rate-
insensitive (as cross-validated by conducting multiple simulations). Nonetheless, the transformation behavior is observed to be strongly affected by the variation in ambient pressure and temperature.

Figure 4.3(c) – Different twinning systems activated under compression/tension due to the unidirectional nature of deformation twinning, thereby giving rise to the constitutive asymmetries.

External pressure quite strongly modifies the NiTi phase transformation behavior, the origin of which is traced to the crystallography of deformation. The martensitic transformation under the tensile (i.e. positive) hydrostatic stress is demonstrably favored over the compression case as in Figure 4.4(a). This behavior has been documented experimentally [167]; however, the physical clarification thereof has remained elusive so far. Per the present simulations, the pressure effects can be attributed to the twinning unidirectionality as explained earlier in Figure 4.3(c). Inherently, a parent austenitic crystal has 24 sets of planes and directions to create a twin-matrix pair (i.e. the so-called “variants”) during transformation. Various hydrostatic stress states (tension or compression) activate multiple variants in different numbers and senses. Therefore, increasing compressive pressure makes the phase transformation process more and more difficult due solely to the various number of active variants.
Figure 4.4(a) – Variation in $\sigma_{\text{transform}}$ under hydrostatic stress, $\sigma_{\text{hydrostatic}} = \pm \frac{\sigma_{\text{transform}}}{3} P_{\text{external}}$ (externally applied pressure, $P_{\text{external}}$ is positive if compressive while $\sigma_{\text{transform}}$ is positive if tension). Note only absolute magnitude of $\sigma_{\text{transform}}$ is however plotted for the convenience of showing the trend.

Figure 4.4(b) – Temperature dependence of the stress-strain curves for NiTi under compression and tension along $\langle 011 \rangle_{\text{a2}}$ orientation. At higher temperature (> 450 K), the NiTi alloy loses superelastic behavior.
On the other hand, the temperature dependency of the NiTi superelasticity is also an interesting phenomenon. Figure 4.4(b) demonstrates that higher temperatures (250K → 300K → 350K → 400K) raise both the lower and upper stress plateaus of the stress-strain hysteresis. This trend agrees with the earlier experimental observations[168] as well as the thermodynamics of transforming alloys[150]. Curiously, this behavior is quite unlike any conventional alloys, which experience decreasing plastic stress levels with rising temperatures. The temperature effects on the NiTi alloy can be rationalized by the fact that the monoclinic B19' structure (constituting the martensite phase) becomes unstable at elevated temperatures. As a result, the austenite-to-martensite transformation becomes more difficult to occur, necessitating additional applied mechanical forces. Simulation-wise, a gradually decreasing volume fraction of the martensitic crystal is noticed at the end of loading (at 5% strain) at higher temperatures. Moreover, above 450K, the original austenitic B2 crystal starts to behave like a common alloy (i.e. undergoes temperature-dependent plastic deformation without any phase transformation), no longer displaying the superelastic properties.

4.5 Conclusions and Future

In summary, we have captured: (i) the reversible B2 ↔ B19' phase changes affecting the NiTi stress-strain behavior, (ii) the tension/compression asymmetries and the associated transformation stresses and strains, (ii) the correct lattice constants and angles for B2 and B19' phases, (iii) the internal twinning planes of martensite, (iv) the atomistic foundation of the strain-rate, temperature and the pressure dependence. However, the true merit of the current modeling endeavor lies at the vast promise that it holds in the realm of computational materials science. With the exponentially-increasing microprocessor power (following the Moore’s law), today we are in a position to advance the existing computational tools to explore the theoretical territories beyond the experimental capacity. To that end, we offer a milestone in predicting the atomistic origin of the superelasticity using NiTi as the representative SMA. This work essentially lays the groundwork for employing computer simulations to address additional problems such as fracture and fatigue. For instance, discrete lattice simulations can be used to study the crack-tip phenomena under static fracture or fatigue condition as has been shown by the authors previously [65]. The poor fatigue and fracture performances are at present a major setback for
further extending the NiTi SMA usage [169] as demonstrated experimentally. Thus, utilizing important atomistic input, accurate prediction of the continuum damage properties could be established [66], a knowledge which would be invaluable for designing better SMAs in the future. Furthermore, understanding the role of coherent \( \text{Ni}_4\text{Ti}_3 \) precipitates [170, 171] is an ongoing research pursuit, which also can benefit immensely from mesoscale simulations.

**Acknowledgments**

The picture courtesies of the NiTi SMA applications are:

1) Cardiovascular stent -

2) X-Ray image of orthopedic staple –

3) Orthopedic staple –

4) Inlet chevron for jet engine -

5) Tilt-rotor V 22 Osprey aircraft –

6) The V 22 Osprey torque tube pictures are taken from the paper by Mabe et al. (2004)[172].

7) See-through car -

8) Actuator valve –

9) Air flow mixer (climate control) –
Chapter 5 Modeling of NiTi superelasticity in presence of nanoprecipitates

5.1 Abstract

The presence of nano-sized coherent precipitates is well known to have crucial impact on the mechanical behaviors of a broad class of superelastic alloys. As a representative material, the pseudoelasticity of austenitic NiTi alloy in presence of a lenticular coherent Ni$_4$Ti$_3$ precipitate is investigated using atomic scale simulations. We predict the local stress gradient at the matrix-precipitate interface induced by inter-lattice atomic disregistry. The calculated stress distribution conforms to the latest high resolution electron microscopy measurements in the literature. Due to the presence of the local disturbance fields, the preference for activating different martensitic variants, given the uni-directionality thereof, is influenced substantially. The resultant constitutive attributes are thus observed to undergo adjustments in terms of reduced transformation stress, strain and hysteresis in general agreement with experimental literature.

5.2 Introduction

Since their discovery in the early 1950s [173, 174], the superelastic shape memory alloys (SMA) have emerged as one of the most widely used multi-functional materials. In today’s technology-driven world, the usage spectrum for these materials has widened extensively to span bio-medical, aerospace and automotive industries [144, 145]. To meet the specific requirements of modern applications, there exists an ever-mounting need for advancing new alloys with superior superelastic potential. To that end, strategies to fine-tune the microstructural features are being pursued rigorously both on experimental and theoretical grounds. Among the ongoing quests, the introduction of nanometer sized coherent precipitates, via optimizing thermo-mechanical treatments, currently stands as the singular most prospective as well as practical tactic [175, 176]. Microstructurally, a stress-induced reversible transformation between two ordered phases triggers the observed strain recovery under isothermal conditions [162, 168]. The presence of nanoscale precipitates is known to drastically affect the transformation hysteresis, the orientation dependence and magnitude of transformation stress as outlined by Sehitoglu and others [177-180]. So influential is the effect of coherent precipitation that there exist newly
proposed alloys, despite not being ordered crystals, demonstrating enhanced recoverability due solely to the prevalence of precipitates [181-183]. The principal role of these coherent precipitates is to create microscopic stress gradients as a direct consequence of the inter-lattice mismatch, which in turn sets preference for uni-directional transformation variants. Evidently, for the current generation of scientists and researchers, an atomic level understanding of the precipitate-matrix interplay can prove instrumental in forwarding new alloys and service components. However, the present limitations of even most modern experimental techniques preclude in-situ investigation of the physical micromechanisms therein with the atomic-scale resolution. Thus, one can immediately notice the critical need for an atomistic theoretical framework, free of adjusting parameters, to examine the mechanistic foundation for the general constitutive behaviors of precipitated superelastic alloys. The present paper addresses these very concerns with molecular dynamics modeling, particularly utilizing a novel improved pair-potential. Figure 5.1 puts the current study into perspective.

For our objective, we select near equiatomic NiTi alloys as the candidate material for study. The NiTi alloys are one of the most important classes of shape memory alloys (exhibiting pronounced superelasticity above austenite finish temperature, \(A_f\)) both from research and
application perspectives. These alloys are studied extensively via experiments, and long known to demonstrate well-defined Ni$_4$Ti$_3$ precipitation upon suitable thermo-mechanical treatments (Figure 5.2). Early x-ray diffraction studies affirmed that the lattice structure of the Ni$_4$Ti$_3$ precipitate is of rhombohedral type [186, 187]. A coherent boundary is characterized by a high degree of atom-by-atom correspondence between the two adjoining lattices (i.e. the cubic matrix and the rhombohedral precipitate). The coherency of a precipitate is a strong function of its size and shape. Through electron microscopy, the Ni$_4$Ti$_3$ precipitates are typically found to be of oblate spheroid geometry, lying on the {111}$^\text{B2}$ family of planes. Figure 5.2 shows the most commonly observed microstructure morphology with the presence of Ni$_4$Ti$_3$ precipitates. Precipitates with relatively small disc-diameters (typically of 5-10 nanometers) maintain coherent boundaries with the matrix material [188]. Thus, with a substantial inter-lattice registry at the shared periphery, the small coherent precipitates induce elastic disturbances fields along the boundary. The origin of these fields can be attributed to the very discreteness of the neighboring crystals, which consist of atoms as building blocks at the sub-crystal level. The non-continuum nature of the atomistically mismatching lattices (i.e. the austenitic B2 matrix and the rhombohedral Ni$_4$Ti$_3$) [171, 185] gives rise to elastically stretched atoms at the boundary. By contrast, semi-coherent to incoherent precipitates (i.e. with diameter $>>$10 nanometers), are characterized by the presence of a gradually increasing number of interfacial dislocations, which serve to mitigate the interfacial disturbances. Essentially, the sub-nanometer sized precipitates are more influential in terms of generating internal stress/strain fields in the NiTi alloy microstructure. Consequently, the coherent precipitates strongly influence the material preference for the nucleation and the growth of the uni-directional martensitic variants [189] at the micro level. The resultant deformation characteristics are macroscopically manifested in terms of decreased transformation stress, strain, and hysteresis as reported in the experimental literature. Most recently, using high resolution electron microscopy, Tirry and Schryvers [171, 190] have measured the strain gradient near a Ni$_4$Ti$_3$ particle in an austenitic matrix, which quite interestingly demonstrates a non-uniform profile. From theoretical standpoint, validity of any model can be checked against such findings. To develop a full understanding of the chain of micromechanisms contributing to the macroscale behaviors, one ought to delve deeper into the atomic level phenomena as outlined heretofore.
A number of theoretical approaches have been undertaken in the earlier literature to understand NiTi constitutive behaviors. Most of these models based on the principles of thermodynamics, finite element and self-consistent methods address the continuum aspects of the problem [148-150, 191-193]. Most noteworthy approach to address the precipitate problem is the Eshelby-type analysis [194] capturing the internal/external stress/strain distributions for various precipitate geometries. Sehitoglu et al. explained the biased variants due to the precipitate fields with micro-mechanical calculations [185]. However, as pointed out earlier, the fundamental effects of a precipitate disturbance fields originate from the atomistic interactions [177] at the discrete lattice level. To that end, with the advent of superior computer power, the last decade has witnessed a surge in the atomic-scale modeling. Most recently, quantum mechanics based treatments have been forwarded, predicting the elastic anisotropy of the Ni<sub>4</sub>Ti<sub>3</sub> lattice founded on the sub-lattice electronic structure [195]. However, the ab initio endeavors are currently limited to small systems due to a requirement of very high computing capacity [153], and hence unable to capture the mesoscopic deformation scenarios. However, one can resort to mesoscale molecular dynamics (MD) simulations to address much larger crystals consisting of millions of atoms, utilizing pair potential based bonding descriptions.
As of today, most MD simulations on the strain-recovering alloys are confined to NiTi crystals in solutionized conditions (i.e. without precipitates) [155-157, 196, 197]. The primary objective has remained as capturing a broad spectrum of NiTi behaviors. To compare predictions with experimental findings, the principal attributes to be modeled are threefold: (a) the size/shape of stress-strain hysteresis, (b) the martensitic phase transformation (i.e. B2 ↔ B19') at the crystal level, and (c) the stability of individual phases under various thermo-mechanical situations. To that end, the existing literature reports several accomplishments. For example, Farkas et al. [155] proposed a pair potential and addressed the B2 lattice cohesive energy. Lai and Liu predicted the melting behavior thereof based on another potential. Most recently, Zhu and co-workers [157, 159] adapted Lai and Liu’s potential to study martensitic phase transformation both in nanowire and bulk crystal configurations. Similarly, Mutter and Nielaba [158, 160] added modifications to Lai’s original potential to predict temperature/composition dependent transformation behaviors.

While the literature models succeeded in theorizing solutionized crystal behaviors, there still exists a need for studying how the aforementioned attributes are modified by nanoprecipitates. It is important to note that the crystallographic interaction between the matrix (cubic B2 or monoclinic B19') and precipitate (rhombohedral) is rather complex and entails a rather stringent accuracy from the pair-potential. Particularly, it is imperative that the potential be capable of predicting elastic moduli accurately of individual crystal structures. In this work, we use a newly developed Finnis-Sinclair type potential (descriptions provided in next section) to achieve such a feat. We employ several improvement tactics such as fine-tuning the cut-off behavior as well as accurately fitting the cross-interaction energy terms using density functional theory parameters.

We particularly aim to investigate the in-situ atomic-scale mechanism of how a coherent Ni₄Ti₃ particle influences: (a) the martensitic phase transformation and (b) the associated stress-strain response.

The current work [198], based on the NiTi austenite precipitated with lens-shaped Ni₄Ti₃, can be deemed as a necessary and timely contribution. This analysis serves to represent the generic effects of a nanoprecipitate on the superelasticity, and essentially pave the way for extending current modeling approach to address similar class of materials.
5.3 MD simulation procedure

Figure 5.3(a) - The currently modeled crystal configuration. A Ni$_4$Ti$_3$ precipitate of rhombohedral primitive unit cell embedded in a CsCl type (i.e. body-centered) austenitic matrix. The precipitate lies on the $\langle 111 \rangle_{B2}$ plane.

First, we created the austenitic (B2) NiTi single crystals of CsCl type unit cells (with $a_{B2} = 3.021$ Å) using the basis: Ni $\equiv (0 0 0)$ and Ti $\equiv (0.5 0.5 0.5)$. Then, separately a lens-shaped Ni$_4$Ti$_3$ precipitate is constructed, to be embedded in a B2 austenite matrix as shown in Figure 5.3(a). The primitive unit cell of Ni$_4$Ti$_3$ precipitate is of rhombohedral type. The atomic positions for the basis atoms for this unit cell are taken from the X-ray diffraction literature [186, 187]. The lattice variables for the rhombohedral unit cell are: $a_R = 6.704$ Å and $\alpha_R = 113.85^\circ$. As presented in Figure 5.3(b), the oblate-spheroid precipitate is constructed with major and minor axis being 70 Å and 24 Å respectively. It consists of 2681 Ni atoms and 2017 Ti atoms. The minor axis of the precipitate is parallel to the [111]$_R$ crystal direction. The host matrix consists of CsCl-type B2 unit cells with lattice constant, $a_{B2} = 3.021$ Å. The oblate ellipsoid is inserted into the austenitic NiTi B2 matrix with the [111]$_R$ plane parallel to the $\langle 111 \rangle_{B2}$ plane (Figure 5.4), and energetically minimized in molecular statics simulations.
Figure 5.3(b) – The atomistic configuration of the lens-shaped $\text{Ni}_4\text{Ti}_3$ precipitate. The oblate spheroid is constructed with the $(111)_R$ plane parallel to $(111)_B$. The Ni atoms are colored blue so that the precipitated can be differentiated from the matrix.

The energy minimization is conducted using the conjugate gradient energy algorithm. The size of the cubic crystal (with each side being 30 nanometers) is selected based on the convergence of physical observables (e.g. temperature, pressure, kinetic and potential energy) to the system size independence. The crystals represent bulk material (i.e. without any free surface or dangling bonds) as ascertained by enforcing periodic boundary condition on the crystal facets [65, 67]. The number of atoms in a typical simulation supercell was about $1 \times 10^6$, which is sufficiently large to avoid any size- and/or periodicity-induced artifacts [199]. An isoenthalpic-isobaric ensemble was employed for non-equilibrium deformation simulations with a constant number of atoms and zero external pressure. The Nose-Hoover thermostat algorithm is utilized to maintain a steady absolute temperature during each simulation. A Velocity Verlet time-integration scheme was used to conduct the time-step advancement during the deformation simulations. The stress-strain responses reported in this letter are computed based on the concept of virial stress (which is the atomistically equivalent quantity of the conventional Cauchy stress) [5].
5.4 Results

5.4.1 Ni$_4$Ti$_3$ Precipitate and Elastic fields

Figure 5.5(a) – The three dimensional stress profile on a plane going through the disc equator and (b) – The same data demonstrating the stress distribution along a line.

Figure 5.5(a) shows the three-dimensional distribution of the normalized stress profile scanned along the center plane of the precipitate disc. The stress data presented are averaged...
over a very thin-sliced plane parallel to the disc equator in order to capture the correct planar stress distribution. The averaging is conducted with a spatial resolution of $2 \AA$. Figure 5.5(b) presents the $\sigma_{zz}$ stress profile along the centerline of the precipitate as shown. The stress fields surrounding the precipitate are axisymmetric about the z axis, and mirror-symmetric about x and y axes. Therefore, the stress components $\sigma_{yy}$ and $\sigma_{xx}$ follow similar profiles (not shown). The stress components are normalized by the precipitate Young’s modulus, $E_{[111]} = 168$ GPa [195], and the eigenstrain, $\varepsilon_{zz} = 0.029$ mm/mm [200]. It is observed that inside the precipitate the stress is tensile and constant, while a compressive stress peak can be discerned along the austenite-precipitate interface.

![Figure 5.6(a)](image1)

![Figure 5.6(b)](image2)

Figure 5.6 (a) – The 3D stress distribution near the surface of the precipitate on a plane parallel to the disc plane and (b) – The near-surface stress profile.

Figures 5.6(a) and 5.6(b) demonstrate the computed stress distribution on a plane very close to the precipitate surface (parallel to the disc plane) as indicated. The computed near-surface stress distribution appears markedly different than the peripheral one as presented earlier in Figures 5.5(a) and 5.5(b). It can be seen that near the pole (i.e. on top of the disc) the stress is constant and compressive in nature. Farther away from the pole (and also from the surface), the
stress reaches a tensile maximum. On reaching the peak magnitude, the stress then gradually subsides to the bulk level (i.e. zero) with increasing distance from the interface.

The characteristic variation of the near-interface stress distribution in the matrix are in general agreement with the most recent measurements using high resolution electron microscopy by Tirry and Schryvers [171, 190]. Their findings suggested a very similar distribution. A maximum strain is found not at the interface itself, rather a distance away from it, which then gradually diminishes (i.e. similar to the present case). These researchers pointed out that there is a strong deviation of the measured gradient from micromechanical predictions. They attributed the apparent discrepancy to: (a) the assumption of an equal stiffness for the precipitate and the matrix, and (b) the deviation of the real precipitate shape from the ideal lenticular one as presumed in the Eshelby formulations. By contrast, in the current calculations, the generated stress profile is obtained as a direct result of the atomistic misfit, circumventing both constancy of stiffness and the perfect ellipsoid shape assumptions. The currently modeled interface is essentially non-continuum, and hence deviates from the perfect ellipsoid outline upon molecular statics relaxation. Also, the moduli of the cubic matrix and the rhombohedral precipitates are not the same. In other words, the physical conditions of the precipitate in the present simulations are significantly close to that found in nature. Thus, the molecular statics based calculations provide better agreement with the experiments, unlike the micromechanical predictions. Figure 5.7 provides a schematic comparison of the precipitate strain gradient (near its top surface (i.e. as highlighted in Figure 5.5(b) with grey shading) against the normalized distance obtained from current molecular statics simulations, high resolution electron microscopy and micromechanical predictions (based on Eshelby inclusion problem.
Figure 5.7 – A schematic comparison of the strain gradient near the precipitate surface (i.e. as in Figure 5.5(a) and 6(b)) obtained from current molecular statics simulations, high resolution electron microscopy by Tirry and Schryvers [16, 17] and micromechanical prediction. The band representation is due to the uncertainty in calculations.

Next, to understand the role of the precipitate-induced internal stresses, we conduct uniaxial compression simulations for the \(\{011\}_{\text{B2}}\) loading orientation. In the following sections, we refer to the pristine NiTi austenitic single crystal (with no precipitate) as the “un-precipitated” and the one with the embedded Ni\(_4\)Ti\(_3\) ellipsoid as the “precipitated” crystals.

### 5.4.2 Stress-strain Behavior

The presence of the precipitate is found to reduce the transformation stress and strain under \(\{011\}_{\text{B2}}\) compression. Figure 5.8 presents the constitutive responses of the austenitic NiTi single crystals in presence/absence of the Ni\(_4\)Ti\(_3\) precipitate at 300K and 340K temperatures. The reported stress-strain curves are obtained for the crystals deformed to a maximum strain level of 5%. It readily follows that both the un-precipitated and the precipitated crystals demonstrate superelastic stress-strain behavior with hysteresis.
Figure 5.8 — The stress-strain responses of the precipitated and the un-precipitated austenitic crystals.

For the un-precipitated NiTi austenite at 300K, a transformation stress, $\sigma_{\text{transform}}$, of 776 MPa (based on 0.2% offset method) is calculated. In comparison, the precipitated crystal at the same temperature experiences a reduced magnitude of $\sigma_{\text{transform}} = 556$ MPa. At a higher temperature (340K), the $\sigma_{\text{transform}}$ for the un-precipitated austenite is about 787 MPa. For the precipitated crystal at 340K, the $\sigma_{\text{transform}}$ drops to approximately 574 MPa compared to the un-precipitated one at the same temperature.

The maximum transformation strain (i.e. $\varepsilon_{\text{transform}} = \varepsilon_{\text{total}} - \varepsilon_{\text{elastic}}$) obtained for the un-precipitated NiTi is calculated to be 4.20%. For the precipitated case, the maximum $\varepsilon_{\text{transform}}$ drops to 3.18%. These observations are consistent with early experimental literature [162, 185]. The calculated $\sigma_{\text{transform}}$ and $\varepsilon_{\text{transform}}$ magnitudes of the precipitated and un-precipitated NiTi are summarized in Table 3.
The aforementioned observations can be summarized as follows.

(a) The precipitated austenite experiences a reduction in the magnitudes of $\sigma_{\text{transform}}$ and $\varepsilon_{\text{transform}}$ compared to those of the un-precipitated one.

(b) With increasing temperature (300K $\rightarrow$ 340K), both the un-precipitated and the precipitated austenite experiences an increased $\sigma_{\text{transform}}$, and smaller hysteresis.

To unravel the mechanistic origin of the observed constitutive responses, next we analyze the atomic-scale evolution of the phase transformation processes.

Table 5.1 – Calculated values of $\sigma_{\text{transform}}$ and $\varepsilon_{\text{transform}}$ for the precipitated and un-precipitated NiTi austenite compressed $\langle 011 \rangle_{B2}$ in direction.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Temperature</th>
<th>Un-precipitated</th>
<th>Precipitated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\text{transform}}$ (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300K</td>
<td>776</td>
<td>556</td>
<td></td>
</tr>
<tr>
<td>340K</td>
<td>787</td>
<td>574</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_{\text{transform}}$</td>
<td></td>
<td>4.20%</td>
<td>3.18%</td>
</tr>
<tr>
<td>Stress hysteresis, H (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300K</td>
<td>620</td>
<td>502</td>
<td></td>
</tr>
<tr>
<td>400K</td>
<td>503</td>
<td>370</td>
<td></td>
</tr>
</tbody>
</table>

### 5.4.3 Reversible B2 $\leftrightarrow$ B19' Transformation

Figure 5.9 demonstrates the atomistic snapshots of the precipitated NiTi single crystal during various stages of deformation at 300K temperature. The crystal is sectioned in the middle to reveal the Ni$_4$Ti$_3$ precipitate. We observe that the initial elastic straining (from 0% to about 1.8%) does not incur any change in the atomistic morphology of the austenitic bulk, as expected.
The matrix phase remains essentially the same as the initial CsCl-type B2 structure, only elastically compressed along the applied loading direction. When the applied stress level reaches the critical magnitude of 556 MPa, the atoms surrounding the precipitate is observed to undergo considerable re-arrangement, indicating the initiation of B2 → B19' martensitic phase transformation. At this stage, some regions of the austenitic lattice (with CsCl unit cells) start transforming into the monoclinic B19' lattice. This can be verified by a careful inspection of the lattice structure of the transformed portion of the crystal. On a closer inspection, the monoclinic non-orthogonal lattice structure can be clearly discernible. The distinctive features of the B19' unit cell are the lattice variables thereof: $a_{B19'} = 4.606 \ \text{Å}, \ b_{B19'} = 4.386 \ \text{Å}, \ c_{B19'} = 2.699 \ \text{Å}$ and $\alpha_{B19'} = \gamma_{B19'} = 90^\circ < \beta_{B19'} (\approx 96.7^\circ)$. The monoclinic unit cell structure is in stark contrast with the body-centered B2 lattice. Thus, the volumes containing the individual phases can be properly identified upon studying the unit cell structure at higher viewing (atomistic) resolutions. With continued compression (i.e. along the stress plateau), the volume fraction of the B19' martensite increases. The atoms part of the newly transformed B19' lattice also create multiple mirrored strips. This phenomenon is the direct evidence of the “internal twinning” of the B19' martensite. Such twinning process is commonly designated as the “compound” type in the literature, occurring on the {001} family of planes.
The internal deformation twinning process continues until the exhaustion of the austenitic material, which occurs at about 3.8% applied strain. At this point, the precipitated single crystal becomes fully martensitic (of internally twinned B19’ lattice) approximately at 4% applied strain. Continuation of applied loading leads to the elastic straining of the twinned martensite, corresponding to the rising portion of stress-strain curve (from about 4% to 5%). It is worth noting that no discernible atomic re-arrangement within the Ni₄Ti₃ precipitate itself is observed, as expected. The final crystal structure (at 5% applied strain) is characterized by multiple internal twins as can be seen in Figure 5.9. This phenomenon is consistent with early experimental
observation that the presence of precipitate curtails the detwinning process, thus facilitating the elastic straining of martensite [188].

Upon unloading, the deformed crystal consisting of twinned martensite fully recovers the total strain of 5%. Mechanistically, the complete deformation recovery can be attributed to a combination of elastic relaxation and a reverse transformation, $B19' \rightarrow B2$. The atomistic snapshot in Figure 5.9 indicates a gradually reduced volume fraction of twinned $B19'$ during unloading. The volume fraction of the martensitic $B19'$ phase continuously diminishes along the lower stress plateau. The phenomenon suggests that the internally twinned $B19'$ structure is stable only under high stress, and hence the removal of stress triggers the $B19'$-to-$B2$ transformation. Figure 5.10 presents a closer atomistic view near the precipitate. Different variants of the martensite structure can be discerned. The predominance of variant 2 can be attributed to the local fields of the precipitate.

Figure 5.10 – Formation of different variants (of monoclinic $B19'$ type lattice) around the ellipsoid $Ni_4Ti_3$ precipitate (of rhombohedral lattice).
5.5 Discussion

5.5.1 Elastic Fields of Precipitate

The presence of Ni$_4$Ti$_3$ precipitate induces substantial local stress concentration at the interface, which strongly influences the dynamics of the matrix-originated defects (e.g. propagation of twins etc.) during deformation. The origins of these stress disturbances can be twofold: (i) the initial atomic misfit at the matrix-precipitate interface (prior to any applied loads), and (ii) the inter-lattice elastic moduli mismatch, which introduces further stress concentrations during loading. Experimentally, the extent of elastic strain fields around the Ni$_4$Ti$_3$ particle has most recently been quantified using high resolution electron microscopy [171]. On theoretical grounds, the problem of precipitate-matrix interaction has most widely been treated within Eshelby-based modeling framework [194], as the so-called inclusion problem. From a physical standpoint, the current simulations provide an important physical foundation to understand the inclusion-type effects (i.e. generation of local fields under zero farfield stress) from the underlying atomistics.

Micromechanically, the origin of the interfacial elastic fields in an otherwise stress-free crystal is modeled via imposing the so-called eigenstrain. In our model, the Ni$_4$Ti$_3$ precipitate is pre-constructed as the Ni-rich rhombohedral lattice of the lens-shaped geometry. On insertion into the B2 lattice, the lenticular-shaped precipitate creates a coherent periphery with the austenitic matrix, free of any interface dislocation. However, the local atomic coordination, adjacent both to the body-centered matrix and the rhombohedral precipitate, differs significantly. The natural tendency of the atoms at the boundary would be to occupy the space in the most energetically favorable positions, thus minimizing the strong inter-lattice disregistry. Following the energy minimization in molecular statics simulations, the peripheral atoms assume metastable and higher potential energy states compared to those in the surrounding crystal. As a result, these atoms create long-range elastic disturbances, which reach the maximum magnitude very close to the interface (several nanometers), and subside spatially away from the precipitate. Thus, the genesis of the interfacial stress fields can be ascribed to the elastic stretching of atomic bonds at the boundary due to local atomic re-arrangement upon the energy minimization. The current predictions of the stress distributions are especially unique, in that these fields are
generated as a direct outcome of underlying atomistic interactions, unlike the micromechanical approach (where separate mathematical terms are incorporated in the strain formulations to account for the existent disturbance). Moreover, in micromechanical approaches, the constancy of stiffness (both of the precipitate and the matrix) and a perfect lenticular shape are assumed, which is generally not the case in nature. From a physical standpoint, the molecular statics crystal configurations are closest to the real material ones. As a result, the currently computed stress gradient is in good agreement with the experimental ones as measured by Tirry and Schryvers [171].

The lenticular geometry of the precipitates plays a crucial role in generating non-symmetric stress fields. Early quantum mechanical calculations demonstrated [195] that the largest difference in elastic moduli between the cubic and rhombohedral lattices exists along the \( \langle 111 \rangle_c || \langle 111 \rangle_{B2} \). As a result, the precipitates are always formed as oblate spheroids with disc-plane parallel to \( \{111\}_{B2} \) family of planes. Due to the same rationale, a lens-shaped precipitate imposes direction-dependent stress fields. As a result of the directional nature of elastic fields, the stress concentrations near the surface experience a peak magnitude (as predicted by the our simulations as well as measured through experiments [171]). The current results, in conjunction with the experimental ones, serve to establish the strongly directional nature of the precipitate fields. This result also bears important implications regarding the experimentally observed multiple variants of the precipitates discussed as follows.

It is known that there exist 4 types of precipitate variants lying of the \( \{111\}_{B2} \) family of planes. The fields associated with each variant would be essentially identical in nature, and differ in orientation only. Thus, in order to isolate the nature/role of individual precipitates, it suffices to investigate only one variant case. It can be reasonably inferred that the presence of multiple precipitates would lead to a complex network of interacting fields in real materials. The mechanistic influences that these localized stresses would have on the phase transformation preferences would be fundamentally similar to the current observations, varying only in intensity and directionality.

5.5.2 Phase transformation and constitutive behavior

Transformation crystallography
The observed difference in the constitutive responses between the un-precipitated and the precipitated NiTi crystals (Figure 5.8) is principally a result of: (a) the uni-directionality of the phase transformation and (b) how the coherent Ni$_4$Ti$_3$ precipitate fields affect the phase transformation preferences [189]. As observed, the B2 → B19' phase transformation is associated with the process of compound twinning on the \{111\}_B2 family of planes. The local fields would essentially result in a large resolved shear stress (RSS) on some variants and a small RSS for others based on: (i) the loading direction (i.e. tension or compression), (ii) crystallographic orientation of the austenite single crystal, and (iii) the orientation of the precipitate. Therefore, for a particular combination of these factors, different sets of transformation systems would be more readily available for activation. As a result, the presence of the precipitate would ultimately dictate the favored activation of certain variant systems (out of 24 possible ones as per the transformation crystallography). For the current case, we have considered only one combination of the precipitate variant and applied loading direction/orientation. Further investigation of different loading type (i.e. tension) and crystal orientation remains a promising future research. We rationalize the currently observed trends in the levels of $\sigma_{\text{transform}}$ and $\varepsilon_{\text{transform}}$ with regard to the crystallography as dictated by the local fields.

**Transformation stress, $\sigma_{\text{transform}}$**

The predicted $\sigma_{\text{transform}}$ level is found to be reduced due to the presence of the precipitate fields (Figure 5.8 and Table 1), in general agreement with the experimental trends in the literature [162, 185]. This behavior is believed to be an outcome of the local stress fields reinforcing the applied RSS. Thus, a lesser degree of externally applied loads would be required to initiate and sustain the progression of phase transformation on the locally favored variant systems. As a result, the $\sigma_{\text{transform}}$ as well as the overall hardening response is decreased. This observation bears important mechanistic implications for the experimental behaviors as well. In real materials, the precipitates, being dispersed on 4 different \{111\}_B2 planes, form a closely-knitted network of intertwining stress fields. Since there exist 24 different sets of potential variants, some variants would always be locally triggered by a favorable field. By studying one
isolated precipitate case, one can extend the current inferences towards elucidating the presence of multi-particles. Earlier literature noted that the precipitate-induced phase transformation is often accompanied by a transient R phase (of orthorhombic lattice type). However, Nishida and Wayman [201] provided evidence that the R-phase is not an essential precursor to martensitic (B19') transformation. Additionally, Treppmann and Hornbogen [202] noted that R-phase transformation occurs only when the precipitates are widely dispersed with interspersed stress fields, which is not the current case. In the present model, the B2 lattice directly converts into the B19' type martensitic lattice in the form of different martensitic variants (via compound twinning).

**Transformation strain, \( \varepsilon_{\text{transform}} \)**

As the martensitic variants grow, the interfacial misfit would be modified, and so would be the extent of the local fields. Once the B2→B19' transformation is complete, a new form of local mismatch would arise at the boundary between the rhombohedral precipitate and the B19' martensite. The newly generated stress fields now governs the reverse B19'→B2 transformation during unloading, and hence the transformation strain, \( \varepsilon_{\text{transform}} \). Upon unloading, the maximum recoverable strain i.e. the \( \varepsilon_{\text{transform}} \) for the precipitated crystal is lower than the recoverable strain of the un-precipitated crystal (3.18% versus 4.20% respectively as in Table 1). This behavior has also been noted in the earlier experimental literature. The currently observed \( \varepsilon_{\text{transform}} \) reduction can be attributed to the combined effects of: (a) the non-transformability of the Ni$_4$Ti$_3$ rhombohedral lattice, (b) the reverse transformation under the influence of a modified local stress concentration as mentioned earlier, and (c) the inhibition of de-twinning of martensite due to the precipitate, thus promoting easily recoverable elastic straining of martensite during loading [188].

**Temperature effects**

In addition, increasing temperature (300K → 340K) is observed to reduce the \( \varepsilon_{\text{transform}} \) as well as increase the \( \sigma_{\text{transform}} \) levels (Table 1) both for the precipitated and the un-precipitated
alloys. These observations from the simulations are in general agreement with literature experimental findings [168]. The temperature effects can be rationalized on the basis of the thermodynamics of transforming alloys [150]. The twinned monoclinic B19' structure constituting the martensite phase becomes unstable at elevated temperatures. In order to sustain the B2-to-B19' transformation, additional mechanical driving force is needed to be applied. As a result, the $\sigma_{\text{transform}}$ levels continue to increase with rising temperature, quite unlike any conventional alloys (which would undergo decreasing flow stress). Simulation-wise, a gradually decreasing presence of the twinned B19' crystal has been noticed on analyzing the atomistic snapshots. At sufficiently high temperature, the parent B2 austenite behaves like a common alloy (i.e. demonstrates temperature-dependent plastic deformation of the austenite phase), no longer displaying any reversible transformation or the superelastic deformation.

![Graphical representation of stress-strain relationship and crystal response](image)

**Figure 5.11 – Schematic summary of the findings from the current modeling.**
**Strain rate effects**

Furthermore, it is important to note that the typical MD simulations are performed over several picoseconds timeframe. As a result, the deformation proceeds with a rather high strain-rate. However, the currently predicted constitutive responses are quite intriguingly in a reasonable agreement with the earlier experimental levels (conducted at a typical laboratory rate) [162, 163]. Experimentally, very high strain-rate deformation of NiTi austenite is associated with an increased hysteresis and the loss of pseudoelasticity due principally to: (a) the slipping of austenite crystal [165] and/or (b) the adiabatic heat generation [166]. However, none of these phenomena is present in the current molecular dynamics deformations, which proceeds solely via compound twinning. Early literature reports that pure twinning is considerably rate-insensitive unlike dislocation slip [11]. In addition, the heat flow rate during the current simulations was kept in synchronization with the strain rates, thereby producing no adiabatic entrapment of deformation-generated heat. As a result, the simulated deformation scenario is mechanistically very similar to the experimental deformation at the laboratory settings. Due to the foregoing factors, the present levels of the stress-strain curves are not affected by the usually encountered high rate-related artifacts in the MD modeling (as cross-validated by performing multiple simulations at different strain rates).

### 5.6 Conclusions

In the current paper, we have predicted the internal/external stress distribution surrounding a coherent Ni$_4$Ti$_3$ precipitate (with a disc diameter of 7nm). The local fields are generated as a direct outcome of the inter-lattice mismatch between the cubic CsCl-type matrix and the rhombohedral Ni$_4$Ti$_3$ precipitate. Hence, the origin of the precipitate stress fields is captured on a physical ground. Next, the constitutive behaviors of the precipitated austenite are studied against the un-precipitated pristine crystal under the $\langle 011 \rangle_{\beta_2}$ compression. The information obtained from the current model is schematically illustrated in Figure 5.11. A reduced degree of the transformation stress, strain and hysteresis is observed to have resulted for the precipitated alloy. The atomistic origins of the overall constitutive behaviors have been correlated with: (a) the unidirectionality of the phase transformation (i.e. internal twinning of
B19’ lattice), (b) the local stress fields setting preference for the activation of different variant systems, and (c) the thermodynamics of the transformation alloys. In addition, the principal merit of the current modeling endeavor is highlighted as unraveling the atomic-scale roles of a coherent precipitate in improving the NiTi superelastic traits. The successful modeling the precipitate problem implies important future extension of the model.

The feasibility of the current atomistic simulations also suggests considerable promise for future research [203]. For example, problems such as fracture and fatigue behaviors of SMAs remain major issues today to be addressed. Atomistic simulations can most effectively be employed to probe into the cracking phenomena under static and/or cyclic loading conditions [204]. The poor fatigue and fracture performances are at present a major setback for further extending the NiTi SMA usage [169] as demonstrated experimentally. Thus, utilizing atomistics, mesoscale defect properties such as Peierls stresses could be predicted [154], which in turn could be used in continuum damage evaluation [66, 205, 206]. Such knowledge would be helpful for designing better SMAs in the future.
Chapter 6 Summary and Future work

6.1 Summary

On the whole, the present thesis contributes to the modeling of materials mechanical properties using atomistic simulations. The materials of interest were fcc alloys, namely, Ni/Co base alloys and shape memory NiTi alloys. A combination of crystal level simulations (molecular dynamics and density functional theory) and continuum mechanics has given rise to accurate prediction of critical resolved shear stresses (CRSS) specific material microstructure. An assortment of experimental techniques is employed to verify the theoretical results. Uniaxial tension/compression tests on single- and poly-crystals samples (of Co-33%Ni and nanotwinned NiCo alloys respectively) were conducted to determine the experimental magnitudes of CRSS.

For the study of NiTi, experimental literature was used to extensively compare the simulation results therewith. A reasonably good agreement is established between the simulations and the experimental discoveries. What such an agreement implies is that the future of materials design benefit hugely from such mesoscopic simulations. Specific to each chapter, we have addressed the following.

In Chapter 2, we have discussed the atomic, continuum and mesoscale treatments of CoNi alloys mechanical properties. Tensile/compressive constitutive responses thereof have been studied using a number of specimens. Extensive characterization on the deformed microstructure was employed to unequivocally establish the predominant deformation mechanism – slip and/or twinning. Both crystal orientation and loading direction have been demonstrated to play a role in dictating the deformation mechanism. The observed experimental discoveries subsequently were rationalized using atomistically calculated fault energetics and elastic theory of dislocations.

In Chapter 3, we have studied polycrystalline NiCo alloys of four compositions whose pre-deformation microstructure was found to be characterized by a prevalence of nano-sized stable annealing twins. Upon uniaxial tests of different Ni-Co alloys, a trend in terms of the respective flow responses was established. The flow response was found to be a non-uniform function of composition. The observed experimental trends were then found to be linked with composition-
dependent fault energetics at the discrete lattice level. Particularly, the role of coherent twin boundaries were investigated in details with molecular dynamics simulations. Various slip transfer mechanisms that are likely to occur during the deformation of the polycrystalline NiCo alloys were identified. The scenarios under which such reactions would transpire is discussed from a mechanistic standpoint. The energy barriers associated with individual slip transmission mechanisms are quantified. A mesoscale model based on the Peierls-Nabarro concepts is forwarded to convert the atomistically computed energy values into mesoscale frictional stresses. The computed stresses were eventually normalized into CRSS values that could be directly compared with the experimentally determined ones. A good agreement between the predicted stresses and the experimental ones lends credibility to the proposed theory.

In Chapter 4, utilizing a newly developed pair-potential, we have performed extensive molecular dynamics simulations to study the constitutive responses and the phase transformation behaviors in near-equatomic NiTi alloys. The stress-strain responses were found to be superelastic i.e. the material was demonstrated to have completely recovered its deformation (of 5% engineering strain) upon unloading. The origin of the superelastic strain recover was linked to a reversible crystal transformation between the cubic B2 (austenite) and monoclinic B19' (martensite) phases.

In Chapter 5, the role of nano-sized coherent precipitates on the superelastic traits of the NiTi alloys are explored. The local stress gradient at the matrix-precipitate interface as induced by inter-lattice atomic disregistry is computed from the atomistic relaxation simulations. The calculated stress distribution is found to agree with the latest high resolution electron microscopy measurements in the literature. On studying the crystallographic evolution during the deformation, the presence of the local disturbance fields surrounding the precipitate is found to create preference for activating different martensitic variants. Due to the very uni-directional nature thereof, the stress-strain response of the precipitated austenitic crystal is found to be influenced substantially. The presence of the precipitate resulted in the reduced transformation stress, strain and hysteresis, a trend which is in general agreement with experimental literature.
6.2 Future work

On the basis of the systematic methodology employed in this thesis, interesting research avenues are expected to be opened up. In essence, what we have shown is that atomic scale simulations can most effectively be scaled to the continuum level deformation behaviors. In doing so, we have avoided using phenomenological constants (i.e. requiring a number of fitting constants for accurate constants). In other words, the primary impact of the current thesis can be deemed as showing a path to create physically based models. To be more specific, we list some promising future issues that could be solved utilizing current approach. We also discuss how the current procedure itself could further be fine-tuned to accommodate existing complexities in materials design.

- One of the most important applications of the predicting mechanistically based CRSS would be to analyze damage behavior. The fracture and fatigue studies of materials have remained a largely phenomenological area. The determination of damage metrics is also experimentally an expensive and strenuous job. Using atomistic simulations, one can explore the crack tip damage mechanisms. Particularly, the fault energetics associated with the near-tip micro-mechanisms can be captured both qualitatively and quantitatively.

- Currently, we have demonstrated the feasibility of atomistic methods for the case of fcc lattice only. It is well known that another important class of materials which are most likely to undergo twinning deformation are the hexagonal closed packed (hcp) materials. These materials are technologically important ones whose current applications span from aerospace to petrochemical industries. Employing physically based models to understand the inherent deformation propensity from the discrete lattice standpoint would certainly be worth pursuing.

- From the viewpoint of further fine-tuning the current methods, one can incorporate the rate and temperature effects therein. Currently, we have demonstrated the temperature- and/or strain rate-independent behaviors. Inclusion of the sensitivity of these important variables would be a major improvement.
Appendix A

Figure A.1

Figure A.2

Figure 2.A1 reports the applied (global) stress-strain ($\sigma - \varepsilon$) curve for polycrystalline Co-33%Ni for small strain. The flow stress demonstrates raggedness to some extent. As no texture preference was found in the polycrystalline specimen, Taylor’s assumption was used to extract the critical resolved shear stress ($\tau_{\text{CRSS}}$) for plastic flow initiation using the following equation.

$$\tau_{\text{CRSS}} = \frac{\sigma_{\text{yield}}}{M}$$

(27)
Where, $\sigma_{yield}$ is the macroscopic yield strength (0.1% offset) from the $\sigma - \varepsilon$ plot ($48 \pm 3$ MPa) and $M$ is the so-called Taylor factor (for isotropic fcc materials, $M = 3.06$). Using this method, $\tau_{CRSS}$ is measured to be $16 \pm 1$ MPa. This result is compared with single crystal experimental data (from $\langle 123 \rangle$ tension and $\langle 111 \rangle$ compression) on $\tau_{CRSS}$ as well as the predicted value as compared in Figure 2.19. It can be concluded from this comparison that the polycrystalline yields corresponds to dislocation slip nucleation. Subsequent flow proceeds in the form of forest dislocation hardening for which the critical stress level is determined to be $25 \pm 6$ MPa as listed in Figure 2.19. We note that twinning in the polycrystalline sample is not evidenced for the initial stage of plasticity (as shown in the TEM images in Figure 2.A2 and 2.A3). However, the raggedness of the flow curve in Figure 2.A1 indicates that twinning may occur at higher strain levels in favorably oriented grains (as the twinning Schmid factor exceeds that of dislocation slip in these grains). For the current modeling considerations, we limit our predictions to initial plasticity (corresponding to the material yield) and post-yield secondary plasticity (immediately following). Hence, latter stage of flow in the polycrystalline material (possibly contributed by twinning in addition to slip) is not investigated (experimentally or theoretically).
Appendix B

Figure B.1 – Two crystal blocks are rigidly shear-displaced on the (111) plane.

Figure B.1 illustrates the crystal configuration for calculating the $\gamma$ surface in DFT simulations. Two crystal blocks adjoining each other on the (111) slip plane are rigidly sheared by the displacement vector, $\vec{u} = \vec{u}_{\{110\}} + \vec{u}_{\{112\}}$. The $\gamma$ energy corresponds to the energy differential between the sheared structure and the original one ($E_{\text{sheared}} - E_{\text{perfect}}$) as normalized by the area ($A$) as in Equation (28) [127].

$$\gamma = \frac{E_{\text{sheared}} - E_{\text{perfect}}}{A}$$  \hspace{1cm} (28)
Figure C.1 – GSFE curve calculated during the actual glide of an extended dislocation in molecular dynamics.

Figure C.1 illustrates the procedure to calculate the γ surface in molecular dynamics simulations during the glide of a dislocation. A row of “tracing atoms” are selected for constantly monitoring the differential between bulk and slip-influenced potential energy, \( \Delta E = E - E_{\text{bulk}} \). The dimensions of the tracing atomic area (w times l) are chosen carefully to ensure convergence of the calculated fault energy levels (which occurs at larger l and smaller w values [67]). The fault energy γ equals to the ratio, \( \frac{\Delta E}{w \ell} \) [127]. The insets in Figure 3.B1 show the location of the extended dislocation with respect to the tracing atoms, and the corresponding γ levels. This method can be used in computing the γ_{us} near a local stress concentration (e.g. a twin boundary, residual dislocation etc.).
Appendix D

Constructing pair-potential

Figure D.1 – The concept of pair-potential in MD simulations. The metallic bonding is reproduced by considering the functions, ρ, φ and F.

Central to the concept of pair potential is the notion that the positively charged atomic nuclei interconnect with each other via homogeneously distributed electron clouds (Figure D.1). This very special electronic bonding landscape can be mathematically re-constructed by considering (i) the pair-wise potential energy, \( \phi_i = \phi_i (r_i) \) representing the close-range repulsive and long-range attractive forces, (between atoms i and j separated by \( r_{ij} \)), and (ii) the embedding energy functional, \( F_i \) which implies energy required to embed atoms into an electronic cloud (as contributed by all other atoms of the system). The total electron density, at the site of a certain atom, i, is approximated by a simple linear superposition of electron cloud contributions of all neighboring atoms, j i.e. \( \rho_i = \rho_i (r_{ij}) \). Thus, the total potential energy surface can be represented by the Equation (29):
where \( i \) and \( j \) represent atoms; \( \phi_{ij} = \phi_{ij}(r_{ij}) \) is the interatomic potential (\( r_{ij} \) being interatomic spacing); \( F_i \) is the embedding energy which in turn is a functional of the electron density function, \( \rho_{ij} = \rho_{ij}(r_{ij}) \). For NiTi binary alloy, one ought to incorporate the following functions to fully describe the bonding energy landscape: \( F_{Ni}, F_{Ti}, \rho_{Ni-Ni}, \rho_{Ti-Ti}, \rho_{Ni-Ti}, \phi_{Ni-Ni}, \phi_{Ti-Ti} \) and \( \phi_{Ni-Ti} \).

The terms representing the pure species are accurately modeled by Mishin and co-workers \[207, 208\], which only leaves the inter-species \( \rho_{Ni-Ti} \) and \( \phi_{Ni-Ti} \) to be established as follows.

Within a cut-off distance of 0.52 nm (which incorporates fourth nearest neighbors in B2 lattice), both \( \rho_{Ni-Ti} \) and \( \phi_{Ni-Ti} \) are modeled as cubic spline of the form:

\[
\rho(r) \text{ or } \phi(r) = \sum_{\alpha} a_{\alpha} (r_{\alpha} - r)^3 H(r_{\alpha} - r)
\]  

where \( \alpha \) denotes a particular knot; the Heaviside function, \( H(r - r_{\alpha}) = 1 \) for \( r - r_{\alpha} \geq 0 \) and \( H(r - r_{\alpha}) = 0 \) for \( r - r_{\alpha} < 0 \). The coefficients \( a_{\alpha} \) are determined at known \( r_{\alpha} \) values up to the cut-off radius by optimization method. First an objective function (\( Z \)) considering the fitting weight \( (w_{\beta}) \) is defined, to be minimized:

\[
Z = \sum_{\beta} w_{\beta} (Y(r, a_{\beta}) - Y_{\beta a})
\]  

(31)
where $Y_{\beta 0}$ is the target value (e.g. elastic constant, energy from experiments and DFT predictions) and $Y(r, a_\beta)$ is fitting value with an adjustable $a_\beta$. With $w_\beta$ set manually, $a_\beta$ values corresponding to the minimized $Z$ is determined and plugged back in Equation (30), thus, numerically re-constructing the $\rho_{\text{Ni-Ti}}$ and $\Phi_{\text{Ni-Ti}}$ functions. Using the foregoing methodology, the target database to be fitted include: (a) the energy versus volume relations for B2, B19, B19', BCO (body-centered orthogonal) crystals and imaginary compounds, B1-NiTi, L1$_2$-Ni$_3$Ti and L1$_2$-NiTi$_3$, as obtained from Quantum Espresso based predictions [209] (b) experimentally determined B2 elastic constants ($C_{11}$, $C_{12}$ and $C_{44}$) [210], and (c) cohesive energies for pure species [207, 208]. Reasonably good agreement with DFT predictions and experiments (where available) is observed, for example, in terms of elastic moduli of both B2 and B19' crystals (Tables D.1 and D.2). The accurate modeling of the elastic moduli has contributed to the realistic predictions (comparable to experimentally observed ones) of the stress-strain hysteresis loops.

Table D.1 – Comparison of elastic constants (in GPa) of B19' from the current potential, literature potential (by Zhong et al. [157]), and DFT predictions [211].

<table>
<thead>
<tr>
<th>Elastic constants (GPa)</th>
<th>B19'</th>
<th>Current potential</th>
<th>Literature DFT [211]</th>
<th>Literature potential [157]</th>
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<tr>
<td>$C_{11}$</td>
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<td>209</td>
<td>692</td>
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<tr>
<td>$C_{12}$</td>
<td>72</td>
<td>114</td>
<td>400</td>
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<td>326</td>
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<tr>
<td>$C_{23}$</td>
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<td>139</td>
<td>222</td>
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<td>$C_{55}$</td>
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<td>23</td>
<td>215</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Current potential</td>
<td>Literature experiment [210]</td>
<td>Literature potential [157]</td>
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</tr>
<tr>
<td>--------------</td>
<td>-------------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td></td>
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<tr>
<td>C11</td>
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<td>162</td>
<td>205</td>
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</tr>
<tr>
<td>C12</td>
<td>122</td>
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<td>136</td>
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</tr>
<tr>
<td>C44</td>
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</table>

Table D.2 – Comparison of elastic constants (in GPa) for B2 crystal from current potential, literature potential (by Zhong et al. [157]), and experiment [210].

**Conducting MD simulations**

The present simulations were performed using the open-source software LAMMPS [212] (*Large-scale Atomic/Molecular Massively Parallel Simulator*) ([http://lammps.sandia.gov](http://lammps.sandia.gov)). The atomic configuration viewer Ovito [213] ([http://ovito.org](http://ovito.org)) was used to reveal the crystal phase transformation processes.

On defining the atomic positions, the crystal structure is first energetically minimized via the conjugate gradient energy algorithm. An isoenthalpic-isobaric ensemble was employed for non-equilibrium deformation simulations with a constant number of atoms and zero external pressure. The Nose-Hoover thermostat algorithm is utilized to maintain a steady absolute temperature during each simulation. A Velocity Verlet time-integration scheme was used to conduct the time-step advancement during the deformation simulations. Further details of MD algorithm adopted for the ensemble averaging can be found at [214].
References


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