ATOMISTIC SIMULATION STUDY OF THE EFFECTS OF POINT DEFECTS ON THE INCEPTION OF PLASTIC DEFORMATION IN METALS

By

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ATOMISTIC SIMULATION STUDY OF THE EFFECTS OF POINT DEFECTS ON THE INCEPTION OF PLASTIC DEFORMATION IN METALS

Abstract

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Atomistic simulations have been used to study the effect of various types of point defects on the mechanical response of FCC single crystals in nanoindentation and uniaxial tests. To study the effect of spatial distribution of defects in nanoindentation testing, various point defects were located in different relative positions to the indenter. When the defect position was close to the regions of high shear stresses the nucleation of dislocations was related to the location of the defect; however homogeneous nucleation of dislocations was also observed for defect-containing crystals. The effect of the point defects was independent of the indenter size, and the applied pressure needed to initiate plasticity, when compared to defect-free crystals, was a reduction of approximately 10%, 20%, 20% and 50% for a single vacancy, di-vacancy, self-interstitial atom and stacking fault tetrahedron (SFT), respectively. The stochastic nature of the pop-in loads was further explored for different orientations using molecular dynamics and complementary nanoindentation experiments on (100), (101) and (111) single crystals of copper and Ni200. The sensitivity of the crystal to the presence of internal structural defects depends strongly on its crystallographic orientation. The simulations suggest that the first event observed experimentally may not correspond to the first plastic deformation event. Anisotropy effects were also studied
for various orientations in uniaxial tests in the presence of a centered SFT. Both the normal stresses to the slip plane and the relative values of Schmid factor in compression and tension affect the observed compression/tension yield asymmetry. The reduction in yield stress was found to be larger in compression than in tension for almost all orientations. The simulations suggest that compression is a more reliable experimental tool for studying the effect of structural defects on the mechanical behavior of the FCC crystals, while tension may be more useful to determine size effects in deformation. Finally, simulations at high temperatures showed that internal defects are capable of reducing the temperature sensitivity of yielding in various crystal orientations, especially when the stress field is mainly compressive like those in nanoindentation and compression tests.
# TABLE OF CONTENTS

ACKNOWLEDGMENT.................................................................................................................. iii

Abstract ........................................................................................................................................ v

Contents ......................................................................................................................................... vii

List of tables .................................................................................................................................. x

LIST OF FIGURES ......................................................................................................................... xi

Chapter 1: Introduction ................................................................................................................. 1

CHAPTER TWO: Effect of vacancies on incipient plasticity during contact loading ............... 12

2.1 Introduction ............................................................................................................................ 12

2.2 Experimental and modeling procedures ................................................................................. 15

2.3 Results and discussion .......................................................................................................... 19

2.4 Conclusions ............................................................................................................................ 34

CHAPTER THREE: The impact of a variety of point defects on the inception of plastic
deformation in dislocation free metals ......................................................................................... 36

3.1 Introduction ............................................................................................................................ 36

3.2 Modeling details ....................................................................................................................... 38

3.3 Results and discussion .......................................................................................................... 39

3.4 Conclusions ............................................................................................................................ 44

CHAPTER FOUR: Inception of plasticity in copper single crystal in the presence of stacking
fault tetrahedra .......................................................................................................................... 46
4.1 Introduction ........................................................................................................................................46

4.2 Modeling ...........................................................................................................................................49

4.3 Results and discussion ..........................................................................................................................50

4.4 Conclusions .......................................................................................................................................56

CHAPTER FIVE: The effect of crystal orientation on the stochastic behavior of dislocation nucleation and multiplication during nanoindentation ........................................................................57

5.1 Introduction ........................................................................................................................................58

5.2 Methods ...........................................................................................................................................61

5.2.1 Modeling ......................................................................................................................................61

5.2.2 Experiments ..................................................................................................................................62

5.3 Results and discussion ..........................................................................................................................64

5.4 Conclusions .......................................................................................................................................77

CHAPTER SIX: Crystal orientation effect on dislocation nucleation and multiplication in FCC single crystal under uniaxial loading ..................................................................................80

6.1 Introduction ........................................................................................................................................80

6.2 Modeling ...........................................................................................................................................84

6.3 Results and discussion ..........................................................................................................................85

6.3.1 Asymmetry in crystals with existing structural defects ................................................................85

6.3.2 Plastic asymmetry in crystals with existing structural defects ......................................................93

6.4 Conclusions .......................................................................................................................................103
CHAPTER SEVEN: TEMPERATURE EFFECTS IN THE PRESENCE OF THE POINT DEFECTS ........................................................................................................................................... 105

7.1 Introduction ................................................................................................................................................................. 105

7.2 Modeling ............................................................................................................................................................................ 107

7.3 Results and discussion...................................................................................................................................................... 109

7.3.1 Nanoindentation ........................................................................................................................................................... 109

7.3.2 Uniaxial loading: .......................................................................................................................................................... 111

7.4 Conclusions ...................................................................................................................................................................... 120

CHAPTER EIGHT: SUMMARY AND FUTURE WORK ........................................................................................................... 122

Bibliography ........................................................................................................................................................................ 127
Table 1- Statistical analysis of pop-in data for all three orientations for each indenter tip. Number of points represents the number of pop-ins observed, the mean is the mean pop-in load for each data set. .................................................................................................................................................. 72

Table 2- P-values for each combination of orientations determined from Wilcoxon-Mann-Whitney rank sum tests. Values lower than 0.05 indicate a greater than 95% probability that the data sets are statistically unique. .............................................................................................................................................. 72
LIST OF FIGURES

Fig. 2-1. Experimental load-displacement curves for four samples, two each with high and low vacancy concentrations. The indenter radius is 250 nm. The dash-dot line in the inset showing elastic loading represents a Hertzian fit to sample number 1 with low vacancy concentration. .. 20

Fig. 2-2. Atomistic configuration of a perfect crystal in 110 plane showing the position of nucleation site of dislocations, atoms are color coded according to centro-symmetry parameter, atoms in perfect lattice are not shown................................. 22

Fig. 2-3. Load-displacement curves, obtained by the simulations, showing the onset of plasticity for a perfect crystal and crystals with a single vacancy at the center of different layers, the indenter radius is 4 nm................................................................. 23

Fig. 2-4. Load-displacement curves and atomic snapshots of particular points during the downward motion of the indenter with the radius of 4 nm; (a) single vacancy at the 4th layer, with x: -7.185 Å and z: 0, A: nucleation from the vacancy, B: propagation to the surface; (b) single vacancy at the 7th layer, with x: -5.748 Å and z: 0, A: before migration, B: during migration, C: vacancy migrated to the 4th layer, D: nucleation from the vacancy, E: propagation to the surface................................................................. 24

Fig. 2-5. Atomistic configurations of several stages of nanoindentation in the presence of a single vacancy on the 7th layer, at x: -5.748 Å, z: 0. The atoms are color coded according to the mean stress value. The tip radius is 4 nm. Here, vacancy migration is clear. Atoms under tensile mean stress are marked with (+) sign. ........................................................................................................ 25

Fig. 2-6. Variations of contact pressure ratios for different positions of a single vacancy along [112] and [110] at different layers for indenter radius of 4 nm, (a) vacancy is along [112] (in 110 plane), (b) position on [112] is fixed while vacancy is translated along [110]. Contact pressures are normalized by the value of the contact pressure at the displacement burst of the perfect crystal........................................................................................................ 26

Fig. 2-7. Equivalent crystallographic directions in the 6th layer shown in the same line pattern; along similar line pattern, vacancies with equal distances to the indentation axis lead to equal yield forces; dotted lines show the region in which a single vacancy in the 6th layer can affect the onset of plasticity, small filled circles show vacancy locations corresponding to the smallest yield force. The dashed circle shows the approximate size of the region at which a single vacancy can impact the material yielding. The radius of this circle and the tip radius are 1.74 nm and 4 nm, respectively. ........................................................................................................ 27
Fig. 2-8. Yield loads at the onset of plasticity for randomly distributed vacancies with different concentrations. Two dashed lines indicate the yield loads for the perfect crystal and the crystal with a single vacancy in a critical spot (at 6th layer, with x: -4.311 Å and z: 0). The indenter radius is 4 nm.

Fig. 2-9. Variations of contact pressure ratios for different positions of a single vacancy along [112] and [110] at different layers for indenter radius of 6 nm, (a) vacancy is along [112] (in 110 plane), (b) position on [112] is fixed while vacancy is translated along [110]. Contact pressures are normalized by the value of the contact pressure at the displacement burst of the perfect crystal.

Fig. 2-10. Modeling (a) and experimental (b) results showing the effect of indenter size on the cumulative distributions of the contact pressure ratios for the Ni single crystal. Experimental data were obtained for specimens with a high concentration of vacancies. The maximum pressures used to obtain these ratios for modeling and experimental data are, respectively, 21.3 GPa and 22 GPa.

Fig. 2-11. Load-displacement curves and atomistic visualization of particular points during the downward motion of the indenter with the radius of 6 nm; (a) single vacancy at the 4th layer, with x: 15.807 Å and z: 0, A: nucleation of dislocation loops from the vacancy under the surface, B: separate nucleation, burst point, C: collision of two separate dislocations, D: propagation to the surface; (b) single vacancy at the 12th layer, on x: 0 and z: 9.956 Å, A: nucleation from the vacancy, B,C: propagation to the surface; (c): single vacancy at the 6th layer, x: 12.933 Å and z: 0, A: nucleation of dislocation loops from the vacancy under the surface, B: propagation to the surface.

Fig. 2-12. Atomistic configurations showing the effect of indenter size on the nucleation mechanisms at onset of plasticity for a crystal with a single vacancy at the 12th layer, x: 0 and z: 9.956 Å, (a) indenter size of 4 nm, (b) indenter size of 6 nm.

Fig. 3-1. Load-displacement curve with snapshots of atomistic configuration at several stages of nanoindentation including the nucleation of dislocations from the defect and the onset of plasticity (marked with *). The defect is a di-vacancy positioned on the 12th layer away from the indentation axis. The position of the di-vacancy (black solid dots) and also the indentation axis (x symbol) are shown at the corner of the graph.

Fig. 3-2. Percentage of weakening effect as a function of normalized depth of a single vacancy (a) and a di-vacancy (b) located on the indentation axis for indenter radii of 6 nm, 10 nm and 15 nm.
Fig. 3-3. Percent reduction in the yield pressure at the onset of plasticity versus indenter size for a single vacancy, a di-vacancy, a SIA and a SFT in copper single crystals ........................................... 42

Fig. 3-4. Variation of the contact mean pressure at the onset of plasticity under the indenter as a function of film thickness for a perfect crystal (triangles), a crystal with a di-vacancy in a critical spot at the 12th layer (circles) and a crystal with a SFT of size 10 centered at the 15th layer on the indentation axis (squares). Predictions of pressures using Eq. 1 are shown using dash-dotted lines for di-vacancy and dashed lines for SFT ................................................................. 44

Fig. 4-1. Maximum percent reduction in the yield pressure (contact pressure at the onset of plastic deformation) in nanoindentation tests on copper single crystals for different point defects ................................................................................................................................................ 48

Fig. 4-2. Atomistic configurations of the simulation box before (a) and after (b) relaxation showing the formation of a downward SFT from a triangle of vacancies in (111) plane. Atoms are color coded using centro-symmetry parameter ........................................................................................................... 50

Fig. 4-3. Load-displacement curves for perfect crystal and crystals having upward and downward SFT. Insets show the shape of each SFT. Indenter radius is 6 nm and SFTs are centered on the indentation axis at the 9th layer from the surface ........................................................................................................... 51

Fig. 4-4. Atomic configurations of deformation mechanisms for copper single crystal having upward (top row) and downward (bottom row) SFT centered on the indentation axis at the 12th layer from the surface; (a-d): initial upward SFT, unzipping the SFT, propagation of dislocations toward bottom surface, propagation of dislocation toward the top surface; (e-h): initial downward SFT, unzipping the SFT, propagation of dislocations toward the top surface. Arrows show the directions of dislocations movement ........................................................................................................................................ 51

Fig. 4-5. Variation of contact pressure ratio at the onset of plasticity vs. the depth of the center of the stacking fault tetrahedron for upward and downward orientations ........................................................................................................... 53

Fig. 4-6. Atomic snapshots showing the deformation mechanisms for the upward SFT centered at (a) 9th, (b) 12th, and (c) 15th layer ........................................................................................................................................... 54

Fig. 4-7. Load-displacement graphs of nanoindentations on (111) copper single crystal including SFT centered on the indentation axis at different layers; indenter radius is 15 nm ........................................................................................................... 55

Fig. 5-1. MD Load-displacement curves for nanoindentation tests on perfect crystals with different orientations ........................................................................................................................................... 65
Fig. 5-2. MD load-displacement curves in nanoindentation tests on perfect crystals and crystals with an SFT in different layers centered close to the indentation axis for a. (100), b. (110) and c. (111) orientations ................................................................. 66

Fig. 5-3. Atomistic snapshots of MD simulations of nanoindentation tests presenting deformation mechanisms in the presence of an SFT under the indenter in crystals with different orientations, a. (100)(a1: initial configuration, a2: homogeneous and heterogeneous dislocation nucleation from bulk and SFT, respectively, a3: dislocation propagation to the surface, a4: surface-dislocation interactions, formation of the dislocation lock); b. (110)(b1: initial configuration, b2: migration of SFT to the surface in (110) direction, vacancy formation at the SFT vertices, b3: dislocation nucleation from SFT in its way to the free surface, b4: dislocation propagation to the free surface, b5: dislocation images including the SFT’s and the image of other dislocations propagated into the crystal); c. (111)(c1: initial configuration, c2: unzipping SFT, c3: dislocation propagation from SFT in three {111} planes; c4: surface-dislocations interactions, c5: triangle image of dislocations on the free surface; atoms are colored according to the centro-symmetry parameter) ........................................................................................................ 68

Fig. 5-4. MD load-displacement curves of nanoindentation on (110) crystal with SFT in 50th layer from the surface centered on different locations in x axis, atomistic snapshots of points 1, 2, 3 and 4 are shown in Fig 5. Points 1 and 2 are on the solid curve and points 3 and 4 are on the dashed curve.......................................................................................................................... 70

Fig. 5-5. Atomistic snapshots of points 1, 2, 3 and 4 on the presented MD curves in Fig. 4. At point 1 complete annihilation of SFT happens when it is located on the indentation axis (a,b). The large burst occurs at a larger indentation force at point 2 where more dislocations hit the free surface (c). When the SFT is off-axis, at point 3, dislocations nucleate and propagate in a plane which intersects the SFT path through the surface (d,e). After the first burst more dislocations are formed (f) under the indenter in comparison to the case with the on-axis SFT......................... 71

Fig. 5-6. Experimental results showing cumulative distributions of the pop-in events vs. pop-in loads for (a) 100 nm radius tip, and (b) 1300 nm radius tip for different crystal orientations ..... 73

Fig. 5-7. MD results showing the effect of an SFT on the mechanical response of (100) single crystal in nanoindentation test by manipulating minor and major events; (a) perfect crystal(a1: homogeneous dislocation nucleation inside the bulk, a2: dislocation propagation to the surface, formation of dislocation lock, a3: dislocation propagation and release from the lock, a4: more dislocation interactions under the indenter leading to hardening); (b) a crystal with an SFT at the 21st layer on the indentation axis(b1: heterogeneous dislocation nucleation from SFT, b2: dislocation propagation to the free surface, formation of dislocation lock, b3: dislocation propagation in another {111} plane from SFT, b4: images of the dislocations already formed in
the crystal on the free surface); (c) a crystal with an SFT at the 25th layer on the indentation axis (c1: homogeneous and heterogeneous dislocation nucleation from bulk and SFT, respectively, c2: dislocation propagation to the surface, c3: surface-dislocation interactions, formation of the dislocation lock, c4: dislocation release from lock and more dislocation interactions leading to hardening); atoms are color coded according to centro-symmetry parameter.

Fig. 6-1. Stereographic triangle showing the investigated orientations. Uniaxial loading is applied along the shown crystal orientation (y axis).

Fig. 6-2. Representative stress-strain curves for compression (solid line) and tension (dashed line) tests on orientations: (a) [001], (b) [405], (c) [417] and (d) [2,1,10]. For both loading directions positive strain and stress are shown to ease recognizing different behavior for each loading direction.

Fig. 6-3. Contour plots of the compressive (a) and tensile (b) yield stresses for a perfect crystal as a function of crystal orientation.

Fig. 6-4. Contour plot of the yielding compression/tension (C/T) asymmetry ratio for a perfect FCC crystal as a function of orientation.

Fig. 6-5. Contour plots of (a) normal factor (NF), (b) Schmid factor (SF) in compressive loading, (c) Schmid factor in tensile loading, and (d) Schmid ratio being the ratio of the compressive Schmid factor to tensile Schmid factor in inverse pole figure.

Fig. 6-6. Contour plot of C/T asymmetry ratio in NF-Schmid ratio coordinate system as a function of crystal orientation.

Fig. 6-7. Stress-strain curves for (a) [417] and (b) [7,5,10] orientations under compression and tensile loading for perfect crystals and crystals with an SFT at the center. The C/T asymmetry ratio is lowered for [417] orientation and it is reversed for [7,5,10] orientation.

Fig. 6-8. Contour plots of the compressive (a) and tensile (b) yield stresses for a crystal with centered SFT, as a function of crystal orientation.

Fig. 6-9. Contour plot of the compression/tension (C/T) asymmetry ratio for crystal, including an SFT at the center, as a function of orientation.
Fig. 6-10. Contour plots of percent reduction in (a) compressive and (b) tensile yield stress due to SFT for considered crystal orientations.

Fig. 6-11. Contour plot of the reduction percent ratio in inverse pole figure. The ratio is calculated as compressive percent reduction over tensile percent reduction. Several orientations have been marked for which deformation mechanisms are shown in Fig. 12.

Fig. 6-12. Snapshots of atomic configuration at the onset of plasticity for several representative crystal orientations. In each orientation, upper snapshot is for compression and lower one is for tension. CSP has been used to color code the defects. Initial configuration of the SFT is presented for some snapshots with the smaller atom size to clarify the deformation mechanism.

Fig. 6-13. Variation of the yield stresses against elastic modulus in tension and compression tests (a) for the perfect crystal and (b) in the presence of an SFT Lines only drawn to guide the eye, and have no functional form.

Fig. 6-14. Actual reduction in yield stress vs. elastic modulus for tension and compression tests on single crystals with an SFT at the center.

Fig. 6-15. Reduction in yield stress vs. yield stress for the perfect crystal under tension and compression for the considered crystal orientations.

Fig. 7-1. Stereographic triangle showing the investigated orientations. Uniaxial loading is performed along the shown orientation that coincides with the y axis.

Fig. 7-2. Load-depth curves in nanoindentation tests at different temperatures on (a) [111] perfect crystal and (b) [111] crystal with an SFT centered at the 15th layer from the surface on the indentation axis.

Fig. 7-3. Variation of maximum shear stress at the first load drop with respect to the temperature for a [111] perfect crystal and [111] crystals holding different types of internal defects.

Fig. 7-4. Stress-strain curves of tension and compression tests on [111] perfect crystals (solid lines) and [111] crystals having an SFT (dashed lines) at the center, at 1 K and 500K.

Fig. 7-5. Yield stress vs. temperature curves for [111] perfect crystals and [111] crystals with centered d-vacancy and SFT in (a) tension and (b) compression tests.
Fig. 7-6. Contour plots of temperature sensitivity ratio, defined as the ratio of the stress gradient with respect to the temperature for the perfect crystal over that for the crystal with the SFT, for (a) tension and (b) compression tests. Note the difference in scales for each figure................. 114

Fig. 7-7. Atomic snapshots of deformation mechanisms for compressive loadings of different crystallographic orientations at 10 K and 500 K; [5,2,10] (a) 10 K, (b) 500 K; [101] (c) 10 K, stair rod dislocation as an SFT edge, (d) 10 K, dislocation nucleation from the stair rod dislocation, (e) 500 K, dislocation nucleation from the stair rod dislocation; [829] (f) 10 K, stair rod dislocation as an SFT edge, (g) 10 K, dislocation nucleation from the stair rod dislocation, (h) 500 K, SFT unzipping and dislocation propagation in one of the SFT sides.................. 116

Fig. 7-8. Contour plots of distribution of the asymmetry ratio in the stereographic triangle at 10 K for (a) perfect crystal and (b) crystals with a centered SFT........................................... 117

Fig. 7-9. Contour plots of distribution of the asymmetry ratio in the stereographic triangle at 500 K for (a) perfect crystal and (b) crystals with a centered SFT........................................... 117

Fig. 7-10. Contour plots of the percent reduction in yield stress due to SFT in compression tests at (a) 10 K, and (b) 500 K.......................................................... 118

Fig. 7-11. Contour plots of the percent reduction in yield stress due to SFT in tensile tests at (a) 10 K, and (b) 500 K.......................................................... 119

Fig. 7-12. Reduction in yield stress (due to the presence of a SFT) vs. yield stress of the perfect crystal for compression and tension tests at (a) 10 K and (b) 500 K................................. 119
Dedication

This dissertation is proudly dedicated to my lovely wife, my wonderful family and my gorgeous in-laws for their constant support and love in my PhD.

I love you with all my heart.
Chapter 1: Introduction

To make a very strong material, it is essential to have dislocations that are both hard to nucleate and also hard to move. Strengthening mechanisms such as solid solution strengthening are mainly used to impede dislocation motion, thus making material harder to deform. In small volumes of materials, with fewer existing dislocations, one open question is how any hardening process used to strengthen materials via impeding dislocation motions will impact the nucleation of dislocations. There are also some other structural defects that can weaken materials by reducing stresses required to nucleate or move the dislocations. The majority of published works about these effects address the motion of pre-existing dislocations [1-3], not the nucleation of dislocations from internal defects. This project focuses on the effects of internal defects in metallic crystals on the nucleation of dislocations. Among different types of defects, those which are most common in nanoscale size metallic single crystals are chosen and their effects on the nucleation of dislocations and consequently on the onset of plasticity will be studied. The study of dislocation nucleation has wide range of applications in thin film deformation [4], shock deformation [5], structural nanolayered materials [6], nanocrystalline solids [7] and fracture processes [8]. When deforming materials, nucleation of dislocations is commonly observed as a pop-in in load-displacement (stress-strain) curves and ascribed to the onset of plasticity. Inception of plastic deformation has been an interesting area of research recent years as modeling methods are being developed to find related governing deformation mechanisms [9-15]. A combination of atomistic simulations and experimental studies will be beneficial, as the simulations may complement the experiments and provide guidelines for future validation of the experiments. Furthermore, simulations provide the ability to study the effect of a particular
defect isolated from the effect of other factors (e.g., other defects) which may not be practical in the experiments where effects due to various variables often merge and intertwine.

There are two categories of dislocation nucleation mechanisms. First, homogeneous dislocation nucleation occurs spontaneously throughout the volume of a material initially free of defects [16-20]. For this deformation mechanism very large stresses are required. Second, heterogeneous dislocation nucleation occurs at defects such as point defects, frees surfaces, voids, grain boundaries. These defects act as stress concentrators and promote emission of dislocations at lower stresses than required for homogeneous dislocation nucleation. Recently, Schuh et al [21] conducted nanoindentation experiments on single crystal Pt at several temperatures and calculated the activation energies and volumes for dislocation nucleation. The calculated activation energies were much lower than that typically associated with homogeneous dislocation nucleation and were reported to be close to that for heterogeneous dislocation nucleation. It is suggested that pop-ins in the indentation curve were in fact associated with dislocation nucleation from heterogeneous sources, such as vacancies or pre-existing dislocations nucleated from surface asperities during contact [21-23]. Tschopp and McDowell [24] calculated the activation volume for homogeneous dislocation nucleation in copper single crystal under uniaxial loading. Furthermore, Zhu et al. [25] computed the activation energy and activation volume for dislocation nucleation from the free surface in copper nanowires. All the reported values of the activation volume were in the same range as those calculated by Schuh and coworkers, which shows that activation volume is not an appropriate tool to distinguish homogeneous and heterogeneous dislocation nucleation.

Crystal defects can be categorized according their dimensionalities. These include point, line, area and volume defects. These defects can act as dislocation nucleation sources and
significantly impact the mechanical behavior of a material. Among several defects in metallic crystals, point defects, and especially vacancies, are very common and also little knowledge is available on the effects of this type of crystal defects on dislocation nucleation. On the other hand, performing experimental studies in this area is feasible which enables us to use them to validate the modeling results.

Point defects, such as impurities and vacancies [26-30] and their clusters may play a significant role in initiation of plastic deformation in crystalline metals. Classical works on solid-solution strengthening clearly demonstrate that impurities increase the flow stress in bulk materials, but that is only accounting for the propagation, not nucleation of dislocations. Literature includes controversial results about the effect of impurities on the mechanical behavior of materials at the onset of plasticity. While using an experimental study, Bahr and Vasquez [26] did not see a remarkable impact of impurities in Ni-Cu diffusion couples; Rajgarhia et al. [28], using MD simulations, showed decreasing trend on the tensile stress required for partial dislocation nucleation in the Cu crystal with increasing the concentration of Sb as substitutional impurities. The strained region around solute Sb atoms acts as a heterogeneous source of partial dislocation loops, thereby reducing the tensile stress required to nucleate dislocations below that needed for homogeneous dislocation nucleation in pure Cu [28]. It was also shown that the distribution of impurities in a crystal may lead to either softening or hardening of the material, both due to dislocation nucleation [31]. Several works have been carried out on the effect of hydrogen on the mechanical properties of metals. It is shown that hydrogen reduces the required stress for the onset of plasticity, by decreasing the defect formation energy and the inter-atomic bonding energy [29,30].
It is well known that vacancies are thermodynamically required in crystals. Certain concentrations of vacancies are present even in supposedly perfect crystals. The equilibrium concentration of vacancies is typically very low; however it grows exponentially with temperature and may become relatively high when temperatures approach the melting point [32]. It is important to note that this equilibrium concentration value represents a bare minimum that can be found in perfect crystals under normal circumstances. The actual concentration of vacancies may be considerably higher than the corresponding equilibrium value due to a number of factors. For example, rapid quenching, when vacancies do not have enough time to diffuse to sinks such as surfaces or grain boundaries, can lead to high vacancy concentrations even at low temperatures. Severe or cyclical plastic deformation also increases the numbers of vacancies through dislocation interactions. Finally, materials subjected to radiation damage, when high-energy particles knock atoms off their equilibrium lattice cites, leads to increased concentrations of vacancies in crystalline metals [33].

The effect of non-equilibrium vacancies on the mechanical response of metals is complex, ranging from strengthening effects due to Cottrell atmospheres, to dislocation motion impacted by climb and jog formation [34]; to weakening effects previously reported to impact dislocation nucleation [35-39].

In materials with a face-centred cubic (FCC) lattice, the agglomeration of vacancies may result in the formation of stacking fault tetrahedra (SFT) from the smallest observable size of several atoms [40], typically generated by collision cascades, to the largest size observed up to several hundred nanometers introduced by quenching. They were evidenced in a number of irradiated pure metals such as Cu [41,42], Ni [43,44] and Pd [45], and in technical alloys such as stainless steels [46]. In FCC crystals, stacking fault tetrahedra are a more common type of vacancy clustered defects than simple planar dislocation loops. The first observation of stacking
fault tetrahedra by transmission electron microscopy was made about 50 years ago [47], and since then they have appeared in a very wide variety of cases, by quenching from high temperatures, irradiation and heavy plastic deformation. These faults have been all confirmed to be vacancy type; it was found that interstitial-type stacking fault tetrahedra do not exist [48]. When the reduced stacking fault energy, $\gamma/\mu b$ (where, $\gamma$ is the stacking fault energy, $\mu$ is the shear modulus and $b$ is the length of the Burgers vector) is smaller than about 1/50, SFTs are favorable [49]. Nurdlund and Gao [50] showed that even at the low temperatures at which the thermal migration of vacancies to form stacking fault tetrahedron is not possible, SFTs are produced. In simulations of 50 keV collision cascades in Cu and Ni they observed the formation of SFTs at temperature close to 0 K. It was also shown that initially quite complex damage at low temperature can rearrange into SFTs during high-temperature annealing. Clustering vacancies may lead to either void or stacking fault tetrahedron. The stability of a void or a SFT depends on its size. For some metals, voids are energetically more stable than SFTs [51].

Focused ion beam (FIB) methods are sample preparation techniques that have been widely used for a couple of decades in materials science [52-56]. In FIB techniques, the shape of the target material is manipulated by bombarding the surface of the target by accelerated heavy ions, usually gallium. One possible issue with the FIB process is that ions can produce defects in the target material and resulting structure. The damage could be in the form of amorphous layer [57], a dislocation network [58], vacancy clusters such as stacking fault tetrahedra and voids [59], and even implanted Ga. Shim et al. [55] showed that compressed Mo-alloy pillars in the as-grown condition behave like dislocation-free crystals, and yield at near-theoretical strength. On the other hand, micropillars that were FIB milled before compression had a much lower strength. These studies suggest that the FIB-altered microstructure could play a significant role in the
micropillar plasticity. On the other hand, other studies suggested that the effects of the FIB milling are negligible if the original crystal has some initial dislocation structure before milling [54,56]. Once the sampling volume of materials reaches the sub-micron length scales, these results imply that a study of the effects of defects on the nucleation and propagation of dislocations is required. By studying different FIB-produced defects one can find the particular impact of each defect and consequently find better explanation about the size effect in micro and also nanopillars.

The field of small scale mechanical testing, of which the most common method is nanoindentation, has made great progress in sampling volume of materials on the µm and sub-µm length scales. While newer methods including in situ mechanical testing during electron microscopy have their own benefits, the simplicity and flexibility of the materials that can be sampled via nanoindentation makes this a technique that has significant strengths in mechanical testing. The traditional methods of nanoindentation involve analysis of the load-depth curves by penetration of a tip into a sample, from which material properties such as hardness and elastic modulus are extracted. Large volume mechanical testing will generally measure the motion of pre-existing dislocations under applied stresses, therefore it limits our understanding about the nucleation of dislocations or the ability to sample dislocation free zones. Because of that, small regions of materials are being sampled to study the nucleation of dislocations. Nanoindentation couples small-scale mechanical testing with materials modeling, as it approaches volumes that can be simulated using atomistic simulations. The Hertzian solution of 3-D spherical indentation of linear elastic half space [60] provides a global view of the stress distribution and indicates that the spherical indenter projects the maximum shear stress to an internal point, a finite distance away from the surface. This minimizes the influence of surface defects and enables us to see how
internal defects affect the mechanical behavior of a particular material. In recent years, atomistic simulations of nanoindentation have also led to a better understanding of deformation at the nanoscale [13,17,18,61,62]. Spherical indenters are commonly used because they are more sensitive to the elasto-plastic transition than sharp tip geometries [63], and more closely match the experimental condition, as no indenter tips are atomistically sharp, the indenter tip is assumed to be close to a sphere. One of the significant differences between experimental and modeling studies in the nanoindentation test is the length scale, particularly the indenter radius and the volume of sampled material [64]. Several literature [62,65-68], using either experimental or modeling methods, have studied the effect of probe size on the mechanical response of perfect crystals.

One interesting observation in nanoindentation testing is the indentation size effect, which is controlled by dislocation propagation and entanglement and manifests as a higher measured hardness either at smaller indentation depths or smaller indenter radii [69,70]. Shim and coworkers [71] and Salehinia et al. [39] reported a different type of indentation size effect of nanoscale size indenters based on maximum shear stress at the onset of plastic deformation which is directly associated with the nucleation of dislocations for nanometer size indenters. Using cumulative distribution curves in nanoindentations with μm sized indenters, Morris et al. [72] showed a narrow distribution of shear stresses at the onset of plasticity for small radii, wide distribution for medium radii and again a narrow distribution of shear stresses for radii of 17.5 μm and larger, i.e. supporting the effect of structural defects on the onset of plasticity.

As the deformed volume of materials decreases, the effect of crystal anisotropy on the mechanical response intensifies. Elastic and also plastic anisotropy have been observed for various materials under different loading conditions such as nanoindentation, shear loading and
uniaxial loading [24,62,73-79]. While both the elastic and plastic responses are affected by the crystal orientation, the orientation effect tends to decrease with plastic deformation. Li et al. [80] performed theoretical calculations and experiments to study the cumulative distribution of pop-in loads for nanoindentation on NiAl single crystal in several crystal orientations. They linked the wide distribution of pop-in loads in (100) orientation to the larger stressed volume (which was calculated theoretically) under the indenter that increases the chance of different types of structural defects to impact the mechanical response of the material.

In uniaxial loading the yield stress in compression is often different than that in tension. This phenomenon is called yield asymmetry or compression/tension (C/T) yield asymmetry [81]. In the presence of dislocations, in contrast to FCC crystals, BCC crystals show the C/T yield asymmetry due to the effect of non-Schmid stresses on the screw dislocation core. With small size scales where the dislocations are rare, the C/T yield asymmetry shows a different trend than the former case where dislocation movement is the main deformation mechanism. It is conventionally accepted that in FCC crystals the yield criterion in the presence of dislocations is critical resolved shear stress (CRSS). In this view, yielding should occur when the maximum resolved shear stress on the slip plane and along the slip direction reaches CRSS, this value is assumed to be constant for a given material. The proper understanding of yielding in the absence of dislocations is lacking in various crystal structures. This study aims to shed light on these phenomena for copper in various crystal orientations. In particular, the compression/tension asymmetry in the presence of point defects will also be considered.

The majority of previous atomistic simulations have excluded the temperature effects to find the effects of the point defects on the dislocation nucleation and onset of plastic deformation that are hard to explore at higher temperatures due to the thermal effects. However, since both
increasing temperature and also point defects lower the yield point, it is important to study their combined effect on the mechanical response of the material. At higher temperatures the diffusion rate of point defects increases and thermal vibrations start to play a bigger role in triggering dislocation nucleation, therefore it would result in reducing the effect of point defects on the mechanical response of the material. Schuh and coworkers [21] showed that for Pt single crystal the distribution of pop-in loads at high temperatures was narrower than at low temperatures. They also showed lower pop-in loads at higher temperature in nanoindentation tests. Salehinia and Medyanik [82] performed atomistic simulations of nanoindentation tests with different single vacancy densities in Ni single crystal at different temperatures. They showed that the vacancies are less effective at higher temperatures. Due to the thermal vibration on the indenter tip, nanoindentation tests are not only hard to perform but also tricky to simulate. Simulations of uniaxial tests at high temperatures may compliment the nanoindentation models and help us to understand the deformation mechanisms in the presence of the point defects.

Overall, this thesis is trying to answer several fundamental questions regarding the onset of small scale plasticity, particularly:

- Is the nucleation of dislocations the dominant factor in deformation of small volumes of metals, even when the stressed volume is small but coupled to larger volumes of material?
- What effects do compositional and structural defects, such as those that may be imposed on purpose (alloy development) or inadvertently (like point defects) have on the onset of plasticity?
- Among different types of point defects and their complexes, which one lowers the nucleation stress the most, and does this effect remain the same over a range of size scale?
- Can details of nucleation mechanisms affect the transition from atomistic (nucleation dominated) deformation to continuum-level plasticity?
- How would crystal anisotropy enter to play a role when point defects exist in the crystal?
- What would be the temperature effect on the mechanical response of the sample when point defects are present?

Chapters in this dissertation are mainly based on some of the published (or submitted) papers in this research. The papers have been slightly modified for consistency through the dissertation and references are moved to the end of the dissertation and duplications have been removed. In chapter two, the experimental and modeling results are given to show the effect of non-equilibrium vacancies on the mechanical response of the material in nanoindentation test performed by different indenter sizes. In this research, all the experiments have been carried out on Ni crystal and simulations have been done on copper single crystal as the model material. In chapter three the impact of several point defects such as single and di-vacancy, self interstitial atoms and also SFT as an example of cluster of vacancies are compared in nanoindentation test for different indenter radii. Since the biggest impact on the mechanical response of the crystal was found for ST, chapter four focuses on the deformation mechanisms in the presence of an SFT in various positions in the copper single crystal under the nanoindentation test. Chapter five investigates the effect of the relative position of the point defects (in particular an SFT) to the indenter for different crystal orientations on stochastic distribution of the pop-in loads in nanoindentation test. Simulation results are used to explain the observed behavior in
nanoindentation experiments for different indenter sizes. Chapter six includes the simulation results of the uniaxial loading applied in several crystallographic orientations on the perfect crystal and on the crystals with an SFT. Deformation mechanisms in compressive and tensile loading senses are used to explain the compression/tension asymmetry in the presence of the defects and for the perfect crystal. Schmid and non-Schmid stresses are taken into account for further clarification of the observed behavior. In chapter seven the temperature effect in the presence of point defects and SFT is investigated in nanoindentation and uniaxial tests in various crystal orientations. Finally, chapter eight covers the main conclusions of this research along with the proposed future work to address new questions that have arisen from the current work.
CHAPTER TWO: Effect of vacancies on incipient plasticity during contact loading
I. Salehinia, V. Perez, D.F. Bahr

Abstract

Atomistic simulations and experimental nanoindentation tests are used in this study to examine the effect of vacancies on the inception of plastic deformation in Ni. Molecular dynamics have shown the effect of vacancy position on the yield load and demonstrate a variety of mechanisms which are responsible for the inception of plastic deformation during indentation. In cases where the vacancy position is close to regions of high shear stresses the nucleation of dislocations is related to the location of a vacancy; however homogeneous nucleation of dislocations is also observed for vacancy-containing crystals. Complementary experiments have been used to demonstrate the effect of indenter size on the onset of yielding in the presence of vacancies. Both the simulations and experiments show that larger indenter tips increase the chance of weakening the material in the presence of vacancies.

2.1 Introduction

The governing mechanisms that control the transition from elastic to plastic deformation during contact loading have not been yet identified thoroughly. In relatively defect free single crystals, the inception of plastic deformation is commonly related to the discrete nucleation of dislocations [9,15,83]. The mechanism by which dislocations nucleate in this process may be either homogeneous or heterogeneous. While many studies of deformation mechanisms at the
onset of plasticity in single crystals have suggested homogeneous nucleation of dislocations [13,16-20] some recent studies have showed that the first displacement burst is more likely to have a heterogeneous nature [21,22,61]. These mechanisms may include the nucleation of dislocations from a vacancy or formation of dislocation rings from pre-existing vacancies condensed into a plate [21-23]. It is well known that vacancies are thermodynamically required in crystals. While the equilibrium concentration of vacancies in most metals is typically very low at room temperature [32], non-equilibrium processes such as quenching, severe plastic deformation and radiation damage can increase the vacancy concentration to a significant degree [33].

The effect of non-equilibrium vacancies on the mechanical response of metals is complex, ranging from strengthening effects due to Cottrell atmospheres, to dislocation motion impacted by climb and jog formation [34]; to weakening effects previously reported to impact dislocation nucleation [35-37,82]. Mukherjee et al. [38] used two dimensional models of nanoindentation tests and showed annihilation of vacancies in the compression zones and enlargement of vacancies in the tension zones under the indenter. Njeim and Bahr [37] also simulated nanoindentation tests in single crystal iron and found out that vacancies, by impacting the stress field in the material, can participate in the small scale deformation mechanisms for which they do not need to be present at the regions with highest resolved shear stress. Atomistic simulations of the inception of plasticity showed nucleation of dislocations from the perfect lattice regions was possible, and it was followed by subsequent interactions of dislocations with vacancies upon further deformation. Very recently, Salehinia and Medyanik [82] modeled nanoindentation test by using both molecular mechanics and molecular dynamics to study the effect of position of a single vacancy, groups of vacancies arranged in a rectangular pattern and random distributions of
vacancies with different concentrations on the onset of plasticity in nickel single crystal. While this work only considered a few particular positions of a single vacancy, it showed that even a single vacancy can have a pronounced effect on the yield load and the magnitude of this effect may significantly depend on the vacancy’s position relative to indenter. It was also shown that at high temperatures the effect of vacancies on the mechanical behavior of materials at the onset of plasticity is less pronounced.

A useful experimental tool for understanding mechanisms which control the nucleation of dislocations is the nanoindentation test. In recent years, atomistic simulations of nanoindentation have also led to a better understanding of deformation at the nanoscale [13,17,18,20,61,62,84]. Spherical indenters are commonly simulated because they are more sensitive to the elasto-plastic transition than sharp tip geometries [63], and more closely match the experimental condition, as no indenter tips are atomistically sharp a spherical cap is commonly assumed to reside at the apex of a given nanoindenter tip.

One of the significant differences between experimental and modeling studies in the nanoindentation test is the length scale, particularly the indenter radius and the volume of material tested [64]. Several papers [38,61,65-68], using either experimental or modeling methods, can be found on the effect of probe size on the mechanical response of perfect crystals. Though Bei and co-workers have recently provided an assessment of size effects on stochastic yield behavior in the presence of dislocations [85], and a previous study using nanoindentation showed similar effects on dislocation density on yielding [83], a study on this effect when vacancies are present in the crystal is still lacking.

The purpose of this current work is to determine the effects of lattice vacancies on the nucleation of dislocations and consequently on the onset of plastic deformation in Ni single
crystal during contact loading. Experimentally it is not possible to know a priori if a given indentation will have the highest shear stresses coincide with the vacancy position. To carry out modeling studies which would mimic this uncertainty, several simulations of nanoindentations with single crystals having a single vacancy in verity of spots can be executed. While having a single vacancy is a condition far from what is observed in experiments, positioning a single vacancy at several spots under the indenter tip is analogous to probing specimens with different vacancy distributions for which vacancies are seen in different spots. In particular, the effect of indenter size in the presence of vacancies is investigated using a combination of simulations and experimental studies that expands this work beyond previous, more limited investigations.

2.2 Experimental and modeling procedures

Nanoindentation experiments were performed on Ni single crystals in the \{111\} orientation. Ni has a low tendency for forming clusters of vacancies due to its high energy of vacancy migration [86]. As the melting temperature of nickel is relatively high, it does not anneal out vacancies quickly, hence even at the room temperature non-equilibrium vacancy concentration can be sustained. In addition, at room temperature only a thin oxide forms which should minimize any effect of an oxide layer on the test results. Specimens were ground to 1200 grit, then mechanically polished with alumina powder to 0.05 \(\mu\)m, and finally electropolished in a solution of 37 ml \(\text{H}_3\text{PO}_4\), 56 ml glycerol and 7 ml deionized water for 2 min at a current density of \(9 – 12\) A/in\(^2\).

Nanoindentation tests were conducted using a Hysitron TI 900 TriboIndenter with two Berkovich diamond tips. The tips had approximate root radii of 250 nm and 70 nm. The experiments were run in load control, and accordingly the onset of plastic deformation is observed as an excursion in depth at a fixed load. The maximum load is 500 \(\mu\)N for the
experiments. Regions of the crystal were examined using scanning probe capabilities of the instrument using a cube corner tip. After electropolishing three 10 \( \mu \)m square regions exhibited an average RMS roughness of 2.65 nm. Positron annihilation spectroscopy (PAS) [87] was then used to estimate the vacancy concentration. Though this method cannot be used to find vacancy concentrations in all metals, successful measurements with nickel have been documented in the literature [88].

To reduce the vacancy concentration the samples were heat treated at 1296 K for about 4 hours in a vacuum of approximately 10^{-6} Torr in a sealed ampule that had been previously backfilled with Ar. The sample was furnace cooled to room temperature over the course of several hours. The average RMS roughness after heat treatment using the previously mentioned cube corner tip was 9.2 nm. While these roughnesses have not been corrected to account for the tip convolution, for the purposes of this study it is clear that the heat treatment increased the surface roughness of the sample. After heat treatment PAS was again performed to determine changes in relative vacancy concentration. X-ray Photoelectron Spectroscopy was carried out to estimate the oxide thickness after heat treating; the oxide after heat treating was on the order of 1.5 nm, similar to a native oxide on Ni and therefore will be viewed as unlikely to have any significant impact on the comparison between the two samples.

For each indenter size 128 indentations were done on two regions of the crystal separated by several mm’s. At each region an 8x8 square array of indentations separated by 15 \( \mu \)m were performed using a loading profile that included a check for elastic behavior at loads lower than 50 \( \mu \)N. Total loads of 500 \( \mu \)N were applied, and a loading and unloading rate of 50 \( \mu \)N/s was used for the tests. Tests were performed on regions of the crystal that had not been imaged using
the scanning probe capabilities of the Triboindenter to minimize any possible effects of contact loading prior to testing.

In the simulations, the atomistic embedded atom method (EAM) was applied to model the nanoindentation process in nickel. The EAM potential used in this work was developed by Voter and Chen [89,90]. The accuracy of this potential for Ni has been verified by Zimmerman et al. [91]. The Ni single crystal chosen for the simulation is a rectangular crystal lattice with dimension $19.2 \times 19.2 \times 9 \text{ nm}^3$ containing about 300,000 atoms. The simulation of nanoindentation was performed using a quadratic repulsive force $F(r) = -K(r - R)^2$ to model rigid spherical indenters with tip radii of 4 nm and 6 nm. $K$ is the force constant equal to 1000 eV/Å³, $r$ is the distance from an atom to the center of the indenter and $R$ is the radius of the indenter. The indentation axis is along [111] direction ($Y$ axis), while the $X$ and $Z$ axes are along [110] and [100] crystallographic directions.

Molecular dynamics simulations were performed using the parallel atomistic simulation program LAMMPS [92,93]. Side faces were fixed while top and bottom faces were allowed to move. The simulation box is large enough to neglect the effect of boundary conditions on the side faces. To be sure about the consistency of the results, simulations were carried out for either fixed or free bottom face and the results showed both quantitative and qualitative agreements. Effect of model size has been also studied by Zhu and coworkers [79] who used both molecular dynamics and finite element method to find the mechanisms of homogeneous dislocation nucleation in copper single crystal which was initially free of defects. The nucleation sites of dislocations agreed well for the both applied methods. Initial relaxation was applied for 10 ps. The indenter speed was 5 m/sec and the time step used was 1 fs. A thorough study of the effect of indenter speed on the simulation results was done. This relatively large indenter speed leads to
high strain rate which is required to achieve plastic strains in MD timescale which is in nanosecond order. Although this speed is much higher than that is used in nanoindentation experiments, it is sufficiently slow to let equilibrium of the indentation as it does not generate any shock loading in the system. It is therefore expected that the deformation characteristics is insensitive to the indenter speed. The temperature of the system was kept close to 0 K by explicitly rescaling the atoms velocities [92]. Therefore our simulations did not consider any of the temperature effects on the nucleation of defects in the material. These effects become more dominant at high temperatures [82] and make it hard to clarify the effect of vacancies on the mechanisms of nucleation of dislocations.

In order to visualize vacancies, partial dislocations, and stacking fault regions the centro-symmetry technique [17] is employed. Since in FCC crystal each atom has twelve nearest neighbors, the centro-symmetry parameter for an atom is defined as

$$CSP = \sum_{i=1}^{6} |R_i + R_{i+6}|^2$$

The centro-symmetry parameter vanishes for the atoms under elastic deformation. Under plastic deformation the centro-symmetry condition no longer holds and the CSP near defects such as partial dislocations, stacking faults or any other type of defects such as vacancies becomes greater than zero. In Ni, the value of this parameter for atoms around a single vacancy and on the stacking faults is in the range 4-6 and for atoms close to the nucleation sites of partial dislocations it is less than 4. For visualization purposes atoms with a CSP less than 0.3, i.e. those belonging to the perfect lattice regions, are not shown in atomistic configurations represented in the following results.
2.3 Results and discussion

Heat treating the sample resulted in a relative decrease in vacancy concentration. Estimation of the relative vacancy concentration was performed by assuming a fixed diffusion constant of 1 cm$^2$/s for positrons in both samples, a life time of 109 ps for positrons in Ni, and a trapping rate of $3e15$ per second. After heat treating the vacancy concentration at a depth of 1 µm was approximately $15x10^{-6}$ for the as-polished sample, while the heat treated sample exhibited approximately 10 times fewer point defects (an atomic fraction of $1.1x10^{-6}$). While both these numbers are substantially higher than the expected room temperature vacancy concentration, the relative differences between the samples should be the same at a given depth. As the concentration varies with depth in both samples an accurate quantification of the vacancy concentration is beyond the scope of this current work; however this technique clearly can identify that the heat treated sample has a much lower vacancy concentration than the initial sample, and therefore for the purposes of this study the samples will be referred to as the “high” and “low” vacancy concentration. These concentrations are similar to the simulations where 1 vacancy in 300,000 atoms was used. However by having a smaller tip the strained region in the simulation is substantially smaller than that in the experiment. Therefore, to first order, the likelihood of probing a single vacancy is similar in the experiment and simulation.
Fig. 2-1. Experimental load-displacement curves for four samples, two each with high and low vacancy concentrations. The indenter radius is 250 nm. The dash-dot line in the inset showing elastic loading represents a Hertzian fit to sample number 1 with low vacancy concentration. (Data were provided by V. Perez)

Fig. 2-1 shows four typical experimental load-displacement curves representing the general effect of vacancies on the mechanical response of Ni single crystal during nanoindentation using a tip with an effective radius of 250 nm. Each indentation began with an initial load, unload, reload sequence to ensure the initial loading was indeed elastic. The results consistently indicate lower yield points for the samples with higher concentration of vacancies. This corresponds to previous works which indicated that the presence of vacancies can decrease the yield point during any mechanical testing [35-37,82]. The observed difference in the initial stiffness (Fig. 1-inset) is due to the different surface roughnesses. Since the elastic portion of the load-displacement curve roughly obeys the Hertzian solution in which a composite radius, R, of the tip/contact surface is used

\[
\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}
\]  

(2)
with subscripts denoting the radii of the two contacting surfaces [60], and since the indenter tip was not changed between each experiment and the oxide thicknesses between the two samples are similar and less than 1.5 nm, the only differences which can account for the slightly stiffer loading in the sample with the higher vacancy concentration is the lower surface roughness or an effect of the vacancies themselves, but since vacancies are unlikely to increase the modulus, the most likely reason for the slight stiffening in the high vacancy concentration sample is a change in roughness. The critical observation from the experimental study is that the major onset of plasticity occurs at lower stresses when the vacancy concentration is increased. Additionally, the experimental distribution in stresses for the onset of plasticity will be discussed at length later in this paper (Fig. 2-10). Because subsequent polishing would potentially add additional defects in the crystal, we do not have the ability to completely separate the effect of roughness, but suspect that the change in vacancy concentration by one order of magnitude is more substantial than any change in roughness. Finally, the overall hardness of the material with fewer point defects is also lower (i.e. the depth of the indentation once plastic deformation has occurred is greater at a given load for the samples with a low vacancy concentration due to solid solution effects). “The mean hardness of the sample with low vacancy concentration was 2.5±0.2 GPa, while the higher concentration exhibited a mean hardness of 2.8±0.1 GPa. The total range of hardness data does suggest that other defects (pre-existing dislocations or other impurities) may also impact the hardness; but as hardness measurements are taken at larger depths and sample much larger volumes we will assume and ascribe the differences in yield point to the smallest defects we could consider, in this case vacancies.”

Fig. 2-2 shows the atomic configuration of a perfect crystal at the onset of plasticity. Atoms in the perfect lattice are not shown while others are colored according to the centro-
cymmetry parameter. The location at which dislocations nucleate is off-axis, along the [11\bar{2}] direction. This location is on the 5th layer (y: -8.129 Å), 0.46a under the top surface and 0.42a in the horizontal plane from the indentation axis, where a is the contact radius. Off axis nucleation of dislocations has been seen previously by several researchers [13,18-20,61,79].

Fig. 2-2. Atomistic configuration of a perfect crystal in (1\bar{1}0) plane showing the position of nucleation site of dislocations, atoms are color coded according to centro-symmetry parameter, atoms in perfect lattice are not shown.

To gain insight regarding the mechanisms governing the initiation of plastic deformation in the presence of vacancies, the simulations consider only a single vacancy in the crystal. This is a reasonable approximation of vacancy concentration in Ni single crystal in the test conditions, and by moving the position of the vacancy closer to regions of higher stresses it is possible to approximate higher vacancy concentrations. For the simulations using an indenter with a 4 nm radius, load-displacement curves showing the onset of plasticity for a perfect crystal and crystals with different vacancy positions along the loading axis are presented in Fig. 2-3. With the indentation geometry used in the simulation, the 3rd (y: -4.065 Å), 6th (y: -10.161 Å) and 9th (y: -16.257 Å) layers are the first three layers that include an atom site on the indentation axis. Even a single vacancy can lead to an inception of plasticity at a lower load during contact loading.
As the vacancy is positioned further from the surface, its effect on the onset of plasticity vanishes and the crystal’s behavior approaches that of a perfect crystal. The yield force for a crystal with a single vacancy on the 6th layer is lower than that when the vacancy is on the 3rd layer. The smaller force corresponding to the yield for the vacancy in the 6th layer is likely because of its shorter distance to the off-axis position of nucleation in perfect crystal (Fig. 2-2) than that of the vacancy in the 3rd layer.

Since a single vacancy can affect the onset of plasticity during contact loading, it is appropriate to investigate the particular mechanisms by which it exerts this influence. Figures 2-4(a) and 2-4(b) show load-displacement curves with snapshots of several particular points during downward motion of the indenter for two particular positions of a single vacancy in the 4th (y: -6.097 Å) and 7th (y: -12.193 Å) layers of the crystal, respectively. In the snapshots the atoms are colored according to the centro-symmetry parameter. In Fig. 2-4(a), the dislocation nucleates at
the vacancy position, and corresponds to the significant load drop. After nucleating, the dislocation propagates on the slip plane. However, in Fig. 2-4(b), the vacancy migrates to a region of higher hydrostatic pressure and the deformation proceeds with the nucleation of dislocations from the vacancy. The small fluctuations in the load-displacement curve before the large event are the results of vacancy migration and the incipient formation of dislocations.

![Graph showing load-displacement curves and atomic snapshots](image)

Fig. 2-4. Load-displacement curves and atomic snapshots of particular points during the downward motion of the indenter with the radius of 4 nm; (a) single vacancy at the 4th layer, with x: -7.185 Å and z: 0, A: nucleation from the vacancy, B: propagation to the surface; (b) single vacancy at the 7th layer, with x: -5.748 Å and z: 0, A: before migration, B: during migration, C: vacancy migrated to the 4th layer, D: nucleation from the vacancy, E: propagation to the surface.

The pressure gradient is the primary mechanism driving the observed vacancy migration [21,22]. Fig. 2-5 shows the distributions of the hydrostatic stresses in the crystal whose behavior has been shown in Fig. 2-4(b). Atomic-level stress-tensor components are obtained using virial formula [94]. Presented snapshots are for different times up to the time at which the migration stops. In this figure, negative values show pressure and positives values show tensile mean stress on a particular atom. In each snapshot atoms under a tensile mean stress are marked with (+) sign. The stress field on some of the atoms around the vacancy at the initial configuration is
tensile. As the deformation proceeds, neighbors of a vacancy fill the vacancy and force it to the upper layer. Migration continues until the time that no more tensile field around the vacancy exists and the vacancy is located in an effectively hydrostatic compressive stress field.

Fig. 2-5. Atomistic configurations of several stages of nanoindentation in the presence of a single vacancy on the 7th layer, at x: -5.748 Å, z: 0. The atoms are color coded according to the mean stress value. The tip radius is 4 nm. Here, vacancy migration is clear. Atoms under tensile mean stress are marked with (+) sign.

By positioning the vacancy at a variety of horizontal and vertical positions in the lattice structure it is possible to find the volume in which a single vacancy affects the onset of plasticity during contact loading. For the 4 nm indenter, variations of contact pressure\(^1\) ratios under the indenter at the first displacement burst for different positions of a single vacancy along [11\(\bar{2}\)] (X

\[^1\] Contact pressures are calculated as: \(P = \frac{F}{\pi R d}\); where R is the indenter radius and F and d are the load, and indentation depth at the displacement burst, respectively.
axis) and [110] (Z axis) directions at different layers are shown in Fig. 2-6(a) and (b), respectively. To be able to compare the results for different indenter radii the contact pressures are normalized by the contact pressure at the displacement burst when a perfect crystal is being indented. We define the area of contact by selecting the total projected area of contact between the tip and the sample. Since we know the load that causes this, we can determine the mean pressure (a Hertzian type approach). We do this for a perfect crystal. When we add a vacancy, the contact area and load are determined at the onset of plasticity and the mean pressure is calculated again. The ratio of these two mean pressures is referred to as the contact pressure ratio. In Fig. 2-6(a), the position of a single vacancy is varied in (110) plane (along the X axis), and in Fig. 2-6(b), for each layer, for a fixed coordinate in the [112] direction (and the closest distance to the indentation axis), a single vacancy is translated in the [110] direction. Due to the symmetric distribution of atoms in (112) plane (X plane) only lattice points in the [110] direction have been studied. On the other hand, since the distribution of atoms is not symmetric in the (110) (Z plane) plane, both [112] and its opposite direction are considered.

![Graphs showing variations of contact pressure ratios](image)

Fig. 2-6. Variations of contact pressure ratios for different positions of a single vacancy along [112] and [110] at different layers for indenter radius of 4 nm, (a) vacancy is along [112] (in 110 plane), (b) position on [112] is fixed while vacancy is translated along [110]. Contact pressures are normalized by the value of the contact pressure at the displacement burst of the perfect crystal.
Several observations can be made from these graphs. For a given tip, the position of the vacancy clearly impacts the yield load. In the case of the tip radius of 4 nm, a single vacancy at the 6th layer is the most leads to the lowest loads needed to initiate plasticity. It is also apparent that a single vacancy along [110] weakens the crystal more than one along [11\bar{2}] does. The lowest recorded yield load was 126.68 eV/Å, a 34% lower load than that for a perfect crystal (191.08 eV/Å). The 34% decrease in load corresponds to a 13% decrease in contact pressure. This shows that even in absence of other defects such as grain boundaries or surface steps, a single vacancy can impact yielding. It is also seen that in every layer the position of a single vacancy which corresponds to the smallest yield load is off-axis.

![Fig. 2-7.Equivalent crystallographic directions in the 6th layer shown in the same line pattern; along similar line pattern, vacancies with equal distances to the indentation axis lead to equal yield forces; dotted lines show the region in which a single vacancy in the 6th layer can affect the onset of plasticity, small filled circles show vacancy locations corresponding to the smallest yield force. The dashed circle shows the approximate size of the region at which a single vacancy can impact the material yielding. The radius of this circle and the tip radius are 1.74 nm and 4 nm, respectively.](image)

Because of the rotational symmetry in the lattice structure, several equivalent positions in other crystallographic directions can be found as well. In particular for the 6th layer and the tip
radius of 4 nm, Fig. 2-7 shows these equivalent directions with the same line patterns. Indeed, crystals with a single vacancy in the directions with the same line pattern and with the same distance from the indentation axis show the same yield load at the onset of plastic deformation. Using this fact, and also Fig. 2-6, it is possible to define a region on the 6th layer in which a single vacancy can affect the onset of plasticity, noted in Fig. 2-7 by dotted lines. This region has a three-fold symmetry around the indentation axis, and the dashed circle in the figure denotes the approximate size of this region. The vacancy locations corresponding to the smallest yield forces are also shown as marked with small solid circles in the figure. Although not explicitly shown in the figure, several positions between the represented lines were also considered and the obtained results validate the marked region.

To address spatial distribution of single vacancies versus concentrations of more than one vacancy, for indenter radius of 4 nm several simulations with random distribution of vacancies with concentrations in the range 3.3e-5 to 0.0033 atomic fractions were carried out. Fig. 2-8 shows the yield loads at the onset of plasticity for these distributions and also two dashed lines indicating the yield loads for the perfect crystal and the crystal with a single vacancy in a critical spot (at 6th layer, with x: -4.311 Å and z: 0). It can be seen that except three points, all other data are between the upper (perfect crystal) and lower (crystal with a single vacancy) bounds. The vacancy concentration of these three points is 0.0033 which is very high and unlikely to happen. This shows the essential need for studying particular locations of vacancies in the crystal.
Fig. 2-8. Yield loads at the onset of plasticity for randomly distributed vacancies with different concentrations. Two dashed lines indicate the yield loads for the perfect crystal and the crystal with a single vacancy in a critical spot (at 6th layer, with x: -4.311 Å and z: 0). The indenter radius is 4 nm.

To identify the effect of indenter size on the onset of plasticity during contact loading in the presence of a vacancy, the indenter radius was increased from 4 nm to 6 nm. Fig. 2-9 shows the contact pressure ratios for several positions under the indenter obtained for this indenter size. By comparing Fig. 2-6 with Fig. 2-9, it can be seen that the region beneath the indenter in which a single vacancy affects the yield point scales with the tip radius. As the indenter radius increases, material in both the vertical and horizontal directions is impacted by the stress field around the indenter.
Fig. 2-9. Variations of contact pressure ratios for different positions of a single vacancy along [11\̅2] and [1\̅10] at different layers for indenter radius of 6 nm, (a) vacancy is along [11\̅2] (in (1\̅10) plane), (b) position on [11\̅2] is fixed while vacancy is translated along [1\̅10]. Contact pressures are normalized by the value of the contact pressure at the displacement burst of the perfect crystal.

Since spatial variations in defect position have now been shown to be able to impact the yield behavior during contact loading, it is possible to more closely compare simulations to experiments by positioning vacancies at random locations in the affected volume and determining the yield point for a large number of runs. Experimentally this is often presented as a cumulative distribution function of yield [21,22,95], where the normalized or raw loads or stresses are noted for a large number of indentations. To examine the sensitivity of the magnitude of the yield point to the indenter size in the presence of vacancies, the cumulative distributions of the contact pressure ratios at the first displacement bursts for two indenter sizes, used in the simulations, are shown in Fig. 2-10(a). The cumulative distributions of the contact pressure ratio at yield for the experimental studies are shown in Fig. 2-10(b) for both indenter tips used in the experiments. The experimental change in contact pressure correlates closely with the change in the load at which a displacement burst occurs; we use both the load and depth at this point to determine the mean pressure using a Hertzian model, and then normalize by the
highest stress measured experimentally. By using the load and depth the impact of roughness is eliminated, as the effective tip radius is removed from the model. This estimate using the Hertzian model will tend to under-predict the actual shear stress [96], but since the loads and depths at yield are similar between the samples with low and high vacancy concentration, the relative underestimate in shear stress should be similar between both samples. While the experiments obviously probe a broader distribution of defects than the simulations (and hence lead to much lower contact pressure ratios at the lower end of the probability curves and also much more scattered points close to the contact pressure ratio of 1), the salient feature of comparison is that it is more probable to observe the decrease in the yield point when sampling a volume of material containing vacancies is done with a larger radius tip than when it is done with a tip of a smaller radius.

Fig. 2-10. Modeling (a) and experimental (b) results showing the effect of indenter size on the cumulative distributions of the contact pressure ratios for the Ni single crystal. Experimental data were obtained for specimens with a high concentration of vacancies. The maximum pressures used to obtain these ratios for modeling and experimental data are, respectively, 21.3 GPa and 22 GPa.

By sampling a large number of vacancy positions, several typical features in load-displacement curves were noted. For the tip radius of 6 nm these features and the corresponding
snapshots of the atomic positions during indentation are shown in Fig. 2-11(a-c). These cases, representative of several simulations, show different mechanisms of nucleation and propagation of dislocations in the Ni crystal when it has a single vacancy. Fig. 2-11(a) shows the nucleation of dislocations from the vacancy which is relatively far from the indentation axis. Propagation of dislocation loops continues under the surface causing fluctuations in the load-displacement curve. The burst then happens when a second set of dislocations nucleate from a region close to the loop which is already created. For the crystal with a single vacancy in the 12th layer (y: -22.353 Å) (Fig. 2-11(b)), the nucleation is again from the vacancy while no migration or propagation of dislocation loops under the surface can be seen. The behavior of the crystal in the last case (Fig. 2-11(c)) is similar to what is observed in Fig. 2-11(a) but with subtle difference. In this case two yield points, one much smaller than the other are seen. The small burst is due to the nucleation and propagation of dislocation loops from vacancy under the indenter while the large yield point happens when other dislocations branch from the dislocation loops which were already generated from the vacancy.
Fig. 2-11. Load-displacement curves and atomistic visualization of particular points during the downward motion of the indenter with the radius of 6 nm; (a) single vacancy at the 4th layer, with x: 15.807 Å and z: 0, A: nucleation of dislocation loops from the vacancy under the surface, B: separate nucleation, burst point, C: collision of two separate dislocations, D: propagation to the surface; (b) single vacancy at the 12th layer, on x: 0 and z: 9.956 Å, A: nucleation from the vacancy, B,C: propagation to the surface; (c): single vacancy at the 6th layer, x: 12.933 Å and z: 0, A: nucleation of dislocation loops from the vacancy under the surface, B: propagation to the surface.

The nucleation of dislocations in single crystals with vacancies is also dependent on the resulting stress/strain field surrounding the indenter. Fig. 2-12 shows two different mechanisms responsible for the onset of plasticity for a single vacancy at the same position for two different
indenter sizes (i.e. at different relative locations in the stress field). As can be seen, for this particular position, nucleation happens from the vacancy for larger indenter (Fig. 2-12(b)) while for the small indenter (Fig. 2-12(a)) the nucleation happens from a site close to the indenter. Here the nucleation site is not the same as that for the perfect crystal (Fig. 2-2). This shows that the role of the vacancy on the location of nucleation of dislocations may depend on the magnitude of either the stress or the stress gradient underneath the indenter tip. This effect is similar to that shown to exist with nanocompression [85] and nanoindentation experiments [83,71] with varying dislocation content. When testing materials with low defect content with a small probe, the likelihood of sampling a perfect area of the crystal and consequently the perceived strength increase. Sampling moderate defect densities or sampling with moderate sized mechanical probes will lead to more stochastic behavior and a broader distribution of yield phenomena, and finally sampling with a large probe or a high defect density should show a lower, but more consistent, stress required to initiate plasticity.

![Fig. 2-12. Atomistic configurations showing the effect of indenter size on the nucleation mechanisms at onset of plasticity for a crystal with a single vacancy at the 12th layer, x: 0 and z: 9.956 Å, (a) indenter size of 4 nm, (b) indenter size of 6 nm.](image)

### 2.4 Conclusions

Both atomistic simulations and experimental data have been used to examine the effect of vacancies on the onset of plasticity in a Ni single crystal under contact loading. Atomistic
modeling has demonstrated that presence and position of a single vacancy can impact the yield load. A single vacancy can lower the yield load even when positioned at depths of approximately one-third of the tip radius. Several mechanisms regarding the nucleation of dislocations in the presence of vacancies have been documented, including nucleation of dislocations from a vacancy, migration of a vacancy prior to nucleation, and the nucleation of a large number of dislocations from a loop already created under the surface. These mechanisms support the theory that nucleation of dislocations during contact loading in the presence of vacancies is heterogeneous; even when a dislocation does not nucleate at a vacancy the vacancy impacts the nucleation event and hence the process is effectively heterogeneous. Finally the atomistic simulations, supported by experimental data, have shown that the yield behavior is more sensitive to the vacancies as the sampled volume increases, and heterogeneous nucleation of dislocations will experimentally manifest in nanoindentation experiments as a probe sample size dependent phenomenon.

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CHAPTER THREE: The impact of a variety of point defects on the inception of plastic deformation in dislocation free metals

I. Salehinia, D.F. Bahr

Abstract

Atomistic simulations of nanoindentation tests were used to quantify the effect of point defects (a single vacancy, a di-vacancy, a self interstitial atom and a stacking fault tetrahedron) on the onset of plasticity in copper. The stacking fault tetrahedron reduces the pressure needed to nucleate a dislocation by almost half of that of the perfect crystal. Reduction in the normalized yield pressure relative to the perfect crystal for a given defect is independent of indenter size.

3.1 Introduction

Focused ion beam (FIB) machining is widely used as a sample preparation technique to form structures for micromechanical testing of materials [55,56,97-101], such as pillars [97,99], cantilever beams [100], or tensile bars [101]. This technique can generate defects in the material so there are efforts to find the possible effect of this method of machining on the mechanical behavior of the target materials. For instance, Van Petegem et al. [102] showed that FIB milling has a small effect on the mechanical properties of pillars whose internal length scale is much smaller than the pillar size. However, Van Swygenhoven and co-workers observed, using Laue diffraction during compression testing, that defects caused by FIB damage can alter the yield strength of single crystals [103]. Shan et al. [56] showed that the deformation of a single crystal Ni pillar was mainly controlled by the nucleation of dislocations once defects which were formed
by FIB milling (primarily dislocations) were “annealed” away with the application of small applied forces. Bei et al. [104] observed that in FIB milling the creation of dislocations was the main controlling mechanism for small scale deformation. These and other work [105] suggest that an examination of the possible influence defects commonly formed during FIB processing on dislocation nucleation is appropriate in understanding the wide range of yield behavior in small scale mechanical tests noted in the literature.

In source-limited deformation conditions (dislocation “starvation”) [56,106,107] or when the sample size is too small to contain a uniform distribution of dislocations, the nucleation of dislocations may be critical for deformation mechanisms. Previous studies have focused on pre-existing dislocations as possible sources [83,85], but FIB milling also generates point defects and their clusters. While these defects have not been widely addressed as possible heterogeneous sources for dislocation nucleation, it has been noted that they are a possible source for the heterogeneous nucleation of dislocations [21].

This paper uses atomistic simulations of nanoindentation to identify the relative impact of four commonly formed point defects in FCC materials (single vacancies, di-vacancies, self interstitial atoms (SIAs), and stacking fault tetrahedra (SFTs)) on yield behavior. In the absence of dislocations, free surfaces and these internal defects are possible sources of dislocation nucleation [21,25]. The simulated mechanical test, nanoindentation, was chosen to minimize the possibility of nucleation of plasticity at the free surface by projecting the maximum shear stress to an internal point, hence increasing the chance of internal defects to dominantly affect the mechanical behavior. The majority of available literature focuses on the effect of these defects when they interact with pre-existing dislocations [108-111], fewer have examined the effect of point defects on the nucleation of new dislocations and most of these focus on single vacancies.
As these defects may not be readily observable by experimental methods [98,56], simulations provide an efficient way to determine if these defects do indeed influence the nucleation of dislocations and could be an important factor in micromechanical testing. The impact of the size of the indenter and the model size will be studied to determine if smaller simulations are applicable to larger experimental results and also to find if the simulation volume can artificially influence the onset of plasticity in the presence of defects. Nanoindentation is only one of several small scale testing methods, but the results should be appropriate to any small scale mechanical test which is impacted by deformation mechanisms such as dislocation nucleation in small scales.

3.2 Modeling details

In the current study the atomistic embedded atom method (EAM) was applied to model the nanoindentation process on copper using the potential developed by Mishin and coworkers [112]. The Cu single crystal film chosen for the simulation is $20 \times 20 \times 20 \text{ nm}^3$ containing about 680,000 atoms. The simulation was performed using a quadratic repulsive force to model a rigid spherical indenter; radii of 6 nm, 10 nm and 15 nm were used in this study [39]. The indentation axis is along the [111] direction (Y axis), while the X and Z axes are along [11\overline{2}] and [1\overline{1}0] directions.

Molecular dynamics simulations were performed using the LAMMPS code [92,93]. The side and bottom faces were fixed while top face was allowed to move (i.e. the simulation is similar to a thin film on a rigid substrate). The simulation box is large enough to neglect the effect of applied boundary conditions on the onset of plasticity; simulations with the other extreme case (free bottom surface) show no statistically different results for the onset of plasticity (of course the subsequent propagation and interactions of the dislocations is greatly
influenced by the boundary condition). The initial relaxation was applied for 10 ps. The indenter speed was 10 m/sec and the time step was 1 fs. The temperature of the system was kept close to 0 K to minimize temperature effects. As thermal activation in general lowers the applied stresses needed to generate plasticity, keeping the system at low temperatures allows for the determination of the maximum effects in applied stresses these defects will have on the nucleation of plasticity. This will enable upper bound estimates of the magnitude each defect type will have on the reduction in applied stress in incipient plasticity conditions. The centro-symmetry technique [17] was employed to visualize defects. Atoms with a centro-symmetry parameter (CSP) less than 0.3 are not shown in the results so as to highlight the particular defects of interest.

Single vacancies were generated by removal of a single atom from the crystal structure. To introduce a di-vacancy, two nearest neighbor atoms were removed on a (111) plane. This resembles one of the most stable configurations of a di-vacancy in FCC metals [113]. The <100> dumbbell configuration has been found to be the stable form for a SIA in Cu [114]. To create a SIA two atoms separated by 2.556 Å were arranged at atomic positions near the atomic site in the lattice from which an atom was already removed. The SFTs were generated by relaxation of a triangular Frank loop platelet of vacancies in one of (111) planes [47]. The SFT was oriented downward and the initial triangle contains 55 vacancies; 10 on each edge. The edge length of the resulting SFT is about 2.2 nm, close to that of experimentally observed SFTs in copper [115].

3.3 Results and discussion

Fig. 3-1 shows a load-displacement graph and the snapshots of atomistic configurations for a representative simulation with a 15 nm-indenter on copper with a di-vacancy at the 12th atomic layer (y=22.96 Å) on the off-axis position. In all simulations the first burst in the load-
displacement graph is picked when the dislocations already generated from the defect hit the surface. Deviation from elastic behavior is more obvious for this point compared to that associated with the nucleation of dislocations, and closer to experimental observations.

Fig. 3-1. Load-displacement curve with snapshots of atomistic configuration at several stages of nanoindentation including the nucleation of dislocations from the defect and the onset of plasticity (marked with *). The defect is a di-vacancy positioned on the 12th layer away from the indentation axis. The position of the di-vacancy (black solid dots) and also the indentation axis (x symbol) are shown at the corner of the graph.

To account for a variety of indenter sizes and positions of defects, the depth of the defect was normalized by the radius of the contact area at the onset of plasticity. For indenter radii of 6, 10 and 15 nm, Fig. 3-2 (a) and (b) show the variation of reduction in the yield pressure relative to the perfect crystal versus non-dimensional depth for a single vacancy and a di-vacancy located on the indentation axis. In the case of a di-vacancy, an atom on the indentation axis and one of its 6 nearest neighbors were removed. The percentage of weakening was calculated by comparing the maximum Hertzian pressure \( p_0 = \left( \frac{6PE^2}{\pi^2R^2} \right)^{1/3} \), where \( P \) is the indentation load, \( R \) is the
indenter radius and $E^*$ is the reduced elastic modulus) [60] at the onset of plasticity for the perfect crystal and the defective crystal. The weakening effect is independent of the indenter size; of course the load required to nucleate the defects scales with the indenter size. The spatial distribution of shear stress underneath an elastic contact, which shows no indenter size dependence, is the likely explanation of this observation. Since bigger indenter sizes require larger simulation boxes and longer simulation time, this suggests that the use of small models to find the effect of particular defects on the onset of plasticity is computationally efficient.

Fig. 3-2. Percentage of weakening effect as a function of normalized depth of a single vacancy (a) and a di-vacancy (b) located on the indentation axis for indenter radii of 6 nm, 10 nm and 15 nm.

To ensure the maximum amount of weakening was determined for a particular defect, each defect was also positioned at off-axis spots. The largest reductions in the yield force for the defects considered in this work occur when the defect is near (not necessarily on) the indentation axis. The impact of the defects on the reduction in shear stress required to nucleate a dislocation is shown in Fig. 3-3 as the variation of maximum reduction in the yield pressure for different types of defects versus indenter radius. The maximum relative weakening effect of a specific defect on the stress required for the initiation of plastic deformation is constant over the indenter
size range; the decrease in yield pressure is 10%, 21%, 22% and 49% for a single vacancy, a di-vacancy, a SIA and a SFT, respectively. The highest impact of a SFT on the maximum contact pressure at the onset of plasticity is comparable to the values reported in literature for other defects such as surface steps [116,117] and grain boundaries [118,119], and suggests that STFs generated during FIB milling could play a significant role on the onset of plastic deformation in micromachined mechanical test specimens.

![Graph showing reduction in yield pressure vs indenter size](image)

Fig. 3-3. Percent reduction in the yield pressure at the onset of plasticity versus indenter size for a single vacancy, a di-vacancy, a SIA and a SFT in copper single crystals.

To ensure no effect of the small sample volume was influencing the various size defects, a study of the effect of the simulation volume was done for a fixed position of a di-vacancy and a SFT. The indenter radius, 15 nm, and the width of the simulation box, 20 nm, were held constant while the thickness of the simulation volume was varied. This effectively produces a film thickness effect, similar to that shown by Nair et al. [118] where they studied the effect of the film thickness on the onset of plasticity in the presence of low angle grain boundaries. Fig. 3-4
shows the variation of the contact mean pressure \( p_m = \frac{P}{\pi R d} \), where \( d \) is the indentation depth) at the onset of plasticity under the indenter as a function of film thickness for a perfect crystal (triangles), a crystal with a di-vacancy in a critical spot at the 12\(^{th}\) layer (circles) (see Fig. 3-1) and a crystal with a SFT of 2.2 nm centered at the 15\(^{th}\) layer on the indentation axis (squares). The contact pressure at the onset of plasticity decreases with increasing the film thickness. This is similar to the effect demonstrated in [37]; the required stress for the inception of plastic deformation could be partitioned into two parts; that of a critical stress, \( \sigma_0 \), needed to nucleate dislocations from the defect in an infinite solid, and a size-dependent term,

\[
\square^* = \square_0 + 2 \square b/L \tag{1}
\]

where the size dependent term requires \( \mu \), the shear modulus (48 GPa for Cu), \( b \), the Burgers vector (0.2556 nm) and \( L \), the dimension of the structure or another barrier to dislocation bowing that would preclude forming a dislocation loop. Here \( L \) is limited by the film thickness. The data for single crystals having defects were fit to this equation and the results are shown in Fig. 3-4 to reasonably fit the MD results. The constant term in this equation is equal to 23.7 GPa and 12.9 GPa for the crystal including a di-vacancy and a SFT, respectively.
Fig. 3-4. Variation of the contact mean pressure at the onset of plasticity under the indenter as a function of film thickness for a perfect crystal (triangles), a crystal with a di-vacancy in a critical spot at the 12th layer (circles) and a crystal with a SFT of size 10 centered at the 15th layer on the indentation axis (squares). Predictions of pressures using Eq. 1 are shown using dash-dotted lines for di-vacancy and dashed lines for SFT.

3.4 Conclusions

In summary, atomistic simulations of nanoindentation tests have been used to study the extent to which common point defects that can be generated from FIB milling may lower the stresses required to initiate plasticity. These defects include a single vacancy, a di-vacancy, a self-interstitial atom and a stacking fault tetrahedron. The amount of reduction on the yield stress has been found for each of the defects and it has been shown that the weakening effect of these internal defects does not depend on the indenter size in nanoindentation test. This work suggests that in dislocation “starved” conditions point defects could be responsible for decreasing the stress needed to nucleate dislocations by up to almost 50%. Any effect of simulation volume on the yield stress in the presence of defects has to be accounted for so that the stress at the inception of plastic deformation in larger volumes can be isolated.
The presence of point defects can help explain the distribution in stresses required for dislocation nucleation observed experimentally in the literature [21]; variations in strength of up to 50% may be observed in FIB machined samples and various annealing and FIB machining conditions could lead to stochastic variations in strength, while vacancies likely can be responsible for reductions in stresses at incipient plastic deformation of about 10%. For more comprehensive comparison between simulations and experiments future studies should include the effect of temperature in the presence of different types of point defects.

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CHAPTER FOUR: Inception of plasticity in copper single crystal in the presence of stacking fault tetrahedra

I. Salehinia, D.F. Bahr

Abstract

Atomistic simulations have been used to investigate the effect of a spatially distinct defect, a stacking fault tetrahedron (SFT), on the inception of plastic deformation in a perfect copper single crystal during nanoindentation. An SFT positioned within a volume under significant stress from an indentation lowers the stress required for dislocation nucleation by up to 50% from that of the perfect crystal when the nucleation event occurs at the SFT. The orientation of the SFT affects the required load for the initiation of plastic deformation, and provides an envelope for the effect an SFT can have in weakening an otherwise perfect crystal. The weakening effect of the upward SFT vanishes faster than the downward SFT when it is lowered along the indentation axis. The load at the onset of plasticity changes with position, and the load drop after the inception of plastic deformation increases with SFT distance from the surface.

4.1 Introduction

Stacking fault tetrahedra (SFTs) are common defects formed in FCC crystals under variety of treatments such as large plastic deformation [120], quenching from high temperatures [121,122], irradiation [123] and FIB milling [124]. SFTs are a special shape of vacancy clusters whose stability depends on the number of initial constituent vacancies [51]. Other structural point defects, such as single and di- vacancies, and impurity atoms can also be formed in the above
mentioned processes. In a sufficiently small volume of a material, in which dislocations are likely not present, these internal defects can alter the mechanical response by lowering the stress required for the initiation of plastic deformation [28,30,37,39,82,125]. Several studies have shown that the onset of plasticity in low dislocation density material is the result of the nucleation of dislocations in the materials either homogeneously from the perfect lattice or heterogeneously from the existing defects; these defects may be point defects or pre-existing dislocations in materials [11,13,17,21,29,61,85,126]. The data presented in the recent paper by Salehinia and Bahr[125], showed that among different point defects in copper single crystal, the SFT has the largest effect on the yield stress, reducing the pressure at the onset of plasticity in nanoindentation test by almost half of that for the perfect crystal. Fig. 4-1 includes a typical comparison on the percent reduction of the pressure at the onset of plasticity (with respect to that for a perfect crystal) for different types of point defects (single vacancy, self-interstitial atom (SIA), di-vacancy and SFT) in that paper. As the SFT has the biggest impact on the mechanical response of the material in the case of incipient plasticity, it is necessary to explore the governing deformation mechanisms in the presence of this defect. Literature on the effects of SFT on the mechanical response of materials is mostly limited to the formation of this defect or its interaction with other structural defects mainly dislocations [122,127,128].
Nanoindentation experiments are capable of testing extremely small volumes of materials containing low amount of pre-existing dislocations \([129,71]\). In the absence of pre-existing dislocations plastic deformation is mainly controlled by the nucleation of dislocations. If the surface of a sample is flat and has few significant asperities, then the maximum shear stress during an indentation test which begins in an elastic manner is in the bulk of the material \([60]\). This makes small scale indentation specifically suitable for studying the effect of internal defects on the mechanical behavior of materials. In indentation testing the onset of plasticity is seen as either an excursion in a load-displacement graph in load-control mode or load drop in load when indentations are run in displacement control mode \([129,74]\).

In this paper, atomistic simulations are used to investigate the effect of stacking fault tetrahedron on the inception of plastic deformation in copper. Different orientations of this defect...
are considered and deformation mechanisms are used to explain the observed mechanical response in load-displacement curves in a nanoindentation test.

4.2 Modeling

Molecular dynamics (MD) as implemented in the LAMMPS code [92,93] using the embedded atom method (EAM) [112] were performed to model nanoindentation tests on copper single crystal having a stacking fault tetrahedron as an internal defect. The size of the simulation box was 20x20x20 nm$^3$, containing approximately 680,000 atoms. The indenter radius was varied between 6 nm and 15 nm. Although these sizes are much smaller than indenter radii in experiments, the applied approach in this work assures getting similar results for larger sample and indenter sizes. The indenter was modeled as a rigid spherical tip using a quadratic repulsive force [17]. Using deformable indenter in the simulations increases the computational cost of the simulations without a remarkable effect on the overall behavior of the crystal with or without a defect. The indentation was performed along the [111] direction (Y axis), while the X and Z axes are along [112] and [110] directions. The top face is allowed to move and the bottom and side faces are fixed within 5 Å. An initial relaxation was applied for 10000 MD steps (10 ps) using time step of 1 fs. The indenter speed was 10 m/sec. The temperature of the system was kept close to 0 K to reduce temperature effects. To visualize defects the centro-symmetry technique [17] was employed. To see particular defects, atoms in the perfect lattice (with a centro-symmetry parameter (CSP) less than 0.3) are not shown in atomistic configurations represented in the results.

The SFTs, centered on the indentation axis, were generated by relaxation of a triangular Frank loop platelet of vacancies in one of the \{111\} planes [47] containing 55 vacancies; 10 on
each edge. The edge length of the resulting SFT is about 2.2 nm, which is similar to the size of SFTs in copper observed in experiments [120]. The density of SFT in the modeling is close to $10^{23} \text{ m}^{-3}$ which was reported for copper [115]. It should also be noted that the obtained results in this paper are applicable to much bigger sample sizes for which the SFT density is even more realistic. Upward and downward SFTs were generated by removing the initial triangle of vacancies in (1 1 1) and (1 1 1) close packed planes, respectively. Fig. 4-2 shows the configuration of the triangle of the vacancies before relaxation (Fig. 4-2 (a)) and the relaxed structure having a downward SFT (Fig. 4-2 (b)).

![Fig. 4-2. Atomistic configurations of the simulation box before (a) and after (b) relaxation showing the formation of a downward SFT from a triangle of vacancies in (1 1 1) plane. Atoms are color coded using centro-symmetry parameter.](image)

### 4.3 Results and discussion

For the simulations using an indenter with a radius of 6 nm, Fig. 4-3 shows the load-displacement curves for a perfect crystal and crystals with SFTs having different orientations, in upward and downward directions and positioned on the indentation axis at the 9th layer from the surface. The shapes of the SFTs are also shown in this figure.
Fig. 4-3. Load-displacement curves for perfect crystal and crystals having upward and downward SFT. Insets show the shape of each SFT. Indenter radius is 6 nm and SFTs are centered on the indentation axis at the 9th layer from the surface.

Fig. 4-4. Atomic configurations of deformation mechanisms for copper single crystal having upward (top row) and downward (bottom row) SFT centered on the indentation axis at the 12th layer from the surface; (a-d): initial upward SFT, unzipping the SFT, propagation of dislocations toward bottom surface, propagation of dislocation toward the top surface; (e-h): initial downward SFT, unzipping the SFT, propagation of dislocations toward the top surface. Arrows show the directions of dislocations movement.
The orientation of the SFT affects the amount of reduction on the yield load at the onset of plasticity. This behavior is best explored using atomistic visualization to define the differences in the mechanisms governing the inception of plasticity. In all simulations with the defect in the crystal, the onset of plastic deformation has been identified as the point in the loading sequence when dislocations already nucleated from the defect reach the top surface of the crystal. This ensures they cause permanent deformation; prior to this condition it is possible for partial dislocations to reverse during unloading in the simulation and provide no permanent deformation. Fig. 4-4 shows the deformation mechanisms for the crystals having SFT on both orientations. The SFTs are centered at the 12th layer and the indenter size is 6 nm. For both orientations the deformation initiates with an “unzipping” of the SFT in the direction with the highest stress which, in the initial state of deformation, is a high compressive stress in the loading direction. The deformation mechanisms are different for the considered orientations after unzipping the SFT is complete. For the downward facing SFT, unzipping is followed by propagation of dislocations on three \{111\} planes creating SFT toward the top surface of the crystal. On the other hand, for the upward SFT after unzipping the SFT, the dislocations continue to propagate into the bulk of the material in two slip planes until dislocations start to propagate toward the top surface in another slip plane. In the case of the upward oriented SFT, the movement of dislocations into the bulk of the crystal delays the onset of plasticity and hence the required load for the initiation of plastic deformation is larger than that associated with the downward SFT. An important observation in here is that for both orientations, the SFT is the source of dislocation nucleation. This, indeed depends not only on the relative position of SFT to the indenter but also on the orientation of the SFT.
Fig. 4-5. Variation of contact pressure ratio at the onset of plasticity vs. the depth of the center of the stacking fault tetrahedron for upward and downward orientations.

Fig. 4-5 shows the variation of contact pressure ratio at the onset of plastic deformation for upward and downward SFTs centered on the indentation axis at different layers. The contact pressure ratio is the ratio of the contact pressures at the onset of plastic deformation of a crystal with a SFT and a perfect crystal. The downward SFT can reduce the pressure at the onset of plastic by up to 50% of that for the perfect crystal. When the SFT defect is located further from the indentation surface, the effect on the yield load at the onset of plasticity is lessened. Furthermore, the weakening effect of the upward SFT vanishes much faster than that of the downward SFT. Visualization of the atomistic configuration prior to the onset of plasticity in Fig. 4-6 shows that when an upward SFT is centered at the 15th layer on the indentation axis, nucleation of dislocations far from the SFT accompanies the unzipping of the SFT. Nucleation of

2 Contact pressures are calculated as: \( P = \frac{F}{\pi d^2} \); where \( R \) is the indenter radius and \( F \) and \( d \) are the load, and indentation depth at the onset of plasticity, respectively.
dislocations from the areas without initial defects will be referred to as homogeneous dislocation nucleation; at this point the crystal is behaving identically to the defect free crystal. When the SFT is placed at the 9th or 12th layer the deformation is heterogeneous and dislocations are formed from the defect.

Fig. 4-6. Atomic snapshots showing the deformation mechanisms for the upward SFT centered at (a) 9th, (b) 12th, and (c) 15th layer.

As the effect of the downward SFT on the yield load is much bigger than that of the upward SFT, this study continues with the focus on the effect of downward SFT on the mechanical behavior of the crystal. Simulations were made using an indenter with a radius of 15 nm. Using this indenter size, it is possible to check the consistency of the results for different indenter sizes (change in indenter size is a factor of two, which makes it within a factor of 3 of experimentally achievable tip radii). Secondly the SFT can be placed in much deeper layers from the surface, as the ratio of contact area to position is a controlling factor in the position sensitivity of the defects.
Fig. 4-7. Load-displacement graphs of nanoindentations on (111) copper single crystal including SFT centered on the indentation axis at different layers; indenter radius is 15 nm.

Fig. 4-7 shows the load-displacement curves for a perfect crystal and crystals with different center positions of SFT along the loading axis. Even a SFT centered at the 42\textsuperscript{nd} layer can weaken the material in the case of the larger tip radius. It is also observed that the amount of load drop at the inception of plastic deformation is increased as the defect is located in lower layers. This behavior is supported by the geometrically necessary loading curve, which is defined by the material properties (modulus and strength) and geometry of the nanoindentation test including indenter shape and indenter size [10]. As the onset of plastic deformation deviates from the geometrically necessary elastic-plastic curve the elastic strain energy is increased, leading to larger load drops are needed to reach the geometrically necessary load-depth curve once plasticity has initiated.
4.4 Conclusions

Atomistic simulations have been performed to explain the mechanical behavior seen in nanoindentation test of copper single crystal having stacking fault tetrahedron as an internal defect. Different orientations of the defect have been examined and it is found that the downward SFT has a larger effect on the mechanical behavior of the copper single crystal than an upward-oriented SFT. This allows an upper and lower bound to be identified for the possible effects this defect has on the inception of plasticity. The weakening effect of the defect vanishes much faster when the SFT is oriented in the upward direction than when it is in a downward orientation. Atomistic configurations of the deformation mechanisms using centro-symmetry analysis were used to explain this behavior. The load at the onset of plasticity and the magnitude of the load drop after the inception of plastic deformation increase as the SFT is positioned farther from the surface, showing the effects of spatially distinct defects on yielding during nanoindentation. The propagation of the dislocations far from the indenter reduces the effect of high compressive stress under the indenter and hence increases the load drop at the onset of plasticity.

Acknowledgement

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CHAPTER FIVE: The effect of crystal orientation on the stochastic behavior of dislocation nucleation and multiplication during nanoindentation

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Abstract

Current methods to measure the theoretical shear strength of metals using nanoindentation often present a stochastic view of the applied stresses needed to nucleate dislocations. In this study a combination of molecular dynamics simulations and experimental nanoindentation tests were used to explore the coupled effects of indenter size, crystallographic orientation, and the presence of internal structural defects on the resulting distribution of loads at the onset of plastic deformation in FCC metals; in this case stacking fault tetrahedra have been selected as a representative structural, rather than chemically distinct, defect. The sensitivity of the crystal to the presence of internal structural defects depends strongly on its crystallographic orientation. Simulations of indentations in the presence of a stacking fault tetrahedra show the highest reduction in the pop-in load for the (111) orientation, while experimentally the effect of orientation is dependent on the size of the indenter used, and hence the volume of material under stress. The simulations suggest that indenting near a defect can either cause small, sub-critical events to occur, which then lead to a large “pop-in” at higher loads; therefore the first event observed experimentally may not correspond to the first plastic deformation event. As internal defects are almost inevitable in materials, a defect based model can be used to explain the stochastic pop-in loads in nanoindentation tests.
5.1 Introduction

Nanoindentation is widely used as a tool for sampling the mechanical response of small volumes of materials [130]. The transition from elastic to plastic deformation, often referred to as the onset of or incipient plasticity, manifests itself in nanoindentation load-displacement curves either as an excursion in displacement in load control or load drop in displacement control tests [10]. However, it is not always true that a yield point at this “pop-in” event is indicative of only incipient plasticity. Kiely et al. [12] noted that this event can be a result of events such as the sudden propagation of dislocations already nucleated in the material to the surface. They also showed that these major events happen after some minor events which include nucleation and also propagation of dislocations under the indenter. Similar observations of “pop-in” after plastic deformation events have been noted by other researchers [131,96]. Minor events are almost not observable in experimental load-displacements curve, however molecular dynamics simulations have shown that nucleation, propagation and entanglement of dislocations are possible below the observable pop-in point [12,66].

One important observation in nanoindentation testing is an increase in hardness for either smaller indentation depth or smaller indenter radii [69,70]. Shim and coworkers [71] and Salehinia et al. [39] reported a different type of indentation size effect of nanoscale size indenters based on the nucleation of dislocations at the onset of plasticity (pop-in) for nanometer size indenters. Morris et al. [72] also did a study on the indenter size effect for the indenter radii in the range of 115 nm-700 μm. Using the cumulative event frequency distribution of pop-in events in load-displacement curves they proposed a defect density (mainly dislocations) based model to explain the observed behavior through changing the indenter size. In that study, a narrow distribution of shear stress at the onset of plasticity for small radii, wide distribution for medium
radii and again a narrow distribution of shear stresses for radii of 17.5 μm and larger supported the effect of structural defects on the onset of plasticity. Although their proposed model works very well for radii larger than 1.5 μm, for smaller radii there are significant deviations from the experimental data. Several researchers have used atomistic and multiscale simulations to address indenter size effect on mechanical properties of different types of materials; these sizes are often using tip radii in this smaller regime [132,133,118].

As the deformed volume of materials decreases, the effect of crystal anisotropy on the mechanical response intensifies. Several studies have shown that for FCC crystals elastic moduli for (111) and (110) are about the same and bigger than that in (100) orientation [62,73-78,132]. The majority of literature examining the effect of orientation on pop-in behavior have shown that the pop-in loads in the (111) orientation are usually largest and those in the (100) are usually the smallest [39,62,75-78]. Among experimental studies, several works have tried to elucidate the stochastic nature of the pop-ins in nanoindentations for several crystal orientations. For instance, Li et al. [80] performed theoretical calculations and experiments to study the distribution of pop-in loads for nanoindentation on NiAl single crystal in several crystal orientations. For an indenter radius of 580 nm, their results showed a narrow distribution of pop-in loads for (111) and (110) orientations, and widely stochastic values for (100) orientation. They linked the stochasticity of data in (100) orientation to the larger stressed volume for this orientation compared to those for (111) and (110), suggesting higher chance for internal defects such as dislocations to be influenced by the indenter stress field, hence contributing to the pop-in statistics. Recently, a combined experimental and modeling study by Wang et al. [134] has explored the orientation effect on the stochastic distribution of pop-in loads, and observed that for indentations into Cu single crystals in (100), (110) and (111) using indenters of 164 nm and 53 nm there is little to no
effect of orientation on the yield behavior. Using Weibull statistics, they suggest that bulk defects are more likely responsible for the displacement bursts for (100) orientation, and surface defects are behind the pop-ins for (111) and (110) orientations. MD simulations of nanoindentation tests then showed that for (111) and (110) orientations the nucleation of dislocations was followed by a sudden load drop, while the (100) orientation exhibited homogeneous dislocation nucleation with only a small load drop, followed by the formation of a dislocation lock under the indenter tip.

Since as the test size decreases the effect of structural defects on the mechanical response of a crystal is enhanced, exploring different defects could be a reasonable way to tailor their possible effect on the onset of plasticity in nanoindentation experiments. Among different structural defects in single crystals, surface defects such as steps [117,135,136], and internal defects such as point defects (vacancies, interstitials, impurities) and their clusters like stacking fault tetrahedra [125] have been of interest in literature. Calculations have shown that the critical stress for dislocation nucleation at surface steps can be half that on the flat surface [135]. Salehinia and Bahr [125] studied the effect of vacancies, self interstitial atoms and stacking fault tetrahedra on the pop-in load in nanoindentation on (111) copper single crystal, and showed up to a 50% reduction in the applied stress at the onset of plasticity in the presence of an SFT under the indenter. As structural defects in materials are common, for better understanding of the observed stochasticity in pop-in loads, we believe simulations should include defects.

In this paper experimental and modeling studies are combined to explore the coupled effects of indenter size, crystallographic orientation, and the presence of structural defects on the distribution of the pop-in loads during nanoindentation in commercially pure nickel, while corresponding MD simulations have been carried out for copper. The choice of two different
materials was made to emphasize the strengths of each technique. The available EAM potentials for Cu are more reliable for dislocation nucleation than those for Ni, while experimentally Ni exhibits a thin oxide layer and less effect from solute oxygen than Cu. The load-depth curves and deformation mechanisms from MD simulations will be used to explain the different distribution of pop-in loads for different indenter radii and crystal orientations in experiments.

5.2 Methods

5.2.1 Modeling

Molecular dynamics simulations were carried out using the LAMMPS code [92,93] applying the EAM potential developed by Mishin et al. [112] to model nanoindentation of copper with (100), (110) and (111) crystallographic orientations. The size of the simulation box was 20x20x20 nm\(^3\) containing around 680,000 atoms. The side and bottom faces were fixed and the top face was allowed to move. The simulation box was large enough that the effect of boundaries on the onset of plasticity is negligible. The indenter was modeled as a rigid sphere of 15 nm radius with a quadratic repulsive potential. The time step was 1 fs and the indenter speed was 10 m/sec. To verify that this velocity was not creating an artificial construct, a velocity of 1 m/s was applied for a few tests; the deformation mechanisms and mechanical behavior of the material was basically unchanged. Energy minimization followed by dynamic relaxation for 50 ps was done before initiation of loading. The temperature of the system was kept close to 10 K to exclude the temperature effect in simulations. Since thermal activation assists the nucleation of dislocations by lowering the required stress for this effect, the use of a low temperature results in upper bound stress estimates in the simulations.

As any indentation with a spherical tip projects the maximum shear stress into the crystal underneath the free surface, internal defects could be highly influenced by the stress field under
the indenter. Previous work has shown that of moderately sized point defects (vacancies, di-vacancies, self-interstitials, and stacking fault tetrahedral (SFT)), the SFT causes a much larger reduction in yield stress when compared to a perfect crystal [125]. Since SFTs are formed by partial dislocations, this defect can also be used as an appropriate representative for dislocations distributed in the crystal. SFTs are formed by the agglomeration of vacancies through Silcox-Hirch mechanism [47] during irradiation, quenching and large plastic deformation [40]. The stable mean size of an SFT in copper is about 2 nm [120]. In simulations, relaxation of a Frank loop triangle of 55 vacancies removed from one of the \{111\} planes, resulted in an SFT with an edge length of 2.2 nm; i.e. containing 10 vacancies on each edge. The relative orientation of an SFT to the loading direction can impact the pop-in load [137], therefore in each orientation the SFT with the largest impact on the onset of plasticity has been used.

The centro-symmetry parameter (CSP) [17] was used to visualize the deformation mechanisms. As this parameter is close to zero for atoms in the perfect lattice, visualizations presented in this paper only include atoms with a CSP greater than 0.3 to highlight the particular defects of interest.

5.2.2 Experiments

Nanoindentation tests were performed on polycrystalline Ni200 with a purity of 99.5%. At room temperature, the thickness of the native oxide layer on Ni200 is on the order of 1 nm, which should minimize any effect of the oxide layer on the measured data. Specimens were cut, then rolled to 20% thickness reduction, annealed in air at 1150 °C for 24 hours and then air cooled. After annealing, specimens were ground through 1200 grit SiC, then mechanically polished with 3μm and 0.5μm diamond compound. Finally, vibropolishing was performed with 0.02μm colloidal silica suspension until a clean, flat, mirror finish was achieved. This heat
treatment resulted in grain diameters of approximately 1mm. Samples then were electropolished in a solution of 37% H$_3$PO$_4$, 56% glycerol, 7%H$_2$O for approximately 5min. Currents and voltages were adjusted to achieve a polished surface. After electropolishing the average RMS roughness for the samples was 2.22±0.07 nm.

Electron backscatter diffraction (EBSD) was performed in an FEI Siron scanning electron microscope to generate inverse pole figures (IPFs) from patterns to identify specific grain orientations. Indentations where then made in grains oriented near the vertices of the stereographic triangle (crystallographic orientations of (100), (110) and (111)). Given the resolution of the instrument the grains selected are within 2° of these orientations. EBSD was performed after both vibropolishing and electropolishing to verify that neither the grain size nor the shape of the exposed grains which were indented had changed. This also implies that the exposed surfaces of the grains selected for indentation were near the center of the 1 mm diameter; it is unlikely that any of the selected grains had sub-surface boundaries within local regions probed using nanoindentation since the size of each grain does not change after removing several 10’s of μm’s of material. To further verify that slight misorientation would not impact measured properties, additional indents were conducted on different nominally (100) and (111) oriented grains within the same sample.

Nanoindentation experiments were conducted using a Hysitron TI 900 TriboIndenter. Two different tips were selected; a cube corner tip with a radius near 100 nm and a Berkovich tip with a tip radius near 1300 nm. Tip radii were determined by applying purely elastic loading on two metallic single crystals ((111) Ni and (100) W). The elastic loading was fit to a Hertzian type loading profile and an effective radius of each tip was determined. More than 10 indentations were carried out on the materials and the depth over which the loading was fit was
to approximately 25% of the effective radius. Of course, the Hertzian assumption is only a first order estimate; as noted by Ma and co-workers [5], this may lead to underestimates in the actual stresses at yield of 30%. The experiments were run in load control mode using two different load functions. First, indentations were made in (111) Ni single crystals at fixed loading rates between 87 and 168 μN/s; no statistical difference was observed in the load at which a yield point occurred for this range of rates and therefore it is assumed that subsequent loading within this range of rates will not impact subsequent yield behavior. Lower loading rates did influence the yield point loads, rates less than 10 μN/s did lead to lower average yield point loads. In one case indentations were made with five segments, partial-unloading load function with peak loads ranging from 250 μN to 7000 μN. Subsequent indentations in other (100) and (111) grains were carried out at loading rates of 87 μN/s to a peak load of 1500 μN. The load-depth curves were analyzed to determine the reduced modulus, pop-in load and depth at the excursion as a function of orientation. Indents were made in arrays where each indentation was spaced 15μm apart from other indentations; the largest plastic zone radius developed for a cube corner indent was 9μm and only 3μm for a Berkovich indent. Therefore the plastic zone developed around a given impression did not affect the measured data for a subsequent indentation. Any indentations which were not verified to be elastic prior to deformation using the partial unload technique were excluded from the analysis of pop-in behavior.

5.3 Results and discussion

Load-displacement curves for simulations of nanoindentations using a 15 nm spherical indenter on (100), (110) and (111) Cu are shown in Fig. 5-1. The effect of elastic anisotropy is observed in the initial loading curves; the (111) orientation is mechanically stiffer than the (100) orientation. Loads at the onset of plasticity, when curve deviates from elastic behavior, have the
same trend as the moduli in the considered orientations. These observations are in very good agreement with the literature [62,73-78,132]. The onset of plasticity for both the (111) and (110) is seen as a sudden drop in the load, while the pop-in in the (100) orientation is more gradual. Once general plastic deformation occurs, the effect of crystal anisotropy decreases and the resulting load-depth curves for different orientations primarily follow a geometrically necessary loading curve, dependent on the shape and size of the indenter and a more isotropic flow rule [10].

![MD Load-displacement curves for nanoindentation tests on perfect crystals with different orientations.](image)

In the presence of structural defects, the mechanical response of the single crystal varies depending on the defect type. Fig. 5-2 shows load-depth curves of nanoindentations on (100), (110) and (111) single crystals, obtained from MD simulations including perfect crystals and also crystals with an SFT centered close to the indentation axis in different layers from the top layer. The maximum depth at which SFT can affect the onset of plasticity for this indenter size is the
29th atomic layer below the surface (y: -5.1 nm) for the (100); the 82nd layer (y: -10.3 nm) for the (110); and the 45th layer (y: -9.2 nm) for the (111) orientations. This supports the observation of more localized plastic zone in (100) orientation than those for (111) and (110) which are more extended into the material [138]. By taking the first deviation from elastic loading as an indication of the inception of plastic deformation, the maximum reduction in pop-in loads in presence of an SFT is 64%, 54% and 87% for (100), (110) and (111) orientations, with a corresponding reduction in shear stresses at the onset of plasticity of 51%, 22% and 29%, respectively.

Fig. 5-2. MD load-displacement curves in nanoindentation tests on perfect crystals and crystals with an SFT in different layers centered close to the indentation axis for a. (100), b. (110) and c. (111) orientations
Fig. 5-3 shows the snapshots of the dislocation activity as the indentation progresses into the crystals with different orientations. For clarification, some snapshots are accompanied by their top view showing the image of dislocations reaching the free surface. While dislocation activities vary with the location of the defect, for each orientation, a representative case is chosen to show the main deformation mechanisms in the presence of the SFT. SFTs are respectively centered at the 25th, 54th and 36th layer for (100), (110) and (111) orientations. In the (100) orientation (Fig. 5-3(a1-a4)), partial dislocations start to propagate from two sides of the SFT, assisting in the formation of a dislocation lock under the indenter. The lock decreases the chance of occurrence of a big load drop by confining the dislocation activities. It also facilitates the hardening process in the nanoindentation test [134]. Homogeneous dislocation nucleation is also seen above the SFT in this orientation for this particular case (Fig. 5-3 (a2,a3)). This is highly dependent on the position of the SFT with respect to the indenter. In the (110) orientation (Fig. 5-3 (b1-b5)), the SFT collapses under applied stress and partial dislocations move in a straight path (channel) to the surface (Fig. 5-3 (b2)). In this orientation, the image size of the SFT on the surface is the same as the SFT size (See Fig. 5-3 (b5)). For this particular position of the SFT, dislocations start to form under the indenter from the moving partial dislocations formed from the SFT (Fig. 5-3 (b3)).Fig. 5-3 (b5) shows the image of the SFT and also the image of the secondary dislocations on the surface. In the (111) orientation (Fig. 5-3 (c1-c5)), the SFT “unzipped” from all three sides (Fig. 5-3 (c2)) and then partial dislocations propagate on {111} planes to the surface (Fig. 5-3 (c3)). In this orientation, partial dislocations diverge from each other and finally form a triangular image much larger than the SFT size (Fig. 5-3 (c4,c5)).
Fig. 5-3. Atomistic snapshots of MD simulations of nanoindentation tests presenting deformation mechanisms in the presence of an SFT under the indenter in crystals with different orientations, a. (100)(a1: initial configuration, a2: homogeneous and heterogeneous dislocation nucleation from bulk and SFT, respectively, a3: dislocation propagation to the surface, a4: surface-dislocation interactions, formation of the dislocation lock); b. (110)(b1: initial configuration, b2: migration of SFT to the surface in (110) direction, vacancy formation at the SFT vertices, b3: dislocation nucleation from SFT in its way to the free surface, b4: dislocation propagation to the free surface, b5: dislocation images including the SFT’s and the image of other dislocations propagated into the crystal); c. (111)(c1: initial configuration, c2: unzipping SFT, c3: dislocation propagation from SFT in three \{111\} planes; c4: surface-dislocations interactions, c5: triangle image of dislocations on the free surface; atoms are colored according to the centro-symmetry parameter.
Fig. 5-2 shows that in the (111) and (100) orientations defects closer to the free surface lead to larger reductions of the pop-in load. However, this behavior is not seen in the (110) orientation; i.e. a SFT does not affect the onset of plasticity up to 50th layer from the top layer, and all of a sudden it has a significant effect when it is centered on the 54th layer. This behavior for the crystal with SFT at the 50th layer can be significantly altered by just a small shift in the position of the SFT in the x or z direction in the same plane. Fig. 5-4 shows the load-depth curves for crystals having an SFT on the 50th layer but in different lateral positions. Fig. 5-5 shows the snapshots associated with the points, 1 and 2, for on-axis SFT and points, 3 and 4, for the off-axis SFT (ref. Fig. 5-4 for the points). Complete annihilation of SFT happens when it is located on the indentation axis (Fig. 5-5 (a,b)). The large burst occurs at a larger indentation force at point 2 where more dislocations hit the free surface (Fig. 5-5 (c)). On the other hand, when the SFT is positioned off the loading axis, at point 3, dislocations nucleate and propagate in a plane which intersects the SFT path through the surface before the annihilation of the SFT on the free surface (Fig. 5-5 (d,e)). In this case more dislocations are formed after the first burst (Fig. 5-5 (f)) and their interactions lead to the several other small bursts in load-depth curve. These observations support the significant effect of spatial distribution of structural defects in materials. This suggests that stochastic behavior reported experimentally could easily be achieved by defects other than dislocation loops, and that this effect is highly dependent on the crystallographic orientation.
Fig. 5-4. MD load-displacement curves of nanoindentation on (110) crystal with SFT in 50th layer from the surface centered on different locations in x axis, atomistic snapshots of points 1, 2, 3 and 4 are shown in Fig 5. Points 1 and 2 are on the solid curve and points 3 and 4 are on the dashed curve.

continued on the next page …
Fig. 5-5. Atomistic snapshots of points 1, 2, 3 and 4 on the presented MD curves in Fig. 4. At point 1 complete annihilation of SFT happens when it is located on the indentation axis (a,b). The large burst occurs at a larger indentation force at point 2 where more dislocations hit the free surface (c). When the SFT is off-axis, at point 3, dislocations nucleate and propagate in a plane which intersects the SFT path through the surface (d,e). After the first burst more dislocations are formed (f) under the indenter in comparison to the case with the on-axis SFT.

It should be reemphasized that the SFT is used here as a representative internal defect in FCC crystals. The observed mechanical response in the presence of SFT can be extended to other internal defects such as dislocation loops from vacancies or interstitial atoms, voids and defects with similar size scale. The selection of the SFT was because it has been shown to be a “worst case” scenario for yield point effects in nanoindentation, and hence is most likely to identify trends in load-depth behavior that may be seen experimentally [137].
Table 1- Statistical analysis of pop-in data for all three orientations for each indenter tip. Number of points represents the number of pop-ins observed, the mean is the mean pop-in load for each data set.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Number of Points</th>
<th>Mean (μN)</th>
<th>Standard Deviation(μN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1300 nm radius tip</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(111)</td>
<td>66</td>
<td>272</td>
<td>155</td>
</tr>
<tr>
<td>(100)</td>
<td>118</td>
<td>357</td>
<td>211</td>
</tr>
<tr>
<td>(101)</td>
<td>19</td>
<td>205</td>
<td>76.4</td>
</tr>
<tr>
<td>100 nm radius tip</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(111)</td>
<td>63</td>
<td>46.3</td>
<td>10.2</td>
</tr>
<tr>
<td>(100)</td>
<td>53</td>
<td>45.6</td>
<td>10.9</td>
</tr>
<tr>
<td>(101)</td>
<td>10</td>
<td>41.8</td>
<td>9.5</td>
</tr>
</tbody>
</table>

Table 2- P-values for each combination of orientations determined from Wilcoxon-Mann-Whitney rank sum tests. Values lower than 0.05 indicate a greater than 95% probability that the data sets are statistically unique.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1300 nm radius tip</td>
<td></td>
</tr>
<tr>
<td>(111)-(100)</td>
<td>0.003</td>
</tr>
<tr>
<td>(111)-(101)</td>
<td>0.09</td>
</tr>
<tr>
<td>(101)-(100)</td>
<td>0.0002</td>
</tr>
<tr>
<td>100 nm radius tip</td>
<td></td>
</tr>
<tr>
<td>(111)-(100)</td>
<td>0.54</td>
</tr>
<tr>
<td>(111)-(101)</td>
<td>0.28</td>
</tr>
<tr>
<td>(101)-(100)</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Fig. 5-6 (a) and (b) show the cumulative distributions of pop-in loads for nanoindentations performed by two different indenter tips on crystal orientations of (100), (110), (111). Due to a limited number and size of (110) orientated grains within the sample preparation area fewer indentations could be made for this orientation than the other two primary orientations. The statistics of yield behavior are presented in Table 1. A Wilcoxon-Mann-Whitney rank sum tests was performed as a quantitative measure of similarity between grains, and the calculated p-values are compiled in Table 2. These values indicate that the data are statistically similar, that is, the yield points measured with the 100 nm tip radius are relatively
insensitive to crystallographic orientation. The cumulative distribution of yield in the different grains using the tip with a radius of 1300 nm (Fig. 5-6 (b)) shows statistically different data between the (100) and the other two orientations. A Wilcoxon-Mann-Whitney rank sum tests of the yield point loads using the 1300 nm tips indicate that the (110) and (111) data sets are statistically indistinguishable, while the other orientation combinations are statistically unique, with p-values of less than 0.05 (greater than 95% probability). These data are also tabulated in Table 2.

The distribution of pop-in loads in (100) has a significantly higher coefficient of variance (ratio of standard deviation to mean value) than those in (111) and (110) orientations. Furthermore, the pop-in loads in (100) are bigger than those for (111) and (110) orientations, which is contrary to the MD simulations for the perfect crystals. The observed trend of the cumulative probability graphs for the tip with a 1300 nm radius is the same as what Li et al. [80] have been reported for NiAl single crystal being indented by a 580 nm radius tip. Additionally, the general shape of the “S-curve” observed for the cumulative fraction of events strongly suggests that the same defect is being sampled by each indent array [22].

The narrower distribution (lower coefficient of variance) of pop-in loads for the smaller radius tip is likely due to the higher probability of indenting a relatively defect-free volume under the indenter [39]. MD curves for perfect crystals in (100), (110) and (111) orientations...
(Fig. 5-1) show that pop-in loads for (100) orientation is much smaller than those for other orientations. This is in contrast to the observation in Fig. 5-6 (a) where median values of pop-in loads are almost the same for the considered orientations. Since in (100) orientation, simulations show the plastic deformation starts with small load drop and load-depth curve stays noisy after the inception of plasticity, in the experiment an observable jump in the load-depth curve can be shifted to larger loads which are comparable to those for other orientations. Further description of this phenomenon follows.

The effect of structural defects is greater for the larger radius tip than that for the smaller radius tip. The larger radius tip creates a larger stress field at a given pressure, which is more likely to sample multiple or larger defects. Fig. 5-2 shows that in the (110) and (111) orientations the effect of the defect is more pronounced and the load drops at the onset of plasticity are large enough to be easily observed. Even when the plasticity initiate at small loads, for almost the same pop-in loads the load drop for the (111) orientation is larger than that for the (100) orientation. For instance, for the (111) sample the load at the onset of plasticity is about 450nN when an SFT is at the 21st layer and the resulting load drop is about 20%; in the (100) orientation at the same load the drop is about 2%. Therefore, the likelihood of capturing the inception of plasticity at low loads is higher for (111) and (110) orientations than that for (100) orientation. The similarity (Ref. Table 2) between the yield distributions in the (110) to (111) orientations in Fig. 5-6 (b) would follow from these observations.

Load-depth curves in the (100) orientation consist of small load drops compared to those in the (110) and (111) orientation. The nucleation of dislocations from the bulk of the material occurs at the first load drop in load-depth curve, which may then be followed by a larger load-depth curve discontinuity (see Fig. 5-2 (a)). Increasing the indenter size in this case causes the
load drop due to nucleation of dislocation loops to decrease [3] making identification of the very first pop-in event more difficult. Furthermore, the larger stressed volume under the indenter results in more dislocation activity, which in general makes a smoother load-depth curve [3]. This suggests that in experiments, imperceptible load drops maybe followed by an observable pop-in due to the effect of other defects, thermal activation of other dislocation sources in the crystal, or a combination of homogeneous and heterogeneous dislocation nucleation in the crystal. This could lead to larger ranges of observed pop-in events during experiments. Fig. 5-7 shows the effect of an SFT on the mechanical behavior of the crystal. Fig. 5-7 (a) shows the load-depth curve and atomistic snapshots of the deformation mechanisms in the absence of the defect. The nucleation of dislocations in the perfect crystal is homogeneous and positioned directly under the indenter. Dislocations continue to propagate until they reach the crystal surface and form two big steps (atoms colored in green in Fig. 5-7 (a3)). Adding a defect changes the load range in which small load drops are likely to happen. As an example, Fig. 5-7 (b) shows that by positioning an SFT at the 21st layer, the relatively large load drops (at displacements of 0.9 nm and 1.3 nm) in load-depth curve of the nanoindentation on the perfect crystal have been removed. When the SFT is positioned at the 21st layer, small load drops are distributed from 430 nN to 2400 nN. As indicated in Fig. 5-7 (b1-b4), in this condition the SFT is the only dislocation source and load drops are small even up to 2 nm indentation depth. The lack of a significant drop in load makes capturing the onset of plasticity difficult in experiments, and consequently the load-depth curves are likely to show either large pop-in loads or no pop-ins in experiment. This could be an explanation behind the lack of pop-ins in more than 70% of the nanoindentation experiments performed in this work.
continued on the next page …
Fig. 5-7. MD results showing the effect of an SFT on the mechanical response of (100) single crystal in nanoindentation test by manipulating minor and major events; (a) perfect crystal(a1: homogeneous dislocation nucleation inside the bulk, a2: dislocation propagation to the surface, formation of dislocation lock, a3: dislocation propagation and release from the lock, a4: more dislocation interactions under the indenter leading to hardening); (b) a crystal with an SFT at the 21st layer on the indentation axis(b1: heterogeneous dislocation nucleation from SFT, b2: dislocation propagation to the free surface, formation of dislocation lock, b3: dislocation propagation in another {111} plane from SFT, b4: images of the dislocations already formed in the crystal on the free surface); (c) a crystal with an SFT at the 25th layer on the indentation axis(c1: homogeneous and heterogeneous dislocation nucleation from bulk and SFT, respectively, c2: dislocation propagation to the surface, c3: surface-dislocation interactions, formation of the dislocation lock, c4: dislocation release from lock and more dislocation interactions leading to hardening); atoms are color coded according to centro-symmetry parameter.

On the other hand, when an SFT is centered on the 25th layer from the top surface in (100) orientation, a comparatively big load drop in load-depth curve can be seen (Fig. 5-7 (c)). In this case, snapshots in Fig. 5-7 (c1-c4) show that partial dislocations in the SFT start to propagate on {111} planes which include two sides of the SFT. As the indenter is going down, dislocation embryos are formed above the SFT and partial dislocations surrounding stacking faults are developed from these embryos. These dislocations reach the surface forming three relatively large steps on the crystal surface which facilitate a bigger load drop in the load-depth curve.

These observations show how a single structural defect can create major yield events during contact loading.

5.4 Conclusions

Molecular dynamics simulations and experimental studies have been combined to demonstrate the coupled effect of indenter size, crystallographic orientation, and structural defects on the mechanisms causing incipient plasticity in FCC single crystals using nanoindentation. Several conclusions can be drawn from these results:
1. The sensitivity of the yield points for crystals in the presence of internal structural defects depends on crystallographic orientation. In the presence of an SFT, as a representative internal defect, the highest reduction in the pop-in loads was seen for the (111) orientation. Defects can either lead to one large yield event or initiate a sequence of small events prior to one large discontinuity in a load-depth curve.

2. The size and shape of the effective volume in which internal defects can affect the mechanical response in nanoindentation test depends strongly on the crystal orientation. The effective volume for (100) orientation is smaller than those for (111) and (110) orientations.

3. For a small (100 nm) indenter radius the cumulative fraction of pop-in loads showed a narrow distribution and a similar medial value for all considered orientations. For this indenter size, the stressed volume is more likely to be defect free, resulting in more deterministic values for pop-in loads.

4. In contrast to the small tip radius, the stochasticity of pop-in loads for a larger nominal tip radius (1300 nm) was dependent on the crystal orientation. Pop-in loads in the (100) orientation are bigger than those for other orientations. For the (100) orientation, load-depth curves obtained from MD simulations showed noisy behavior after the inception of plasticity indicating minor events may occur during what appears to be elastic loading. These minor events can lead to major discontinuities in the load-depth curve by a combination of homogeneous and heterogeneous dislocation nucleation in the crystal. While minor events are difficult to capture in experiments, major events are likely observable in nanoindentation tests.
5. As internal defects are almost inevitable in materials, a defect based model might be the best way to explain the stochastic behavior in pop-in loads in nanoindentation tests. This model should include different concentrations and spatial distributions of various types of structural defects with several sizes.

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CHAPTER SIX: Crystal orientation effect on dislocation nucleation and multiplication in FCC single crystal under uniaxial loading

I. Salehinia and D.F. Bahr

Abstract

Molecular dynamics simulations are applied to study the effects of orientation and the presence of structural defects on the compression/tension asymmetry of copper single crystals. A stacking fault tetrahedron (SFT) was used as representative defect to investigate both homogeneous and heterogeneous deformation mechanisms. Both the normal stresses to the slip plane and the relative values of Schmid factor in compression and tension impact the C/T asymmetry. The presence of an SFT lowers the applied stress required for plastic deformation, but this effect is highly dependent on the crystal orientation and loading direction. The reduction in yield stress is larger in compression than in tension for almost all orientations. Results show that in general a structural defect would decrease the C/T asymmetry in copper, corresponding closely to previous experiments. The reduction in yield stress in tension is less sensitive to defects than that in compression, suggesting that compression is a more reliable experimental tool for studying the effect of different types of structural defects on the mechanical behavior of the FCC crystals, while tension may be more useful to determine size effects in deformation.

6.1 Introduction

Crystal orientation can significantly affect the mechanical response of a material in various loading conditions. While both the elastic and plastic responses are affected by the crystal orientation, the orientation effect tends to decrease with plastic deformation [10,139]. Since yield stress at the inception of plasticity is also dependent on the direction of uniaxial
loading, an asymmetry is often seen between yield stress in compression and tension. Compression/tension (C/T) asymmetry has been studied in various materials, to name a few, including metals with BCC [140-143] and FCC [144,145,24] structures, intermetallic compounds [146,147], ceramic-metal composites [148], super alloys [149,150]. Normally, BCC structures show C/T asymmetry due to the effect of non-Schmid stresses on the screw dislocation core [141,151-153], however the C/T asymmetry is not expected for FCC crystals in the presence of glissile dislocations [154].

The observed C/T asymmetry for FCC crystals in experiments has been often explained by differences in sample geometry, test setup, initial microstructure, definition of the flow stress and surface conditions for different sense of the uniaxial loading [142,155-158]. As a particular example, Kiener et al. [154] showed that lateral stiffness of the loading system was a significant source of different stress levels in micro-tension and micro-compression experiments. In these experiments samples are often fabricated on the micrometer length scale or larger, and often the material has a nominal dislocation density of $\rho \sim 10^{12} \text{ m}^{-2}$. Kiener and Minor [159] showed that, in compression, dislocation nucleation rather than propagation became the controlling deformation mechanism for plastic deformation of micromachined pillars with a diameter less than 600-800 nm.

In the absence of pre-existing dislocations, the inception of plasticity in single crystals is directly related to the nucleation of dislocations, either homogeneously from the perfect lattice or heterogeneously from structural defects including free surfaces [21,39,139,135]. The Schmid law states that for yielding the shear stress on the slip plane, in the slip direction, should occur once the critical resolved shear stress (CRSS) is achieved. Conventionally it is assumed that this CRSS is constant for a given material, regardless of the loading condition. This law is well
established for FCC structures when pre-existing dislocations are present in the material, a condition for which deformation mechanisms are more stress dependent than being thermally controlled. However, at small size scales for materials with a limited dislocation density, dislocations are more unlikely to be present; therefore the deformation mechanism can be dominated by dislocation nucleation rather than dislocation propagation, multiplication and interactions. Additionally, at very small length scales and in perfect (or near perfect) materials, it is likely that stresses much higher than those in a conventional bulk strength regime can be sustained prior to plastic deformation. Ogata et al. [160] performed ab initio simulations of nanoindentation and show that non-glide stresses can impact dislocation nucleation in Al and Cu. Tchoppe and McDowell [24] have used molecular dynamics simulations of compression and tension tests on several crystallographic orientations and found the same influence for the non-glide stresses in Cu single crystal.

Since at very small sample sizes it is unlikely that dislocation loops will be stable, the influence of point defects should be considered for micro and nanoscale testing. Point defects, which are inevitable in materials, can be in the form of vacancies, impurities and self-interstitial atoms. Among different point defects, the density of vacancies and their clusters can be large at high temperatures and also in out-of-equilibrium conditions such as exposure to radiation, quenching and large plastic deformation [161]. In FCC crystals, vacancies agglomerate and form clusters such as void and stacking fault tetrahedra (SFT), depending on their stacking fault energy [120]. These relatively large defects can act as dislocation sources [125,137,139,162,163] or interact with dislocations inside a material [164-168]. At small size scales, where dislocations are less likely to be present, dislocation nucleation dominates the deformation mechanisms at the inception of plasticity in the materials. Performing atomistic simulations of nanoindentation,
Salehinia and Bahr [125] showed that a SFT can lower the yield pressure at the onset of plasticity by up to 50% of that for the perfect crystal. Since SFT’s are formed by stair rod dislocations and stacking faults [34] they can serve as effective representations of dislocations in small volumes. Previous atomistic simulations on the C/T asymmetry in FCC single crystals have primarily focused on perfect crystals [24,81] or nanocrystalline materials [144,145]. To mimic common experimental conditions in small scale testing, where samples are often manufactured using focused ion beam milling, we feel it is appropriate to consider the impact of internal defects in the crystal.

In the present work, the C/T asymmetry is investigated in copper for several crystal orientations. Both Schmid stresses (resolved on the slip plane along the slip direction) and non-Schmid stresses (resolved normal to the slip plane) are taken into account to better understand the observed C/T asymmetry in both elastic and plastic deformation in the material. It is found that both normal factor and the “Schmid ratio” (defined as the ratio of the Schmid factor in compression over that for tension) affect the C/T asymmetry in Cu single crystal. In addition to the simulations on the perfect crystal, SFT is positioned at the center of the full-periodic simulation box to study the effect of internal defect on the C/T asymmetry in Cu single crystal. In the presence of an SFT, the C/T asymmetry is lessened and even reversed for some crystallographic orientations. The impact of the SFT on the yield stress is compared for tension and compression and deformation mechanisms are investigated to explain it. In most orientations, SFT is unzipped and dislocation start to propagate from its faces in compression, while in tension it is often seen that new dislocations nucleate from the SFT while it is almost intact. Effects of elastic modulus and yield stress for the perfect crystal on the SFT impact are also studied.
6.2 Modeling

Molecular dynamics simulations were performed in LAMMPS code [92,93]. An embedded atom method [169] potential for copper [112] is used in this work. Periodic boundary conditions have been applied for all sides, while uniaxial loading at the constant strain rate of 3e8 1/s was applied on the y direction which is on the orientation of the crystal. The simulation cell size for a given orientation was chosen to lessen the effect of periodic boundaries on the result; all cells used in this study were between 10-20 nm$^3$ for each considered orientation, in order to assure small effect of boundaries on the results. Fig. 6-1 shows the orientations examined in this work within the inverse pole figure with [001], [101] and [111] vertices.

![Stereographic triangle showing the investigated orientations](image)

Fig. 6-1. Stereographic triangle showing the investigated orientations. Uniaxial loading is applied along the shown crystal orientation (y axis).

An initial minimization was performed using the conjugate gradient method and initial relaxation for 50 ps using isobaric-isothermal (NPT) ensemble at a pressure of 0 bar and a temperature of 10 K before loading to equilibrate the atomic configuration for each orientation. The yield stress (stress at the onset of plastic deformation) is defined as the maximum uniaxial
compressive (tensile) stress. The centro-symmetry parameter [17] was used to visualize defects in the crystal configuration.

The SFT were formed by the relaxation of a removed Frank loop triangle of atoms from one of the \{111\} plane at the center of the simulation cell. The triangle contains 55 atoms; i.e. 10 on each edge. The resulting edge length of the SFT is about 2.2 nm, close to the experimentally observed size of SFTs in copper [115].

6.3 Results and discussion

6.3.1 Asymmetry in crystals with existing structural defects

Stress-strain curves for compression and tension are shown for several crystallographic orientations in Fig. 6-2. There are two features that will be discussed separately; the non-linear elastic behavior at high stresses and strains (which will be noted as elastic hardening or softening, where the non-linear elastic stress-strain behavior either exceeds or is lower than the expected value assuming pure linear elastic conditions) and the magnitude of stress at which plasticity commences, which will be described as yielding asymmetry. Both types of asymmetric behavior occur in almost all orientations examined in this work, however both the direction of asymmetry and the magnitude are strongly affected by the relative loading orientation.
Fig. 6-2. Representative stress-strain curves for compression (solid line) and tension (dashed line) tests on orientations: (a) [001], (b) [405], (c) [417] and (d) [2,1,10]. For both loading directions positive strain and stress are shown to ease recognizing different behavior for each loading direction.

6.3.1.1 Elastic asymmetry in perfect crystals

First, to consider the non-linear elastic asymmetry, it is possible to find a variety of conditions in which either elastic hardening or softening occurs. For instance, Fig. 6-2 (a) shows that in the [001] orientation, tension produces elastic hardening and compressive loading exhibits elastic softening. This behavior is reversed for the [405] (Fig. 6-2 (b)) and the [417] (Fig. 6-2 (c)) orientations, where elastic softening is seen in tension and elastic hardening is seen in compression. In the case of the [2,1,10] orientation there appears to be no elastic hardening in compression and only a minor amount of elastic softening in tension (Fig. 6-2 (d)). Elastic hardening and softening has been observed in several works including uniaxial [24] and shear [79] loading conditions. In theory normal stresses to the slip plane can affect the friction between the atomic planes with higher friction in compression due to compressive normal stress to the slip planes and lower friction in tension due to tensile normal stress to the slip planes. Increasing (decreasing) friction may lead to hardening (softening) in compression (tension). However, Zhu et al. [79] showed that elastic hardening (softening) is seen even for shear loading where the normal stress to the slip plane is zero. Furthermore, normal stresses are not enough to explain observed behavior for [001] and also [2,1,10] orientations. With these examples one finds that
not only the normal stress but also other stress components such as resolved shear stresses on the closely packed planes is necessary to explain the observed mechanical asymmetry between compression and tension tests. The combined effects of resolved normal and resolved shear stresses (on the slip plane) on the compression/tension asymmetry will be addressed in the next sections.

6.3.1.2 Plastic yield asymmetry in perfect crystals

The onset of plastic deformation in relatively defect free solids (i.e. low dislocation density solids of limited sample size, such as observed experimentally in nanoindentation [129,170], micropillar compression [159,171], or microtensile testing of whiskers [172,173]) is the second form of asymmetric mechanical deformation. Fig. 6-3 shows the distribution of yield stresses in tensile and compression tests for perfect crystal; yield was determined as the maximum stress prior to permanent deformation and the formation of dislocations within the sample. In this current study contours of yield stresses for various crystallographic orientations agree well with those reported by Tschopp and Mc Dowell [24]. In compression, the maximum and minimum yield stresses are for the [111] and [001] orientations, respectively. In a tensile test, [111] shows the highest yield stress and orientations close to [110] show the lowest yield stress.
Fig. 6-3. Contour plots of the compressive (a) and tensile (b) yield stresses for a perfect crystal as a function of crystal orientation.

Yielding asymmetry is best noted by the compression/tension (C/T) asymmetry ratio; described as the ratio of the magnitude of the uniaxial stress at yield in each loading condition. Fig. 6-4 shows the contour graph of C/T asymmetry ratio for the considered orientations mapped to an inverse pole figure. The orientation effect on the C/T asymmetry ratio agrees well with the results given by Tschopp and McDowell [24], with the lowest value (≈0.4) for the [001], a moderate value (≈1.6) for the [111] and the biggest value (≈3.3) for the orientation close to [101]. Orientations on the [001]-[111] edge of the stereographic triangle have C/T asymmetry ratio close to 1 indicating that the yield asymmetry is small for these orientations.
Fig. 6-4. Contour plot of the yielding compression/tension (C/T) asymmetry ratio for a perfect FCC crystal as a function of orientation.

Ab initio studies on Cu and Al [160], showed that normal stresses to the slip plane can affect the critical resolved shear stress, raising the importance of non-Schmid terms on dislocation nucleation in these materials. So, to better understand the variation in C/T asymmetry ratio, which changes significantly between the [001] and [101] orientations, it is instructive to study the Schmid and non-Schmid effects in uniaxial loading. Activated slip systems for tensile and compression loadings can be found using the slip vector analysis [135]. Orientations in the interior of the stereographic triangle have single slip system and those on the exterior of the triangle deform with double slip systems. The slip system for the cases studied here is (11̅1)[2̅11] in compression and (11̅1)[112] for tensile loading. For the exterior of the triangle, slip systems of (111)[11̅2] and (111)[11̅2] are also active for compression and tension, respectively. The resulting Schmid and non-Schmid values are calculated for each slip plane and slip direction for partial dislocations through the following relations:

\[ SF = l_{y'y}l_{x'y}, \quad NF = l_{y'y}^2 \]  

(1)
where $l_{ij}$ are the direction cosines relating the coordinate axes fixed to the slip system ($x'$ is the slip direction and $y'$ is normal to the slip plane) to a fixed sample coordinate system with $y$ as the loading direction. Another non-Schmid factor (coslip factor) can be found by projecting the uniaxial stress on the slip plane normal to the slip direction; this has been proven to have no effect on dislocation nucleation in copper [174] and so will be ignored for the rest of this current study. $NF$ and $SF$ values are the same for active slip systems in orientations on the exterior of the stereographic triangle.

Fig. 6-5 (a), (b) and (c) show the orientation dependence of the normal factor, the Schmid factor in tension, and the Schmid factor in compression. The normal factor does not depend on the loading direction (i.e. the slip plane is the same for compression and tension), and so only one plot is shown for normal factor (Fig. 6-5 (a)). In contrast, the Schmid factor is not identical for tension and compression as a result of different partial slip directions. The maximum Schmid factor in compression is at the [001] orientation and its minimum is at the [111] orientation. On the other hand, the maximum Schmid factor in tension is for orientations close to [101] and its minimum value is at the [001] orientation. Since the actual values and also the distribution of Schmid factors for compression and tensile loadings are different, it is convenient to define a Schmid ratio as the ratio of Schmid factor in compression to the Schmid factor in tension; this ratio is shown in Fig. 6-5 (d). This parameter is smallest for all orientations on [101]-[111] edge of the IPF and it is the highest at [001] orientation.
Fig. 6-5. Contour plots of (a) normal factor (NF), (b) Schmid factor (SF) in compressive loading, (c) Schmid factor in tensile loading, and (d) Schmid ratio being the ratio of the compressive Schmid factor to tensile Schmid factor in inverse pole figure.

Fig. 6-6 shows the contour plot of the C/T asymmetry ratio as a function of both Normal Factor and Schmid ratio. For a constant Schmid ratio, the C/T asymmetry ratio increases with increasing $NF$, and in general for a constant $NF$ the C/T asymmetry ratio decreases as Schmid ratio increases. Therefore, normal stresses on the slip plane do significantly affect the C/T asymmetry in FCC crystals in the perfect crystals, which are dominated by dislocation nucleation. However, an important observation in here is that the $NF$ cannot independently
determine the C/T asymmetry. An example is the [001] orientation with a $NF=0.333$ and a C/T asymmetry ratio of 0.45. Despite having a medium value for the $NF$, this orientation indicates a higher yield stress in tension than compression (asymmetry ratio less than 1). As can be seen in Fig. 6-5 (d), for this orientation the Schmid ratio is the largest, i.e. the $SF_{tension}$ is much smaller than $SF_{comp}$. Molecular dynamics simulations on the [001] orientation show the same range of virial [94] resolved shear stresses on the slip plane along the slip direction for both loading conditions at the onset of yielding. With that, tensile loading, which has the smaller $SF$, shows a higher stress at yield that consequently leads to the C/T asymmetry value of less than 1. Since the other stresses, such as those resolved on the slip plane normal to the slip direction, are not responsible for the dislocation nucleation in the FCC crystals, the Schmid ratio should be an important factor affecting the C/T asymmetry in this type of crystals. From both observations in elastic (Fig. 6-2) and plastic deformation, one can see that $NF$ and Schmid ratio are both required to explain the asymmetry between elastic behavior and also yield stresses in compression and tension loading conditions in perfect crystals.

![Contour plot of C/T asymmetry ratio in NF-Schmid ratio coordinate system as a function of crystal orientation.](image)

Fig. 6-6. Contour plot of C/T asymmetry ratio in NF-Schmid ratio coordinate system as a function of crystal orientation.
6.3.2 Plastic asymmetry in crystals with existing structural defects

Since chemically indistinct structural defects (such as vacancies, self interstitials and their clusters) are inevitable within experimentally achievable volumes of materials, it is worth considering their effects on the subsequent mechanical behavior and C/T asymmetry in the current system of interest. Based on previous studies of structural defects [125] a stacking fault tetrahedra (SFT) was selected as a typical defect that tends to emphasize the impact of the defect over considering only vacancies or self-interstitials. Fig. 6-7 shows typical stress-strain curves of compression and tension; in this case the orientations of [417] and [7,5,10] were selected to demonstrate the difference between the perfect crystals and crystals with an SFT as the representative internal defect. The C/T asymmetry ratio is lowered from 2.58 to 1.86 for the [417] orientation, and it is even reversed, from 1.87 to 0.79, for the [7,5,10] orientation. Therefore, in experimental conditions where defects are likely to occur (such as conditions where focused ion beams are used to machine micro- or nano-sized samples [55,56,175]), the compression/tension asymmetry can be altered, removed or even reversed as compared to the perfect crystal condition.

Fig. 6-7. Stress-strain curves for (a) [417] and (b) [7,5,10] orientations under compression and tensile loading for perfect crystals and crystals with an SFT at the center. The C/T asymmetry ratio is lowered for [417] orientation and it is reversed for [7,5,10] orientation.
Fig. 6-8 shows the distribution of yield stress of tension and compression tests for a crystal with an SFT at its center. In tensile tests and almost in entire inverse pole figure for compression tests, contours for crystals with SFT show a generally similar behavior as those for the perfect crystals (Fig. 6-3 (a) and (b)), although the yield stresses are smaller in the presence of the defect.

Fig. 6-8. Contour plots of the compressive (a) and tensile (b) yield stresses for a crystal with centered SFT, as a function of crystal orientation.

The contour of yielding C/T asymmetry ratios for the considered orientations in the presence of an SFT is shown in Fig. 6-9. Significant differences between the perfect crystal case (Fig. 6-4) and this case are obvious. First, the total range of asymmetry ratios is much smaller in a crystal with a defect, from a factor of almost 8 to a factor of less than 4. In orientation space, almost half of the inverse pole figure has an asymmetry value of 1 or less than 1, while for the perfect crystal this area is just concentrated around the [010] orientation (Fig. 6-4). These observations show that structural defects could lower the yield asymmetry in FCC crystals.
Of course, the impact of orientation must be normalized by the behavior of a perfect crystal of a given orientation. This is shown in Fig. 6-10 as the percent reduction in yield stress at the onset of plasticity for both compression and tensile tests due to the presence of an SFT at the center of the periodic cell. The reduction in yield stress due to the defect is highly orientation dependent, and the impact for compression loading is larger than that for tensile loading for almost all the orientations except [001] for which the percent reduction in yield stress in tension is larger than that in compression and [103] for which the percent reduction is almost the same for both loading directions. The largest reduction in yield stress during a compression test happens for orientations inside the stereographic triangle and not on the vertices. Of particular note is that the maximum reductions in yield stress occur for different orientations in tension and compression. For instance, the maximum impact of an SFT in compression is to reduce the yield stress by 67% from the yield stress of the perfect [5,2,10] crystal, while the maximum reduction in yield stress is 44% in tension for the [2,1,10] orientation.
Fig. 6-10. Contour plots of percent reduction in (a) compressive and (b) tensile yield stress due to SFT for considered crystal orientations.

Fig. 6-11. Contour plot of the reduction percent ratio in inverse pole figure. The ratio is calculated as compressive percent reduction over tensile percent reduction. Several orientations have been marked for which deformation mechanisms are shown in Fig. 12.

To understand the different reductions in yield stresses in tensile and compression loading for a particular orientation, it is useful to examine the deformation mechanisms at the onset of plastic deformation. Fig. 6-11 shows the contour plot of the reduction percent ratios
(compression reduction over tensile reduction), and notes specific orientations that are instructive in explaining the differences between orientations with regard to C/T yield asymmetry. Fig. 6-12 shows the snapshots of the atomic configuration at the yield point for several representative orientations marked in Fig. 6-11. The upper snapshots are for compression and the lower ones are associated with tensile loading. The centro symmetry parameter [17] has been used to color code the atoms which are displaced from their FCC lattice positions, only atoms with a CSP greater than 0.3 are shown in Fig. 6-12. In contrast to the perfect crystal, where the onset of plasticity is directly related to the nucleation of dislocations, in the presence of the SFT, dislocations can be formed and propagate before the onset of plastic deformation. There is a distinct difference in the mechanism of plasticity between compression and tension. For most orientations the onset of yielding in compression involves the SFT unzipping and subsequent dislocation propagation; in tension the onset of plasticity is caused by the nucleation of a dislocation from the stair rod dislocation on the edge of the SFT. As the required stress for dislocation propagation is much lower than that for dislocation nucleation, the relative change in macroscopic stress needed to generate subsequent plastic deformation scales accordingly. Dislocation nucleation is, obviously, the main deformation mechanism at the onset of plasticity for the perfect crystal in both tension and compression. However, in the presence of the SFT, some orientations don’t follow this behavior. For [001] the reduction in yield stress for tensile loading is bigger than that for compression loading, whereas for the [103] the values are almost equal. For [334], [4,3,10], and [528] orientations unzipping the SFT is followed by dislocation propagation in compression, while in tension the SFT is intact and dislocations nucleate from the SFT edges. This behavior is reversed for [001], where in tension the SFT is unzipped and dislocations propagate in the two slip planes, while in compression the SFT behaves as a
nucleation source and as a result the reduction in yield stress for tension is bigger than that for the compression. For [2,1,10], the deformation mechanism in compression also includes dislocation propagation from one of the SFT faces, however in tensile loading dislocations are formed from the SFT edge and then the SFT collapses. This deformation mechanism is different from those observed for the [334], [4,3,10] and [528] orientations for which the SFT remained intact.
Fig. 6-12. Snapshots of atomic configuration at the onset of plasticity for several representative crystal orientations. In each orientation, upper snapshot is for compression and lower one is for tension. CSP has been used to color code the defects. Initial configuration of the SFT is presented for some snapshots with the smaller atom size to clarify the deformation mechanism.

An important feature of the [2,1,10] orientation is that its C/T asymmetry ratio (for the perfect crystal) is close to 1. This orientation demonstrates that the yield stress is not enough to explain the different reduction in yield stress due to the SFT. As in compression, dislocation propagation is the dominant deformation mechanism in this orientation, the reduction in yield stress is bigger than that for the tensile loading for which formation of dislocations from SFT edges is happening. The percent reduction ratio for [103] orientation is also close to 1, even though the C/T asymmetry ratio is 1.64. However, the deformation mechanisms in this orientation resemble those for orientations with the high differences in compression and tensile loading. The atomic configurations for compression loading in this orientation show that the yield point on the stress-strain curve is not associated with unzipping the SFT (which happens at
6.4 GPa), but it is postponed to much larger stress of 9.23 GPa, as seen in Fig. 6-12. Tensile loading in this orientation is the same as that observed for [2,1,10] orientation both including the formation of dislocations from stair rod dislocations in SFT followed by destruction of SFT. Delayed yielding in compression lowers the reduction in yield stress (due to the presence of the SFT) and consequently the percent reduction becomes almost the same for compression and tensile loadings.

Since copper shows a high degree of elastic anisotropy, it is instructive to examine the differences based on changes in modulus. The elastic modulus for tensile and compression loading is calculated in a given \([hkl]\) by:

\[
\frac{1}{E_{[hkl]}} = S_{11} + (2S_{12} - 2S_{11} + S_{44}) \frac{(k^2l^2 + l^2h^2 + h^2k^2)}{(h^2 + k^2 + l^2)}
\]  

(2)

where \(S_{ij}\)s are elastic compliances for a given crystal calculated from the elastic constant \(C_{ij}\)s in EAM potential for copper [112]. The stiffest orientation is [111] and the most compliant one is [001].

As one might expect, in the case of a perfect crystal in general the yield stress increases as a function of increasing elastic modulus, as shown in Fig. 6-13 (a). In the presence of a defect the overall yield stresses also increases with increased modulus (Fig. 6-13 (b)), though more modestly than in the case of the perfect crystal, while the C/T asymmetry is significantly reduced compared to the perfect crystal.
Fig. 6-13. Variation of the yield stresses against elastic modulus in tension and compression tests (a) for the perfect crystal and (b) in the presence of an SFT Lines only drawn to guide the eye, and have no functional form.

Fig. 6-14 shows the reduction in yield stress due to the inclusion of an SFT in the crystal as a function elastic modulus for tensile and compression loading. In tensile loading, the yield behavior is relatively insensitive to the presence of the defect. However, the reduction is significant for stiffer orientations in compression. This is likely caused by the change in deformation mechanism in tension from SFT unzipping and dislocation propagation for [001] to dislocation nucleation from SFT edges for [111]. This is in contrast to compression where dislocation propagation and SFT destruction are the main deformation mechanisms in stiffer orientations and dislocation formation from SFT edges happens for orientations with lower elastic modulus. The scatter in the data is indicative that in addition to the elastic modulus, orientation parameters are required to explain the mechanical response in the presence of structural defects.
Fig. 6-14. Actual reduction in yield stress vs. elastic modulus for tension and compression tests on single crystals with an SFT at the center.

For designing experiments to probe high strength, source limited deformation conditions, it is worth considering the effect of the yield stress for the perfect crystal and the resulting reduction due to presence of the stacking fault tetrahedra. Fig. 6-15 shows the variation of reduction in yield stress with respect to the yield stress for the perfect crystal. In general orientations with a higher yield stress in a perfect crystal will demonstrate higher reductions in yield stress (i.e. they have farther to fall). However, the differences in compression are in general well in excess of the differences in tension. This suggests that examining C/T asymmetry and yield behavior in small samples with limited dislocation sources in compression will be much more sensitive to the existence, type, and placement of said defect than similar tests in tension. Experimental studies exploring size effects in plastic deformation in tension would be more likely to be able to separate phenomena based on size rather than the type and location of structural defects.
6.4 Conclusions

Molecular dynamics simulations have been used to study the compression/tension asymmetry in copper single crystal for various crystallographic orientations. Both homogeneous (perfect crystals) and heterogeneous (crystals with an SFT at the center) dislocation activity has been considered. Differences in deformation mechanisms can be used to explain the C/T asymmetry ratio in the presence of an SFT. Based on this study, the following conclusions can be drawn:

- Compression/tension asymmetry in relatively defect free FCC materials is a result of normal stresses and different Schmid stresses for compression and tensile loadings. While the normal factor has an effect on the C/T asymmetry, by itself it cannot explain the observed variation in asymmetry. A new parameter, the Schmid ratio (the ratio of Schmid factor in compression to the Schmid factor in tension), also plays an important role in determining the asymmetry.

Fig. 6-15. Reduction in yield stress vs. yield stress for the perfect crystal under tension and compression for the considered crystal orientations.
- Compression/tension asymmetry is generally lowered in the presence of an internal structural defect (SFT) and can even be reversed for some crystallographic orientations. The inclusion of a single structural defect (an SFT) provides an explanation for observations in which the C/T asymmetry increases in some orientations and decreases in other orientations.

- The impact of a defect on the mechanical response of the crystal is highly dependent on the crystal orientation and loading direction. The reduction in the yield stress is larger in compression than in tension for almost all orientations.

- The differences in yielding C/T asymmetry in the presence of a defect arise from different plasticity mechanisms. In tension dislocation nucleation from the SFT edges is the main deformation mechanism, while in compression, unzipping of the SFT followed by dislocation propagation is the dominant deformation mechanism. Even though this is frequently seen, some orientations show the opposite behavior.

- The presence of a structural defect will always lower the resulting yield stress, and this reduction increases as the yield stress of the perfect crystal increases. However, the reduction in yield stress in tension is less sensitive to defects than that in compression, suggesting that experimental observations in tension are more suitable than those in compression for future size dependence studies.

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CHAPTER SEVEN: TEMPERATURE EFFECTS IN THE PRESENCE OF THE POINT DEFECTS

Abstract

Molecular dynamics simulations have been performed to study the effect of temperature and the presence of various types of point defects on the mechanical response of copper. Nanoindentation and uniaxial tests have been modeled to compare different loading conditions. Anisotropy effects have been also added to the study by applying the uniaxial load in various crystallographic orientations. The general decreasing trend of yield stress with the temperature has been seen for the perfect crystal and also the crystals with any type of point defect for all loading conditions and also for all studied orientations. Temperature sensitivity of the yield stress was significantly lowered by the presence of defects in nanoindentation and compression tests. This is dependent on the loading condition and the defect size, and consequently on the impact of the defect on the yield stress; the temperature sensitivity is lower for the orientations that are more influenced by the presence of defects. The effect of point defects on the yield drop with temperature in tensile tests is less than in other loading conditions. Deformation mechanisms have been explored to better understand the observed behavior.

7.1 Introduction

Atomistic simulations and experiments have been widely used to explore the effect of point defects and their clusters on the mechanical behavior of materials in various loading conditions such as nanoindentation and uniaxial tests [1,7,21,23,28,35-39,53,82,125,139]. Internal point defects may act as a source of dislocation nucleation, an effect which is strongly
dependent on the position of the defects in relationship to the applied stress field. This effect is particularly discernible when a small volume of a material is being sampled, or when the stress field is highly concentrated in a small volume.

Many previous atomistic simulations have excluded temperature effects to find the effects of the point defects on the dislocation nucleation and onset of plastic deformation that are hard to explore at higher temperatures due to thermal effects. However, since both increasing temperature and point defect concentration lowers the yield point, it is important to study their combined effect on the mechanical response of the material. The density of the point defects grows exponentially with the temperature [176] and at elevated temperatures it is more likely that the point defects affect the mechanical behavior of the material if a stress field is applied to a small volume (i.e. there is more likelihood to sample defects as temperature increases). Schuh and coworkers [21] showed that for Pt single crystal the distribution of pop-in loads at high temperatures were narrower than at low temperature. They also showed lower pop-in loads at higher temperature in nanoindentation tests. Salehinia and Medyanik [82] performed atomistic simulations of nanoindentation tests with different single vacancy densities in Ni single crystal at different temperatures. They showed that the vacancies are less effective at higher temperatures. At higher temperatures the diffusion rate of point defects increases and thermal vibrations start to play bigger role in triggering dislocation nucleation, so reducing the effect of point defects on the mechanical response of the material.

In this work molecular dynamics simulations were performed to explore the effects of several types of point defects, such as single and di-vacancies, and their clusters such as stacking fault tetrahedra, on the mechanical response of copper. Two types of loading mechanisms, which correspond to viable experimental test conditions were selected; nanoindentation and uniaxial
tension and compression. These simulations were performed at various temperatures ranging from 1K to 500 K. Nanoindentation tests project the highest shear stress into a small volume of material at which dislocations are rare and the effect of point defects are more noticeable [39]. However, it is hard to distinguish the onset of plastic deformation in nanoindentation tests due to the fluctuations in the load-depth curves which are the results of the contact between the indenter and the free surface of the sample. Compression and tensile tests with full periodic boundary conditions and less fluctuation in output data (such as stress-strain curves) are practically more efficient than nanoindentation tests to find the exact moment of the incipient plasticity in the presence of the point defects. Uniaxial tests have been carried out in several crystallographic orientations and the effect of temperature on the impact of the point defects on the yield stress and also on the compression/tension yield asymmetry (in the presence of the point defects) have been scrutinized.

7.2 Modeling

This study utilized molecular dynamics simulations in LAMMPS [92,93] using an EAM potential for copper [112]. and focused on three types of point defects: vacancies, di-vacancies and stacking fault tetrahedral (SFT). Single vacancies were generated by removal of a single atom from the crystal structure. To introduce a di-vacancy, two nearest neighbor atoms were removed; this is one of the most stable configurations of a di-vacancy in FCC metals [113]. The SFTs were formed by the relaxation of a removed Frank loop triangle of atoms from one of the \{111\} plane at different positions under the indenter in nanoindentation test and at the center of the simulation box in uniaxial tests. The triangle contains 55 atoms; i.e. 10 on each edge. The resulting edge length of the SFT is about 2.2 nm, which is close to the experimentally observed
size of SFTs in copper [115]. For each orientation, the size of the simulation cell was chosen between 10-20 nm$^3$ which assures the negligible effect of boundaries on the results.

In nanoindentation simulations, the side and bottom faces were fixed and the top face was allowed to move. The indenter was modeled as a rigid sphere of 15 nm radius with a quadratic repulsive potential [17]. The time step was 1 fs and the indenter speed was 1 m/sec. The indenter velocity was chosen not only to minimize the fluctuations in load-depth curves but also to guarantee the low time cost in simulations. Energy minimization followed by dynamic relaxation for 60 ps using a NVT ensemble was done before initiation of loading. Nanoindentation was performed on (111) crystal orientation. The SFT points downward and was centered on the indentation axis and located either at 15$^{th}$ or 27$^{th}$ layer from the surface. Previous studies have shown this geometry has the largest impact on yielding, and in the interest of determining trends the most dramatic condition possible was felt to be a useful first step in analyzing the coupled effects of defect type and temperature.

In uniaxial tests, periodic boundary conditions were applied to all sides, while loading at a constant strain rate of 3e8 1/s was applied in the y direction, coinciding with stated crystal orientation. An initial minimization was performed using the conjugate gradient method, and at each temperature an initial relaxation for 60 ps using isobaric-isothermal (NPT) ensemble at a pressure of 0 bar was applied before loading to equilibrate the atomic configuration for each orientation. The yield stress (stress at the onset of plastic deformation) is defined as the maximum uniaxial compressive (or tensile) stress.

Fig. 7-1 shows the orientations examined in this work within the inverse pole figure with [001], [101] and [111] vertices.
The centro-symmetry parameter (CSP) [17] was used to visualize defects in the crystal configuration.

Fig. 7-1. Stereographic triangle showing the investigated orientations. Uniaxial loading is performed along the shown orientation that coincides with the y axis.

7.3 Results and discussion

7.3.1 Nanoindentation

Fig. 7-2 (a) and (b) show the load-depth curves of nanoindentations at several temperatures on the perfect crystal and crystal with a single SFT centered on the 15th layer from the surface and along the indentation axis. When the SFT is present, the entire load-depth curves are shown as an inset with an annotated region around the onset of plasticity showing the close view of the mechanical response of the materials at different temperatures. Fluctuations in load-depth curves are seen at temperatures larger than 1 K. As noted before, the indenter velocity and the indenter stiffness have been chosen to minimize the fluctuations and also the run time of the simulations.
Fig. 7-2. Load-depth curves in nanoindentation tests at different temperatures on (a) [111] perfect crystal and (b) [111] crystal with an SFT centered at the 15th layer from the surface on the indentation axis.

Fig. 7-3 shows the variation of the maximum shear stress under the indenter with respect to the temperature for the perfect crystal and the crystal with different types of defects. A decreasing trend of the stress with the temperature is seen for all cases; however, the rate of change of stress with temperature is highly influenced by the internal defect in the crystal. Even for a small defect such as a di-vacancy the temperature effect on the yield stress is much lower than that for the perfect crystal. Despite the larger size of the SFT, it’s impact on the temperature sensitivity of the yield stress is almost the same as that for the di-vacancy. Crystals with SFTs located at different layers from the surface show similar trend for the change in yield stress with the temperature. These curves show the significant effect of the internal defects on the temperature sensitivity of the yielding provided that the defect is positioned on the effective volume where its effect on the yield stress is large enough even at the high temperatures. Less stochastic yield stresses at higher temperatures agree well with the data given by Schuh et al. [21] who showed more narrow distribution of pop-in loads in experimental nanoindentation tests on Pt single crystals at higher temperatures.
7.3.2 **Uniaxial loading:**

Fig. 7-4 shows the stress-strain curves in compression and tension simulations at 1 K and 500 K for the [111] perfect crystal and a [111] crystal having an SFT at the center. SFT only impacts the yield stress, not the elastic modulus. As it is expected the elastic modulus is lower at higher finite temperature.
Fig. 7-4. Stress-strain curves of tension and compression tests on [111] perfect crystals (solid lines) and [111] crystals having an SFT (dashed lines) at the center, at 1 K and 500K.

Fig. 7-5 (a) and (b) show the variation of yield stress with respect to the temperature for [111] single crystal under tensile and compressive loading, respectively. Overall, the trend of the curves in compressive loading for perfect crystal and those when a di-vacancy or SFT are present resembles those shown in Fig. 7-3. This is due to the similar stress field in the compression and nanoindentation tests; Although the stress field in nanoindentation is non-uniform, in contrast to the compression test.

Fig. 7-5. Yield stress vs. temperature curves for [111] perfect crystals and [111] crystals with centered d-vacancy and SFT in (a) tension and (b) compression tests.
As the stress change with temperature is almost linear, the remainder of this work will consider primarily simulations at the ends of the studied temperature range, i.e. 1 K and 500 K. As the effect of the SFT is much bigger than that of di- and single vacancy, from now on simulations compare the mechanical behavior of the perfect crystal and crystals with the SFT as a representative internal defect in an effort to determine the largest possible observable impacts of the coupled temperature–defect combination. Fig. 7-6 (a) and (b) show the contour plot of the temperature sensitivity ratio (TSR) for tensile and compressive loadings for a wide range of selected crystallographic orientations in a stereographic triangle (see Fig. 7-1). This ratio is defined as the ratio of the stress gradient with respect to the temperature for the perfect crystal over that for the crystal with the SFT.

The TSR values in compression tests are more than 3 in a big portion of the inverse pole figure, while on the other hand the maximum value of the TSR in the tension test is 2.5. The general conclusion is that internal defects lower the temperature sensitivity of the yield stress at the onset of plasticity in uniaxial tests. However, this suppressing effect is not uniform for different crystallographic orientations and also different loading senses.
Fig. 7-6. Contour plots of temperature sensitivity ratio, defined as the ratio of the stress gradient with respect to the temperature for the perfect crystal over that for the crystal with the SFT, for (a) tension and (b) compression tests. Note the difference in scales for each figure.

Atomistic snapshots at the onset of plasticity showed that for orientations with the TSR value of larger than 3, the SFT is unzipped at least from one side and dislocation propagation continues from the same side. Fig. 7-7 (a) and (b) show the atomistic snapshots of deformation mechanisms for the [5,2,10] orientation (the one with the highest TSR) at 10 K and 500 K, respectively. An interesting observation is that in this orientation SFT forms dislocation loops similar to a Frank-Read source. This behavior has been seen in compression tests on several orientations, such as [528], [718], [8,1,11], [2,1,10], at both low and high temperatures. At 10 K atoms with CSP less than 0.3, and at 500 K atoms with CSP less than 4 are not shown in these snapshots. For the orientations with low TSR, two mechanisms are observed; either dislocation propagation and SFT unzipping are not in the same plane or deformation mechanisms at low temperature is different from that at high temperature. As an example of the former case, Fig. 7-7(c-e) shows the atomic snapshots for the [101] orientation in compression. Fig. 7-7 (c) shows the unzipped SFT, however dislocations stopped to propagate from the sides of the SFT. After 63 ps, nucleation of dislocations starts from the stair rod dislocation at the SFT edge (see Fig. 7-7 (d)). At 500 K, the deformation mechanism is the same for this orientation (Fig. 7-7 (e)). Finally,
as an example of the latter case, Fig. 7-7 (f-h) show the atomic snapshots for [829] orientation, where the stair rod dislocation followed by dislocation nucleation at 10 K are seen in Fig. 7-7 (f) and (g). Fig. 7-7 (h) shows different deformation mechanism at 500 K which resembles that for [5,2,10] orientation under compression. Here, a general rule is that the existence of an SFT can suppress the temperature effect on the yield stress when the main deformation mechanism is unzipping the SFT followed by dislocation propagation. On the other hand, the SFT does not have as much influence if dislocation nucleation from stair rod dislocations in the SFT happens, or different deformation mechanisms are active at low and high temperatures.

continued on the next page …
Fig. 7-7. Atomic snapshots of deformation mechanisms for compressive loadings of different crystallographic orientations at 10 K and 500 K; [5,2,10] (a) 10 K, (b) 500 K; [101] (c) 10 K, stair rod dislocation as an SFT edge, (d) 10 K, dislocation nucleation from the stair rod dislocation, (e) 500 K, dislocation nucleation from the stair rod dislocation; [829] (f) 10 K, stair rod dislocation as an SFT edge, (g) 10 K, dislocation nucleation from the stair rod dislocation, (h) 500 K, SFT unzipping and dislocation propagation in one of the SFT sides

In tensile loading, the same statement can be used to explain TSR values in the inverse pole figure; i.e. the main deformation mechanism for the orientations with high TSR values is the dislocation propagation and it is dislocation nucleation from the stair rod dislocations at the SFT edges for orientations with low TSR values.

Another promising feature in mechanical response of the copper single crystal is the yield stress asymmetry in compressive and tensile loadings [24]. In this work, temperature effect on the yield asymmetry ratio is studied. Fig. 7-8(a) and (b) show the distribution of asymmetry ratio at 10 K for different orientations in inverse pole figure for perfect crystals and crystals with centered SFT. In the presence of the SFT, the asymmetry ratio is generally lowered at 10 K due to larger influence of SFT on compressive yield stress than that on the tensile yield stress for almost all the orientations in stereographic triangle.
Fig. 7-8. Contour plots of distribution of the asymmetry ratio in the stereographic triangle at 10 K for (a) perfect crystal and (b) crystals with a centered SFT.

Fig. 7-9(a) and (b) show the distribution of asymmetry ratio at temperature of 500 K for different orientations in the inverse pole figure for perfect crystals and crystals with a centered SFT.

In general, the asymmetry ratio for the perfect crystal is unchanged at high temperature. This is in agreement with the results given by Tchopp and McDowell [24]. An unchanged asymmetry ratio means that the temperature has the same effect on both compressive and tensile
yield stresses. The asymmetry ratio at 500 K, in the presence of the SFT, is lowered for almost all the orientations in inverse pole figure.

Contour plots of the percent reduction in yield stress in the presence of the SFT in compression test at 10 K and 500 K are shown in Fig. 7-10(a) and (b). The reduction due to the presence of an SFT at 500 K is generally smaller than (but close to) that at 10 K, showing that for larger internal defects (such as SFT) the increased temperature would be a less important effect on the mechanical response of the material than the defect itself. Also, at 500 K the effect of the defect is increased for orientations close to [110]. Atomic snapshots reveal that for these orientations, the main deformation mechanism is dislocation nucleation from stair rod dislocations on the SFT edges. Since dislocation nucleation is a temperature-controlled process, high temperature assists crystal yielding which results in a larger drop on the yield stress.

Fig. 7-10. Contour plots of the percent reduction in yield stress due to SFT in compression tests at (a) 10 K, and (b) 500 K

Contour plots of the percent reduction in yield stress in the presence of the SFT in the tensile tests at 10 K and 500 K are shown in Fig. 7-11(a) and (b). Similar to the compression test, the percent reduction in yield stress at 500 K is smaller than that at 10 K.
Fig. 7-11. Contour plots of the percent reduction in yield stress due to SFT in tensile tests at (a) 10 K, and (b) 500 K.

Fig. 7-12(a) and (b) show the actual reduction in yield stress versus the yield stress of the perfect crystal for tension and compression tests in the presence of the SFT at 10 K and 500 K, respectively. Generally, the effect of the SFT is larger for perfect crystals with higher yield stresses. In compression, the data at high temperature are more deterministic than those at 10 K. At high temperatures, deformation mechanisms are mainly dislocation propagation and movement which lead to less stochastic data than those based on the dislocation nucleation which mostly happens at low temperatures and are more stochastic.

Fig. 7-12. Reduction in yield stress (due to the presence of a SFT) vs. yield stress of the perfect crystal for compression and tension tests at (a) 10 K and (b) 500 K.
7.4 Conclusions

Molecular dynamics simulations have been performed to study the combined effect of elevated temperature and the presence of point defects on the mechanical response of copper using both nanoindentation and uniaxial loading tests. A variety of crystallographic orientations have been investigated in uniaxial loading to better understand the anisotropy effect in the presence of the point defects at high temperatures. This study has resulted in the following conclusions:

- Yield stress, associated with the dislocation nucleation, is lower at higher temperature regardless of the loading condition, defect type and size.

- The temperature sensitivity of the yield can be significantly influenced by the presence of the internal defects. This is dependent on the loading condition and the defect size, and it is lower for the orientations that are more influenced by the presence of defects. In nanoindentation tests, where stress field is highly concentrated in a small volume, a di-vacancy positioned in a specific lattice sites in the crystal can decrease the temperature sensitivity as much as the much larger defect, i.e. SFT, does.

- The observed variation in temperature sensitivity is mainly due to the different deformation mechanisms at the onset of plastic deformation. In particular for the SFT, the yield drop due to the temperature is the same as that for the perfect crystal when dislocations nucleate from one of the SFT edges. On the other hand, when the SFT is being unzipped and dislocations propagate, the temperature sensitivity is much smaller than that for the perfect crystal. Therefore, care must be taken in ascribing effects noted in experiments if they are not sampling the same deformation mechanism.
- Temperature has the same effect on the yield stress of a perfect crystal in compression and tension. However, the asymmetry ratio at high temperatures, in the presence of the SFT, is a bit lower for almost all the orientations in the inverse pole figure.

- Generally, the effect of the SFT is larger for perfect crystals with higher yield stresses. At high temperatures, in compression, deformation mechanisms are mainly dislocation propagation and movement which lead to more predictable data than those based on the dislocation nucleation which mostly happens at either low temperatures or in tensile loading.

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CHAPTER EIGHT: SUMMARY AND FUTURE WORK

Atomistic simulations have been used to study the effect of various types of point defects on the mechanical response of FCC single crystals in nanoindentation and uniaxial tests. To study the effect of spatial distribution of defects in nanoindentation tests various point defects were located in different relative positions to the indenter.

Simulations of nanoindentations demonstrated that presence and position of (even) a single defect can impact the yield load. The studied defects include single vacancy, di-vacancy, self-interstitial atom and stacking fault tetrahedron (SFT). Nucleation of dislocations during contact loading in the presence of point defects is heterogeneous; even when a dislocation does not nucleate at a point defect, the defect still impacts the nucleation event and hence the process is effectively heterogeneous. The impact of the point defects on the initial yield behavior is not indenter size dependent.

The study continued with molecular dynamics simulations and experimental studies to demonstrate the coupled effect of indenter size, crystallographic orientation, and structural defects on the mechanisms causing incipient plasticity in FCC single crystals using nanoindentation. The sensitivity of yield points in the presence of internal structural defects depends on crystallographic orientation. In the presence of an SFT, as a representative internal defect, the highest reduction in the pop-in loads was seen for the (111) orientation. Defects can either lead to one large yield event or initiate a sequence of small events prior to one large discontinuity in a load-depth curve. The size and shape of the effective volume in which internal defects can affect the mechanical response in nanoindentation test depends strongly on the crystal orientation. The effective volume for the (100) orientation is smaller than those for (111)
and (110) orientations. The stochastic distribution of pop-in loads can be explained by including the point defects in the crystal at various locations.

Compression/tension asymmetry in copper for various crystallographic orientations in the presence of point defects has been studied. Differences in deformation mechanisms were used to explain the C/T asymmetry ratio in the presence of an SFT. Compression/tension asymmetry in relatively defect free FCC materials is a result of normal stresses and different Schmid stresses for compression and tensile loadings. Compression/tension asymmetry is generally lowered in the presence of an internal structural defect (SFT) and can even be reversed for some crystallographic orientations. The impact of a defect on the mechanical response of the crystal is highly dependent on the crystal orientation and loading direction. The reduction in yield stress in tension is less sensitive to defects than that in compression, suggesting that experimental observations in tension are more suitable than those in compression for future size dependence studies.

Finally, effect of temperature in nanoindentation and uniaxial tests in the presence of point defects has been explored in this research. The general decreasing trend of yield stress with the temperature has been seen for the perfect crystal and also the crystals with any type of point defect for all loading conditions and also all studied orientations. The temperature sensitivity of the yield stress is significantly lowered by the presence of defects in nanoindentation and compression tests. The effect of point defects on the yield drop with the temperature in tensile tests is less than that in other loading conditions.

Despite that these studies have shed light into the mechanical response of the FCC crystals, many subjects are still open for further exploration. The main goal of this research is finding a model to describe the observed stochastic data in experimental investigation of metallic
structures. Atomistic simulations are being used as a tool to extend our ability to explain phenomena in experiments by probing in more detail the mechanisms controlling small scale deformation, particularly those that could be the source of major events which are large enough to be detected by the experiments. The following suggestions for future work could be used to further achieve this purpose:

- As internal defects are almost inevitable in materials, a defect based model might be the best way to explain the stochastic behavior in pop-in loads in nanoindentation tests. This model should include different concentrations and spatial distributions of various types of structural defects with several sizes. Cumulative distribution of pop-in loads at the onset of plasticity can be used to formulize the problem.

- Temperature effects require further examination in nanoindentation tests. Simulations should be carried out for different temperatures in various crystallographic orientations and the results should be compared to those in the complementary nanoindentation experiments that are equipped with a proper heating stage.

- Large difference between the time and length scales in molecular dynamics simulations and those in experiments can be removed by using other simulation methods. For instance, the quasicontinuum (QC) method [177] can be used which is capable of modeling larger length scales. Length scales include the indenter radius and also the volume of materials being sampled. By doing that, the quantitative and qualitative comparisons between simulation results and experimental data make more sense and consequently the findings are more practical. The quasicontinuum method combines the atomistic and finite element region in a problem to extend the length scale beyond that in molecular dynamics. Both quasistatic (zero temperature) and finite temperature versions
of this method are available. Accelerated molecular dynamics methods such as temperature accelerated dynamics can be used to achieve longer time scales even close to a second [178].

It is also important to explore the effect of point defects and various other types of internal defects on the mechanical response of the other metallic crystals with BCC and HCP structure. The Schmid stresses in BCC crystals play an important role on their mechanical behavior and this could be hugely impacted by the presence of different internal defects. HCP structures have less slip systems than FCC and BCC structures, however different slip systems (on basal planes, prismatic planes and pyramidal planes) depending on their c/a ratio can be activated in these crystals. Different distributions of point defects on various slip planes might lead to stochastic results in the highest bearable shear stress in the material, i.e. an approach to explain the experimental observations for these structures.

Other point defects, particularly impurities, may also have a strong effect on the mechanical behavior of materials on the inception of plastic deformation. As noted in the introduction chapter (chapter 1) classical works on solid-solution strengthening clearly demonstrates that impurities will increase the flow stress in bulk materials, but that is only taking into account the propagation, not nucleation of dislocations. Literature includes controversial results about the effect of impurities on the mechanical behavior of materials at the onset of plasticity [26,28,31]. Considering these works, study of the effect of solid solutions on the onset of plastic deformation is not yet complete. It is not yet known that in what circumstances substitutionals can impact the flow stress and what the atomistic mechanisms of this impact are. Difference in stacking fault energies, atomic
radius mismatch, and different crystal structures can be the reason for the influence of the solid solution atoms and the impurities on the mechanical behavior of the binary systems. Effects of other types of impurities such as oxygen, hydrogen and nitrogen on the mechanical behavior of materials are also interesting. These studies are easy to do as long as the proper interatomic potential is available for this purpose. These potentials are available for hydrogen as impurities in metals such as Ni, Al. More research is needed to find appropriate potentials for proper describing of these impurities in metallic crystals.
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