Investigation of Grain Boundary Segregation and Embrittlement Mechanisms of the Cu-Bi System by Analytical Electron Microscopy

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Investigation of Grain Boundary Segregation and Embrittlement Mechanisms of the 
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Table of Contents:

Acknowledgements: .............................................................................................................. iv

Table of Contents: ................................................................................................................. v

List of Tables: .......................................................................................................................... viii

List of Figures: ........................................................................................................................ vi

Abstract: .................................................................................................................................. 1

1. Introduction: ....................................................................................................................... 2

2. Background: ....................................................................................................................... 4

2.1 Grain boundaries in crystalline materials: ...................................................................... 5

2.1.1 Investigation of the structure of GBs and interfaces via electron microscopy
.................................................................................................................................................. 15

2.2 Grain boundary segregation: ........................................................................................ 21

2.3 The Cu-Bi system: ........................................................................................................ 29

2.4 Currently proposed mechanisms of grain boundary embrittlement in the Cu-Bi system:
.................................................................................................................................................. 30

2.5 Past investigations of Bi induced embrittlement of Cu: .............................................. 38

2.5.1 Auger electron spectroscopy ....................................................................................... 38

2.5.2 X-ray energy dispersive spectrometry ........................................................................ 48

v
2.5.3 Electron energy loss spectrometry ........................................... 65

2.5.4 Mechanical testing of Bi doped Cu grain boundaries .............. 71

3. Statement of problems and objectives: ........................................ 77

4. Experimental Procedures: .......................................................... 78

   4.1 Bi doping of Cu polycrystalline bulk specimens: .................... 78

   4.2 Bi doping of Cu bicrystal bulk specimens: .............................. 82

   4.3 Metallographic preparation of pure and Bi doped Cu bicrystal specimens: ..... 85

   4.4 Observation of Cu bicrystals via scanning electron microscopy: ........... 86

   4.5 Focused ion beam specimen preparation for TEM and mechanical testing: ..... 86

   4.6 Micro-tensile mechanical testing procedure: ............................... 97

   4.7 TEM/STEM procedure: ......................................................... 99

      4.7.1 Low magnification specimen characterization ....................... 99

      4.7.2 High resolution TEM and STEM imaging ............................ 99

      4.7.3 STEM through-focus imaging: ....................................... 100

      4.7.4 Analytical X-ray energy dispersive spectroscopy in STEM ........... 104

      4.7.5 Grain boundary analysis through electron energy loss spectroscopy .... 104

5. Results and Discussion: ............................................................. 105

   5.1 Specimen misorientation analysis .......................................... 105

   5.2 Micro-mechanical testing of FIB prepared Bi doped Cu Bicrystals ........ 117
5.3 Bicrystal Specimen Characterization .......................................................... 123

5.3.1 Microscopic characterization ...................................................................... 123

5.3.2 Mesoscopic characterization ..................................................................... 133

5.3.3 Nano and atomic scale characterization .................................................... 140

5.4 3-dimensional imaging of Bi doped Cu grain boundaries ......................... 160

5.4.1 Choice of convergence semi-angle ............................................................ 160

5.4.2 STEM TFI of Bi Doped Cu Bicrystals ...................................................... 163

5.5 Electronic structure at the Cu GB ................................................................. 176

5.6 GB compositional analysis via XEDS ........................................................... 186

5.7 Comparison of GB compositional quantification through imaging and X-ray
analysis ............................................................................................................. 212

5.8 Interpretation of micro-mechanical testing results through STEM analysis ... 216

6. Conclusions: .................................................................................................... 221

7. Suggested Future Work: .................................................................................. 223

8. References: ..................................................................................................... 225

9. Appendix: ...................................................................................................... 234

10. Vita: ............................................................................................................... 237
List of Tables:

Table 1 – Summary of possible grain boundaries using an interface-plane scheme [2]. 9
Table 2 – Embrittlement Mechanisms and their proposed effect on GB properties (G_{disl} and G_{cleav}) ............................................................................................................................................. 35
Table 3 – Results of segregation XEDS measurements for a Σ19a Cu GB doped with Bi [66]............................................................................................................................................. 60
Table 4 – Fracture toughness values for various Cu [100] tilt bicrystals as reported by Mclean [75]. ............................................................................................................................................. 118
Table 5 – Observable Change in GB Morphology upon Bi Doping ........................................ 125
List of Figures:

Figure 1 - Variables that define a GB. \( x_A, y_A, z_A \) and \( x_B, y_B, z_B \) are the crystallographic directions for grains A and B, respectively. \( O \) is the rotation axis and \( \Theta \) is the rotation angle necessary to bring grain A to the orientation of grain B and vice versa. \( n \) is the orientation of the GB plane at the interface between grain A and grain B [2].

Figure 2 – Schematic diagram showing a tilt GB (top) and a twist GB (bottom) between two grains (blue and green outlined cubes) where the misorientation axis appears in bold [6].

Figure 3 – Structure of three [100] symmetrical tilt GBs in a BCC material (a) \{013\} singular GB, (b) \{024\} singular GB, and (c) \{037\} general GB. Circles and triangles represent parallel (100) planes [7].

Figure 4 - HRTEM micrograph of a \( \Sigma 51 \) [110] tilt Cu doped Bi grain boundary with symmetrical (s) and asymmetrical (as) GB planes [21].

Figure 5 – Darkan-Gurry map of Cu showing solubility of atoms inside ellipse (\( X < 0.3 \) difference and \( r < 15\% \) difference from Cu).

Figure 6 - Grain boundary enrichment ratio vs. bulk atomic solid solubility [27].

Figure 7 – Schematic diagram of an atomically sharp, stationary crack tip (left) showing the competition between blunting dislocation emission (upper right) and GB decohesion (lower right) [49].
Figure 8 - Scanning electron micrograph of a 3Cr1Mo rotor steel which fractured in a completely intergranular fashion due to temper embrittlement [51].............37

Figure 9 - The three steps of the Auger electron formation process [54]....................45

Figure 10 - Micrographs of 3 fracture surfaces analyzed by AES with the top micrograph showing a general view of the fractured specimen, the middle micrograph showing an area found to have a low concentration of Bi, and the bottom micrograph showing a fractured surface found to have a high Bi concentration [34]..................................................................................46

Figure 11 - A histogram of the number of Bi monolayers determined to exist on the fracture surface of a Bi doped Cu polycrystalline specimen analyzed with AES, 700°C corresponds to the heat treatment applied to the specimen during its fabrication [29]...................................................................................47

Figure 12 - A flow chart of the quantification procedure for the ζ-factor method including X-ray absorption correction [61]..................................61

Figure 13 – Histogram comparing the proportion of GBs displaying different boundary coverage, as measure in monolayers of Bi, for AES and XEDS studies of the Cu-Bi system...................................................................................62

Figure 14 – Quantitative XEDS Bi map of a Bi doped Cu GB (left) and a Bi segregation profile extracted from the XEDS map along a line crossing the GB at a right angle with analysis points taken 1.3 nm apart (right) ......................63
Figure 15 – Bright-field STEM micrograph showing Σ19a Cu GB doped with Bi (25 at ppm) and annealed at 800 ºC with arrows pointing to the intersection between two GB facet types [66].

Figure 16 – Cu L23 edge showing the difference in EELS spectra between a boundary and a bulk region in Bi doped Cu [70].

Figure 17 – EELS Cu L3 energy edge showing the difference between the GB and bulk spectra for a clean Cu 36.8 tilt about a [001] axis° symmetrical bicrystal boundary [46].

Figure 18 - EELS Cu L3 energy edge showing the difference between the GB and bulk spectra for a Bi doped Cu 36.8 tilt about a [001] axis° symmetrical bicrystal boundary [46].

Figure 19 – Graph of the predicted cleavage response vs. dislocation emission response for Cu bicrystals according to the Rice-Thomson model. Open circles correspond to pure Cu GBs while triangles correspond to Bi doped GBs, (+) and (-) correspond to different crack growth directions compared to the crystallographic directions in the material [49].

Figure 20 – The dependence on fracture toughness (σf) of various symmetric [001] tilt bicrystals at multiple Bi doping levels for Cu bicrystals fractured in tension [73].

Figure 21 – Ion channeling contrast of a GB from a Bi doped Cu rod showing the GB plane of the boundary inclined with respect to the specimen surface.
Figure 22 – Schematic diagram of a Cu bicrystal sample cross-section after being doped with Bi. The bicrystal boundary is running vertically through the middle of the sample. ................................. 84

Figure 23 - Bi doped Cu [001]/33° bicrystal TEM coupon specimen mounted on Mo half-grid secondary ion image generated with a 30 kV Ga ion-beam; contrast between the two grains of the bicrystal is due to differences in ion channeling effects in each grain................................................................. 93

Figure 24 – Schematic diagram of FIB specimen GB orientations with yellow representing the GB plane ................................................................. 94

Figure 25 – Top-down view of FIB TEM specimen during thinning showing a plane-view GB specimen orientation for FIB specimen fabrication where (1) Grain 1 mills at a slower rate than grain 2, (2) Grain 1 mills at the same rate as Grain 2, and (3) Grain 1 mills at a faster rate than Grain 2. Note the GB is lost in (1) and (3) due to asymmetric milling rates between Grain 1 and Grain 2............ 95

Figure 26 – Top-down view of FIB TEM specimen during thinning showing the benefit of a near plane-view GB specimen orientation for FIB specimen fabrication where (1) Grain 1 mills at a slower rate than grain 2, (2) Grain 1 mills at the same rate as Grain 2, and (3) Grain 1 mills at a faster rate than Grain 2 ................................................................. 96

Figure 27 – Load schedule used during micro-tensile mechanical test showing loading ramps where the load is increased and holds where images were acquired during testing [75]. ................................................................. 98
Figure 28 - Schematic representation of a Bi doped Cu bicrystal specimen showing the effect of changing the objective lens current on the electron probe crossover point through the depth of the specimen. ................................................................. 102

Figure 29 - Schematic representation of a Bi doped Cu bicrystal specimen displaying the two specimen orientations used to acquire the STEM TFI image series with the possible location of Bi atoms through the thickness of the inclined boundary. ........................................................................................................... 103

Figure 30 - An EBSD map of a 6° [100] twist Cu GB used to confirm the bicrystal orientation and boundary regularity .......................................................................................................................... 110

Figure 31 - A pole figure generated from an EBSD map of a 6° [100] Cu twist bicrystal confirming an approximate misorientation of 6° ......................................................... 111

Figure 32 - A pole figure generated from an EBSD map of a 13° [100] Cu twist bicrystal confirming an approximate misorientation of 13° [75]. ......................... 112

Figure 33 - A pole figure generated from an EBSD map of a 33° [100] Cu twist bicrystal confirming an approximate misorientation of 33° [75]. ......................... 113

Figure 34 – Illustration showing the selection of the reference frame RF denoted by (X_R, Y_R, Z_R) and the pattern frame PF denoted by (X_P, Y_P, Z_P), and the angles δ and γ which must be measured in order to establish the matrix [CR] [77]. 114

Figure 35 – Schematic representation of the relation between two crystal coordinate frames and a reference coordinate frame. Various stages of rotation are indicated by the arrows and the corresponding rotation matrices. [M12] is a
matrix specifying the rotation of CF1 to CF2. \([R12]\) is a matrix representing
the rotation of \(v_1\) into \(v_2\) by referring to RF [77].

Figure 36 – Sample CBED pattern showing the values to be measured for
misorientation analysis.

Figure 37 – Stress-strain curves generated from two DENT 6° Cu [100] twist bicrystal
specimens; note the extensive plastic behavior in both the Bi doped and pure
Cu conditions prior to failure [75].

Figure 38 - Stress-strain curves generated from two DENT 33° Cu [100] twist
bicrystal specimens; note the plastic behavior in both the Bi doped and pure Cu
conditions prior to failure as well as the significantly reduced elongation at
failure of the doped condition [75].

Figure 39 - SEM micrograph of a pure Cu 33°[100] twist bicrystal after transgranular
shear-like failure has occurred [75].

Figure 40 - SEM micrograph of a Bi doped Cu 33°[100] twist bicrystal after
intergranular failure has occurred due to Bi embrittlement [75].

Figure 41 – BF-TEM image of a Bi doped 6° Cu bicrystal GB.

Figure 42 – BF-TEM image of a pure 6° Cu bicrystal GB taken from a post-heat
treatment sample.

Figure 43 – BF-TEM image of a near plane-view orientation specimen showing
second phase particles along the GB with two arrows indicating points A and
B, the GB region of the specimen.
Figure 44 – HAADF-STEM image of a 33° [100] twist Cu GB doped with Bi imaged at a location between two second phase GB particles rich in Bi on an edge on GB orientation specimen. ................................................................. 130

Figure 45 - BF-STEM image of a 33° [100] twist Cu GB doped with Bi imaged at a location between two second phase GB particles rich in Bi on an edge on GB orientation specimen ................................................................. 131

Figure 46 – DF-TEM image (200) reflections from lower grain of 33° Cu bicrystal GB showing 3 different dislocation lines in red. ......................................................... 132

Figure 47 - BF-TEM image of a 33° [100] twist Cu GB doped with Bi showing a network of dislocations across the inclined GB. .............................................. 136

Figure 48 - BF-TEM image of a 33° [100] twist Cu GB doped with Bi showing a network of dislocations across the inclined GB, the change in contrast conditions from one side of the GB to the other is due to changing diffraction conditions across the dislocation. ......................................................... 137

Figure 49 – HRTEM image of a 33° [100] twist Cu GB doped with Bi showing a network of dislocations across the inclined GB. ........................................... 138

Figure 50 - HRTEM image of a 33° [100] twist Cu GB doped with Bi showing a network of dislocations across the inclined GB, note the change in dislocation appearance in the upper left corner due to GB faceting. ................................. 139

Figure 51 – HAADF-STEM image of a Bi doped 13° Cu bicrystal viewed in a near edge on GB orientation showing bright contrast at the GB due to Bi as well as facets along the GB. ................................................................. 146
Figure 52 - HAADF-STEM image of a Bi doped 13° Cu bicrystal viewed in a near edge on GB orientation showing an apparent “bilayer” if Bi on this particular GB facet. ............................................................................................................ 147

Figure 53 – Ni bicrystal showing the presence of a Bi bilayer at the GB [82]. ........ 148

Figure 54 – Line profile taken across the GB “bilayer” shown in Figure 52 displaying the measured distance between the two layers forming the “bilayer”............. 149

Figure 55 – Possible Bi atomic arrangements that may lead to a “bilayer” appearance when imaged with Z-contrast through HAADF or ABF-STEM techniques. 150

Figure 56 – HAADF-STEM image of a GB Bi oxide particle contained on a Bi doped Cu 33° bicrystal GB showing atomically resolved Bi columns surrounding the Bi oxide. ............................................................................................................ 151

Figure 57 – BF-STEM image of a GB Bi oxide particle contained on a Bi doped Cu 33° bicrystal GB showing atomically resolved Bi columns surrounding the Bi oxide. ............................................................................................................ 152

Figure 58 - HAADF-STEM micrograph Bi-doped Cu [001]/33° twist bicrystal boundary with right grain oriented to a <001> direction showing periodic Bi atoms on GB with distances between two Cu containing atomic columns as well as the distance between two Bi containing atomic columns labeled..... 153

Figure 59 – Images of periodic spacing of areas containing Bi along a Bi doped 33° Cu bicrystal GB, (a) showing BF-STEM and (b) showing HAADF-STEM with Bi atoms labeled along the GB with the spacing between areas containing Bi measured to be approximately 2.5 nm................................................................. 154
Figure 60 - BF-STEM image (a) and HAADF-STEM image (b) of inclined grain boundary with probe focused on the left side of the boundary showing the location of Bi atoms.................................................................155

Figure 61 - BF-STEM image (a) and HAADF-STEM image (b) of inclined grain boundary with probe focused on the middle of the boundary showing the location of Bi atoms.................................................................156

Figure 62 - BF-STEM image (a) and HAADF-STEM image (b) of inclined grain boundary with probe focused on the right side of the boundary showing the location of Bi atoms.................................................................157

Figure 63 – HAADF-STEM image showing GB with Bi present at boundary along with magnified section showing filtered images highlighting edge dislocations with Bi atoms near dislocation cores marked in blue along with an extra half plane of Cu atoms marked in red.........................................................158

Figure 64 – HAADF-STEM images of a pure Cu (top) and Bi doped (bottom) 36.8° symmetric tilt GB showing a repeated structural unit schematically represented on the images [46]. .................................................................159

Figure 65 - Graph of probe-forming semi-angle (mrad) vs 59% probe diameter (nm) for a STEM with a Schottky FEG, a cold FEG, and an idealized geometric probe with comparison to the diffraction limit for a 200 kV accelerating voltage. [84]........................................................................................................162
Figure 66 - An inclined Bi-doped Cu [001]/33° twist bicrystal boundary viewed by HAADF-STEM imaging with an electron probe focused on (a) the top surface and (b) the bottom surface of the specimen..........................171

Figure 67 - Selected images from a STEM TFI image series with black arrows indicating the depth of the probe focal point moving toward bottom surface of specimen from the top surface. An individual Bi atom is indicated with a red arrow as it is resolved during the image series..........................172

Figure 68 - Sum STEM TFI image showing Z-contrast lateral atomic resolution (Top) with extracted x plane projections showing Bi atomic positions through thickness of the specimen (Bottom), with reference axes (Left).............173

Figure 69 - Intensity profiles taken from the x plane projection of a sum STEM TFI image from a STEM TFI image series acquisition showing FWHM imaging intensity of (a) a Bi atom near the top surface of the specimen, (b) a Bi atom in the interior of the specimen, and (c) a Bi atom near the bottom surface of the specimen. FWHM values are plotted against Bi position from the top surface in (d) showing increasing FWHM as Bi atoms farther into the depth of the specimen are imaged. .................................................................174

Figure 70 – HAADF-STEM images of two observed atomic configurations of Bi atoms along a 33° Cu twist bicrystal with the depth of the atoms determined through STEM TFI. (a) corresponds to an atomic arrangement yielding 0.02 monolayers of Bi and (b) corresponds to an atomic arrangement yielding 0.09 monolayers of Bi. .................................................................175
Figure 71 – 3 EELS spectra from a Bi doped 6° Cu GB overlay showing the bulk, GB, and spatial difference (bulk spectrum less the GB spectrum). ................................ 181

Figure 72 - 3 EELS spectra from a Bi doped 13° Cu GB overlay showing the bulk, GB, and spatial difference (GB spectrum less the bulk spectrum) ................. 182

Figure 73 – 3 EELS spectra from a Bi doped 33° Cu GB overlay showing the bulk, GB, and spatial difference (bulk spectrum less the GB spectrum) ................. 183

Figure 74 – 3 EELS spectra from a pure 33° Cu GB overlay showing the bulk, GB, and spatial difference (bulk spectrum less the GB spectrum). ...................... 184

Figure 75 – 3 EELS spectra from a pure 33° Cu GB overlay showing the bulk, GB, and spatial difference (GB spectrum less the bulk spectrum). ...................... 185

Figure 76 - XEDS spectrum obtained on a Bi doped 6° Cu bicrystal GB showing the location of the Cu K$_\alpha$ and K$_\beta$ X-ray peaks along with the Mo K$_\alpha$ X-ray peak originating from the Omniprobe half-grid.................................................... 195

Figure 77 - XEDS spectrum obtained on a Bi doped 6° Cu bicrystal GB showing the location of the Cu K$_\alpha$ and K$_\beta$ X-ray peaks along with the Mo K$_\alpha$ X-ray peak originating from the Omniprobe half-grid, additionally the energy location of the expected Bi peaks are labeled................................. 196

Figure 78 – XEDS spectrum obtained on a Bi doped 13° Cu bicrystal GB showing the location of the Cu K$_\alpha$ and K$_\beta$ X-ray peaks along with the Mo K$_\alpha$ X-ray peak originating from the Omniprobe half-grid and a Ga K$_\alpha$ X-ray peak originating from the FIB specimen preparation................................................. 197
Figure 79 - XEDS spectrum obtained on a Bi doped 13° Cu bicrystal GB showing the location of the Bi X-ray energy peaks and possible small X-ray peaks due to Bi. .......................................................... 198

Figure 80 - XEDS spectrum obtained on a Bi doped 33° Cu bicrystal GB............. 199

Figure 81 - XEDS spectrum obtained on a Bi doped 33° Cu bicrystal GB showing the location of the Cu and Mo X-ray peaks along with the Bi Lα X-ray peak significantly above the background of the X-ray spectrum......................... 200

Figure 82 – XEDS spectrum taken from a BISSCO powder specimen showing a typical spectra obtained from BISSCO powder of any thickness. ................ 201

Figure 83 - XEDS spectrum taken from a BISSCO powder specimen showing a typical spectra obtained from BISSCO powder of any thickness with major X-ray peaks identified................................................................. 202

Figure 84 – XEDS spectrum showing the windows taken for background subtraction around the Cu Kα – Ni Kβ peak overlap highlighting the need to remove the Ni Kβ peak intensity from that of the Cu Kα peak intensity. ......................... 203

Figure 85 - XEDS spectrum showing the Gaussian fitting of the Ni Kβ peak leaving a residual signal or the Cu Kα X-ray peak with 1.2FWHM labeled as signal...204

Figure 86 – Graph showing the relationship between Cu intensity in the measured X-ray spectra and the Cliff-Lorimer ratio of Cu Kα to Bi Lα calculated from the BISSCO specimen. ................................................................. 205

Figure 87 – BF-STEM image of a Bi doped 33° Cu bicrystal GB showing the region of interest (ROI) for a XEDS map................................................................. 206

xx
Figure 88 – Color overlay (left) of X-ray signal intensity from Cu K\textsubscript{\alpha} X-ray line and the Bi L\textsubscript{\alpha} X-ray line (right). ................................................................. 207

Figure 89 – Thickness map of Bi doped 33° Cu bicrystal GB inclined with respect to beam direction. ................................................................. 208

Figure 90 – Bi wt% map of Bi doped 33° Cu bicrystal GB inclined with respect to beam direction. ................................................................. 209

Figure 91 – Integrated line profile extracted across the GB from Figure 90 showing both the Bi wt% with 95% confidence limits and the minimum mass fraction (MMF) at each point................................................................. 210

Figure 92 – GB Bi excess across GB in XEDS ROI with 95% confidence limits..... 211
Abstract:

Grain boundary (GB) segregation and embrittlement of copper (Cu) by small amounts of bismuth (Bi) has been investigated on 6°, 13°, and 33° Cu twist bicrystals. The results from micro-mechanical double edge notched testing showed no embrittlement effects in the 6° GB. The 33° GB has been shown to be significantly embrittled by the introduction of Bi. Single edge notch testing of the 13° GB also showed a reduction in fracture toughness. These mechanical results have been interpreted through the use of analytical electron microscopy (AEM) studying the GB geometry, the atomic structure, the electronic structure, and the chemical compositions of the GBs. The 6° and 33° GBs were found to be close to pure twist boundaries but with more accurate twist angles of 4.3° and 38.0°, respectively. The electronic structure of the GBs was not found to be a good indication of the presence of Bi, which was confirmed on the 13° and 33° GBs. The Bi GB coverage was confirmed via quantitative XEDS on the 33° GB to correspond to 0.12 ± 0.03 monolayers of Bi and through 3-dimensional scanning transmission electron microscope (STEM) through focus imaging to be 0.02 – 0.09 monolayers of Bi. The presence of edge dislocations along the 33° GB was confirmed with Bi segregating to edge dislocation cores. The Bi atoms on the dislocation cores embrittle the GB by increasing the energy required to move a dislocation in response to an applied stress resulting in reduced plasticity at the crack tip which promotes GB cleavage.
1. Introduction:

Grain boundary (GB) segregation induced embrittlement is a well-known phenomenon encompassing many types of metal and ceramic materials having first been observed well over 100 years ago [1]. In general, GB segregation induced embrittlement causes a reduction in the fracture toughness of materials and causes them to behave in a brittle manner where there is little to no plastic deformation prior to the point of failure. To date, the mechanism responsible for this observed embrittlement effect in many materials is unknown or has an unsatisfactory enough explanation. In this study, the particular system of Copper-Bismuth has been investigated. The Cu ore from which Cu metal is created naturally contains a small amount of Bi. Due to the typical processing techniques used on Cu metal (e.g. tube and pipe rolling, wire drawing, and other cold forming processes), a ductile metal is needed to ensure that forming equipment and personnel are not harmed as the result of unexpected brittleness in a material during processing can be catastrophic. The need for removal of Bi from Cu is obvious from a manufacturing standpoint; however, the key mechanism causing this embrittlement is poorly understood.

Past studies of the Cu-Bi system have typically focused on three types of investigation: mechanical properties, segregation behavior, and theoretical thermodynamic modeling. The mechanical properties of the Cu-Bi system have typically been investigated in a small range of special bicrystals or over a wide array of general/random bicrystals, by measuring a variety of mechanical properties to
deduce the amount of embrittlement present related to macroscopic boundary
variables such as misorientation angle. GB segregation behavior studies have typically
been performed on an extremely small set of well characterized special bicrystals,
allowing direct observation of Bi atoms and determination of Bi coverage at the Cu
GBs. Thermodynamic modeling studies have applied solute adsorption theories to the
perceived structure of Cu GBs in an attempt to determine the change in GB cohesion
energy when Bi atoms are introduced to the GB. From these three distinct and isolated
types of Cu-Bi studies minimal conclusions can be drawn as there has not been
consistency among specimens across the investigatory techniques. In this study,
tensile testing of specific GBs has been performed to determine the mechanical
behavior of the Cu GBs and an in-depth study of the chemical segregation behavior
including atomic structure of the GB has been performed. This thorough investigation
of individual boundaries allows observation and degree of embrittlement to be
correlated with the structure and chemistry of the Cu GB—starting at general GB
orientation and even down to individual atomic positions of Bi on the Cu GB. The
mechanical properties and the structural and chemical compositions of the GBs
studied here have been characterized via micro-mechanical testing and electron
microscopy, both scanning electron microscopy (SEM) and scanning transmission
electron microscopy (STEM/TEM), to determine the cause and contributing factors of
the drastic reduction in fracture toughness that is observed when Cu is embrittled by
Bi.
The sections of this dissertation will now be briefly described. Section 2 covers the background information on geometric descriptions of GBs, the different models describing GB segregation and GB embrittlement, along with an overview of the Cu-Bi system and the observed embrittlement and proposed embrittlement mechanisms therein. Section 3 outlines the Materials Science problems addressed in this work and the objectives for the research presented. Section 4 contains all of the experimental procedures for the fabrication of specimens, the geometric characterization of these specimens, the mechanical testing performed, and the chemical, electrical, and microscopic characterizations of the GB atomic structures. Section 5 interprets the results of the experimental procedures performed and includes discussion of the implication of the findings on the Cu-Bi system and the current understanding of GB embrittlement. Section 6 presents the conclusions that can be formed from this study. Proposals for future work related to understanding GB embrittlement in the Cu-Bi system are presented in Section 7. A compilation of the works referenced in this dissertation is presented in Section 8. Section 9 provides an appendix showing the software code used to calculate misorientation using the CBED technique. Finally, Section 10 gives a brief biographical background on the author.

2. Background:

The background section of this dissertation will begin with a general overview of the meaning and definition of GBs, GB segregation, and GB embrittlement in
materials as well as recent investigatory techniques for the study of GBs. This section will also cover the past investigations of Bi induced GB segregation and embrittlement of Cu as well as modern experimental techniques used to investigate these phenomena. The selection of the Cu-Bi system as a model system for all GB segregation induced embrittlement will also be covered and the major proposed mechanisms leading to this embrittlement will be addressed. In addition to studies on the Cu-Bi system, electron microscopy studies of various other GB systems will be introduced to provide whole context to the reader for the microscopy techniques employed in this study.

2.1 Grain boundaries in crystalline materials:

A GB is defined as an interface separating two crystals of different crystallographic orientations in a polycrystalline material of the same phase [2]. The introduction of GBs and similar homophase interfaces in a material may so drastically alter the material properties that many studies of the properties of polycrystalline materials require the study of the GBs present in the material. GB strengthening is an example of one of many such effects.

GB strengthening occurs as the average grain size in a crystalline material is reduced. This reduction in grain size leads to an increase in that total GB volume in the material, providing greater resistance to the motion of dislocations and thereby increasing the yield strength of the material. Conversely, various effects at a GB may also prove detrimental to the mechanical properties of a material as the disorder at a GB may lead to an increase in average atomic bond length across the interface.
meaning that there is a decrease in the energy required to separate two atoms compared to the energy of the pure crystal. Kurishita et al. showed that the fracture behavior of molybdenum twist bicrystals is strongly dependent on the character of the GB, with fracture stress varying as much as ~60% for Mo <110> bicrystals with different misorientation angles [3].

Due to the numerous and dramatic effects that GBs can have on materials it is necessary to have a manner to completely and unambiguously define a GB. GBs can be described according to the five macroscopic geometric degrees of freedom (DOF) that are properties of each GB. Three of the geometric DOF parameters correspond to a rotation of one of the two crystal lattices onto the other crystal lattice about a common rotation axis. Here there are two DOF defining a vector along the rotation axis and one DOF defining the rotation angle. The other two geometric DOF are parameters that describe the orientation of the GB plane normal separating the two crystals at the GB. Together these five geometric DOF can be thought of as simply all the parameters needed to manufacture a bicrystal from two separate crystals with a particular rotation between the two crystals and a particular GB plane [4]. Figure 1 shows a schematic representation of the parameters that can be used to define a GB. With the variables found in Figure 1 a GB can then be defined as $\Theta^o[h_o,k_o,l_o]$, $(h_{An},k_{An},l_{An})$ where the rotation axis $O = [h_o,k_o,l_o]$ and $(h_{An},k_{An},l_{An})$ describes the GB plane as it relates to one crystal. Though only five parameters are needed to fully define a GB it is often easier to understand the GB boundary plane and misorientation relationship between the two crystals if the GB is over-defined, giving the GB plane as
related to both of the crystals that comprise the GB. Using the above notation, an over description of the GB describing both boundary planes is as \( \Theta^o[h_o,k_o,l_o], (h_{Ao},k_{Ao},l_{Ao}) \) / \( (h_{Bn},k_{Bn},l_{Bn}) \). For much of this dissertation the misorientation of GBs will be used and compared to one another utilizing rotation axis and angle notation (i.e. \( \Theta^o[h_o,k_o,l_o] \)) with boundary plane information only present when available. In addition to noting the misorientation angle, axis, and boundary planes, GBs are often described by the density of coincident lattice sites on both sides of the GB, which is so called coincident site lattice (CSL) theory to describe the geometries of GBs. This description is occasionally used in this paper to denote specific boundaries (as CSL boundaries are often thought of as “Special” lower energy GBs compared to other random GBs).

In addition to the five macroscopic geometric DOF defining the misorientation between two crystals, there also exist four additional microscopic DOF that describe the local atomic structure at interface. Three of these microscopic DOF define periodic rigid-body displacements along the boundary regarding local atomic structure. If there is no periodicity along the interface. These three microscopic DOF reduce to one microscopic DOF used to define a volume expansion across the interface. An additional DOF is used to describe the position of the interfacial plane. Together, these four microscopic DOF parameters determine the atomic structure of the interface and are a result of stress relaxation from the conditions imposed by the five macroscopic geometric DOF; thus the four microscopic DOF are not completely independent variables and are constrained by boundary conditions imposed by the five macroscopic
geometric DOF [4]. In total, these nine DOF defining a bicrystal boundary lead to an enormous number of possible GB conditions for investigation even prior to the addition of other variables such as segregant species on the GB.

Two special categories of GBs result from consideration of the rotation axis between the two grains and its orientation with respect to the GB plane. When the rotation axis of misorientation is parallel to the GB plane, a special boundary called a pure tilt GB is formed. This tilt boundary is in contrast with the rotation axis of misorientation being perpendicular to the GB plane. When the rotation axis of misorientation is parallel to the GB plane normal vector, a pure twist GB is formed. These two special types of GBs have been the focus of many studies due to the relative ease of fabricating bicrystals with these specific geometric requirements; it is much more difficult to repeatedly reproduce a general GB that has a rotation axis of misorientation unrelated to the GB plane. Figure 2 shows a schematic representation of these two special GB types. In Figure 2 the rotation axis of misorientation can be seen in the tilt bicrystal being in the GB plane, where the rotation axis of misorientation for the twist bicrystal below is perpendicular to the GB plane. A full systematic description of all possible GBs proposed by Wolf and Lutsko is based on a so-called interface-plane scheme [5]. Here the miller indices of each of the two GB planes present at the interface are related through a twist angle, $\varphi$. The use of the two GB plane normals and the rotation angle between them allows the unrelaxed bicrystal GB to be easily conceptualized. Table 1 shows a summary of the four possible categories of GBs using the interface-plane scheme.
Much of the current electron microscopy work on bicrystals has been conducted on symmetric tilt bicrystals as they allow observation across the bicrystal boundary from a specimen orientation that contains identical directions in both grains, i.e. observation directly down the misorientation axis direction while still observing the specimen across the GB. This type of orientation is not possible in a twist GB as observation along the twist misorientation axis would yield a specimen orientation not across the GB but rather through the GB. For practical reasons of specimen preparation, this through-GB orientation is very difficult to fabricate as the necessity to keep the entire GB plane within the electron transparent thin specimen is quite difficult. Hence the overwhelming use of tilt GBs in electron microscopy studies of fabricated bicrystals.
GBs can additionally be broken into two separate categories based on the degree of misorientation between the two grains, forming high-angle and low-angle GBs. High-angle GBs typically have a degree of rotation from one grain to the other of greater than 10-15°, whereas low-angle GBs are those with rotation angles less than this amount. The choice of this angle is not arbitrary but related to the ability of the system to accommodate the strain across the GB interface by the generation of an array of misfit dislocations. These misfit dislocations provide relief of strain caused by the misorientation across the GB. The misorientation of a pure tilt low angle GB can be accommodated by an array of edge dislocations. The misorientation of a pure twist low-angle GB can be accommodated by an array of screw dislocations. The delineation between low- and high-angle GBs is formed as misorientation increases and the density of misfit dislocations cannot increase any more. When the dislocation cores of the strain relieving dislocations in the material can no longer remain separated and begin to overlap, the misorientation can no longer be accommodated by misfit dislocations and the boundary is then considered as a high-angle boundary.

High-angle GBs may further be broken down into three separate groups: singular, general, and vicinal. Singular GBs are high-angle GBs that have accommodated the misorientation between the two grains by the formation of periodic atomic structural units along the GB. These singular GBs often exhibit a sharp minima in energy as they are composed of a single type of atomic structural unit. General GBs are composed of two or more parodic atomic structural units and are high-energy GBs. Vicinal GBs are energetically situated between singular and general GBs; they are
composed of the closest singular GB structural unit and an array of secondary GB misfit dislocations. Figure 3 shows the structure of two singular boundaries in (a) and (b) and a third general GB in (c) being a combination of the two structural units from boundaries \{013\} and \{024\} forming the structural units of an \{037\} symmetric tilt GB. Clearly, with the large number of DOF possible (9 if inversion boundaries are not considered), there exist a vast amount of possible GB arrangements even prior to considering the effects of segregation, heat treatment, and other non-geometric or purely crystallographic variables.
Figure 1 - Variables that define a GB. $x_A, y_A, z_A$ and $x_B, y_B, z_B$ are the crystallographic directions for grains A and B, respectively. $O$ is the rotation axis and $\Theta$ is the rotation angle necessary to bring grain A to the orientation of grain B and vice versa. $n$ is the orientation of the GB plane at the interface between grain A and grain B [2].
Figure 2 – Schematic diagram showing a tilt GB (top) and a twist GB (bottom) between two grains (blue and green outlined cubes) where the misorientation axis appears in bold [6].
Figure 3 – Structure of three [100] symmetrical tilt GBs in a BCC material (a) \{013\} singular GB, (b) \{024\} singular GB, and (c) \{037\} general GB. Circles and triangles represent parallel (100) planes [7].
2.1.1 Investigation of the structure of GBs and interfaces via electron microscopy

The small lateral dimension of GBs requires investigation by techniques with high resolution if analytical results of any quality are to be generated. Due to this high resolution need, electron microscopy (EM) has traditionally been a primary investigatory tool for materials scientists interested in studying and analyzing GBs in a wide variety of materials.

Developing a full understanding of material behavior at the nanometer level often greatly benefits from the ability to accurately image atomic structure in three dimensions. One approach for achieving this goal is to employ transmission electron microscopy (TEM) imaging. In general, TEM offers 2-dimensional projection views of 3-dimensional objects even though electron transparent TEM specimens are very thin. Figure 4 depicts a Bi doped \(\Sigma 51\) GB in Cu in an edge-on orientation showing the GB very sharply along with multiple facets. Here only a 2-dimensional projection is observable with no information through the thickness of the specimen. However, multiple methods have been suggested for obtaining 3-dimensional information from thin specimens in TEM. One method that is already widely used in biological sciences and increasing in the physical sciences is electron tomography [8].

In electron tomography a microscope is operated in either TEM or scanning transmission electron microscope (STEM) mode to collect a series of images at multiple specimen tilt angles. The image series is then processed by computer to develop a 3-dimensional reconstruction of the specimen. The advantage of high-angle
annual dark-field (HAADF)-STEM imaging for this purpose is the reduced or completely eliminated diffraction and phase contrast effects, especially in crystalline specimens, which can reverse image contrast and cause difficulty interpreting images. So, image interpretation 3-dimensional reconstruction becomes straightforward when a tilt series of images are acquired by HAASD-STEM imaging. The atomic number sensitivity of HAADF-STEM can also be utilized to observe buried structures of different chemical compositions.

Alternatively, 3-dimensional information is also obtained by scanning confocal electron microscopy (SCEM) [9]. The SCEM approach is the electron microscopy analog to the confocal optical microscopy technique. The goal of SCEM is to form a transmitted image using only the electrons that are scattered from the portion of the specimen that is in the focus, i.e. scattering from the focal volume. This approach offers improved image resolution in the z-direction and, as such, is a powerful tool for 3-dimensional imaging. To achieve atomic resolution, however, SCEM has many precise instrumentation requirements [10]. The first requirement is a set of two aberration correctors for illumination and projection, to achieve the best possible resolution in all 3 directions. The second instrumentation requirement is a pinhole aperture that limits the electrons entering the detector to only those that passed through the focus of the beam. Additionally, with the use of two sets of scan coils, the first to raster the beam and the second to refocus the beam on the detector, problems arise keeping the imaging conditions constant throughout the raster; thus, the use of a static beam and stage raster may also have to be considered. These instrumentation
requirements only allow a few microscopes (designed with this particular goal in mind) to be converted to SCEM capable machines, necessitating the need for a more practical 3-dimensional imaging technique.

Recently, a combination of TEM/STEM tomography and atom probe tomography (APT) has been used to obtain 3-dimensional information at the nanoscale while simultaneously removing some of the artifacts present in TEM tomography and APT when these techniques are used individually [11]. Work has also been performed by Raabe et al. (2014) correlating TEM nano-diffraction crystallographic information with APT results to study GB segregation [12]. APT, while useful for studying 3-dimensional morphological and compositional information, lacks the required resolution to observe specific atomic placement of individual segregant atoms on GBs.

The use of aberration-correction for STEM offers a dramatic increase in the range of aberration-free angles for electron probe formation. Increasing the aberration-free angular range allows the use of a larger probe formation angle, \( \alpha \), without the occurrence of resolution limiting lens aberrations. The immediate result of the aberration-correction technology has been a significant improvement in the lateral resolution possible with STEM systems, as the lateral resolution is inversely related to \( \alpha \). Atomic column structures separated by as few as 47 pm have been resolved successfully with the latest aberration-corrected STEM instruments [13], [14]. In addition to improved lateral resolution, a larger probe-forming semi-angle effectively reduces the geometric depth of field (DOF) of the electron probe. The geometric DOF is a region of defocus for which the image contrast intensity is not significantly

17
reduced from the maximum value [15]. The relationship between the geometric DOF, \( \Delta z \), and \( \alpha \) is given as [16]:

\[
\Delta z = 1.77 \frac{\lambda}{\alpha^2},
\]

*Equation 1*

where \( \lambda \) is the wavelength of the electrons used to form the electron probe. Here \( \Delta z \) is defined as the full width at half-maximum along the optic axis. For improving the depth resolution, \( \Delta z \), it is essential to employ as large a probe-forming aperture as possible to maximize \( \alpha \). Therefore, larger aberration-free angular ranges provided by aberration correction are essential to improve the depth resolution.

By employing an aberration-free electron probe formed with relatively large angles and sufficiently small focus steps, images can be simultaneously optimized for both high lateral and high vertical resolutions. This STEM through-focus imaging (TFI) technique seeks to use the height sensitivity along the z direction with large probe-forming semi-angles to extract 3-dimensional information. 3-dimensional resolution is achieved by taking a series of images with different focal plane positions through the thickness of the specimen [17]. A focal image series obtained by STEM TFI contains both high lateral resolution, provided by the inherent high resolution of modern aberration-corrected STEM instruments and information at different depths through the sample, provided by the smallest DOF possible with large probe forming apertures. Results from STEM TFI in a limited number of material systems have revealed both promising efficacy of the technique in specific circumstances but also
potential limiting factors for its general application. Sensitivity to individual dopant atoms has been reported in single crystal silicon doped with Bi, and in calcium titanate (CaTiO2) with an imbedded half monolayer film of lanthanum [18]; individual hafnium atoms have also been detected in semiconductor gate oxides [19].

The ability to directly image buried structures in TEM specimens at the atomic scale is necessary for proper investigation of GB segregants. In GBs that contain segregant atoms, the atomic structure can change significantly compared to a clean boundary. However, the exact form of this change is not always immediately apparent from traditional microscopy investigations without extensive and difficult sample preparation. For example, alumina GBs doped with yttrium (Y) have been viewed using a plane-view orientation allowing the detection of a monolayer distribution of Y atoms occurring along the GB [20]. In these plane-view specimens the projection of the boundary plane was imaged to determine the spacing of individual dopant atoms at the boundary, requiring the creation of a specimen containing the whole width of the boundary in an electron transparent section. Projection-based techniques such as TEM and STEM can only accurately show spatial distributions in the lateral directions; no depth information can be directly inferred from conventional projected images. To properly and more easily characterize the atomic structure of an interface, information, 3-dimensions must be able to be observed.
Figure 4 - HRTEM micrograph of a Σ51 [110] tilt Cu doped Bi grain boundary with symmetrical (s) and asymmetrical (as) GB planes [21]
2.2 Grain boundary segregation:

Segregation in materials is the enrichment in the concentration of a solute at some site specific feature. These features may include surfaces, dislocations, stacking faults, and precipitates or other phase boundaries (both homo and hetero). For the discussion of segregation related to the work performed in this study, only GB segregation will be covered in depth. GB segregation is, quite simply, the enrichment in the concentration of some solute species on all or some of the GBs present in the matrix material. The first possible recording of GB segregation (and GB embrittlement) was in the book “De Re Metallica” by Georgius Agricola in 1556 [22]. Agricola describes in his book the “hot shortness” of steel, the propensity for steel to crack along GBs while being forged at high working temperatures, even becoming brittle at temperatures above the recrystallization temperature. The segregation of sulfur and other low-melting point constituents causes a weakening across the GB of the iron (Fe) and causes it to literally fall apart under hot forging or rolling conditions.

Qualitatively the propensity for GB segregation can be predicted by the Hume-Rothery rules [23]. These rules describe the necessary conditions for either substitutional or interstitial dissolution of a solute atom in a solid matrix formed of solvent atoms.

Substitutional Solid Solution Criteria:
1. The atomic radii of the solvent and solute atoms may differ by no more than 15%.
2. The crystal structure of the solute and solvent species must match.
3. The solute and solvent atoms must have similar valency.
4. The solute and solvent atoms must have similar electronegativity.

**Interstitial Solid Solution Criteria:**

1. The atomic radius of the solute atoms must be smaller than those of the solvent atoms.
2. The solute and solvent atoms must have similar electronegativity.

Using these Hume-Rothery rules, an idea of what elements can be alloyed can be graphically represented with a Darken-Gurry Map [24], which is a diagram of the electronegativity of each element plotted against the atomic radius of each element. These Darken-Gurry maps can be used to quickly determine the potential for solid solubility based on atomic difference in radii and electronegativity for two elements. Further considerations need to be taken to assess the crystal structure and valence state of the atoms involved in determining the final potential for the formation of a solid solution. For the solubility of elements in Cu, as show in Figure 5, it is quickly observed that an element such as nickel (Ni) will have high solubility in Cu while an element such as Bi will have little to no solubility.

Thermodynamic descriptions of segregation in metals were first derived from Langmuir gas-adsorption theories by McLean [25]. Here McLean used a statistical
mechanical approach to express the internal energy of the GB as a function of solute concentration, $C$, randomly distributed on $N$ lattice sites, as well as $c$ solute atoms distributed on $n$ GB sites as shown in Equation 2, with $k$ being the Boltzmann constant.

$$U = cu_1 + CU_1 - kT[\ln (n!N!) - \ln(n - c)!c!(N - C)!C!]$$

*Equation 2*

The equilibrium state of this system will be reached when the internal energy $U$ is at a minimum. To determine the minimum value of $U$, the equation for internal energy of this binary system can be differentiated with respect to $c$ to develop the Langmuir-McLean segregation isotherm as shown in Equation 3.

$$\frac{X^\Phi}{1 - X^\Phi} = \frac{X^C}{1 - X^C} \exp\left(-\frac{\Delta u}{kT}\right)$$

*Equation 3*

Here $X^\Phi = c/n$, $X^C = C/N$, and $\Delta u = u_1 - U_1$. In the derivation of this Langmuir-McLean isotherm it is assumed that all GB sites are able to accommodate solute atoms and the only entropy concern is that of configuration, as expressed in the right-hand term in Equation 2 [2]. Entropy concerns may be addressed by replacing $\Delta u$ with a corresponding Gibbs free energy of GB absorption, $\Delta g$. By adding a GB solubility limit to Equation 3 of $X^\Phi_0$, Equation 4 is formed which more accurately predicts solute segregation to GBs for sub-monolayer segregation.
As expected, Equation 4 correctly predicts increases in GB solute concentration, $X^\Phi$, with decreases in temperature, $T$, and increases with bulk solute concentration, $X^C$. However, this equation is limited in its predictive ability to systems that may form sub-monolayer GB segregant distribution. For study of those systems that may display multilayer GB segregation, the work of Brunauer et al. and their development of the Brunauer–Emmett–Teller (BET) isotherm to describe how gas molecules may form multilayers on a free surface according to the energies of atoms present in different layers was adapted to internal interfaces in materials by Seah and Hondros. Additionally, Seah and Hondros described multilayer segregation in specific systems such as tin in body centered cubic Fe and Sulphur, phosphorus and antimony segregation in face centered cubic Fe and Ni. [26], [27], [28]. A truncated version of the BET isotherm applying to monolayer GB segregation is shown in Equation 5 where the only difference between the truncated BET isotherm and the McLean isotherm given in Equation 4 is that an upper concentration limit, $X^C_0$, is imposed in the bulk material.
Using Equation 5, Seah and Hondros were able to create a comparison between the solute solubility in the bulk material and the solute existing on the GB. The GB enrichment factor, \( \beta \), is defined in Equation 6.

\[
\beta = \frac{X^\Phi 1}{X_0^\Phi X_0^C}
\]

If the GB of a system is assumed to be saturated to the GB solubility limit, the GB enrichment factor is then inversely proportional to the bulk solid solubility limit of the system. This atomic solubility to GB enrichment factor relation is graphically represented in Figure 6 where the Cu-Bi system can be seen as having the highest GB enrichment ratio as well as the lowest bulk atomic solid solubility.

The result from this collection of thermodynamic analysis of GB segregation is that models can be developed to help predict the occurrence and degree of GB segregation present in a binary, or even multi-component system. The theoretical prediction is key here as thermodynamic analysis of GB segregation treats each GB nearly identically in that at thermodynamic equilibrium there should be an equal amount on all GBs present. This thermodynamic approach does not take into account the geometric DOF in actual crystallographic structures nor the DOF related to GB relaxation as discussed in section 2.1. Powell and Woodruff first reported a high degree of segregation anisotropy in the Cu-Bi system in 1976, meaning that
segregation occurs at very different levels on different GBs throughout a polycrystalline specimen [29]. A relation between crystallographic misorientation at GBs and the present level of GB segregation was confirmed by Fraczkiewics and Biscondi in 1985 [30]. This means that until a more rigorous thermodynamic description of GBs and GB segregation is available, thermodynamic modeling is useful for predicting only if GB segregation can occur in a given system. For a more accurate understanding of the amount of segregant on specific GBs, experimental verification is needed.
Figure 5 – Darkan-Gurry map of Cu showing solubility of atoms inside ellipse ($X < 0.3$ difference and $r < 15\%$ difference from Cu)
Figure 6 - Grain boundary enrichment ratio vs. bulk atomic solid solubility [27].
2.3 The Cu-Bi system:

Bi has also been known to severely embrittle Cu, a phenomenon first observed and attributed to Bi over 100 years ago [1]. Bi acts as a GB embrittlement agent in Cu and is naturally contained in Cu ore. To purify the resulting Cu from the ore and allow it to reach a level of ductility suitable for drawing and other processing techniques, expensive and time consuming purification steps are needed to ensure the concentration of Bi is below ~10 ppm [31], [32]. Without the purification steps, Cu will fracture in an intergranular fashion with fracture surfaces running along the Cu grain boundaries [33].

For this study the Cu-Bi system has been selected due to several of the intriguing properties of this system. Bi has almost no solubility in Cu; this lack of solubility has importance when studying the chemical nature of the interface between two Cu grains. As a dopant atom in Cu, Bi cannot be dissolved in the bulk Cu matrix and hence segregates toward any type of interface in the material, i.e. a GB, second phase particle, inclusion, or surface [34], [29]. The low solubility combined with a feature such as a GB gives Bi a very high enrichment factor for Cu as shown in Figure 6, which is the GB enrichment factor for multiple systems plotted against the solubility of the segregant atoms in those systems. The Cu-Bi system has the highest GB enrichment ratio and the lowest atomic solid solubility of any system [27].
Recently Bi has been added to certain Cu alloys to enhance the machinability of the alloys as a substitute for the hazardous Pb used previously [35]. Though the machinability has been increased, the lack of full understanding of the process of Bi embrittlement of Cu has led to other elements and compounds being used to increase machinability of Cu and its alloys. Being an ideal system for the study of GB embrittlement, there is an abundance of literature on the segregation of Bi to Cu GBs and the brittle intergranular fracture that results from Bi doped Cu polycrystalline specimens, even though debate still remains among the mechanisms and exact processes that cause GB embrittlement of Cu by Bi [36], [37], [38], [39], [40].

2.4 Currently proposed mechanisms of grain boundary embrittlement in the Cu-Bi system:

One frequent consequence of GB segregation is the altering of mechanical, electrical, or chemical properties at GBs that have been populated with some amount of a segregant species. There are many possible GB effects caused by GB segregation such as: enhanced creep embrittlement, temper embrittlement, enhanced GB stress corrosion cracking, altered sintering kinetics, hydrogen embrittlement, among others [41]. This study exclusively focuses on mechanical embrittlement of GBs due to GB segregation.

McLean first proposed GB segregation induced embrittlement was due to rearrangement of solute atoms exactly along the GB plane as segregant atoms [25]. On the GB the segregant atoms changed the ideal work of fracture, the required work to
cause fracture absent any other changes in the system such as dislocation motion or phonon propagation, \( \gamma \). Building on the fracture mechanics work of Griffith, McLean wrote the following equation describing rapid fracture in a GB embrittled solid [42].

\[
\gamma = 2\gamma'_s - \gamma_b
\]

*Equation 7*

Where \( \gamma_b \) is the GB energy per unit area prior to fracture and \( \gamma'_s \) is the surface energy per unit area immediately after fracture. McLean argued that with this type of GB segregation-induced embrittlement the total work of fracture was determined by the ideal work of fracture due to the small boundary area over which fracture and crack tip propagation may occur [43]. If the surface energy of a system is reduced, then it can become energetically favorable to relieve stress through the propagation of a crack rather than the typical method of plastic deformation in normally ductile materials. These two competing energies, the energy required to cleave the boundary and create new surfaces, \( G_{\text{cleave}} \), and the energy required to initiate dislocation motion, \( G_{\text{disl}} \), can be used to predict whether a GB will likely crack or plastically deform when a sufficient stress is applied. Mason adapted the Rice-Thomson model of crack blunting dislocation behavior to compare these two values, \( G_{\text{cleave}} \) and \( G_{\text{disl}} \), in an effort to determine which stress relieving behavior is more likely to occur on a given GB [44], [45]. If \( G_{\text{cleave}} < G_{\text{disl}} \) then cleavage along an atomically sharp crack will occur to relieve stress at the crack tip, and if \( G_{\text{disl}} < G_{\text{cleave}} \) then crack tip blunting dislocations will be emitted from a dislocation loop at the crack tip to relieve stress at the crack tip.
When $G_{\text{cleave}}$ is reduced to a level below that of $G_{\text{disl}}$, through a reduction in temperature, GB segregation, or any other means, a ductile to brittle transition (DBT) has occurred. Intergranular fracture seen in brittle materials, resulting in fracture surfaces similar to those in Figure 8, occur when $G_{\text{cleave}} < G_{\text{disl}}$.

There also exists multiple explanations of the observed embrittling effect of Bi in Cu using arguments of electronic structure at the GB. The first argument is that the presence of Bi at the GB causes a weakening of the Cu-Cu bonding where the more electronegative Bi atom draws charge from the Cu-Cu bond across the GB. Here, $G_{\text{cleave}}$ is reduced in comparison to $G_{\text{disl}}$ to bring about the DBT [46]. A second electronic structure argument exists wherein the presence of embrittling atoms cause strong hybridized bonds to form thereby stiffing bonding in a directional manner across the boundary making plastic deformation much more difficult to initiate, i.e. increasing $G_{\text{disl}}$ [47]. A third electronic effect has also been proposed that is contradictory to the second for noble metals which are strengthened by directional bonding. This electronic effect is that the presence of Bi reduces the directional bonding in Cu, i.e. the 3d 4s hybridization, and increases the number of electrons occupying the Cu 4s states [46]. This hybridization effectively weakens the Cu-Cu bonding at the GB, thereby decreasing $G_{\text{cleave}}$ to a lower energy per unit area than $G_{\text{disl}}$ and causing a DBT to occur [46], [48].

Wang and Anderson used the Rice-Thomson model to explain GB embrittlement of face centered cubic (FCC) metals as a function of GB geometry and
structure related to available slip planes for dislocation emission competing with GB
decohesion due to GB segregation [49]. This embrittlement mechanism was derived
from the result of being fairly insensitive to absolute GB segregation levels, consistent
with some mechanical testing of specific bicrystals. It is important to note that in this
GB embrittlement mechanism the GB segregant atoms serve only to reduce GB
cohesion and do not interact with dislocations. Wang and Anderson reported that $G_{\text{disl}}$
can vary as much as 300% due to geometrical differences on different boundary planes
concerning the number of available slip systems while the GB structure responsible
for allowing Bi on the boundary to decrease cohesion only caused a variability in
$G_{\text{cleave}}$ of 36% [49].

From this relatively simple Rice-Thomson model on the brittle-versus-ductile
behavior in materials exhibiting GB segregation can be qualitatively explained. In the
Cu-Bi system the atomic size effect of GB embrittlement supposes a decrease in $G_{\text{cleave}}$
to a level below that of $G_{\text{disl}}$ through the stretching of Cu-Cu atomic bonds across the
GB due to the significantly larger atomic radii of Bi atoms compared to the radii of Cu
atoms. Due to this large size difference, the free volume typically found at a Cu GB
can hardly contain the Bi atoms without stretching—and thus weakening—the Cu
bonds. This explanation of embrittlement has been used by Schweinfest et al. to
atomistically model GBs in the Cu-Bi system, and they have been able to show a large
reduction of $G_{\text{cleave}}$ due solely to the accommodation of Bi into the Cu GB through
stretching of the Cu-Cu atomic bonds [50].
To summarize the currently proposed mechanisms of segregation induced GB embrittlement, the following list is provided along with Table 2 showing the proposed effect of each mechanism on the GB properties responsible for dislocation movement and GB cleavage.

1. Atomic size effect, or the reduction of GB cohesion due to the stretching of the Cu-Cu boundary bridging bonds in response to the incorporation of large Bi atoms into the free volume of the Cu GB.

2. Electronic effect via difference in electronegativity between solute and matrix atoms; the more electronegative Bi atoms present at the GB removes charge from the Cu-Cu GB bridging bonds leading to a reduction in GB cohesion.

3. Electronic effect via increased hybridization of Cu-Cu bonding, where the increase in the hybridization leads to a more directional covalent bond between the atoms increasing stiffness and preventing plasticity.

4. Electronic effect via decreased hybridization of Cu-Cu bonding, where the presence of Bi atoms prevents the Cu-Cu bond forming 3d 4s hybrid states and leads to an increase in the occupancy of the 4s state thereby weakening the Cu-Cu GB bridging bonding.

5. Slip plane availability effect at the crack tip, where the dominating feature determining the possible embrittlement of a GB by Bi is the activation energy required for the emission of a crack tip blunting dislocation, which has a high degree of variability due to the large number of GB planes possible. In this
mechanism Bi serves to reduce $G_{cleave}$ into a range where competition between crack tip blunting dislocation emission and GB decohesion becomes possible.

### Table 2 – Embrittlement Mechanisms and their proposed effect on GB properties ($G_{disl}$ and $G_{cleav}$)

<table>
<thead>
<tr>
<th>Embrittlement Mechanism</th>
<th>Effect on $G_{disl}$</th>
<th>Effect on $G_{cleav}$</th>
</tr>
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<tbody>
<tr>
<td>Atomic Size Effect</td>
<td></td>
<td>Decrease Energy</td>
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<tr>
<td>Charge Transfer</td>
<td></td>
<td>Decreases Energy</td>
</tr>
<tr>
<td>Increased Hybridization</td>
<td>Increase Energy</td>
<td></td>
</tr>
<tr>
<td>Decrease Hybridization</td>
<td></td>
<td>Decrease Energy</td>
</tr>
<tr>
<td>Slip Plane Availability</td>
<td>Increase Variability (depending on crack direction)</td>
<td>Decrease Energy</td>
</tr>
</tbody>
</table>
Figure 7 – Schematic diagram of an atomically sharp, stationary crack tip (left) showing the competition between blunting dislocation emission (upper right) and GB decohesion (lower right) [49]
Figure 8 - Scanning electron micrograph of a 3Cr1Mo rotor steel which fractured in a completely intergranular fashion due to temper embrittlement [51].
2.5 Past investigations of Bi induced embrittlement of Cu:

The observation of Bi causing the embrittlement of Cu was first made in a technical journal in 1874 [1]. In the time that has passed between the initial observation of the embrittling effect Bi has on Cu and the writing of this dissertation, many advancements in scientific understanding of materials and instrumentation advancement for the study of materials have occurred.

2.5.1 Auger electron spectroscopy

Compositional analyses of Bi embrittled Cu have been conducted using Auger electron spectroscopy (AES). AES is a surface characterization technique in which a high energy photon or electron beam is rastered over the surface of a specimen causing ionization of atoms near the surface of the specimen resulting in the production of Auger electrons [52]. The Auger electrons have characteristic kinetic energies dependent on the element from which the Auger electrons were emitted from. The creation of an Auger electron for analysis results from a three electron process. During the incident beam ionization process, an electron A from a core shell of a near surface atom, having an energy of $E_A$, may be ejected from the atom creating a core shell hole. This now excited atom may non-radiatively decay by the demotion of an outer shell electron B, having an energy of $E_B$, filling the core shell hole. This outer shell electron loses energy equal to the difference between the binding energy of the ejected core shell electron and the demoted outer shell electron; this energy may then
be transferred to a second outer shell electron C, which is then released from the atom to be collected by the Auger analyzer and have its kinetic energy measured. The kinetic energy of this Auger electron, $E_{ABC}$, is given by Equation 8, as follows:

$$E_{ABC} \approx E_A - E_B - E_C,$$

*Equation 8*

Figure 9 shows a schematic representation of the three steps for the release of an Auger electron beginning with (A) the ionization of the atom due to the ejection of electron A, then (B) the relaxation due to the demotion of electron B down to the core shell, and finally (C) the emission of the outer shell electron C as the Auger electron with a kinetic energy of $E_{ABC}$. Due to the discrete energy levels of the electron shells in each element, the kinetic energy of the Auger electron collected prior to any inelastic scattering event is characteristic of the element the electron was emitted from. There are some minor corrections to these characteristic energy levels, such as the slight change in $E_C$ due to the presence of a core hole in the particular shell and the effect of the electron analyzer’s work function due to electrical contact with the specimen; however, these may be ignored for the ease of understanding the basic principles involved in the AES technique.

AES is a surface analysis technique, only gathering information from ~100 Å of depth in a specimen, which has the advantage of being non-destructive and only requires a specimen with a clean surface that can be fit into a high-vacuum chamber. AES allows relatively high spatial resolution in modern instruments and is capable of
analysis achieving a lateral resolution of less than 100 Å and depth sensitivity of less than ~100 Å, so that AES only probes a few atomic layers from the surface ensuring that only near-surface elements are detected, seemingly making it ideal for fracture surface study. Moreover, the AES technique is relatively sensitive with a detection limit of ~0.1 atomic % which is more than adequate for Cu-Bi segregation studies where the AES analysis volume on the GBs may have a very large Bi atomic %.

There are, however, some important limitations with the AES technique. Foremost is that AES can only observe interfaces after fracture, and any change in the chemistry or structure of the interface during fracture or between fracture and the AES observation will affect the accuracy of the results. Even if it can be assumed that the structure of the boundary does not change dramatically during the in-situ fracture of the interface, the resolution of AES is not capable of the atomic level sensitivity that is needed to determine the exact positioning of Bi atoms on the Cu GBs. For this reason, a method to study the pre-fracture interface with extremely high spatial resolution is required.

Previous studies of Bi doped Cu polycrystalline samples have been performed using AES to determine the presence and amount of Bi on specimen fracture surfaces. Most of these AES studies were conducted on polycrystalline Cu samples containing a multitude of general GBs [34]. Typically a Cu polycrystalline samples were heated in contact with Bi both directly or from a vapor source and held at an elevated temperature to allow Bi to run into the Cu GBs. After a sufficient soak time, the
samples were quenched and then inserted into an AES spectrometer and fractured under ultra-high vacuum conditions via an external extensometer operated through a bellows to preserve the chemistry of the fractured interface [27]. Due to the nature of AES analysis, only fracture surfaces that break cleanly and in a brittle manner can be analyzed since the GB surface after fracture of a ductile interface cannot be directly observed in any meaningful way. AES has been used in the particular case of the Cu-Bi system to identify GBs that present fractured surfaces containing Bi and to quantify the amount of Bi on the surfaces of these GBs.

The AES quantification technique will now briefly be addressed to understand the results of AES on Bi embrittled Cu GBs. AES quantification relies on forming a ratio in the intensity of characteristic auger electron signals between the adsorbate species and the bulk species and then converting this ratio to a more easily interpretable monolayer description of adsorbate amount. For the case of Bi embrittled Cu, the adsorbate species is Bi and the bulk species is Cu. Like most other forms of spectrometry, standard specimens containing known surface composition and containing both of the species of interest must be used to form a calibration ratio of adsorbate auger electron intensity to bulk auger electron intensity. Once this calibration ratio has been obtained the experimental AES results may be interpreted, determining $X_s$, the coverage of adsorbate A on a substrate S using Equation 9 [36]:

$$X_s = \lambda_A \frac{I_A}{I_S} \frac{I_A^0}{I_S^0},$$  

Equation 9
Where $I_S^0$ and $I_A^0$ are the bulk auger electron intensities from a standard specimen for the substrate and the adsorbate, respectively, and $\lambda_A$ is the attenuation thickness of the adsorbate in monolayers. The attenuation thickness is a measure of the reduction in detection of the characteristic auger electrons as the number of monolayers of an adsorbate is increased. AES experimental results for Bi embrittled Cu can then be discussed in terms of monolayers of Bi existing on a Cu GB surface based on the intensity ratio of the Bi auger electron signal intensity to the Cu auger electron signal intensity.

Past AES studies of Bi doped Cu have yielded insight into the presence of Bi on intergranular fracture surfaces of the bulk Cu metal [34] [29]. Early findings in these studies suggested that Bi was evenly distributed on any given GB with multiple points of investigation on any particular boundary yielding similar amounts of Bi. Bi was also measured on opposing sides of the same fracture surface where Bi concentrations were generally found to correspond with one another [34]. Using a combination of argon ion bombardment to remove surface materials, AES was performed at a range of depths from the Cu fracture surface and Bi was found to exist mostly within the first 10 Å of the surface. However, Auger electron peaks measured between different grains fractured on the same sample showed a large variability in the calculated amount of Bi on the surface. Figure 10 shows three micrographs obtained from a specimen after AES was performed on the fractured surface of the Cu. The top micrograph gives a low magnification view of the fractured polycrystalline Bi doped Cu specimen post in-situ fracture where multiple Cu grains can be seen on the fracture
surface. The middle micrograph displays a pocked surface with a low concentration of Bi displaying what appears to be a fracture surface more indicative of ductile fracture. The final micrograph at the bottom of Figure 10 shows a fracture surface with a relatively high amount of Bi and presenting with a sharp intergranular fracture indicative of the embrittling effect of Bi in Cu. The work of Wolski et al. also showed a dependence on time and temperature of Cu-Bi doping and the formation of intergranular Bi films of multiple nanometers in thickness confirmed via AES [53].

The results from these early AES studies proved to be repeatable but not above reproach due to the experimental limitations of AES. In particular AES of fractured surfaces needs to be analyzed vary carefully. Due to the nature of AES, the crystallographic orientation of the surface being investigated may lead to significant (10%) differences in the generated Auger electron signals due to the electron channeling effects that may be considerably different between any two grains. These large effects add a high degree of uncertainty, not only between measurements comparing Bi concentrations of two grain on the surface of a single fractured specimen, but also when comparing the concentrations of Bi between two complementary surfaces of an intergranular fracture. Here, crystallographic changes and take-off angle changes between the surfaces analyzed make it wholly unclear if the assumption that each side of a fractured surface contains an equal amount of Bi. Additionally, AES fails to provide a direct way of observing Bi atoms as they sit on the GB. Even if the assumption is made that the Bi atoms do not move locally when fracture occurs, the spatial resolution of AES is too poor to observe the Bi atomic
structure at the boundary; at best it gives a quantitative measure (albeit with a high
degree of uncertainty) of the amount of Bi at Cu GBs. From this calculated amount of
Bi an assumption of the Bi structure at the grain boundary is made to aid in
visualization of possible atomic arrangements at the GB. Bi is typically thought to
form a number of monolayers at the GB determined by assuming a Bi layer at the
interface will contain a density of 9.78 g cm$^{-3}$. Figure 11 shows a histogram of the
number of Bi monolayers determined to exist on fractured boundary surfaces in a
polycrystalline Bi embrittled Cu AES sample. Here it can be seen that even when there
is no Bi monolayer determined to exist on the fracture surface, the material still
behaved in a brittle manner. This brittle behavior is known to have existed for this
specimen as it is mentioned in Powell’s work that GBs which fracture in a ductile
manner are incapable of being analyzed via AES as there is too great an amount of
surface deformation to yield any meaningful results from the analysis [29]. This lack
of a detectable monolayer on a seemingly embrittled Cu GB means that the sensitivity
of AES is not sufficient to detect extremely small amounts of Bi on Cu GB surfaces.
As evidenced by the brittle fracture of the Cu GB and non-detection of Bi by AES, a
more robust analytical technique is needed if GBs with small amounts of Bi are to be
studied.
Figure 9 - The three steps of the Auger electron formation process [54].
Figure 10 - Micrographs of 3 fracture surfaces analyzed by AES with the top micrograph showing a general view of the fractured specimen, the middle micrograph showing an area found to have a low concentration of Bi, and the bottom micrograph showing a fractured surface found to have a high Bi concentration [34].
Figure 11 - A histogram of the number of Bi monolayers determined to exist on the fracture surface of a Bi doped Cu polycrystalline specimen analyzed with AES, 700°C corresponds to the heat treatment applied to the specimen during its fabrication [29].
2.5.2 X-ray energy dispersive spectrometry

X-ray energy dispersive spectrometry (XEDS) is a materials characterization technique that uses the characteristic X-rays emitted from atoms to identify the chemical species and thus, the composition of a specimen [55]. This X-ray emission process is stimulated by the high energy electron beam in an electron microscope. The principles of this technique arose from electron probe microanalyzers (EPMA) and were later converted to an analysis technique possible in TEM / STEM systems thereby increasing the lateral resolution at a sacrifice of detection efficiency due to the reduction in the analysis volume. XEDS produces an X-ray signal in a similar fashion to the Auger electron signal produced by AES. Whereas in AES an ionized atom uses a two electron relaxation process to return to the ground state resulting in the release of a characteristic Auger electron, XEDS measures the resultant characteristic photons that are released from a single electron relaxation process to return the atom to the ground state [55]. By use of a solid-state detector an energy dispersive spectrum of characteristic X-rays can be recorded and analyzed using the energy peaks themselves for finger-print identification or the areas under these energy peaks for quantification [56].

As mentioned previously XEDS evolved from EPMA in a search for greater lateral resolution of analysis areas. Due to a use of bulk specimens in EPMA, quantification procedures to determine the exact compositional information is complicated by the effects of the atomic number (Z), the absorption of X-rays in the...
bulk sample (A), and the fluorescence of X-rays in the bulk sample (F) [55]. These hindrances impeding quantification using bulk specimens were first predicted by Castaing, contributing to the K sensitivity term in Equation 10 where \( C_i \) and \( C_{(i)} \) refer to the composition of the unknown specimen and a standard specimen, respectively, and \( I_i \) and \( I_{(i)} \) refer to the collected X-ray intensities from the unknown specimen and a standard specimen, respectively [57], [55].

\[
\frac{C_i}{C_{(i)}} = [K] \frac{I_i}{I_{(i)}},
\]

Equation 10

The relation expressed in Equation 10 allows the ability to calculate the composition of samples using EPMA but is limited by the ZAF corrections needed due to the entire incident electron beam being absorbed by the specimen in a relatively large interaction volume. The effects of A and F can be greatly reduced or completely ignored if a thin specimen is used—in which not all of the electrons are completely absorbed by the specimen—or even if the specimen is sufficiently thin to only allow single scattering events for individual incident electrons. The use of these thin specimens lead to the Cliff-Lorimer ratio technique for standard-less analytical electron microscopy (AEM) XEDS quantification [55], [58]. The poor vacuum and low brightness of early AEMs made quantification using standards during each acquisition impractical (as is necessary in EPMA) due to the need to turn off the electron gun and change standards multiple times only to have contamination build up.
and different conditions inside the AEM from standard to specimen making
meaningful comparisons difficult [55]. The Cliff-Lorimer ratio technique assumes the
“thin-foil criterion”, i.e. there is no effect of A and F and the incident electron does not
lose the energy during interaction with the specimen, so the K sensitivity ratio
between the composition and peak intensities of Equation 10 is only effected by Z.
This allows the composition of a binary system to be determined directly from the
ratio of the peak intensities of two elements in an XEDS spectrum using Equation 11
and Equation 12 forming a new sensitivity factor, the $k_{AB}$ factor.

\[ C_A + C_B = 100\% \],

*Equation 11*

\[ \frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B} \],

*Equation 12*

Here, a binary system is considered where the weight % of each element, $C_A$
and $C_B$, constitute the 100% of the specimen, and $I_A$ and $I_B$ are the elemental peak
intensities above background for elements A and B [55]. For many years the Cliff-
Lorimer ratio method has been the primary means of accomplishing quantitative
XEDS in an AEM. In order to obtain an acceptable degree of error in measuring the
$k_{AB}$ factor many spectra need to be taken, and many specimens need to be used
especially for complex multi-component systems. This time-consuming process has
led to a practicality limit for the Cliff-Lorimer ratio method as, for many AEM

operators, it is much easier and faster to calculate $k_{AB}$ factors than to accurately measure them. Though $k_{AB}$ factors may be calculated, this can lead to errors in excess of ±15%, diminishing the accuracy possible in modern AEMs even with the technological advancements modern AEMs have made over the years [59]. Another limiting factor of the Cliff-Lorimer ratio method is the assumption of total absence of fluorescence or absorption of X-rays during acquisition, i.e. the thin-film approximation. To overcome this obstacle a complicated correction factor may be incorporated into the Cliff-Lorimer ratio making the X-ray generation, and therefore collection, dependent on the mass thickness ($\rho t$) of the individual analysis point on the specimen. Independent determination of $\rho t$ is often very complicated or very inaccurate, adding another practicality barrier to the Cliff-Lorimer ratio method if X-ray absorption cannot be ignored.

To overcome these limitations of the Cliff-Lorimer ratio method and to take advantage of modern instrumentation that accompany some AEM (e.g. faraday-cup holders, ultra-high vacuum columns, and high-brightness and high-stability electron sources), the zeta ($\zeta$) factor method was developed by Watanabe and Horita [60]. The description of the $\zeta$ factor that will follow is based on the work of Watanabe and Williams using modifications made to the “original” $\zeta$ factor, and which formed the “new” $\zeta$ factor which will henceforth be referred to as the $\zeta$ factor [61]. Beginning with the thin-film approximation used in the Cliff-Lorimer ratio method, the measured characteristic X-ray intensity of an elemental component of a system is proportional to the $\rho t$ of the specimen, i.e. a thinner specimen yields fewer X-rays and a thicker
specimen yields more X-rays incident on an XEDS defector for a given experimental set up. This relationship between characteristic X-ray intensity and $\rho t$ for a given element A may be expressed as shown in Equation 13.

$$\rho t = \zeta_A \frac{I_A}{C_A D_e}$$

*Equation 13*

Where $\zeta_A$ is the $\zeta$ factor for elemental component A, $I_A$ is the characteristic X-ray intensity above background for component A, $C_A$ is the weight % of element A in the specimen, and $D_e$ is the total electron dose during acquisition defined in Equation 14.

$$D_e = N_e I_p \tau$$

*Equation 14*

Where $N_e$ is the number of electrons per unit charge, $I_p$ is the probe current, and $\tau$ is the total acquisition time. These two equations show that the $\zeta$ factor for a particular element is independent of composition, beam current, acquisition time, mass, and thickness, i.e. specific experimental conditions. By using a theoretical expression for the intensity of a characteristic X-ray as presented by Armigliato in Equation 15, the theoretical expression for a $\zeta_A$ can be developed [62] [61].

$$I_A = N_V \frac{Q_A \omega_A a_A}{M_A} C_A \rho t D_e \left( \frac{\Omega}{4\pi} \right) \varepsilon_A$$
Where $I_A$ is the characteristic X-ray intensity of element A above background, $N_V$ is Avogadro’s number, $Q_A$ is the ionization cross-section of element A, $\omega_A$ is the fluorescence yield of element A, $a_A$ is the relative transition probability of the characteristic X-ray peak of element A, $M_A$ is the atomic weight of element A, $\Omega$ is the X-ray detector collection angle in steradians, and $\varepsilon_A$ is the X-ray detector efficiency for collection of X-rays at the energy level of the characteristic X-ray of element A that is used. This equation can simply be understood as showing the likelihood, from a given number of atoms interacting with a given number of electrons, that a particular type of characteristic X-ray will be generated and then detected by an X-ray detector. Equation 14 can be combined with Equation 15 to form a theoretical expression for a $\zeta_A$ as shown in Equation 16.

$$\zeta_A = \frac{M_A}{N_V Q_A \omega_A a_A [\Omega/(4\pi)] \varepsilon_A}$$

Equation 16 represents the $\zeta$ factor equation assuming the thin-film approximation is accurate. This equation shows that the $\zeta$ factor is dependent only on the experimental conditions of accelerating voltage and the choice of the characteristic X-ray energy peak. This independence from experimental conditions means that the $\zeta$ factor can be applied to a wide variety of experiments needing only a well-characterized detector and a Faraday cup to measure the electron probe current. If one
assumes a binary system is being analyzed, much in the same way as the development of the original Cliff-Lorimer ratio method, and Equation 11 is still valid, then relationships between \( C_A \), \( C_B \), and \( \rho t \) can be developed as seen in Equation 17 [61].

\[
\rho t = \frac{\zeta_A I_A + \zeta_B I_B}{D_e},
C_A = \frac{\zeta_A I_A}{\zeta_A I_A + \zeta_B I_B},
C_B = \frac{\zeta_B I_B}{\zeta_A I_A + \zeta_B I_B}
\]

*Equation 17*

Where \( \zeta_B \) and \( I_B \) are the \( \zeta \) factor for specimen component B and the characteristic X-ray intensity above background for component B, respectively. Equation 17 allows simultaneous determination of \( \rho t \), \( C_A \), and \( C_B \) based only on the \( \zeta \) which is only sensitive to accelerating voltage and X-ray energy [61]. Equation 17 can be rearranged into a format very similar to Equation 12, as seen in Equation 18.

\[
\frac{C_A}{C_B} = \frac{\zeta_A I_A}{\zeta_B I_B}
\]

*Equation 18*

Here the advantage of the \( \zeta \) factor over the Cliff-Lorimer ratio method becomes very obvious, as the \( \zeta \) factor method does not rely on a parameter relating two X-rays from different elements but rather on two parameters unique to the X-rays of each element. Though Cliff-Lorimer \( k \) factors are not needed for independent
determination of ζ factors, if one ζ factor and the Cliff-Lorimer $k_{AB}$ ratio is known for a given binary system, the second ζ factor may be determined using Equation 19, a combination of Equation 12 and Equation 18.

$$\zeta_A = \zeta_B k_{AB}$$

Equation 19

The quantification method using the ζ factor is straightforward and easily adapted to use with X-ray absorption correction. In order to adapt the ζ factor method for use with absorption correction, it is necessary to develop an equation predicting the amount of X-ray absorption for a particular X-ray line and detector configuration. Equation 20 shows the absorption correction equation in relation to specimen thickness and detector position.

$$A_A = \frac{(\mu/\rho)^A_{sp} \rho t \csc \alpha}{1 - \exp[-(\mu/\rho)^A_{sp} \rho t \csc \alpha]}$$

Equation 20

Here, $(\mu/\rho)^A_{sp}$ is the mass absorption coefficient for the characteristic X-ray line and $\alpha$ is the X-ray detector take-off angle. This absorption correction term may then be added to Equation 17 to create the absorption-corrected ζ factor equations seen in Equation 21.
\[ \rho t = \frac{\zeta_A I_A A_A + \zeta_B I_B A_B}{D_e}, \quad C_A = \frac{\zeta_A I_A A_A}{\zeta_A I_A A_A + \zeta_B I_B A_B}, \]

\[ C_B = \frac{\zeta_B I_B}{\zeta_A I_A A_A + \zeta_B I_B A_B} \]

*Equation 21*

Due to the dependence on mass thickness of all the terms as a result of the absorption correction, the system of equations presented in Equation 21 cannot be solved analytically and must be determined using an iterative approach. However, this series will converge to a solution in a relatively small number of iterations (10-15) with reasonable accuracy (0.001 wt% composition and < 0.01 nm thickness differences) [61]. A flow chart showing the quantification procedure using the \( \zeta \) factor method is shown in Figure 12; here it is assumed that the \( \zeta \) factors for the system under investigation have previously been determined, then the quantification procedure is strictly dependent on the acquisition parameters chosen and the accuracy of the X-ray peak intensity determination (i.e. signal to noise ratio of the peaks concerned). The ability to directly determine \( \rho t \) allows the use of the \( \zeta \) factor method in combination with experimental techniques focused on GB plane segregation to determine GB plane segregation behavior more accurately than most other approaches [58], [63]. The GB coverage of a solute element A can be determined using Equation 22.
\[
\Gamma_{A}^{ex} + \Gamma_{A}^{bk} = N_{B} \frac{C_{A} M_{B} V}{C_{B} M_{A} A}
\]

*Equation 22*

Where \( \Gamma_{A}^{ex} \) and \( \Gamma_{A}^{bk} \) are the number of solute A atoms per unit area on the GB and in the bulk, respectively, \( N_{B} \) is the number of B atoms per unit volume in the bulk material, \( M_{B} \) is the atomic mass of element B, \( V \) is the interaction volume of the electron probe, and \( A \) is the GB area inside the interaction volume. The \( V \) and \( A \) terms in Equation 22 require precise knowledge of the thickness of the specimen, and can be defined assuming that Gaussian beam broadening occurs within the specimen in the following equation [64]:

\[
\frac{V}{A} = \frac{\pi q}{32} \frac{8\sigma^{2}t + \beta t^{4}}{\int_{0}^{t}(\sigma^{2} + \beta z^{2}/2)^{1/2} dz}
\]

\[
\sigma = \frac{d_{TM}}{4.29}, \quad \beta = 500 \left(\frac{4Z}{E_{0}}\right)^{2} \left(\frac{\rho}{M}\right).
\]

*Equation 23*

Where \( q = 4.29 \) for a spatial resolution containing 90% of the incident electron beam intensity, \( \sigma \) and \( \beta \) are terms associated with incident beam size and beam broadening, respectively, \( t \) is specimen thickness, \( z \) is a particular depth through the specimen, \( d_{TM} \) is the diameter of the incident electron beam at full width tenth
maximum beam intensity, $\bar{Z}$ is the average atomic number of the specimen, $E_0$ is the accelerating voltage, and $\bar{M}$ is the average atomic weight of the specimen. The integration in Equation 23 cannot be solved analytically and must be solved using a numerical integration technique. Despite this drawback, this technique is slightly more accurate than others which use an estimation of beam broadening or a truncated cone approximation to determine the interaction volume and the boundary plane area inside that volume [64].

The ability to analyze GBs through the use of XEDS to detect the amount of Bi present has allowed access to GB unavailable to AES studies. This is due to the fact that non-brittle boundaries cannot be studied in AES and, therefore, it is not possible to obtain an accurate measure of the anisotropy of Bi on Cu GBs with AES by itself. Keast et al. reported the finding of low Bi segregation on non-special low energy GBs meaning that misorientation alone cannot be responsible for determining Bi segregation and the embrittlement that it may cause [48]. Figure 13 shows a histogram comparing the results of a XEDS study to those of an AES study. It can be seen in this figure that the two methods of study yield very different results, as the AES study skews the results so that a disproportional number of boundaries appear to have 1-1.5 monolayers of Bi present when in fact this artifact is due to the AES technique being wholly incapable of measuring ductile boundaries, i.e. boundaries displaying small levels of Bi segregation.
XEDS studies using tilt boundaries, such as the work of Alber et al., have been able to show Bi segregation dependence on GB plane inclination as seen in Figure 4 where the as\(\Sigma 51\) GB facets displayed Bi segregation of 1.7 Bi atoms per nm\(^2\) and no Bi segregation was measured on the s\(\Sigma 51\) GB facets [21]. Figure 14 shows the results of a study conducted by Keast and Williams demonstrating the high localization of Bi to the Cu GB via a quantitative XEDS map. Associated data extracted from the map allow profiles to be generated in order to observe the change in Bi concentration as a function of distance from the GB as well as obtain the absolute boundary coverage of Bi on any given boundary [65].

The ability of the AEM to obtain high magnification images and extract quantifiable spectra from such small locations has allowed comparison between GB areas separated by mere nanometers. Sigle et al. used XEDS in an AEM to compare GB facets in \(\Sigma 19a\) Bi-doped Cu GBs to compare both bulk concentration and annealing temperature with these factors influence GB segregation and faceting [66]. The results of this investigation are summarized in Table 3; it was found that increasing the annealing temperature and Bi bulk concentration led to an increase in faceting and general segregation level. It is interesting to note that the segregation levels between a GB facet and a non-facet along the same GB were significantly different with more Bi being present on the GB facet. Figure 15 shows a bright-filed STEM image displaying one such GB investigated by Sigle et al. where the GB facets can clearly be seen along the GB.
Table 3 – Results of segregation XEDS measurements for a Σ19a Cu GB doped with Bi [66].

<table>
<thead>
<tr>
<th>Annealing temperature (ºC)</th>
<th>Bi bulk concentration (at. ppm)</th>
<th>Segregation level, non-faceted regions (ML (atoms nm(^{-2})))</th>
<th>Segregation level, facets (atoms nm(^{-2}))</th>
<th>Amount of faceting (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>14</td>
<td>0.6 ± 0.2 (4.2 ± 1.5)</td>
<td>–</td>
<td>0</td>
</tr>
<tr>
<td>700</td>
<td>24</td>
<td>0.64 ± 0.1 (4.5 ± 0.7)</td>
<td>16.8 ± 4</td>
<td>7</td>
</tr>
<tr>
<td>800</td>
<td>25</td>
<td>1.2 ± 0.2 (8.4 ± 1.8)</td>
<td>12.5 ± 5</td>
<td>38</td>
</tr>
<tr>
<td>800</td>
<td>64</td>
<td>–</td>
<td>21 ± 4</td>
<td>100</td>
</tr>
</tbody>
</table>
Quantification procedure in $\zeta$-factor method

Measured X-ray intensities: $I_A, I_B, \ldots, I_j, \ldots, I_N$
Acquisition parameters: $D_o = N_o I_o \tau$

Calculate initial mass thickness and compositions:
$$\rho t = \frac{N}{j} \frac{\zeta_i}{D_e} I_i, \quad C_A = \frac{\zeta_A I_A}{\sum_j \zeta_j I_j}, \quad \ldots, \quad C_N = \frac{\zeta_N I_N}{\sum_j \zeta_j I_j}$$

Calculate corrections terms:
$$A_j = \frac{(\mu/\rho)^{sp}_j \rho t \cosec \alpha}{1 - \exp[-(\mu/\rho)^{sp}_j \rho t \cosec \alpha]}$$

Calculate mass thickness and compositions:
$$\rho t = \frac{N}{j} \frac{\zeta_i}{D_e} A_j, \quad C_A = \frac{\zeta_A I_A A_A}{\sum_j \zeta_j I_j A_j}, \quad \ldots, \quad C_N = \frac{\zeta_N I_N A_N}{\sum_j \zeta_j I_j A_j}$$

Check convergence

Yes

Final mass thickness and compositions: $\rho t, C_j$

No

Figure 12 - A flow chart of the quantification procedure for the $\zeta$-factor method including X-ray absorption correction [61].
Figure 13 – Histogram comparing the proportion of GBs displaying different boundary coverage, as measure in monolayers of Bi, for AES and XEDS studies of the Cu-Bi system.
Figure 14 – Quantitative XEDS Bi map of a Bi doped Cu GB (left) and a Bi segregation profile extracted from the XEDS map along a line crossing the GB at a right angle with analysis points taken 1.3 nm apart (right)
Figure 15 – Bright-field STEM micrograph showing $\Sigma 19_a$ Cu GB doped with Bi (25 at ppm) and annealed at 800 °C with arrows pointing to the intersection between two GB facet types [66].
2.5.3 Electron energy loss spectrometry

Electron energy loss spectroscopy (EELS) is a TEM/STEM spectroscopic technique where electrons with a narrow and well defined kinetic energy are passed through a material specimen having the kinetic energies measured again after the electrons are emitted from the exit surface via a post column electron detector. If electrons have undergone inelastic scattering as they passed through the specimen, the amount of energy lost by the scattering process can be measured and used for a number of various analyses such as: quantitative elemental analysis, specimen thickness, bonding and band-structure effects, short-range ordering in the specimen, and plasmonic effects [67] [68].

EELS is often presented as a complementary technique to XEDS. Where XEDS uses the X-rays emitted from atoms relaxing after inner-shell ionization has occurred due to inelastic scattering from incident electrons, EELS measures the energies of these same electrons after an inelastic scattering event has occurred by collecting them after the specimen in a post-column energy filter. If it can be assumed that only one or very few scattering events have occurred through the thickness of the specimen, then the energy lost due to an individual event can be measured. The form of specific energy loss signals in an EELS spectrum can be used to identify changes in the interatomic bonding relationships between atoms allowing information not only on the physical location of segregant elements to be determined but also provide insight
into the mechanisms by which the segregant atoms impact the material properties in their environment.

EELS spectra of the 3d transition metals is typically dominated by the presence of white lines at the L_{23} energy edge. These white lines are a result of the unoccupied 3d electron states present in the material, the white lines being indicative of transitions from the 2p electron states to the 3d electron states [69]. In the case of Cu there exist no white lines at the L_{23} edges as the 3d electron band in Cu is completely filled. Changes observed in the near edge structure of the Cu L_{23} edge indicate changes in the 3d orbitals, such as 3d-4s hybridization as suggested by Duscher et al. or partial removal of electrons from the Cu 3d orbitals as suggested by Keast et al. [46], [70].

Figure 16 shows an experimental EELS spectra obtained by Keast et al. where the spectra from the GB region can clearly be seen to have enhanced electron energy-loss counts at the L_{3} edge onset indicating a lower density of occupied 3d electron states for Cu atoms at the GB [70]. Keast et al. concluded that the change in the L_{23} edge feature corresponded to the hybridization of the Cu 3d orbital with the Bi 6p orbital and also caused a decrease in the occupied d density of states resulting in a change in the Cu elastic constant and subsequent weakening of the GB. The presence of a white line at the L_{23} edge can also be explained by oxide formation on the GB.

Conversely, Duscher et al. presented experimental EELS data showing a change not in the L_{23} onset edge, but rather in the fine structure corresponding to Cu 3d-4s hybridization changes which are located between L3 and L2 edges [46]. For the
Cu L₃ edge; these transitions are due to mixing of the 3d and 4s orbitals present in the atom. All EELS spectra shown in Figure 16 through Figure 18 clearly exhibit two extra small “bumps” in the energy-loss spectra between the L₃ and L₂ energy loss edge onsets. The work presented by Duscher et al. take alleged differences in these two bumps between spectra taken on and off the boundary as evidence of a decrease in the mixing of the 3d and 4s states [46]. The mechanism causing the reduction in hybridization in the presence of Bi is the metallic bonding of Bi to Cu at the GB. Metallic bonding involves the delocalization of Bi electrons, allowing the Bi electron cloud to encompass multiple Cu atoms. This delocalization of electrons leads to an increase in the occupancy of the Cu 4s orbital, which is normally only half full in bulk Cu. The result of this increase in 4s occupancy of the Cu atoms near Bi atoms on the boundary is a decrease in the ability of these Cu atoms to hybridize, and thus a decrease in the directionality of the Cu bonding. Reducing the directionality of bonding in noble metals like Cu leads to a weakening of the Cu-Cu bond, causing embrittlement through a decrease in the stacking fault energy [71]. This effect may also be thought of simply as adding electrons to an orbital that is less than half full leads to an increase in bond strength while adding electrons to an orbital that is more than half full leads to a decrease in bond strength [72]. Due to the structural independence of this effect, Duscher et al. argue that this mechanism of embrittlement is independent of atomic arrangement at the GB, although they concede that this embrittlement mechanism may not be the only embrittlement mechanism that may affect the mechanical behavior of Cu GBs that have been exposed to Bi.
Figure 16 – Cu L$_{23}$ edge showing the difference in EELS spectra between a boundary and a bulk region in Bi doped Cu [70].
Figure 17 – EELS Cu $L_3$ energy edge showing the difference between the GB and bulk spectra for a clean Cu 36.8 tilt about a [001] axis° symmetrical bicrystal boundary [46].
Figure 18 - EELS Cu L₃ energy edge showing the difference between the GB and bulk spectra for a Bi doped Cu 36.8 tilt about a [001] axis° symmetrical bicrystal boundary [46].
2.5.4 Mechanical testing of Bi doped Cu grain boundaries

Multiple studies have been performed on the mechanical properties of the Cu-Bi system. This section will focus on the results of 3 studies probing the mechanism behind the embrittlement effect of Bi on Cu GBs and the relation of this mechanism to the macro scale degrees of freedom used to describe such boundaries as noted in Section 2.1. A 4th study intimately related to the work presented in this dissertation will also be addressed as the purpose of this study was to accurately define the mechanical behavior of the GBs under investigation in this electron microscopy study of the Cu-Bi system.

The first study to be discussed is that of Wang and Anderson, as mentioned previously in section 2.4. In this study Cu-0.02 wt% Bi bicrystal GBs were used with orientations of 129.5°[110],(1\overline{1}3)/(1\overline{1}3) a symmetrical Σ5 GB, 38.9°[110],(\overline{2}2\overline{1})/2\overline{2}1) a symmetrical Σ9 GB, 37°[100],(031)/(031) a symmetrical Σ11 GB, and an asymmetrical random GB. Notched samples of these GBs were deformed and/or fractured by tension, bending, or ramp loading fatigue [49]. The Rice-Thomson model was used to explain the energetics of the formation of fracture by cleavage or deformation by dislocation emission by comparing $G_{\text{disl}}$ to $G_{\text{cleav}}$. The Σ11 GB showed no capacity to become embrittled, while the Σ5 GB showed high susceptibility to Bi induced embrittlement. The Σ9 GB varying susceptibility depended on the crack growth direction. This strong dependence of crack growth direction means that a
misorientation argument alone cannot fully describe the fracture behavior of Cu GBs in the presence of Bi [49]. It is important to note in this study that it was assumed that the Bi segregants on the GB did not interact with dislocations at the GB, and the only role of the Bi on the boundary was to lower the interfacial energy. This change in the interfacial energy is seen in Figure 19 where the only difference between the Bi doped and pure Cu GBs is a horizontal shift along the $G_{\text{cleav}}$ axis.

Shortly after Wang and Anderson had published their study, Li and Zhang published the results of a more comprehensive look at the effect of misorientation on the fracture toughness of a wide range of Cu bicrystal GBs that had been doped with Bi [73]. In this study, various CSL symmetrical [001] tilt GBs were broken in tension to determine the fracture toughness at multiple Bi doping levels. Figure 20 shows a graph of the change in fracture toughness as the misorientation angle of [001] tilt Cu bicrystal boundaries are increased from 0° to 90° for the pure Cu condition, and two Bi doped conditions. From this figure it can clearly be seen that increasing misorientation up to 45° continuously leads to a decrease in fracture toughness, showing a very strong dependence of the fracture behavior of the boundary to the misorientation of the two crystals composing the bicrystal. There also seems to be a limit around 15° of misorientation for the doped cases where fracture toughness drastically falls to near maximum values.

Li and Zhang were also able to conclude that there is no relationship between GB embrittlement and CSL density. Their work also suggested that the undoped GB
energy present in a boundary was indicative of the amount of mechanical embrittlement observed in the doped GBs of the same misorientation. Unfortunately, no AES spectroscopy was performed on the GBs to have any sense of the amount of segregation to each GB, as it may well be the case that the observed embrittlement present in this study is proportional (or not) to the amount of Bi atoms actually present on the boundary, but without any experimental verification of Bi on the boundary the actual link between the Bi and the Cu boundary segregation and embrittlement is purely speculative.

Armstrong et al. used micro-mechanical cantilever bending specimens on a wide variety of random GBs in an attempt to correlate GB plane, misorientation, and fracture toughness [74]. This method allowed the testing of a wide variety of very different GBs in a doped polycrystalline sample. The results showed nearly no correlation with any of the macroscopic parameters that were defined for the GBs, and it may be that the GBs studied were far too random in nature for a well-controlled study that would highlight specific GB behavior. The one conclusion that Armstrong et al. did reach was that, of the GBs that were studied, some either failed in a brittle manner or showed nearly no effects of embrittlement. Likewise, corresponding XEDS showed Bi present on the GBs that had failed in a brittle manner, and no Bi present on the GBs that had failed in a ductile manner. This result is similar in nature to the results based on AES studies and AEM studies such as those by Keast et al [29], [34], [48]. Most of the mechanical testing work that has been done on the Cu-Bi system has lacked the analytical work pinpointing the location and structure of Bi on the GB. This
lack of analytical work limits the veracity of conclusions that can be drawn and how well Bi can be tied to the observed mechanical embrittlement phenomena.
Figure 19 – Graph of the predicted cleavage response vs. dislocation emission response for Cu bicrystals according to the Rice-Thomson model. Open circles correspond to pure Cu GBs while triangles correspond to Bi doped GBs, (+) and (-) correspond to different crack growth directions compared to the crystallographic directions in the material [49].
Figure 20 – The dependence on fracture toughness ($\sigma_f$) of various symmetric [001] tilt bicrystals at multiple Bi doping levels for Cu bicrystals fractured in tension [73].
3. Statement of problems and objectives:

The Cu-Bi system is currently understood to exemplify both GB segregation and GB embrittlement. Though the effect of Bi on Cu GBs is easily demonstrated and has been well known for over a century, the underlying cause of this phenomenon is still poorly understood. The main purpose of this study is to address the questions of why and how this embrittlement occurs. To do this, this study will employ both mechanical testing and quantitative analysis of Bi embrittled Cu bicrystals. Of major concern in the quantitative analysis of the GB are the chemical composition, the atomic structure, and any possible electronic structure discrepancies from the undoped GB condition. Unlike previous studies the crystals being mechanically tested will be the same as the crystals being quantitatively observed. This comparison of mechanical testing specimens directly to microscopic characterization specimens is possible by new advances in micro-mechanical testing and electron microscopy so that mechanical properties and microstructural information of specimens may be collected in close proximity to one another ensuring identical physical and chemical makeup. This approach will allow simultaneous measurement of the degree of embrittlement and the micro-characteristics of the boundary, which will provide a basic understanding of this phenomenon which can then be applied to the case of bulk polycrystalline materials.

In this study, it is proposed that the mechanical embrittling of Cu bicrystals is primarily a function of boundary misorientation and subsequent relaxation, with the addition of Bi allowing faceting along the boundary by promoting rearrangement of
the boundary into geometries that both accommodate the size of Bi and degrade the mechanical properties of the Cu through the presence of specific pinned dislocations at relaxed GBs, moderate plastic behavior present in certain Bi doped boundaries being the result of the presence of dislocations unable to accommodate Bi atoms in large number.

4. Experimental Procedures:

4.1 Bi doping of Cu polycrystalline bulk specimens:

Initial attempts were made in this study to investigate the segregation behavior and mechanical properties of general or random polycrystalline GBs in Cu that had been doped with Bi. An outline of the successful doping procedure of these rods and a brief description of why this approach was abandoned follows.

¼-inch diameter 99.99% pure oxygen free Cu rod containing random GBs were selected for this study. Bi doping of these rods was performed by submerging the Cu rods in molten Bi at a temperature just above the Bi melting point of 271 °C for several hours, allowing the Bi to coat the entire surface of the Cu rod. After this was completed the Bi coated Cu rods were removed and placed inside quartz tubes which were then evacuated of air, backfilled with argon, and sealed to prevent oxidization of the Cu during the subsequent Bi diffusion portion of the heat treatment. To allow the Bi to diffuse into the Cu rod along the GBs a higher temperature heat treatment step was needed to increase the rate of Bi diffusion along the Cu GBs. This was performed
by heating the encapsulated Bi-coated Cu specimens at a temperature of 900 °C for 24 hours in a solutionizing step as the solid solubility of Bi in Cu was increased at this elevated temperature allowing a greater amount of Bi to be incorporated into the Cu rod than possible at lower temperatures. After this solutionizing step, the rods were cooled to and held at 500 °C, and finally held at temperature to allow migration of the Bi from the bulk to the GB as the solid solubility of Bi in Cu decreased in tandem with the temperature. The rods were then water-quenched to prevent any migration of Bi out of the Cu GBs and the formation of second phase particles that may occur using slower cooling rates.

The result of this doping method was brittle Cu rods successfully doped with Bi. The success of the doping process was confirmed by the fact that these once tough Cu rods, incapable of being deformed by hand, could be broken with a moderate application of force using nothing more than one’s own gloved hands. To characterize the grain size of these Cu rod specimens, the electron backscatter diffraction (EBSD) method was performed in a Hitachi 4300 S/N scanning electron microscope (SEM). The results showed grain size on the order of 100 µm, ideal for producing TEM and micro-mechanical test specimens with a very flat and straight GB plane. Further investigation of the GBs present in these rod specimens via ion beam imaging using a FEI DualBeam-235 focused ion beam (FIB) instrument showed that many of the grains did not have GB planes running perpendicular to the sample surface. This seemingly random orientation of the GB planes with respect to the specimen surface made reliable fabrication of both TEM and micro-mechanical test specimens from the
same GBs almost impossible. Figure 21 shows a micrograph of a GB from a Cu rod sample obtained from the secondary electron signal generated by a 30 kV gallium (Ga) ion beam. The contrast across the boundary is due to the channeling difference of the Ga ions in each grain caused by the change in crystallographic orientation across the GB. Prior to ion milling to observe the GB into the depth of the bulk sample, it is not possible to ascertain the orientation of the GB plane. Due to the time intensive nature of the ion milling technique, it was deemed infeasible to fabricate the number of specimens needed using the random GBs found in the Cu rod; therefore another means to create Bi doped boundaries for investigation was needed.
Figure 21 – Ion channeling contrast of a GB from a Bi doped Cu rod showing the GB plane of the boundary inclined with respect to the specimen surface.
4.2 Bi doping of Cu bicrystal bulk specimens:

Due to the random orientation of GB planes with respect to the specimen surface of Cu polycrystalline rod samples, an alternative method of producing single GB micro-tensile mechanical testing and TEM specimens was needed. Like many previous studies of GB features and mechanical properties, the decision to use specially prepared bulk bicrystals was made. These bicrystals allow a degree of control over some of the geometric DOF that define a GB—in particular the axis of rotation is often controlled during the bicrystal fabrication process to yield specimens of either pure tilt or pure twist character. For this study, bicrystal specimens of pure twist character were used. Unfortunately, the exact fabrication method of these particular bicrystals and their thermal history after fabrication was completely unknown. The bicrystals used in this study were twist bicrystals with a rotation axis along a \(<100>\) direction meaning that the GB plane normal in both grains is in a symmetric direction. This consideration is important for helping the calculations needed for mechanical testing as a common loading axis in both crystals of the bicrystal micro-mechanical testing specimen ease interpretation of the results.

Having pure a twist bicrystal GB for TEM analysis means that specimens extracted in the traditional FIB-coupon extraction process where the bicrystal GB plane is perpendicular to the specimen surface and that the bicrystal misorientation rotation axis will be perpendicular to the TEM optic axis. The effect of studying specimens with this orientation will be further discussed in later sections; however, multiple TEM specimen fabrication techniques will be addressed in this experimental
section to demonstrate the efforts made to effectively change the specimen orientation for TEM analysis.

For fabrication of the doped bicrystal specimens, premade bicrystal samples were used with nominally marked misorientations of 6, 13, and 33° [100] twist. These bicrystal rods were sectioned on a Buehler Isomet Low Speed Saw using a diamond abrasive blade to create small samples that could be heat treated to allow doping, and prepped for SEM observation. Due to the small size of the bicrystal samples, the Bi doping method applied to the polycrystalline Cu rod would not be practical since submersion of the small bicrystal samples in Bi would result in loss of the sample. To dope these Cu samples with Bi a doping technique was developed that allowed a single side of the bicrystal sample to be coated with Bi. This was performed by placing the Cu sample in physical contact with 99.99% pure Bi shot in a tube furnace. The tube furnace, with a positive pressure of Ar to help prevent oxidation of the samples, was heated to 600°C for 72 hours and then allowed to cool to room temperature. A schematic diagram of the cross-section of the resulting Bi doped Cu bicrystal is shown in Figure 22. The remaining Bi present on the surface of the specimen was removed with 400 grit SiC grinding paper prior to metallographic preparation.
Figure 22 – Schematic diagram of a Cu bicrystal sample cross-section after being doped with Bi. The bicrystal boundary is running vertically through the middle of the sample.
4.3 Metallographic preparation of pure and Bi doped Cu bicrystal specimens:

After heat treatment, the Bi doped Cu bicrystal samples, approximately 5 x 10 x 5 mm\(^3\) in size, were mounted in Bakelite for metallographic preparation using a Struers Pronto Press 20 along with the undoped Cu bicrystal samples that did not undergo heat treatment. These metallographic mounts were ground with silicon carbide abrasive papers of 400, 600, and 1200 grit prior to polishing. Polishing was performed at 6 µm diamond for 2 minutes, 1 µm Al\(_2\)O\(_3\) for 30 seconds, and 0.3 µm Al\(_2\)O\(_3\) for 30 seconds. The final polishing step used 0.05 colloidal silica in a Buehler Vibromet I vibratory polisher for 15 minutes. It was found that times greater than 15 minutes in the vibratory polisher would lead to slight etching of the GB which is less than ideal for mechanical testing specimen fabrication. So while some scratches may have remained at such a short vibratory polishing time, these could be avoided during subsequent specimen fabrication steps while etching of the entire GB could not. After metallographic sample preparation, a 5 nm Ir coating was applied to the surface of the specimens to enhance conductivity and help prevent charging when the samples were viewed in an SEM.
4.4 Observation of Cu bicrystals via scanning electron microscopy:

Following metallographic preparation and Ir coating of the bicrystal samples mounted in Bakelite, they were observed first with a Hitachi 4300 S/N SEM microscope. The primary function of this observation was to collect EBSD patterns and maps to find the nominal macroscopic misorientation of the bicrystal boundary, as well as verifying the regularity of the GB. The samples were also observed in the FEI DB-235 and the FEI Scios through electron and ion beam imaging prior to specimen fabrication. Ion beam imaging allows the ion channeling effect to be used to find and orient the GB in the microscope without the need of diffraction patterns. This method was employed to orient the samples in the FIB instrument for specimen preparation.

4.5 Focused ion beam specimen preparation for TEM and mechanical testing:

Due to the strict dimensional requirements of the micro-mechanical testing specimens and the need for complimentary TEM specimens from adjacent locations along the bicrystal GBs under investigation, specimen preparation was performed using a FIB instrument over other techniques such as electrochemical-polishing. Initial micro-mechanical testing and TEM specimens were prepared with a FEI DB-235 instrument; however, during the course of this investigation, Lehigh University acquired a new FEI Scios instrument; thus specimens made later during this research
were produced on the FEI Scios instrument. The specimen preparation steps for micro-
tensile mechanical specimens will be described first.

To begin specimen preparation, the GB of interest is located using secondary
electrons produced by the ion beam of the FIB. The ion channeling contrast caused by
the crystal structure difference across the GB allows the GB to be oriented at the
proper angle for ion milling. Once the Cu bicrystal GB is aligned to the proper
orientation in the FIB, specimen fabrication can begin. By tilting the sample to an
angle of 52°, the ion beam in the FEI DB-235 and the FEI Scios was made
perpendicular to the specimen surface; this angle was used for the primary milling of
the bicrystal specimens. To prevent damage or over-milling of the specimens, a
platinum (Pt) protective layer of an area size 2 x 25 µm² with a thickness of 2 µm is
deposited over the area of interest using an ion beam current of 300 pA, taking care to
ensure that the GB is in the middle of the Pt protective strip. With the stage
sufficiently stable, rectangular trenches with an area of 30 x 10 µm² and a depth of 10
µm were cut into the specimen with the 30 µm wide side of the trench parallel to the
Pt strip and offset from the strip by ~2 µm. For this rough trenching cut a FEI serial
cross-sectioning scan pattern was used with a current of 7 nA on the FEI DB-235 and
a current of 50 nA on the FEI Scios. The FEI cleaning cross-sectioning pattern was
used at a current of 1 nA to remove the material between the end of the rough trench
and the Pt strip to a depth of 10 µm and to clean the face of the specimen.
Once the specimen thickness measured between 1 and 2 µm, the specimen was extracted by a so-called lift-out method. First the stage was tilted to an angle of 6° and a J-cut was performed with an ion beam current of 500 µm. This J-cut frees the specimen from the substrate everywhere except a small upper corner on the opposite side from where the plucker needle can be attached. The width of the J-cut boxes were kept at ~ 1 µm to ensure milling completely through the thickness of the specimen without any redisposition occurring in the milled area. Following the J-cut, the stage was tilted back to 0° and the plucker needle brought into near contact on the corner of the freed side of the specimen. A Pt tack was used to attach the specimen to the needle using a current of 30 pA. Once physically attached to the plucker needle the specimen was completely detached from the sample by milling the material bridging the specimen – sample gap using an ion beam current of 300 pA. From here the specimen was mounted on a Cu Omniprobe half-grid for final thinning to be performed. Figure 23 shows a bicrystal coupon specimen mounted onto an Omniprobe grid prior to final thinning; the two crystals that comprise the bicrystal can clearly be seen due to ion channeling contrast.

After the specimen was secured to the Cu Omniprobe half-grid via a Pt tack deposited with an ion beam current of 100 pA at a stage tilt of 0°, the plucker needle was freed from the specimen by milling with a 30 pA ion beam current and retracted from the FIB chamber. The stage was then tilted to 52° and thinning of the specimen using the FEI cleaning cross-section patterning tool was used at ion beam currents down to 100 pA to improve the surface quality of the specimen while thinning to the
required thickness of ~1 µm. Following this final thinning the half-grid was rotated so that it was flat on a typical sample stub; this brought the specimen into an orientation such that the specimen surface normal vector parallel with the ion beam direction and the specimen itself was in the proper 3-dimensional orientation as it would be on the micro-mechanical testing device. This orientation allowed the specimen to be shaped to the desired dimensions (15 x 6 µm²) with the ion beam and then attached to the plucker needle and moved on the Hysitron Inc. push-to-pull (PTP) micro-mechanical testing device. The micro-mechanical testing specimen was secured across the testing gap on the PTP device via a platinum tack to both ends, being sure that the boundary running through the specimen was parallel with the testing gap on the device, i.e. the rectangular specimen was mounted so that the edge testing gap in the device met the edge of the specimen at a right angle to prevent any side pulling of the specimen during testing. Edge notches were then milled along the boundary for ~1.5 µm towards the interior of the specimen on each side of the specimen using 10 pA and then a 1 pA ion beam current.

Preparation of TEM specimens was performed using identical milling parameters for the removal from the bulk of the Cu bicrystal as those of the micro-mechanical testing specimens. After removal from the bulk sample, the TEM coupon specimen was tacked onto a molybdenum (Mo) Omniprobe half-grid. Mo was used over a Cu half-grid to enable quantitative X-ray analysis to be performed without interference in the form of X-ray signal from the grid. Final thinning of TEM specimens was achieved by using the FEI cleaning cross-section patterning tool at ion
beam currents from 500 pA to 50 pA at an accelerating voltage of 30 kV. Each milling step consisted of tilting the specimen face ~2° into the ion beam, taking care to mill the protective Pt layer as little as possible. This was then also performed on the other face of the specimen and repeated on each face at lower and lower beam currents. The specimen was judged to be sufficiently thin once secondary electrons could be seen coming through the specimen, effectively making the specimen appear bright in the electron-beam induced secondary electron image. Once the specimen was electron transparent, the sample was tilted into the ion beam ~10° and ion surface polishing was performed at an ion beam current of 16 pA and an accelerating voltage of 5 kV. The use of lower beam currents can remove the damage layer on the surface of the specimen caused by higher beam currents. The final polishing step at a lower accelerating voltage removes ion implanted material from the surface of the specimen while also limiting ion implantation with a less energetic beam. The last specimen preparation step prior to TEM observation was a final milling using a Fischione 1040 NanoMill. Here an accelerating voltage of 900 eV and an argon (Ar) ion beam current of 130 pA was used to remove damage from the specimen cause by the much heavier Ga ions. The specimens were milled at angles of ± 9° for 10 minutes a side, removing approximately 10 nm from each surface.

Three types of specimens were prepared for investigation via TEM in this study. The first two types of specimens share a common orientation of the GB plane with respect to the overall specimen geometry, that is, the GB plane bisects the specimen and is perpendicular to the specimen surface. Figure 24 shows this
orientation in the top schematic where the GB plane is in the middle of the specimen and allows the observation of an edge-on orientation of the GB as it runs through the thickness of the specimen. This orientation was used for micro-tensile mechanical testing specimens as well as TEM specimens. In order to observe the boundary plane itself, a different orientation of the specimen is needed where the boundary plane is parallel to the surface of the TEM specimen. Ideally this would result in a specimen such as the middle diagram in Figure 24, a plane-view specimen. However, this orientation is difficult to produce because of the difference in milling rates between the two grains while the specimen is being fabricated and this milling rate difference can cause bending or the loss of one grain completely before the specimen is sufficiently thin. To mitigate these fabrication difficulties a third orientation was selected, that of a near plane-view specimen as seen in the bottom diagram in Figure 24.

Often the two grains comprising the bicrystal specimen mill at very different rates due to the twist nature of the GB since a different crystallographic direction will be parallel with the ion beam in each grain. This problem is not encountered using tilt bicrystals to such a degree as a pure tilt bicrystal will have identical crystallographic directions parallel with the GB plane. When using bicrystals that have a large degree of twist character, the only symmetrical direction in both crystals is one perpendicular to the GB plane, i.e. the axis of misorientation. It is therefore not possible to fabricate a twist bicrystal TEM specimen using a FIB with identical milling conditions on both sides of the GB. One of the two grains comprising the bicrystal will inevitably mill
faster than the other. Using a GB orientation where the GB plane is parallel to the long axis of the specimen is ideal for creating a plane-view specimen when the milling rates of the crystals on both sides of the GB mill at approximately the same rate when exposed to an ion beam. Figure 25 shows the effect of the grain ion beam milling rate on the final location of the GB in the thin specimens. As seen from this figure, when one grain mills at a higher rate than the other grain it will lose material much faster leading to the complete removal of one grain before the specimen is sufficiently thin.

The near plane-view orientation allows the operator to mostly ignore the different milling rates on each side of the specimen and still be able to produce a specimen containing the GB at a near plane-view orientation. Figure 26 shows the benefits of using a near plane-view specimen when fabricating a coupon TEM specimen of a GB. By placing the protective Pt strip at an angle across the GB it is possible to preserve the GB in some location along the length of the specimen regardless of which grain mills at an increased rate. This method of thinning using near plane-view GB orientation was selected over the traditional plane-view specimen orientation where it is quite easy to completely mill through one grain and the GB prior to the specimen becoming acceptably thin for TEM observation.
Figure 23 - Bi doped Cu [001]/33° bicrystal TEM coupon specimen mounted on Mo half-grid secondary ion image generated with a 30 kV Ga ion-beam; contrast between the two grains of the bicrystal is due to differences in ion channeling effects in each grain.
Figure 24 – Schematic diagram of FIB specimen GB orientations with yellow representing the GB plane
Figure 25 – Top-down view of FIB TEM specimen during thinning showing a plane-view GB specimen orientation for FIB specimen fabrication where (1) Grain 1 mills at a slower rate than grain 2, (2) Grain 1 mills at the same rate as Grain 2, and (3) Grain 1 mills at a faster rate than Grain 2. Note the GB is lost in (1) and (3) due to asymmetric milling rates between Grain 1 and Grain 2.
Figure 26 – Top-down view of FIB TEM specimen during thinning showing the benefit of a near plane-view GB specimen orientation for FIB specimen fabrication where (1) Grain 1 mills at a slower rate than grain 2, (2) Grain 1 mills at the same rate as Grain 2, and (3) Grain 1 mills at a faster rate than Grain 2.
4.6 Micro-tensile mechanical testing procedure:

Micro-tensile mechanical testing was performed in situ using one of the following: a FEI DB-235, a FEI XL30 ESEM, or a FEI Scios. A Hysitron Inc. PI-85 nanoindentation system was used along with the PTP silicon devices manufactured by Hysitron Inc. A thorough description of the testing procedures is provided by McLean, 2013 [75]. In short, the PI-85 nanoindentation system was operated in load-control mode allowing the load to be increased in 50 or 25 µN increments with periodic holds in place to allow secondary electron images to be captured during testing. One such schedule using 50 µN load steps can be seen in Figure 27. The micro-tensile mechanical tests were performed until failure, upon which an extended hold period was used to allow multiple images to be taken of the fractured micro-tensile mechanical testing specimen. Load displacement data collected by the Hysitron PI-85 nanoindentation system was used to calculate the stress and strain behavior of the test specimens.
Figure 27 – Load schedule used during micro-tensile mechanical test showing loading ramps where the load is increased and holds where images were acquired during testing [75].
4.7 TEM/STEM procedure:

4.7.1 Low magnification specimen characterization

Initial observations of TEM specimens prepared from the Bi doped Cu [100] twist bicrystal specimens were observed at lower magnifications using a JEOL JEM-2000FX TEM. The goal of this observation was to look for any irregularity at the GB of interest (large second phase, obvious orientation or structural changes). XEDS was also performed on these specimens using an Oxford Instruments 5947 X-ray detector in the JEM-2000FX microscope. Convergent beam electron diffraction (CBED) patterns were collected from each crystal of the bicrystal at two separate tilt conditions to determine the misorientation between the two grains. Bright-field images of the GB were also collected at these tilt conditions for grain boundary plane determination.

4.7.2 High resolution TEM and STEM imaging

High resolution TEM and STEM imaging of Cu bicrystals doped with Bi was performed using JEM JEOL-ARM200CF and JEM JEOL-2200FS aberration-corrected TEM/STEM instruments. For typical observation a particular zone axis (typically [001]) of one side of the GB was aligned parallel with the electron optic axis. Bright-field (BF) -TEM, HAADF-STEM, and HRTEM images were acquired at multiple locations along the GB to observe the presence of Bi, GB facets, and second phase particles. The BF-TEM method forms an image using only the direct electrons that are transmitted through the sample without undergoing any diffraction, while the
HRTEM method uses all possible electrons from both the direct beam and all of the diffracted beams relying on interference between the electron waves to form an image. HAADF-STEM imaging allows diffraction and phase effects to be avoided completely, making the formed image of the specimen completely dependent on the mass thickness of the area imaged.

4.7.3 STEM through-focus imaging:

To perform STEM TFI imaging TEM specimens made with a near edge on GB plane FIB fabrication technique were imaged using a JEOL JEM-ARM200CF aberration-corrected TEM/STEM. The Cu bicrystal specimens were oriented such that the [001] direction of one crystal was parallel to the beam direction. Once the specimen was oriented and the instrument was sufficiently stabilized, including the stage, various sets of STEM TFI image series were acquired in the vicinity of the boundary areas of interest. Each STEM TFI image series was acquired with a 2 nm focal step by controlling the objective lens strength from the underfocus condition toward the overfocus condition. Prior to each STEM TFI image series acquisition, the objective lens was degaussed to reduce lens hysteresis. It should be noted that the focal step was calibrated beforehand and the STEM TFI image series acquisition was automated by developing scripts in Gatan DigitalMicrograph. Figure 28 shows the effect of changing the objective lens current on the electron probe crossover position through the depth of the specimen, allowing an image stack with depth dependent information to be gathered. An identical focal series acquisition process was also
carried out with the specimen turned over in the specimen holder to bring the other surface of the specimen closer to the electron source ensuring that both surfaces of the specimen were imaged as the beam-entrance surface. Figure 29 schematically displays the two orientations of the Cu bicrystal used for investigation where one grain was oriented along a [001] zone axis during the initial STEM TFI set, and the same grain was returned to this zone axis with the specimen turned upside down in the specimen holder to bring the other surface closer to the electron source. For HAADF-STEM imaging a beam convergence angle of ~37 mrad was selected as the largest convergence angle possible using the JEM-ARM200CF convergence aperture system while still being able to reasonably minimize the influence of lens aberrations.
Figure 28 - Schematic representation of a Bi doped Cu bicrystal specimen showing the effect of changing the objective lens current on the electron probe crossover point through the depth of the specimen.
Figure 29 - Schematic representation of a Bi doped Cu bicrystal specimen displaying the two specimen orientations used to acquire the STEM TFI image series with the possible location of Bi atoms through the thickness of the inclined boundary.
4.7.4 Analytical X-ray energy dispersive spectroscopy in STEM

XEDS analysis was performed on Bi doped Cu bicrystal specimens using JEOL JEM-ARM200CF and JEOL JEM-ARM300F aberration-corrected electron microscopes. For use of the JEM-ARM200CF spot size 6C and a convergence aperture of ~37 mrad was used (pA beam current). Point spectra from various bulk and GB regions and second phase particles were collected along with line scans and maps for further analysis discussed in Section 4. Experiments were performed at accelerating voltages of 80 and 200 kV. To determine Cliff-Lorimer $k_{\text{Bi}Cu}$ factors for conversion to $\zeta_{\text{Bi}}$ factor, bismuth strontium calcium copper oxide (BSSCO) or $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8+x}$ was used as a standard specimen with a known stoichiometric composition containing both Cu and Bi. A map using the JEM-ARM300F was collected at the JEOL facility in Japan making use of its high solid-angle X-ray detection system.

4.7.5 Grain boundary analysis through electron energy loss spectroscopy

EELS analysis was performed on a FEI Titan TEM/STEM microscope at the National Institute of Technologies and Standards in collaboration with Dr. Herzing. Here, EELS spectra of Cu bicrystal specimens both pure and doped were collected from both sides of the GB and along the GB using both raster scanning and spectrum-imaging.
collection modes followed by a three window analysis technique discussed in Section 5. Experiments were performed at accelerating voltages of both 80 and 200 kV.

5. Results and Discussion:

5.1 Specimen misorientation analysis

Initial misorientation analysis of specimens was performed via EBSD in a Hitachi 4300 S/N SEM. The goal of this preliminary analysis was to determine the approximate misorientation between the three types of twist bicrystal specimens used in the study. The results of this misorientation analysis were presented in previous work related to this project but are summarized in the following section [75].

Pole figures for each of the bicrystal specimens were created by EBSD indexing on both sides of the bicrystal GB for each specimen. One example of a pole figure map showing the GB can be seen in Figure 30 where the two colors of the map each denote a separate crystallographic direction perpendicular to the surface of the specimen. Such maps were generated for each specimen, and each map showed roughly the expected morphology along the GB; the GBs were straight and near featureless in the undoped pure Cu bicrystal specimens. Figure 31, Figure 32, and Figure 33 show <100> pole figures for the 6, 13, and 33° GBs, respectively. These maps represent surface normal crystallographic direction of each crystal composing the bicrystal. When plotted on a stereographic projection, the angular distance between the two normal vectors can be calculated and related as a misorientation angle about
the <001> axis. These values were determined to be in accordance with the expected values for each of the bicrystal samples [75].

One drawback of using EBSD to calculate misorientation angles is that it requires the user to set an acceptable confidence interval for the indexing of the backscattered electron patterns as well as a threshold for the degree of error acceptable for each pattern, i.e. the angular accuracy of the measurement. In addition to these limitations, EBSD misorientation measurements take the average value of the entire field of similarly indexed area and takes no account for the possibility of changes under the threshold values near features in the grains, such as the GBs themselves. For this reason a more accurate method in terms of spatial resolution and angular error is needed to study the misorientation at the GB and not merely between the two bulk grains.

To accomplish the measurement of the local misorientation at the GB with a higher degree of accuracy than can be provided via EBSD, convergent beam electron diffraction (CBED) patterns acquired via TEM were used. Following the work of C.T. Young et al. (1973) CBED patterns were taken from areas near (<50 nm) the GB in each grain of the specimens using the JEOL JEM-2000FX TEM. The recorded diffraction patterns were indexed and analyzed using a MatLab script written to duplicate the work of C.T. Young et al. The MatLab script is provided in Appendix 1. Figure 34 shows the selection of the parameters for the three matrices from each grain needed to perform the misorientation analysis. The first set of axes are those belonging
to the crystal frame, [CF], which is simply the primary crystallographic directions for
the crystal, in this case since Cu is cubic, these directions are of the [001] family. The
second axes are those of the pattern frame, [PF], which is defined using a pole and a
Kikuchi band present on the CBED pattern. The third and final set of axes needed for
each crystal is the reference axes, [RF]; these axes are determined by an invariant
reference direction in each diffraction pattern. Historically, when operating with
photographic plates, these axes would be determined by the beam stop, however with
the advent of CCD camera technology for TEMs the x and y directions on the
diffraction pattern itself can be used as common axes between any two diffraction
patterns.

Figure 35 shows the process of relating the CF for each grain to the PF for
each grain; these are then both related to the shared RF. The rotation matrices, [CR1]
and [CR2], needed to rotate each CF to the RF can be multiplied together to generate a
rotation matrix, [M12], that rotates CF1 onto CF2. With this rotation matrix the angle
of misorientation can be determined by performing a trace of [M12] as shown in the
MatLab code in Appendix 1. The axis of misorientation can also be determined from
[M12] by calculating the eigenvectors of the matrix. To account for all possible
misorientations present in a cubic system, [M12] may be multiplied by the 23 other
possible symmetry operations of the cubic system resulting in a total of 24 possible
misorientation axis and angle pairs. By convention the lowest angle misorientation, or
disorientation, is typically used.
With each pattern indexed (meaning both a pole and a band have been completely identified and indexed) the final measurements can be determined in order to calculate the misorientation between the two crystals. These measurements are that of $D$, $\gamma$, and $\delta$. $D$ is the distance between the pole axis and the center beam position on the CBED pattern. $\gamma$ is the angle between the line connecting the center beam position with the zone axis pole and the Kikuchi band normal (taken as to not cross the Kikuchi band) measured in a clockwise direction. $\Delta$ is the angle from the Kikuchi band normal and the x reference axis measured in a clockwise direction. Figure 36 shows a sample CBED pattern with the location of all the measurements needed to determine the misorientation between any two crystal grains. Identical measurements need to be carried out in the other grain to obtain the disorientation, or lowest possible angular rotation and axis, and all other possible misorientations between the two crystals with this method.

Application of the CBED method for determination of misorientation was performed on the 6° and the 33° Cu twist bicrystals. For consistency these GB will still be referred to as the 6° and 33° bicrystals, respectively, throughout the rest of the dissertation. The 6° bicrystal was found to have a misorientation of 4.3° about the [100] axis, and the 33° bicrystal was found to have a misorientation of 38.0° about the [.94, .1, .1] axis. The axis of misorientation for the 6° bicrystal being [1, 0, 0] confirms this bicrystal to be a pure twist $\Sigma 1$ GB. The 33° GB was found to not be purely twist in character meaning that there is a small degree of tilt component to the GB, additionally the value of 38° about a near [1, 0, 0] axis places this GB very close,
though not precisely, at the misorientation of a twist in Cu $\Sigma 5$ GB, whose twist angle was 36.87° [76]. The values from the CBED technique vary slightly with the values calculated from the EBSD technique, though both arrive at twist angles within 5° of one another. As seen in Figure 31, the relatively large size of the different spots of the pole figure diagram shows there can be a large amount of spread in the data collected through the EBSD method. In addition, the CBED method allows comparison of patterns directly across the GB as the electron probe size is much smaller than that of an SEM. Ultimately, EBSD is useful for quickly determining an approximate misorientation axis and angle, but if a higher degree of accuracy and precision is needed other techniques such as the CBED method can be employed.
Figure 30 - An EBSD map of a $6^\circ$ [100] twist Cu GB used to confirm the bicrystal orientation and boundary regularity
Figure 31 - A pole figure generated from an EBSD map of a 6° [100] Cu twist bicrystal confirming an approximate misorientation of 6°.
Figure 32 - A pole figure generated from an EBSD map of a 13° [100] Cu twist bicrystal confirming an approximate misorientation of 13° [75].
Figure 33 - A pole figure generated from an EBSD map of a 33° [100] Cu twist bicrystal confirming an approximate misorientation of 33° [75].
Figure 34 – Illustration showing the selection of the reference frame RF denoted by \((X_R, Y_R, Z_R)\) and the pattern frame PF denoted by \((X_P, Y_P, Z_P)\), and the angles \(\delta\) and \(\gamma\) which must be measured in order to establish the matrix \([CR]\) [77].
Figure 35 – Schematic representation of the relation between two crystal coordinate frames and a reference coordinate frame. Various stages of rotation are indicated by the arrows and the corresponding rotation matrices. \([M12]\) is a matrix specifying the rotation of CF1 to CF2. \([R12]\) is a matrix representing the rotation of \(v_1\) into \(v_2\) by referring to RF [77].
Figure 36 – Sample CBED pattern showing the values to be measured for misorientation analysis.
5.2 Micro-mechanical testing of FIB prepared Bi doped Cu Bicrystals

In work associated with the particular bicrystals used for STEM, EELS, and XEDS analysis in this dissertation, McLean et al. studied the fracture behavior of three separate [100] twist Cu bicrystals in both Bi doped and pure Cu conditions using micro-mechanical tensile testing at right angles across GB to fracture double edge-notched micro-tensile (DENT) test specimens [78]. The GBs investigated in this study were $33^\circ [100]$ twist, $13^\circ [100]$ twist, and $6^\circ [100]$ twist. From stress-strain curves generated from the experiments, as seen in Figure 37 and Figure 38, fracture toughness values were calculated to assess the reduction in toughness that Bi causes on these twist bicrystal GBs. The results from this analysis are presented in Table 4. It is important to note that the $13^\circ$ specimens tested in this study were only tested using single edge-notched specimens (SENT), meaning that the calculated fracture toughness values cannot be used as a direct comparison to the $6^\circ$ and $13^\circ$ DENT specimens. The $13^\circ$ SENT specimens are still important to note because of the apparent reduction in fracture toughness even if the numbers cannot be directly compared elsewhere.

Compared to other studies, the study by McLean et al. showed significant plasticity after yielding for Cu bicrystal specimens that were known to contain Bi, and also showed significant reduction in fracture toughness. Currently, there is no proposed mechanism by which Bi is capable of GB cohesive strength (i.e. causing
embrittlement) and yet allowing for a degree of plastic deformation to still occur prior to brittle failure. By comparing the fractured specimen images provided in Figure 39 and Figure 40 it can clearly be seen that the presence of the Bi on the Cu GB is responsible for a drastic change in fracture behavior yet the plasticity present in both specimen failures remains unexplained. The specimens used in the work of McLean et al. are used in this electron microscopy study of Cu embrittlement by Bi presented in this dissertation, and as such an explanation for the seemingly anomalous plastic behavior of the “embrittled” Cu will be sought.

*Table 4 – Fracture toughness values for various Cu [100] tilt bicrystals as reported by Mclean [75].*

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Fracture Toughness $K_C$ (MPa$\sqrt{m}$)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td><strong>Pure</strong></td>
</tr>
<tr>
<td>6° DENT</td>
<td>0.54 ± 0.08</td>
</tr>
<tr>
<td>13° SENT</td>
<td>2.24 ± 0.98</td>
</tr>
<tr>
<td>33° DENT</td>
<td>0.54 ± 0.06</td>
</tr>
</tbody>
</table>
Figure 37 – Stress-strain curves generated from two DENT $6^\circ$ Cu [100] twist bicrystal specimens; note the extensive plastic behavior in both the Bi doped and pure Cu conditions prior to failure [75].
Figure 38 - Stress-strain curves generated from two DENT 33° Cu [100] twist bicrystal specimens; note the plastic behavior in both the Bi doped and pure Cu conditions prior to failure as well as the significantly reduced elongation at failure of the doped condition [75].
Figure 39 - SEM micrograph of a pure Cu 33°[100] twist bicrystal after transgranular shear-like failure has occurred [75].
Figure 40 - SEM micrograph of a Bi doped Cu 33°[100] twist bicrystal after intergranular failure has occurred due to Bi embrittlement [75].
5.3 Bicrystal Specimen Characterization

Over the course of this study a multitude of TEM and STEM instruments have been used to observe the GBs of the various tilt bicrystal specimens in Bi doped and pure Cu conditions. These instruments include: JEOL JEM-2000FX, JEOL JEM-2200FS, JEOL JEM-ARM200CF, and a FEI Titan. The following sections of this dissertation will discuss and interpret images of the Cu bicrystal GBs obtained with various TEM and STEM imaging modes in terms of what can be deduced about the structure of the Cu GBs, the change that occurs when Bi is added to the GBs, and the positioning of Bi on the Cu GBs.

5.3.1 Microscopic characterization

Low magnification TEM imaging was used to assess the general shape and regularity of the various GBs studied. For typical observation, one side of the GB was oriented to a <001> or <011> zone axis, with the latter only being achievable through specimen tilting in the JEOL JEM-2000FX for edge on GB orientation specimens. The alignment of the Cu crystal near the GB to a common low index zone axis allowed for repeatable imaging conditions across multiple specimens, a convenient starting point for any imaging analysis to be performed on the specimens. For undoped GBs it was observed that the GB lines tended to be extremely straight and almost completely featureless with a lack of faceting or any second phase particles. Undoped GBs were observed in two separate conditions; the first observation condition being as received, and the second observation condition being as annealed. The as received condition
was identical to the condition that the mechanical testing specimens were tested under, have undergone no heat treatment except that related to the mounting procedure. A second set of pure bicrystal specimens were observed after undergoing a heat treatment with the same temperature and time as that of the Bi doped specimens. This second observation was to rule out any changes to the GB structure due to relaxation or the heat treatment environment to ensure that all observed boundary structures were due to the presence of Bi or a combination of Bi and the heat treatment environment.

Figure 41 and Figure 42 show images of the GBs from two 6° Cu bicrystal specimens; the first being that of a Bi doped specimen, and the second being that of a pure Cu specimen that has undergone an identical heat treatment to the Bi doped specimen. The heat-treated specimen showed no increase in second phase particles along the GB or any evidence of GB relaxation, meaning that the heating during the doping procedure, by itself, cannot be responsible for any observed changes in mechanical behavior of the Cu specimens.

Upon observation of the pure specimens in the as received condition and the as heat treated condition, there was very little difference in the structure of the GB via SEM observation and low magnification TEM observation. Comparison between the pure and Bi doped specimens, however, revealed a change in the GB appearance for the 13° and the 33° GBs that was observable at low magnification (<200 kX) in the TEM. A summary of the qualitative yet observable morphology change of the different GBs is presented in Table 5. The 33° GB showed the largest change in morphology after Bi doping. GB faceting was observed along the length of Bi doped
33° Cu GBs. This faceting is thought to be the result of GB relaxation to accommodate the large Bi atoms on the GB and relieve stress in and around the GB by changing the GB plane [79]. Large second phase particles periodically appear on the GB throughout the specimen thickness. Figure 43 shows a BF-TEM image of the GB in a 33° Bi doped Cu bicrystal fabricated in a near plane-view orientation. The second phase particles can be seen between the points labeled A and B indicating the beginning of each side of the GB. XEDS analysis, discussed further in section 5.6, revealed these second phase particles to be a Bi heavy oxide most likely Bi$_2$O$_3$.

Table 5 – Observable Change in GB Morphology upon Bi Doping

<table>
<thead>
<tr>
<th>GB Misorientation Angle</th>
<th>Change in GB Morphology</th>
</tr>
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<tbody>
<tr>
<td>6</td>
<td>No</td>
</tr>
<tr>
<td>13</td>
<td>Yes</td>
</tr>
<tr>
<td>33</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Viewing specimens fabricated in a near edge-on orientation as shown in Figure 44 and Figure 45, it is possible to see the different GB plane sections present along the GB due to faceting from the addition of Bi and subsequent rearrangement on the atomic-level (which may lead to relaxation) during the heat treatment. The HAADF image in Figure 44 also shows bright areas along the top and bottom surface of the specimen in this transmission view. These bright areas correspond directly to an increase in the average atomic number of the elements present in that area and are in
fact due to an increase in Bi concentration at the GB. Figure 45 shows a STEM-BF image of the same GB displaying sharper contrast features on the top and bottom of the GB than are observable in the HAADF image of the same GB. The increase in contrast in the STEM-BF image is due to the additional contribution of the diffraction of electrons transmitted through the sample as well as the effect of incoherent scattering due to any changes in atomic number in areas close to the GB. With BF-STEM it is often easier to observe certain crystal defects that may disrupt the periodicity of the crystal lattice leading to local changes in the diffraction conditions. Defects such as GBs, stacking faults, and dislocations are then very easy to discern in a BF-STEM image.

GBs fabricated with a slight inclination of the GB plane to the specimen surface, making it easier to view the GB in a near plane-view orientation, provided some insight into the structure of the GB. Operating a TEM at 80 kV allowed the dislocation structure to be viewed under very specific conditions. Figure 46 shows a DF-TEM image of a 33° GB where dislocations on the GB can be seen. There appear to be three separate types of dislocations: two orthogonal to one another and a dislocation line that runs parallel to the GB. Burgers vector analysis was not capable of being performed on these dislocations as sufficient two-beam conditions were not achievable on the GB area.
Figure 41 – BF-TEM image of a Bi doped 6° Cu bicrystal GB
Figure 42 – BF-TEM image of a pure 6° Cu bicrystal GB taken from a post-heat treatment sample
Figure 43 – BF-TEM image of a near plane-view orientation specimen showing second phase particles along the GB with two arrows indicating points A and B, the GB region of the specimen.
Figure 44 – HAADF-STEM image of a 33° [100] twist Cu GB doped with Bi imaged at a location between two second phase GB particles rich in Bi on an edge on GB orientation specimen.
Figure 45 - BF-STEM image of a 33° [100] twist Cu GB doped with Bi imaged at a location between two second phase GB particles rich in Bi on an edge on GB orientation specimen.
Figure 46 – DF-TEM image (200) reflections from lower grain of 33° Cu bicrystal GB showing 3 different dislocation lines in red.
5.3.2 Mesoscopic characterization

The ability to directly image crystal defects using BF-STEM imaging was mentioned in the previous section concerning low magnification imaging of the Cu bicrystal specimens. In this section higher magnification images and the features visible at those high magnifications will be discussed. The first feature observable on certain facets of the Bi doped 33° Cu bicrystal GBs are GB dislocations. Figure 47 and Figure 48 show BF-TEM images of a Bi doped 33° Cu Bicrystal GB while Figure 49 and Figure 50 show HRTEM images of the same GB. Both of these methods show a continuous array of fringes with a spacing of ~2.5 nm perpendicular to, and along, the GB.

There are multiple sources for alternating contrast features in a specimen observed through TEM. Some of the possible sources for these fringes are: thickness variations, Moiré interference fringes, and dislocation diffraction contrast. Here, the possible source of these fringes appearing in the BF images is explored as follows.

The possibility of thickness variations causing these fringes can be rejected because of the spacing of the fringes and their angle with the GB. If we assume a change in thickness occurred at the GB due to specimen preparation via ion milling, resulting fringes would be parallel to the GB—not perpendicular. In addition to the fringes being oriented in the wrong direction for a thickness change across the GB, the close spacing of the fringes would require an incredibly steep and large change in thickness over mere nanometers to induce such a high number fringes. Thickness
fringes are a result of oscillations in the intensity of the direct and diffracted beams as they travel through the specimen. At intervals of one half the extinction distance ($\xi_g$) the intensity of the diffracted beam is at a maximum while the intensity of the direct beam is at a minimum [55]. By calculating the extinction distance it can be shown that the likelihood of thickness fringes appearing at the measured spacing of ~2.5 nm is unlikely. Equation 24 can be used to calculate the $\xi_g$ for any diffracted beam vector (g) with components h, k, and l where $V_c$ is the unit cell volume, $\theta_B$ is the Bragg angle for reflection g, $\lambda$ is the electron wavelength, and $F_g$ is the structure factor of the material.

$$\xi_g = \frac{\pi V_c \cos \theta_B}{\lambda F_g},$$

Equation 24

Williams and Carter provide a table of extinction distances for various g vectors of Cu at an accelerating voltage of 100 kV listing the smallest of these $\xi_g$ values as $\xi_{111} = 28.6$ nm. The experiments performed in this study were conducted at 200 kV, the effect of raising the accelerating voltage decreases both $\lambda$ and $F_g$ through decreasing the elastic scattering factor [55]. With $0.5\xi_g$ being greater than 14 nm under the imaging conditions present in Figure 47, the specimen would need to change in thickness by over 100 nm along any given 20 nm long GB section. Such a drastic change in thickness is not possible in a FIB prepared specimen where parallel milling has ensured the near uniformity of specimen thickness. Therefore, according to the
calculated extinction distance, the fringe spacing of ~2.5 nm measured from BF images (Figure 48 - Figure 50) is unlikely to be thickness fringes.

The fringes present in the images provided in this section must then be accounted for by either dislocation contrast from a network of parallel misfit dislocations along the GB, or by the presence of Moiré fringes due to the misorientation of the lattice between the two grains composing the bicrystal. Previous studies have attempted to remove the ambiguity between contrast from closely spaced dislocation networks and Moiré fringes [80], [81]. Tholen concluded that at approximately a dislocation spacing of <0.3 $\xi_g$ individual dislocations in a network of dislocations cannot be individually resolved and that it is not possible to distinguish the fringes observed from Moiré fringes [80]. Kamiya et al. interpreted the ambiguity between dislocation diffraction contrast and Moiré fringes as the result of a relationship between the two fringe generation mechanisms in certain cases. The diffraction contrast from dislocations requires adequate dislocation spacing and the strain resulting from the presence of the dislocation be localized near the dislocation core. If the strain is spread over an area the contrast from the dislocation begins to broaden, becoming what can be described as a Moiré fringe [81]. The inability to resolve potential dislocations spaces as closely together as the fringes present in Figure 47 requires additional imaging experiments that may be able to discern the presence of dislocations, such as HAADF-STEM imaging.
Figure 47 - BF-TEM image of a 33° [100] twist Cu GB doped with Bi showing a network of dislocations across the inclined GB.
Figure 48 - BF-TEM image of a 33° [100] twist Cu GB doped with Bi showing a network of dislocations across the inclined GB, the change in contrast conditions from one side of the GB to the other is due to changing diffraction conditions across the dislocation.
Figure 49 – HRTEM image of a 33° [100] twist Cu GB doped with Bi showing a network of dislocations across the inclined GB.
Figure 50 - HRTEM image of a 33° [100] twist Cu GB doped with Bi showing a network of dislocations across the inclined GB, note the change in dislocation appearance in the upper left corner due to GB faceting.
5.3.3 Nano and atomic scale characterization

6° Cu Bicrystal Boundary –

The 6° Cu bicrystal boundary remained unchanged and uniform through all of the low magnification imaging addressed in the previous sections whether the boundary was doped with Bi or was observed in the pure Cu form. Unsurprisingly, high resolution HAADF and BF-STEM imaging showed no formation of second phase particles or the presence of Bi along the GB.

13° Cu Bicrystal Boundary –

The 13° Cu bicrystal showed clear GB faceting when doped with Bi. On these facets it was possible to obtain Z-contrast from the Bi present at the GB through HAADF-STEM imaging. Figure 51 shows the faceting behavior of the boundary where there is a clear change in GB plane orientations along the particular facets of the GB. According to an increase in image contrast at the GB, it can be concluded that the presence of Bi is only located along the GB. Figure 52 shows the same GB at a higher magnification where the appearance of an apparent bilayer is observed. This particular bilayer is very similar to previous work done on the Ni-Bi system by Lou et al. where it was argued that the presence of a bilayer structure at the GB (Figure 53) was responsible for the embrittlement observed in the Ni-Bi system through the breaking of the relatively weak Bi-Bi bonds at the GB [82].
Figure 54 shows a line profile across the bilayer extracted from Figure 52, displaying a spacing of 0.58 nm between the two layers. This distance is larger than the lattice constant of both Cu and Bi in their native crystal structures and is, therefore, also much larger than the interatomic spacing between two Bi atoms if they were to be directly bonded to one another. Due to the large spacing between the two layers of atoms composing the “bilayer,” the embrittlement of the Cu-Bi system cannot be due to fracture along Bi-Bi bonds across the GB as was proposed for the embrittlement mechanism in the Ni-Bi system. This observation is also in agreement with previous AES studies where the fracture surfaces of embrittled Cu GBs was found to be caused by a weakening of and fracture along Cu-Cu bonds across the GB [29], [43], [34]. It is also unclear, from the image in Figure 52, if the lines of Bi along each side of the GB are in fact formed by a continuous monolayer of Bi as the individual atoms composing the layer cannot be resolved laterally from the edge on GB orientation of the specimen. Attempts to tilt this particular specimen to other viewing directions resulted in the loss of any contrast from Bi atoms on the GB, leaving this question of exact Bi atom spacing along the GB unanswered.

Possible Bi atomic arrangements that could lead to a bilayer appearance in a HAADF-STEM image of the GB in a near edge on orientation are schematically shown in Figure 55. An atomic bilayer could give rise to such a contrast feature; however, the large distance of the bilayer spacing eliminates this possibility as mentioned earlier. A
second Bi atomic arrangement that may lead to bilayer-like features through the thickness of the specimen is that of a boundary jog. Here, with a boundary jog, the atomically sharp boundary, considered vertically through the thickness of the specimen, steps horizontally over one or more lattice spacings prior to continuing vertical propagation though the thickness of the specimen. A third Bi atomic structure that may lead to a bilayer-like appearance is that arising from segregation to the top and bottom surfaces of the specimen. With segregation to the surface the images of GB are understood to be close but not exactly parallel to the optic axis of the microscope. If Bi atoms then move to the top and bottom surfaces of the specimen, the Z-contrast generated by each surface, top and bottom, may lead to two strong areas of Z-contrast running parallel to each other, as observed in Figure 52, with the spacing between the two lines being a function of specimen thickness. To help characterize the boundary and the origin of features such as the “bilayer” seen in Figure 52 a 3-dimensional imaging method is needed.

33º Cu Bicrystal Boundary –

Of the three types of bicrystals observed in this study, the 33º Cu bicrystal was the only bicrystal to routinely show marked transformation in the GB appearance and structure when doped with Bi. This GB was also the only boundary to constantly show direct and observable Bi atomic segregation to the GB in clearly resolved individual Bi atomic columns. The first observation of Bi on the GB came in the form of a small boundary feature or second phase Bi oxide particle that was imbedded in the GB.
These oxide particles are routinely found on the 33° bicrystal GBs once they have been
doped with Bi, and while most of the analysis areas used in this study were
sufficiently far away from such oxide particles, the strong atomic contrast of the Bi
surrounding this particular oxide particle is worth noting first. Figure 56 and Figure 57
show HAADF-STEM and BF-STEM images of this Bi oxide particle on the GB. The
arrangement of the Bi atoms is of particular importance; visible along the GB in
multiple other locations is this alternating Cu – Bi – Cu formation of Bi atomic
columns. This shows direct evidence that there is no continuous monolayer of Bi
laterally present along the GB in the 33° Cu bicrystal specimens, and by extension,
these 33° bicrystal specimens contain a higher amount of Bi that is present or
detectable in any of the other specimens studied, making it unlikely that a continuous
monolayer exists in any of the GBs studied in this work.

Figure 58 shows an identical Bi atomic arrangement as observed along the Bi
oxide particle on a clean part of the boundary containing no second phase. On the
particular GB facet observed in this figure, the spacing of the Bi atoms along the GB is
exactly twice that of the spacing of the Cu atoms, when observed with one grain
oriented to the <001> direction. With one side of the bicrystal oriented so that the
<001> direction is parallel to the optic axis of the microscope it is seen that, laterally
along the GB, Bi atoms are present once per unit cell. This figure shows the 180 pm
spacing between neighboring Cu atoms as well as the spacing of 360 pm between any
two Bi atoms. It is also important to remember that this type of imaging only provides
information in 2-dimensions, so that the actual atomic arrangement may be different.
through the thickness of the specimen, meaning that the Bi atoms observed in these atomic columns may be in neighboring atomic positions, or considerably more spread out through the thickness of the specimen with electron channeling along the atomic columns keeping contrast strong for any column containing Bi regardless of the dispersion of Bi atoms along a particular column.

Figure 60, Figure 61, and Figure 62 show three sets of BF/HAADF-STEM images taken at 3 different focal positions of the electron probe through the thickness of an inclined Bi doped 33º specimen by varying the objective lens current values, where both Z-contrast from the heavier Bi atoms and slight diffraction contrast from dislocations across the GB can be seen in HAADF and BF images, respectively. As the probe moves up through the boundary in the three images, the area in focus moves from left to right across the GB, showing that the GB near the top surface of the specimen is closer to the left side of the field of view. Bi atoms on the boundary at this location are in close proximity to the dark areas of the dislocation fringes in the BF-STEM images and the bright areas of the dislocation fringes in the HAADF-STEM images.

To investigate the possibility of dislocations and Bi atom interaction an image from this GB was processed by Fourier filtering, which is filtering using a mask for only specific reflections (or frequencies) on the fast Fourier transformation (FFT) of the raw image, followed by the inverse FFT application [83]. The raw image of the GB, along with a magnified view of the HAADF-STEM, the filtered images, and a
BF-STEM image are presented in Figure 63. Here edge dislocations can be more easily seen in the filtered images. When compared to the raw image, showing the location of Bi atoms, it is has been found that the Bi atoms are present near the extra half-plane of atoms forming an edge dislocation core. The Bi atoms may be attracted to the dislocation cores due to the lattice tension present near the core of the dislocation which allows the relatively larger Bi atom to sit at and relieve some of the stress induced by the dislocation in the crystal, lowering the overall energy of the system. In short, the addition of Bi to the GB causes faceting to increase the free volume at the GB and allow the accommodation of the Bi; upon relaxation dislocations are formed allowing Bi to sit in the tensile stress field below the dislocation core.

Taken to the extreme, if a GB is composed purely of edge dislocations, as with pure twist bicrystals, Bi should sit precisely on the dislocation cores present in the boundary. With Bi on the dislocations in the GB, the energy required to move the dislocations increases and may cause embrittlement if the number of slip systems available to move the dislocations is limited. This mechanism is a combination of the Rice-Thomson model of GB embrittlement, where the primary determining factor of selection between GB cleavage and dislocation motion is the number of slip systems available at the GB crack tip, and the segregant species at the GB previously not taken into account in physical models of GB embrittlement. Duscher et al. imaged one such twist bicrystal in the Cu-Bi system, shown in Figure 64 [46]. Here, the periodic
structural unit described by Duscher et al. can be accurately called an edge dislocation core with Bi sitting at the center of this structure in the Bi doped boundary.

Figure 51 – HAADF-STEM image of a Bi doped 13° Cu bicrystal viewed in a near edge on GB orientation showing bright contrast at the GB due to Bi as well as facets along the GB.
Figure 52 - HAADF-STEM image of a Bi doped 13° Cu bicrystal viewed in a near edge on GB orientation showing an apparent “bilayer” if Bi on this particular GB facet.
Figure 53 – Ni bicrystal showing the presence of a Bi bilayer at the GB [82].
Figure 54 – Line profile taken across the GB “bilayer” shown in Figure 52 displaying the measured distance between the two layers forming the “bilayer”.
Figure 55 – Possible Bi atomic arrangements that may lead to a “bilayer” appearance when imaged with Z-contrast through HAADF or ABF-STEM techniques.
Figure 56 – HAADF-STEM image of a GB Bi oxide particle contained on a Bi doped Cu 33° bicrystal GB showing atomically resolved Bi columns surrounding the Bi oxide.
Figure 57 – BF-STEM image of a GB Bi oxide particle contained on a Bi doped Cu 33° bicrystal GB showing atomically resolved Bi columns surrounding the Bi oxide.
Figure 58 - HAADF-STEM micrograph Bi-doped Cu [001]/33° twist bicrystal boundary with right grain oriented to a <001> direction showing periodic Bi atoms on GB with distances between two Cu containing atomic columns as well as the distance between two Bi containing atomic columns labeled.
Figure 59 – Images of periodic spacing of areas containing Bi along a Bi doped 33° Cu bicrystal GB, (a) showing BF-STEM and (b) showing HAADF-STEM with Bi atoms labeled along the GB with the spacing between areas containing Bi measured to be approximately 2.5 nm.
Figure 60 - BF-STEM image (a) and HAADF-STEM image (b) of inclined grain boundary with probe focused on the left side of the boundary showing the location of Bi atoms.
Figure 61 - BF-STEM image (a) and HAADF-STEM image (b) of inclined grain boundary with probe focused on the middle of the boundary showing the location of Bi atoms.
Figure 62 - BF-STEM image (a) and HAADF-STEM image (b) of inclined grain boundary with probe focused on the right side of the boundary showing the location of Bi atoms.
Figure 63 – HAADF-STEM image showing GB with Bi present at boundary along with magnified section showing filtered images highlighting edge dislocations with Bi atoms near dislocation cores marked in blue along with an extra half plane of Cu atoms marked in red
Figure 64 – HAADF-STEM images of a pure Cu (top) and Bi doped (bottom) 36.8° symmetric tilt GB showing a repeated structural unit schematically represented on the images [46].
5.4 3-dimensional imaging of Bi doped Cu grain boundaries

5.4.1 Choice of convergence semi-angle

Lateral resolution and geometric DOF are both directly influenced by the probe-forming semi-angle in STEM. Increasing the probe-forming semi-angle (α) will reduce both the lateral resolution and the geometric DOF. The inability to completely correct all of the electron probe aberrations limits the possible probe-forming semi-angles usable for a suitable lateral resolution. Due to this limitation of aberration correction, the geometric DOF must be balanced with reasonable lateral resolution via the selection of an appropriate probe-forming semi-angle. Figure 65 shows the relationship between the electron probe diameter that contains 59% of the total intensity (d_{59}) and the probe-forming semi-angle in mrad units. From Figure 3 it can be seen that probe-forming semi-angles below approximately 20 mrad can be reduced nearly to the diffraction limit with sufficient lens aberration correction commercially available today. The 59% probe diameters at α > 20 mrad are dependent on the choice of electron source for the STEM system, due to the effect of chromatic aberration mainly caused by the energy spread (ΔE) of the electron source. In an aberration-corrected STEM equipped with a Schottky field emission gun (FEG), the optimum probe-forming angle is ~25 mrad. If α > 25 mrad, the probe size is degraded by the contribution of chromatic aberration. In contrast, the ΔE value of a cold FEG is better than that in the Schottky FEG, and hence the influence of the chromatic aberration is reduced and the optimum probe-forming angle is expanded to ~35 mrad.
A cold FEG system is employed in the JEOL JEM-ARM200CF used in this study, so a larger probe-forming angle could be selected without limitation of probe diameter by chromatic aberration. For the STEM TFI, the probe-forming angle of 37 mrad was selected. This probe-forming angle is slightly higher than the optimum angle for the best lateral resolution in this instrument as shown in Figure 65. However, this larger probe-forming semi-angle improves the geometric DOF. According to Equation 1, the geometric DOF at 37 mrad is improved by over 50% in comparison with that at 25 mrad, one of the commonly used probe-forming angles for the optimized lateral resolution in Schottky-FEG instruments. This large improvement in geometric DOF more than justifies the use of larger probe-forming semi-angles even with a slight degradation in the ultimate achievable resolution caused by the chromatic aberration.
Figure 65 - Graph of probe-forming semi-angle (mrad) vs 59% probe diameter (nm) for a STEM with a Schottky FEG, a cold FEG, and an idealized geometric probe with comparison to the diffraction limit for a 200 kV accelerating voltage. [84]
5.4.2 - STEM TFI of Bi Doped Cu Bicrystals

The features observed in STEM TFI images acquired from the near-GB region of a Bi-doped Cu bicrystal exhibited a noticeable dependence on local specimen thickness as well as the depth of the focused probe through the thickness of the specimen. Thus, it is useful to separate the areas of observation into "thick" and "thin" areas. Likewise, it is important to differentiate between the behavior of the beam-entrance and beam-exit surfaces. For simplicity, the beam-entrance and beam-exit surfaces are denoted as the top and bottom surfaces, respectively, throughout the rest of the manuscript.

STEM TFI of thicker areas in the near-GB vicinity showed a visible difference in atomic number contrast (Z-contrast) at different boundary depths, with the near surface locations (either top or bottom surface) producing greater image intensity than interior locations. Figure 66 shows two HAADF images taken at different defoci on the same lateral boundary area. Figure 66a shows two bright areas along the boundary: area 1 with bright atoms of Bi relatively well resolved, and area 2, a few nanometers away from area 1, with a diffuse increase in Z-contrast intensity as compared to the regions immediately on either side of it; both of these two regions of interest lie on the intentionally inclined GB. Figure 66b shows the same regions of interest except that now area 1 is no longer in focus and appears as a region of diffuse, higher intensity. Whereas in the first image there was only a slightly blurred region of high intensity in area 2, the second image contains a slightly better resolved area 2 with even higher intensity. The change in intensity between these two images is due to a difference in
the focused position of the electron probe through the thickness of the specimen. With the probe focused at a location farther through the thickness of the specimen in the second image, it is possible to see that the resolution of Bi atoms on the boundary is degraded compared to the first image, which has the electron probe focused on the top surface of the specimen. This lack of resolution at the bottom surface is due to beam broadening through the specimen prior to interacting with the strong contrast generating features, i.e. Bi atoms at the focal point, resulting in the degradation of resolution. It is also important to note that there is a gap of a few nanometers between the two Bi rich areas along the inclined boundary. The first Bi rich area is on or near the top surface of the specimen while the second area is on or near the bottom surface of the specimen. In the gap between the two Bi rich areas there were no Bi atoms visible when this particular STEM TFI image series was acquired, implying that there was little or no Bi along the boundary between the two surfaces of the specimen. It is important to examine the specimen with both surfaces closer to the electron source prior to making this assessment. Any changes in the STEM TFI imaging results when observed from just one side may have possible compositional or structural changes in the specimen through the vertical direction. To avoid this ambiguity it is necessary to perform STEM TFI over the area twice, with both sides of the specimen closer to the electron source.

Moving to thinner regions of the specimen allowed the imaging of individual Bi atoms at multiple locations through the thickness of the bicrystal boundary. STEM TFI performed over these thin boundary areas were collected as a 3-dimensional
vertical image stack, as a function of the defocus (i.e. the depth). After collection of this image stack, spatial drift occurring during the acquisition of the image stack was compensated for by use of the Statistically Determined Spatial Drift (SDSD) program [85]. Figure 67 shows selected frames from one such image stack with a Bi atom indicated as it is resolved through the depth of the material and then unresolved as the probe moves down through the specimen. To visualize the ability to resolve a Bi atom through the thickness of the material, it is necessary to obtain an image containing information parallel to the optic axis of the microscope; conventional imaging techniques in STEM or TEM only contain information perpendicular to this axis. In order to gather this information parallel to the optic axis, a profile along any lateral direction in a summed STEM TFI image may be extracted. To form a summed TFI image, the Z-contrast intensity of each individual image in a drift-corrected STEM TFI image stack is integrated in the vertical (optic axis) direction. With the summed STEM TFI image formed, a profile may be taken in any lateral direction. This profile provides a Z-contrast intensity image containing Z-contrast distributions through the thickness of the specimen with pixel dimensions equal to the lateral pixel dimensions in the original image multiplied by the electron probe focal step used during the STEM TFI image series acquisition. Figure 68 shows a summed STEM TFI image along with the x plane Z-contrast intensity images associated with various profile lines on the sum STEM TFI image. Each of the extracted profiles contains both information of the lateral y direction as well as information along the vertical optic axis.
If an intensity variation of individual atoms in the vertical direction is considered, the full-width half-maximum (FWHM) of the Z-contrast intensity can be used to approximate the depth resolution of an individual Bi atom. Figure 69a shows one such intensity profile. In the case of this particular Bi atom, the FWHM, indicating the depth resolution, was 4.57 nm. The FWHM of the raw image intensity was found by subtracting the average Cu image intensity taken from Cu atomic columns both above and below the Bi atom of interest. With the background subtraction in the extracted line profiles, the remaining image intensity can be regarded as signals generated by the Bi atom. It is this remaining Bi-generated image intensity that the FWHM is taken from that results in a value between 4.5-5 nm. Due to the inability to distinguish individual electrons scattered from the metal matrix and the heavy dopant atom, certain materials and specimen conditions will increase the heavy dopant atom signal, effectively lowering the obtainable vertical resolution. These conditions include imaging from a thin region of the specimen, imaging with the matrix on an off-major zone axis orientation, and using dopant elements that have a much larger atomic mass than the matrix elements. All of these conditions aim to increase the signal from the dopant atoms and to reduce the signal from the matrix atoms that will decrease the achievable FWHM of the dopant atom’s image intensity closer to the geometrically imposed limitation of the system.

Atoms farther from the surface of the specimen tend to have a larger FWHM when imaged with this STEM TFI technique. This increase in FWHM is due to the increased effect of beam broadening prior to interaction with the high signal-
generating Bi atom. This effect can be seen in the FWHM of the intensity profiles shown in Figure 69b and Figure 69c. Figure 69b displays the FWHM of the intensity profile of a Bi atom toward the middle of the specimen, leading to an increase in the resolution (4.9 nm) with which the atom can be resolved in comparison to the Bi atom in Figure 69a that is closer to the entrance surface of the specimen. Figure 69c shows the even further increase in resolution (5.2 nm) when imaging a Bi atom close to the exit surface of the specimen. The FWHM of each of these three Bi atoms plotted against the position from the top surface are shown in Figure 69d, revealing the general increase in achievable resolution as imaging of dopant atoms farther from the entrance surface of the specimen is attempted. In these thinner regions individual Bi atoms were capable of being imaged with a FWHM resolution routinely below approximately 5 nm in the vertical direction. The measured FWHM value is in close agreement with Equation 1 if a Bi atom is considered to be a point-like object. It is worth mentioning that lateral resolution was mostly unaffected as the specimen was not sufficiently thick to cause degradation of resolution from beam scattering, i.e. the specimen thickness was much less than the mean free path of the incident electrons in Cu at 200 kV.

This elongation and the FWHM of the Bi atoms are also in agreement with the object elongation factor calculated by Xin and Muller [86]:

\[
\text{elongation factor} = \sqrt{\frac{3}{2}} \frac{1}{\alpha_{max}},
\]

Equation 25
where $\alpha_{\text{max}}$ is the maximum electron probe convergence angle. As predicted in Xin and Muller’s work, the elongation of objects in the vertical direction is extremely large, though not necessarily disastrous for imaging point-like objects such as atoms. In this experiment, it was found in the Cu-Bi system that the elongation was not significant enough to routinely cause overlap between the observations of two or more Bi atoms on the Cu GB. This ability to resolve atoms without an overlap of signal makes STEM TFI with an inclined boundary an attractive option for the exploration of boundary segregation where small amounts of segregant atoms are widely distributed on the GB. Previous work imaging the distribution of segregant atoms on a boundary involved the extremely tedious task of thinning a specimen (mechanically, electrochemically, or via FIB) so that the GB was oriented approximately perpendicular to the beam axis and the entirety of the GB was contained in the electron transparent region of the specimen. This plane-view approach is typically only possible with highly specialized bicrystals and in systems that do not exhibit a change in boundary morphology when they are doped. In the case of the Cu-Bi system, a change in morphology (specifically, faceting) along the GB occurs, with each boundary facet having a different boundary plane than those surrounding it. Due to the presence of multiple facets throughout the GB of the Bi-doped Cu bicrystals, creating a specimen that contains a representative sample of each type of facet in a plane-view orientation may not be practical, if even possible. With these faceted GBs, STEM TFI of inclined GBs is a straightforward and useful technique to quickly extract information about the 3-dimensional distribution of Bi on the GB. Figure 70 shows
two different atomic arrangements of Bi observed on a single GB facet. Using the STEM TFI technique, the depth location of each atom can be determined, and with simple geometric considerations the planar density of the dopant atoms on the GB plane can be directly calculated. Figure 70a yielded a GB excess of 0.3 Bi atoms per nm$^2$ while Figure 70b yielded a GB excess of 1.4 Bi atoms per nm$^2$. These two GB excess values correspond to monolayer coverages of 0.02 and 0.09 monolayers, respectively. This monolayer coverage result shows an anisotropy in Bi coverage of GBs not only between GB facets, as observed by Powell and Woodruff, but also an anisotropy in coverage along a single GB facet [29].

The STEM TFI technique also enables observation of certain atomic movements during electron beam irradiation. It was observed during the acquisition of some STEM TFI image series that Bi tended to move out of the GB and accumulate on both surfaces of the specimen. Individual atoms were seen to move between image acquisition steps at 200 kV. This movement and rearrangement of Bi may be brought about by the diffusion of Bi to GB surface locations on the top and bottom of the specimen, as seen in Figure 66. During the specimen preparation—in particular the FIB final thinning—the ratio of surface area to volume of the specimen is greatly increased. Bi, with its large atomic radius which may strain the boundary, may diffuse to areas near the GB and specimen surface to take advantage of the extra degree of freedom associated with the surface. Once Bi atoms are at these near-surface locations on the GB, the Bi atoms, induced by the high energy electron beam, may be moved farther out and along the surface of the specimen. Bi atoms observed at positions
through the boundary far from the specimen surface did not move as easily as those at positions near the surface and were able to be imaged multiple times. Experiments were also conducted at an accelerating voltage of 80 kV to reduce the energy transfer to the Bi. Under this condition, no Bi atoms were seen to move and relocate along the surface; however, depth resolution at 80 kV is greatly degraded due to the longer wavelengths of the electrons constituting the electron beam.
Figure 66 - An inclined Bi-doped Cu [001]/33° twist bicrystal boundary viewed by HAADF-STEM imaging with an electron probe focused on (a) the top surface and (b) the bottom surface of the specimen.
Figure 67 - Selected images from a STEM TFI image series with black arrows indicating the depth of the probe focal point moving toward bottom surface of specimen from the top surface. An individual Bi atom is indicated with a red arrow as it is resolved during the image series.
Figure 68 - Sum STEM TFI image showing Z-contrast lateral atomic resolution (Top) with extracted x plane projections showing Bi atomic positions through thickness of the specimen (Bottom), with reference axes (Left)
Figure 69 - Intensity profiles taken from the x plane projection of a sum STEM TFI image from a STEM TFI image series acquisition showing FWHM imaging intensity of (a) a Bi atom near the top surface of the specimen, (b) a Bi atom in the interior of the specimen, and (c) a Bi atom near the bottom surface of the specimen. FWHM values are plotted against Bi position from the top surface in (d) showing increasing FWHM as Bi atoms farther into the depth of the specimen are imaged.
Figure 70 – HAADF-STEM images of two observed atomic configurations of Bi atoms along a 33° Cu twist bicrystal with the depth of the atoms determined through STEM TFI. (a) corresponds to an atomic arrangement yielding 0.02 monolayers of Bi and (b) corresponds to an atomic arrangement yielding 0.09 monolayers of Bi.
5.5 Electronic structure at the Cu GB

To observe changes in the electronic structure at the GB in the pure and Bi doped conditions for the Cu bicrystal specimens, EELS was used in consultation with Dr. Herzing at the National Institute of Standards and Technology. The goal here being to replicate the work done by Duscher et al. and determine if, indeed, there is any change in the Cu L\textsubscript{2,3} energy-loss near edge structure when Bi is added to the Cu GBs. In this section, the EELS spectra for the GB specimens will be presented and their attributes discussed in terms of possible implications of the electronic structure at the Cu GBs as well as difficulties in direct comparisons to previous work done by Duscher et al. (2004) and Keast et al. (2007).

To begin discussion of the EELS results, the method of comparing the GB to the bulk Cu material must be discussed. The GB of the specimens is extremely limited in spatial extent and only occupies a very small portion of the atoms in any EELS spectral image (SI) or raster scan taken over a boundary area. When comparing EELS spectra from a GB region to those from a bulk area, detailed care needs to be taken to remove (or attempt to) the influence of the bulk-like material inherently occupying a large portion of the volume of the material probed in a GB EELS SI. To do this a 3-spectra technique is employed [46]. With this technique, 3 spectra—one from the GB and one from each side of the GB in the bulk material—are obtained under identical acquisition parameters. Once the spectra are acquired the two bulk spectra can be averaged together to approximate the contribution of the bulk-like material to the GB spectrum. By determining the difference between the average bulk spectra and the GB
spectra, the influence of the bulk-like material at the GB on the GB spectra can be removed, ideally leaving behind only EELS information from the GB itself.

The Bi doped 6º EELS results are shown in Figure 71. Here the intensity of the GB spectrum is slightly under the intensity of the bulk spectrum. This drop in intensity at the GB may be an artifact of the 3-spectra method, occurring if the 3 analyzed areas are not of uniform thickness. Due to the milling process in TEM specimen preparation in this study, a change in thickness occurs across the GB. This change in thickness is a result of preferentially fast milling in one grain over the other, due to the change in crystallographic direction along the milling direction across the GB. As a result of the change in thickness across the GB, the analyzed areas used to form the average bulk contribution may not be uniform in thickness; this will then skew the bulk average spectra higher than what actually may be the average contribution at the GB itself. To help mitigate this effect the three spectra used in this analysis were normalized using the post-edge intensity over a range of 20 eV beginning at 1060 eV; though this post-edge normalization did not always completely remove the effect. In the case of the doped 6º EELS results, the lower value of the GB spectrum is consistent; there is no change in the spatial difference spectrum throughout the Cu L_{23} edge though the spatial difference is non-zero. This relatively constant spatial difference for the 6º Cu specimen indicates that there is no effect of Bi on the electronic structure at the GB. Though there is no effect of Bi observed, EELS alone cannot eliminate the possibility of there being Bi present at the GB.
The Bi doped 13° Cu bicrystal GB showed results similar to that of the 6° Cu bicrystal GB. The EELS spectra for the 13° Bi doped GB are presented in Figure 72. The spectrum collected on this GB matches very well with the bulk average spectrum and also shows little variation from that average leading to a near zero spatial difference spectrum. Though Bi is known to be on specific facets in this GB, as evidenced by HAADF-STEM imaging, there appears to be no effect of the Bi on the GB region observed. The lack of an electronic effect can be interpreted three ways: the amount of Bi on the GB is not sufficient enough to statistically appear in EELS spectra, the Bi is not on the GB in the observation area, or the Bi has no effect on the electronic structure at the GB. Additionally, if the 13° Cu bicrystal GB is found to be embrittled through the micromechanical DENT specimen, as is suggested in the SENT specimen results, then the electronic structure argument can be dismissed as the primary cause of GB embrittlement in the Cu-Bi system.

The doped 33° Cu was the only GB orientation studied that showed a significant change in the spatial difference spectrum. Figure 73 shows the three spectra collected on a Bi doped 33° Cu bicrystal GB. In this figure the spatial difference is larger at the onset of the L_{23} edge when the spatial difference is found by subtracting the GB intensity from the bulk, indicating a decrease in the “white line” at the GB compared to the bulk material. This white line indicates electron orbitals in the 4d electron shell that are vacant and promotion from the 2p electron shell to the 3d electron shell is possible. An increase in the likelihood of this 2p to 3d transition leads to an increase in the intensity of the onset of the L_{23} energy edge of a spectrum [48]. If
this particular transition is less likely to happen in the GB of the material compared to the bulk of the material, then the spatial difference spectrum will also have an increased intensity at the energy location corresponding to the “white line”. Figure 73 shows an overlay of the 3 spectra forming the spatial difference taken of the GB and bulk material in a Bi doped 33º Cu bicrystal. The increase in the spatial difference spectrum at 931 eV can be clearly seen while the rest of the spatial difference remains relatively flat until the second discrete shell transition at 952 eV. This may indicate that the presence of Bi at the GB causes a higher occupancy of 3d electron states in the Cu, opposite the trend observed by Keast et al.

If Bi at the GB is donating a partial electron to the atomic orbitals of the neighboring Cu atoms, partially filling the one remaining vacant 4s electron orbital in Cu, then hybridization between the 3d and 4s orbitals could be expected to decrease resulting in a decrease in the “white line” of the absorption edge as the 3d orbitals are now completely full [70]. This is equivalent to the argument that the Cu bonds are weakened by being donated a partial electron from the Bi atom causing the 4s antibonding state in the Cu to become partially full [87]. The problem with this argument is that Cu typically displays no “white line” as the 3d shell is usually full in the bulk material.

To investigate the reason for the occurrence of a “white line” in the near edge structure taken in the doped 33º Cu bicrystal, results of 3-spectra analysis were compared with similar results from the pure GB. This also has the effect of observing
changes occurring in the spatial difference spectrum when Bi is added to the specimen. Figure 74 and Figure 75 show two sets of different 3-spectra analysis performed on a pure 33° Cu bicrystal specimen. In Figure 74 the bulk average spectrum is larger than that of the GB spectrum while the opposite trend can be found in Figure 75. In both of these figures a prominent peak is seen at the L₃ onset energy, indicating that both on and off the GB there seems to be a depletion in the occupancy of 3d states for the Cu. A surface oxide is one possible explanation for this observation, as both cupric oxide and cuprous oxide lead to dramatic increases in the “white line” of the L₂3 energy edge. Upon comparison of results from 3 EELS spectra in the pure and Bi doped 33° Cu bicrystal specimen, it is apparent that an oxide is present on both samples. This makes it very difficult to form any hard conclusions from these spectra as the potential contribution of the Bi to the spectra observed at the Bi is distorted by the contribution of any oxide film present on the surfaces of the specimen.
Figure 71 – 3 EELS spectra from a Bi doped 6° Cu GB overlay showing the bulk, GB, and spatial difference (bulk spectrum less the GB spectrum).
Figure 72 - 3 EELS spectra from a Bi doped 13° Cu GB overlay showing the bulk, GB, and spatial difference (GB spectrum less the bulk spectrum).
Figure 73—3 EELS spectra from a Bi doped 33° Cu GB overlay showing the bulk, GB, and spatial difference (bulk spectrum less the GB spectrum).
Figure 74 – 3 EELS spectra from a pure 33° Cu GB overlay showing the bulk, GB, and spatial difference (bulk spectrum less the GB spectrum).
Figure 75 – 3 EELS spectra from a pure 33° Cu GB overlay showing the bulk, GB, and spatial difference (GB spectrum less the bulk spectrum).
5.6 GB compositional analysis via XEDS

Of great importance in this study is how the chemical composition changes across and along the GB in the specimen. These compositional changes may occur over very limited spatial extents (less than 2 nm), and may also be very great in magnitude. To study these changes with the appropriate spatial resolution required to isolate their precise location, XEDS using TEM and STEM was performed.

Initial qualitative observation of the GB was performed via TEM using a condensed beam placed over the GB area, which was conducted to see if any signal from Bi could be observed on the GBs, similar to the analysis done by Armstrong et al. [74]. No useful Bi signal from the GB was detectable through this method in the 6° Bi doped Cu bicrystals. Two spectra from a Bi doped 6° Cu bicrystal specimen are shown in Figure 76 and Figure 77; there are no observable bismuth peaks at any of the X-ray energy values corresponding to Bi. The Bi doped 13° Cu bicrystal GB occasionally showed possible trace amounts of Bi X-ray signals. Figure 78 and Figure 79 show a spectrum from a Bi doped 13° Cu bicrystal GB. In this spectrum a very low signal can be seen at the expected X-ray energies for Bi L lines, meaning that Bi (in a qualitative sense) may be detected on the GB. To actually determine if the signal can be attributed to the presence of a small amount of Bi, the intensity of the Bi peak above background can be compared to the background intensity under the Bi peak in quantitative manner through Equation 26 [88].

\[ I = 3\sqrt{2B} \]
Where $I$ is the Bi peak intensity above background over an energy range, and $B$ is the integrated background average of a pre and post peak energy window of the same energy width as that of $I$. This detectability criterion was not met for the $6^\circ$ and $13^\circ$ Cu GBs, indicating that there is either no Bi on the GB or the Bi present on the GB is below the detectability under the experimental conditions. The first possibility of no Bi on the GB cannot be ruled out for the $6^\circ$ GB since no direct imaging of Bi was possible. Bi was, however, directly imaged on the $13^\circ$ GB meaning that the amount of Bi on the GB investigated was too low to be detectable, or possibly, the GB inclination led to a decreased Bi signal with less Bi in the beam interaction volume at any given point when compared to an edge on GB.

The Bi doped $33^\circ$ Cu showed the presence of detectable Bi on the GB in accordance with Equation 26. Figure 80 and Figure 81 show two spectra collected from spot analysis on a Bi doped $33^\circ$ Cu GB with and without peak labels, respectively. Long acquisition times were not needed to resolve Bi peaks above the background X-ray intensity if an electron beam of sufficiently small diameter was placed over the Cu GB with point spectra being collected for 100 seconds live time. Following successful qualitative observation of Bi on the GB of the $33^\circ$ Cu GB via XEDS, quantification of the amount of Bi present on the GB was performed using the $\zeta$-factor technique described in section 2.5.2.

In order to determine the proper $\zeta_{\text{Bi}}$ factor, a specimen containing a known composition was needed. One of the few such materials is Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_{8+x}$ (BSSCO)
oxide. XEDS spectra were collected from a powdered form of this material mounted on a Ni holey Carbon grid in the JEOL JEM-ARM200CF for the purpose of developing a Cliff-Lorimer $k_{\text{BiCu}}$ factor. Figure 82 and Figure 83 show a BSSCO spectrum with and without elemental peak labels, respectively. Of interest in the BSSCO spectrum are the peaks of Cu Kα and Bi Lα. The Bi peak is relatively easy to extract and apply background subtraction due to the increased energy spacing between discrete electron shell transitions of higher energy; Bi Lα overlapped no other X-ray peak. The Cu Kα peak was much more difficult to decouple from the overlapping Ni Kβ X-ray peak. This Ni peak was a result of the use of a Ni holey C grid to support the BSSCO powder. Typical TEM grids manufactured with holey C are available in Ni and Cu. To accurately measure the Cu X-ray ratio to Bi, no Cu may be present in the grid supporting the BSSCO specimen, leaving Ni as the only economical choice of material for analysis (Be is also a candidate material but cost prohibits the use of this material unless absolutely necessary). Removing the contribution of the Ni grid to the X-ray intensity of the Cu Kα peak was accomplished in a two-step process. The first being to remove the background under the two overlapped peaks by modeling the background intensity using a pre and post peak edge and extracting the signal of the overlapped peaks; this process is shown in Figure 84. After the background in the two X-ray peaks was removed, the Ni Kβ X-ray peak was fit to a Gaussian distribution allowing the residual signal not encompassed in the Gaussian distribution to be removed, as demonstrated in Figure 85. This residual signal, when integrated over the peak energy window, is the Cu Kα X-ray intensity.
To accurately establish this $k_{BiCu}$ factor, multiple spectra were taken at various thicknesses in the BSSCO powder so that thickness variation effects in the individual spectra could be assessed and, if necessary, mitigated. As shown in Figure 86, there is a thickness dependence that decreases once the BSSCO powder is moderately thick.

Here the relative thickness can be determined by means of the Cu K$_\alpha$ X-ray peak intensities as all spectra were acquired for the same live time, beam current, and specimen tilt meaning that a higher number of X-ray counts is caused by increase in specimen thickness. To account for the thickness changes in the analysis areas when acquiring spectra from the BSSCO specimen, the average k factor and the associated error must be weighted to reflect the change in X-ray peak intensities with analysis area [61]. The weighted arithmetic mean of the measured k factor, $\bar{k}_{BiCu}$, can be calculated along with the k factors error, $\Delta k_{BiCu}$, with Equation 27 through Equation 30 shown below [89], [55]:

$$\bar{k}_{BiCu} = \frac{\sum_{i=1}^{n} w_i k_i}{\sum_{i=1}^{n} w_i},$$

*Equation 27*

$$w_i = \frac{1}{k_i \bar{c}_{Bi} c_{Cu} \left( \sqrt{\frac{2}{I_{Cu,i}}} \right)^2 + \left( \frac{2}{I_{Bi,i}} \right)^2},$$

*Equation 28*
\[ \Delta k_{BiCu} = (t_{95})^{n-1} \sqrt{\frac{s^2}{n}}, \]

Equation 29

\[ s^2 = \frac{\sum_{i=1}^{n} w_i}{(\sum_{i=1}^{n} w_i)^2 - \sum_{i=1}^{n} w_i^2} \sum_{i=1}^{n} w_i (k_i - \bar{k}_{BiCu})^2, \]

Equation 30

where \( w_i \) is the weight of the \( i^{th} \) k-factor measurement, \( k_i \) is the \( i^{th} \) k-factor measurement, \( C_{Bi} \) is the weight percent of Bi in BSSCO, \( C_{Cu} \) is the weight percent of Cu in BSSCO, \( I_{Cu,i} \) is the \( i^{th} \) intensity measurement of the Cu K\( \alpha \) X-ray peak above background, \( I_{Bi,i} \) is the \( i^{th} \) intensity measurement of the Cu K\( \alpha \) X-ray peak above background, \( n \) is the total number of measurements taken, \( (t_{95})^{n-1} \) is the Student’s t distribution value at a 95% confidence interval for \( n \) measurements, and \( s^2 \) is the weighted variance of the measured k-factors. The results of this analysis provided a \( \bar{k}_{BiCu} \) value of 3.23 with an error of ±0.03. Using this measured k-factor in Equation 19 with the previously measured \( \zeta_{Cu} \) K\( \alpha \) value of 279.6 ± 5.0 kg·electron/(m\(^2\)·photon), the value of \( \zeta_{Bi} \) L\( \alpha \) was calculated to be 902.3 ± 25.7 kg·electron/(m\(^2\)·photon).

With the \( \zeta \)-factor of both Cu K\( \alpha \) and Bi L\( \alpha \) determined quantitative compositional analysis of the Bi doped 33° Cu bicrystal GB was performed on XEDS maps of Bi doped 33° Cu bicrystal GBs inclined with respect to the optic axis. Figure 87 shows a BF-STEM image of one such GB with the region of interest (ROI) highlighted in red; the ROI is the area of acquisition for the XEDS map. Figure 88
shows a composite peak intensity map of the Bi and Cu X-ray peaks where the increase of the Bi signal at the GB can clearly be seen as well as the lack of much Bi signal elsewhere in the specimen as the Cu signal dominates outside of the GB. The peak intensity above background maps alone show an increase in Bi signal at the GB and a slight decrease in the Cu signal at the GB; however, to determine how the composition changes in a quantitative sense more analysis is needed.

The thickness of the Bi doped 33° Cu bicrystal determined by the $\zeta$-factor method is shown in Figure 89. In this figure the thickness can be seen to remain relatively constant in the left grain at approximately 15 nm. The thickness of the right grain is significantly larger at a value of 25 nm or greater. This change in thickness across the GB is a result of the FIB specimen preparation in which the crystallographic direction in each grain—relative to the milling direction—is very different, leading to a change in milling rates. The change in milling rates across the GB manifests itself in a thickness gradient across the GB as shown in Figure 89; the right side of the GB appears as thick as the right grain itself and the left side of the GB appears as one of the thinnest areas in the ROI.

With this thickness determined, quantitative descriptions of the composition can be generated. The first considered is the weight percent (wt%) of the Cu and Bi in the mapped GB region. The nearly pure Cu outside the GB is expected in the Cu-Bi system since Bi has an extremely low solid solubility in Cu. On the GB itself the wt% of Cu drops to a low of 70%. The Bi wt% map, shown in Figure 90, displays a near
inverse of the Cu wt% map. The Bi wt% climbs from near zero outside of the boundary to around 30% at some locations on the GB. It is also seen through the use of these two maps that there is an increase in the wt% of Bi at the edges of the GB shown in the map. This increase in Bi indicates that the Bi that resides on the GB is migrating to the top and bottom surfaces of the TEM specimen itself.

To improve accuracy in the compositional measurements of these maps, better counting statistics are needed, which can be performed by extracting an integrated line profile from the compositional X-ray maps. Each pixel in this integrated line profile was formed by taking the sum of 50 pixels perpendicular to the GB line. ζ-factor analysis was applied to the extracted line profile and generated a Bi wt% line profile as seen in Figure 91. In this plot the minimum mass fraction (MMF) of wt% Bi is overlaid on the Bi wt% profile to show the detectability of Bi across the GB. The MMF of Bi was determined by using Equation 31 [61].

\[
MMF_{wt\%\ Bi} = \frac{\zeta_{Bi}3\sqrt{2B_{Bi}}}{D_e\rho t}
\]

Equation 31

Where B_{Bi} is the average of the pre and post-peak background intensities of the Bi L\alpha X-ray line. Off the GB the Bi wt% calculated through the ζ-factor method is almost in the same range as the MMF or slightly less, which means that any Bi determined to be off the boundary is below the detectability limit, and hence can be excluded from analysis. Figure 91 clearly shows an enrichment of Bi on the GB near
the surfaces of the specimen as the XEDS map was taken over an inclined 33° Cu bicrystal GB. This enrichment of Bi is most likely due to electron beam induced migration of Bi atoms towards free surfaces during analysis and/or specimen preparation by FIB. The FIB preparation effectively increases the surface to volume ratio of the specimen providing ample room for Bi to migrate to and along the surface from the interior of the GB. The electron beam induced migration of Bi has been observed prior to XEDS in TFI where upon reimaging the specimen after an image series acquisition, Bi atoms were observed to have migrated along the surface of the specimen, occasionally rearranging themselves in periodic clusters. This Bi migration is significant even during relatively low dose imaging and especially when a higher probe current used as in XEDS. Increased Bi migration out of and away from the GB during XEDS most likely leads to Bi concentration values lower than those actually on the GB in the Cu GB specimen. With this in mind, the XEDS results should be viewed as a lower limit to the possible Bi concentration levels in the specimen.

With the Bi wt% of the integrated line profile obtained, the enrichment of Bi can be calculated using Equation 22 with the volume and area terms also determined for each point in the line profile, based on the specimen thickness determined through the $\zeta$-factor method. This analysis results in an excess Bi profile. To determine the bulk excess of Bi line profile, equal areas off the GB on both sides were averaged and subtracted from the total excess to yield only GB Bi excess as shown in Figure 92. With the excess Bi being contained to only on GB locations, the total GB excess from the inclined GB can be found by adding all of the points in the line scan. It is
important not only to add that the on-boundary points as the average excess across the
two bulk grains has been subtracted effectively negating any contribution from off
boundary locations. The total Bi GB excess was calculated to be $1.82 \pm 0.42$ Bi atoms
$\text{nm}^{-2}$. If a (001) plane is considered to be the plane that Bi predominantly inhabits, as
observed in HAADF & BF-STEM imaging, the calculated Bi GB enrichment
corresponds to $0.12 \pm 0.03$ monolayers of Bi.
Figure 76 - XEDS spectrum obtained on a Bi doped 6° Cu bicrystal GB showing the location of the Cu K\(_\alpha\) and K\(_\beta\) X-ray peaks along with the Mo K\(_\alpha\) X-ray peak originating from the Omniprobe half-grid.
Figure 77 - XEDS spectrum obtained on a Bi doped $6^\circ$ Cu bicrystal GB showing the location of the Cu $K\alpha$ and $K\beta$ X-ray peaks along with the Mo $K\alpha$ X-ray peak originating from the Omniprobe half-grid, additionally the energy location of the expected Bi peaks are labeled.
Figure 78 – XEDS spectrum obtained on a Bi doped 13° Cu bicrystal GB showing the location of the Cu Kα and Kβ X-ray peaks along with the Mo Kα X-ray peak originating from the Omniprobe half-grid and a Ga Kα X-ray peak originating from the FIB specimen preparation.
Figure 79 - XEDS spectrum obtained on a Bi doped 13° Cu bicrystal GB showing the location of the Bi X-ray energy peaks and possible small X-ray peaks due to Bi.
Figure 80 - XEDS spectrum obtained on a Bi doped 33° Cu bicrystal GB.
Figure 81 - XEDS spectrum obtained on a Bi doped 33° Cu bicrystal GB showing the location of the Cu and Mo X-ray peaks along with the Bi L\(\alpha\) X-ray peak significantly above the background of the X-ray spectrum.
Figure 82 – XEDS spectrum taken from a BISSCO powder specimen showing a typical spectra obtained from BISSCO powder of any thickness.
Figure 83 - XEDS spectrum taken from a BISSCO powder specimen showing a typical spectra obtained from BISSCO powder of any thickness with major X-ray peaks identified.
Figure 84 – XEDS spectrum showing the windows taken for background subtraction around the Cu $K_\alpha$ – Ni $K_\beta$ peak overlap highlighting the need to remove the Ni $K_\beta$ peak intensity from that of the Cu $K_\alpha$ peak intensity.
Figure 85 - XEDS spectrum showing the Gaussian fitting of the Ni Kβ peak leaving a residual signal or the Cu Kα X-ray peak with 1.2FWHM labeled as signal.
Figure 86 – Graph showing the relationship between Cu intensity in the measured X-ray spectra and the Cliff-Lorimer ratio of Cu $K_\alpha$ to Bi $L_\alpha$ calculated from the BISSCO specimen.
Figure 87 – BF-STEM image of a Bi doped 33° Cu bicrystal GB showing the region of interest (ROI) for a XEDS map.
Figure 88 – Color overlay (left) of X-ray signal intensity from Cu K_α X-ray line and the Bi L_α X-ray line (right).
Figure 89 – Thickness map of Bi doped 33° Cu bicrystal GB inclined with respect to beam direction.
Figure 90 – Bi wt% map of Bi doped 33° Cu bicrystal GB inclined with respect to beam direction.
Figure 91 – Integrated line profile extracted across the GB from Figure 90 showing both the Bi wt% with 95% confidence limits and the minimum mass fraction (MMF) at each point.
Figure 92 – GB Bi excess across GB in XEDS ROI with 95% confidence limits.
5.7 Comparison of GB compositional quantification through imaging and X-ray analysis

Through the experiments presented in this dissertation, the GB of the Bi doped 33° Cu bicrystal was quantified, in terms of GB coverage, through XEDS and STEM TFI. XEDS quantification of the GB yielded a monolayer coverage of Bi to be approximately 0.12 monolayers compared to a range of 0.02 – 0.09 monolayers determined via STEM TFI. This section briefly describes the reasons for the discrepancy in monolayer coverage determined through the two techniques and discusses the advantages of using one technique or the other in particular situations.

The STEM TFI technique is appropriate for determining GB coverage only when atomic resolution is possible in all 3 dimensions. To properly use this technique in determining GB coverage, the segregant atoms of interest must be sufficiently spaced apart in the z-dimension to allow the separation of atoms in this direction. In practical terms this means that the atomic spacing of atoms in a vertical line through the thickness of the specimen must be greater than the resolution of the technique; for example, in the JEOL JEM-ARM200CF using a 37 mrad beam convergence half-angle this spacing must be greater than ~ 5 nm. The use of a pseudo-plane-view projection (PPP), achieved by inclining the GB with respect to the optic axis of the microscope, may be helpful in providing lateral displacements of GB segregant atoms that would typically be vertically aligned on a GB. The PPP orientation can then be used in conjunction with STEM TFI to study GB segregant concentrations high
enough that individual atoms cannot normally be resolved in 3 dimensions. However, there still is an upper bound in GB segregant concentration that the STEM TFI technique cannot usefully distinguish between adjacent segregant atoms limiting the systems of study to those with less than ~ 25% coverage for close packed systems. This coverage percentage is an estimation for close packed metallic crystal structures where a 25% GB coverage is roughly equivalent to having 4 unit cells between solute atoms providing reasonable lateral spacing between atoms if the PPP orientation is used. Additionally, with higher boundary coverages the possibility of having two segregant atoms in neighboring lattice sites rises; this increases the overlap in HAADF signal from the two atoms making determination of their z-position extremely difficult. Systems with larger lattice spacings or more open crystal structures benefit from having a larger distance between atoms in the bulk material, and if GB segregation occurs substitutionally the segregant atoms will have a larger spacing, possibly allowing higher boundary coverages to be studied.

STEM TFI GB coverage determination is also limited by the field of view achievable at the high magnification required for atomic resolution imaging. While this high magnification can be useful in observing inhomogeneity in GB coverage over small spatial distances, as shown in Figure 70, it is not practical to study an entire GB through this technique as information over ranges of microns may be desired. For observation over larger distances, STEM XEDS provides a robust approach for determining average GB coverage information. In this study, XEDS was used at an intermediate magnification (1 - 3 MX) to observe several microns of the GB at once;
higher magnifications were not used due to the drift inherent in the long acquisition times needed to obtain sufficient enough X-ray counts for appropriate quantification. The high electron dose required for suitable X-ray analysis induces migration of solute atoms during acquisition, which has the effect of possibly lowering the quantified amount of segregant on the GB, thereby decreasing the measured GB coverage. XEDS in TEM also has a relatively poor MMF detectability compared to the detectability limits of bulk techniques such as EPMA. Segregant concentrations below ~5 wt% may not be quantifiable through this XEDS technique.

STEM TFI and XEDS quantification of GB segregation can be used as complimentary techniques. STEM TFI has a much lower electron dose suitable for study of segregant atoms that have a propensity to move when under an electron beam, such as Bi in Cu. STEM TFI also has a much higher sensitivity, being able to directly image individual atoms, meaning that cases of low-level segregation can be effectively studied. STEM TFI, however, can only be extended to homogeneous distributions of segregant atoms on GBs as it would be very labor intensive if it is applied to large areas of the GB. Here, XEDS is preferable for determining average GB coverage. In this study XEDS quantification was able to show an average GB coverage of 0.12 monolayers of Bi where STEM TFI showed 0.02 – 0.09 monolayers of Bi depending on what specific area of the GB was studied. Monolayer coverages were determined using the atomic planar density of the Cu (001) plane as representing one complete monolayer since Bi atoms were routinely imaged to inhabit lattice positions on the (001) plane, this results in an atomic planar density of 15.3 atoms nm\(^{-2}\) comprising one
complete monolayer. Previous work using XEDS mapping showed comparable numbers for GB segregation (0.05 – 0.7 monolayers) [65].

The observed difference between the Bi concentrations on the interior of the GB and the near-surface locations of the GB, observed through both STEM TFI and XEDS, indicates that the distribution of GB segregant atoms is not homogeneous in the single GB. This inhomogeneity in Bi distribution means that the specimens observed via TEM could represent a different GB distribution of Bi than is present in bulk samples. It remains unclear when during specimen preparation the migration of Bi to the surfaces of the FIB lamella specimen occurs. It is possible this migration is inevitable with specimens prepared at room temperature. If Bi at room temperature has enough kinetic thermal energy to diffuse at an appreciable rate, it may routinely migrate to areas of greater free volume, first to the GB and then to the surface of the specimen along the GB. Due to this migration, XEDS provides a more accurate assessment of the actual GB coverage as X-ray signals are taken from all of the Bi in the specimen and near the GB.

The GB coverage determined through XEDS provides a lower limit to the possible coverage of the GB in the bulk material. The coverage is considered as a lower limit due to the mobility of Bi under the electron beam; the longer acquisition times are needed (and/or the higher currents of XEDS analysis) cause some of the Bi to move out of the GB and along the surface of the specimen, potentially leaving the analysis area during the acquisition. The movement of the Bi from the GB results in a
lower collection of characteristic X-rays from the Bi than would be generated from a non-mobile segregant species.

Overall the combined approaches to measure GB coverage of Bi through STEM TFI and XEDS allow measurements to be performed over smaller spatial extents and at detectability levels higher than is capable using XEDS alone, and over a large portion of the GB generating average coverage values that are not capable by STEM TFI alone. The presence of migration from the interior of the GB to the surface and possibly away from the GB along the surface raise questions as to the absolute quantification previously performed and, indeed, if Cu-Bi specimens observed in past TEM investigations accurately reflect the composition, location, and electronic structure of Bi as it exists on bulk Cu GBs.

5.8 Interpretation of micro-mechanical testing results through STEM analysis

This section discusses results presented in sections 5.1-5.6 in terms of the significance of these results to the understanding of the Cu-Bi system and the GB segregation and GB embrittlement observed therein. Of particular interest is what can be determined about the relationship between the mechanical testing results of the Cu bicrystals and the structure and chemistry of the bicrystal as observed through TEM and STEM techniques.

Analysis of the misorientation across the Cu bicrystal GBs through EBSD and CBED patterns yielded similar results showing the bicrystal to have misorientations of
approximately 6, 13, and 33°. The CBED analysis showed slightly more accurate results and also allowed for misorientation measurements to be taken in a much closer proximity to the GB (< 20 nm) than the EBSD measurements. The misorientation resulting from CBED analysis also confirmed that the misorientation axis is close to, but not exactly, <100>. Due to the axis not being directly on the <100> direction, the bicrystals have a small degree of twist character; a possible source for the edge dislocations observed in the high angle GB though GB faceting is also capable of explaining the occurrence of edge type dislocations irrespective of the actual misorientation axis.

The mechanical testing conducted in this work has confirmed that the 33° twist bicrystals were embrittled upon Bi doping. This result is consistent with previous mechanical testing of Cu twist bicrystals insofar as the fracture toughness was observed to be reduced [73]. In contrast, unique to this study is the observed plasticity that was present in the micro-mechanical test specimens. Previous studies of Bi embrittled Cu showed no plasticity during mechanical testing once embrittlement was achieved through Bi doping; specimens were either brittle and broke immediately after exiting the elastic regime or they were not brittle and behaved as pure Cu would [74].

One possible mechanism helping to create an embrittlement effect due to Bi while still allowing the Cu bicrystal to remain somewhat ductile is the migration of Bi to dislocation cores due to the character of the dislocation and the available free volume at the dislocation core. During mechanical testing, this Bi migration causes the
pinning of these specific GB dislocations, increasing the energy required to move the dislocation. Bi atoms were directly imaged on edge dislocation structures on the Cu GB in the 33° bicrystals as shown in Figure 63. The Bi atoms appear to be surrounding edge dislocation cores. This result appears to be consistent with dislocation structures observed in Figure 46 where three different dislocation lines were images; the one parallel to the GB confirmed to have more edge character via HAADF-STEM and the other two dislocation lines ostensibly being screw character. Having large solute atoms on the edge dislocation cores may prevent the dislocation from moving along or from the GB when a crack is propagating along the GB. If the dislocation is prevented from blunting the crack tip due to the pinning effects of the Bi on the dislocation core, then GB cleavage may be a preferable mechanism to relieve localized stress at the GB in front of a crack, making brittle failure of the GB more likely. The possibility of solute dislocation interaction on the GBs in this system has not been previously studied, but provides a further enhancement of the Rice-Thomson model where GB facetting in the presence of Bi determines not only the available number of slip systems for dislocation motion near the crack tip but also a further embrittling effect if the GB facet contains a high number of dislocations with edge character. These edge character dislocations both accommodate a large amount of Bi on the GB and to also limit dislocation movement via solute pinning.

This dislocation pinning by solute atoms on the GB not only explains the reduction in fracture toughness observed on Cu GBs when exposed to Bi, but also explains the observed middling plasticity seen in the case of the 33° twist GB and the
non-embrittlement of particular other Cu GBs. The mechanical properties observed in the 33° twist bicrystal show that an intermediate level of “brittleness” is achievable in the Cu-Bi system through the introduction of secondary GB dislocations (SGBD) which then become pinned by the Bi atoms. SGBD are GB dislocations present on high-angle GBs (> approximately 10-15°) and are often observed between misorientations constituting special low energy CSL GB configurations [90], [91].

GBs in FCC materials of purely twist character form square networks of screw SGBDs and GBs of purely tilt character form edge character SGBDs [92], [93]. These dislocations serve to accommodate regions of the GB where slight deviation from “good fit” high CSL GB arrangements can be corrected by small rotational or tilt displacements of the atoms near the GB [94]. Consequently, the density of SGBDs increases as the misorientation of the GB diverges from low energy CSL arrangements as more SGBDs are needed to accommodate the mismatch across the interface. The faceting of the GB present in 33° twist bicrystals of Cu when exposed to Bi necessarily creates portions of the GB where the misorientation axis is not perpendicular to the GB plane as is typical in a twist bicrystal. The change in GB plane may provide GB structures with mixed dislocation character, in effect adding some tilt character to the GB. The addition of tilt character to the GB misorientation indicates the potential for edge character SGBDs to be present on portions of the GB. Such edge dislocations were directly observed on the 33° Cu bicrystal GB with Bi imaged at the dislocation cores. The intermediate level of brittleness measured on this GB is due to the primarily tilt character of the GB where the portion of dislocation
structures are able to accommodate Bi and then become pinned at the GB is not sufficiently high to cause a completely embrittled GB.

In addition to, or perhaps enhancing, the role GB faceting plays in the occurrence of edge character SGBDs on the 33° twist bicrystal, the slight deviation from the [100] axis in the misorientation of the crystal may also increase the likelihood of edge character SGBDs to form along the GB. This deviation from the [100] axis in effect adds a slight tilt character to the GB causing the formation of edge dislocations along the GB to be more likely. Regardless of the source of the dislocations observed on the 33° twist bicrystal, atomic resolution imaging shows evidence of Bi interaction with edge dislocations along the GB making a Bi induced increase in the energy required to move the GB dislocations likely. The presence of GB dislocation and solute interaction indicates that there may be a change in the energy required to move these dislocations and that calculations of the dislocation energy must take solute effects into account. Therefore, dismissal of a change in the energy to move dislocations as being a contributor to GB embrittlement cannot be simply dismissed as in Schweinfest et al. and their first principle calculations [50].

This edge dislocation pinning effect also explains the middling amount of embrittlement of the 33° twist bicrystal which is expected to have a large degree of screw character dislocations unable to accommodate Bi and a low density of edge character dislocations. The results from the mechanical testing of the twist bicrystals
presented in this and related work are lower than that observed in tilt bicrystals studies due to the increase in the edge dislocation character expected in tilt bicrystals [75].

6. Conclusions:

The work presented in this dissertation has allowed for the advancement of 3-dimensional atomic imaging of GB segregants in metallic systems via the STEM TFI technique which has been applied to the atomic characterization of a [001]/33° Cu bicrystal doped with Bi. Compositional characterization of the [001]/33° GB has confirmed observations of segregant migration. SGBDs have also been observed on this GB allowing a better understanding of the mechanical mechanisms responsible, in part, for the observed GB embrittlement of Bi in Cu. From this work the following conclusions have been made:

(1) Single dopant Bi atoms can be resolved along metallic Cu GBs in 3 dimensions using STEM TFI of traditionally FIB prepared TEM coupon specimens without the need to ensure the boundary plane is parallel to optic axis of the instrument. The PPP orientation of specimens increases the detectability of Bi atoms by laterally displacing atoms on the GB plane through the thickness of the specimen.

(2) The depth resolution of a single Bi atom in the JEOL JEM-ARM200CF aberration corrected electron microscope at 200 kV with a ~37 mrad probe-forming semi-angle is approximately 5 nm.
(3) There are no continuous layered Bi atomic arrangements laterally along the boundary or through the thickness of the boundary indicating that the embrittlement mechanism for [001]/33° and 13° Cu bicrystals doped with Bi is not dependent on the fracture of Bi-Bi bonds present in a prewetting GB film.

(4) Investigation of certain GBs may be aided by the use of an inclined GB with respect to the microscope optic axis allowing depth profiles of GB segregant atoms to be obtained along with information of the arrangement of segregant atoms that may not be available through an edge-on GB approach. The presence of segregant migration from the interior of GBs to the surface of the specimen observed through STEM TFI has been quantitatively confirmed via STEM XEDS.

(5) The Bi GB coverage of [001]/33° Cu bicrystal has been determined to have an average value of 1.82 ± 0.42 Bi atoms nm\(^{-2}\) corresponding to 0.12 ± 0.03 monolayers of Bi as measured by XEDS.

(6) STEM TFI measured GB coverage varied locally along individual GB facets indicating anisotropy of segregation even within a single GB facet with Bi planar atomic densities of approximately 1.37 – 0.28 Bi atoms nm\(^{-2}\) corresponding to coverage values of 0.02 – 0.09 monolayers of Bi.

(7) The resolution of Bi atoms on and around edge dislocation cores on [001]/33° Cu GB show interaction between Bi and SGBDs of edge character potentially increasing \(G_{\text{diss}}\) promoting GB cleavage as a mechanism for relieving stress at a crack tip along the GB.
(8) The presence of edge dislocations and their interaction with Bi on the moderately brittle 33° GB indicates that the embrittlement effect is related to how easily edge dislocations are incorporated into a GB. Twist bicrystals are then expected to have a lower degree of embrittlement which has been confirmed through the mechanical testing presented in this and previously related work where the fracture toughness of the twist bicrystals do not drop to the same severely embrittled level of tilt bicrystals.

7. Suggested Future Work:

To further understand the role that GB dislocations may play in GB segregation induced embrittlement, the detail influence of solute atoms to dislocations needs to be investigated. To begin, the activation energy for dislocation motion while dragging Bi solute in Cu needs to be calculated and compared to typical Cu dislocation activation energy. Essentially, this would be a slight modification of the work done by Wang and Anderson but now incorporating the role of Bi on GB dislocation cores. To experimentally validate these calculations, well defined GB geometries are needed that are known to display secondary GBs containing edge character. Obvious choices would be either low angle tilt GBs with sufficient edge dislocation density to allow Bi to embrittle the boundary (and to observe if it can with low angle tilt GBs) but not high enough to make routine observation of the dislocations difficult via TEM since dislocation spacing diminishes with increasing dislocation density.
The study of dislocations on the GB requires almost perfect plane view specimens making epitaxial growth of Cu thin-films followed by Bi doping via a precisely controllable atomic deposition process and finally welding the two crystals to form the GB interface. Formation of bicrystals through this method lends itself most easily to twist bicrystals; however, Cu crystals with well-defined orientation may be grown on other substrates, such as sapphire, allowing well defined tilt GBs to be formed [95]. This permits the formation of bicrystal specimens that need only release from the substrate to be studied via TEM. Mechanical testing specimens may also be formed, although the method of testing will need to be appropriate for both tilt bicrystals as well as thin-films. Ultimately, however, if the pure and doped GBs can be directly compared through any mechanical testing means and embrittlement is observed, then the testing has served a useful purpose even if dislocation energy information cannot be extracted. A study such as this would allow a much more detailed approach to investigating the dislocations, the GB, and their contribution to embrittlement. It would also allow comparison of dislocation activation energy to previous studies and other systems that exhibit GB embrittlement.
8. References:


232


9. Appendix:

1. MatLab code used for determining bicrystal misorientation:

```matlab
fprintf('\n Misorientation Calculation for Cubic Crystals \n \n');
% Camera length L should be constant for both patterns
L=input('Enter calibrated camera length for the kikuchi patterns:');
% First Grain Information
% XP_1 is the index of the kikuchi band
% ZP_1 is the index of the pole
% YP_1 is the cross product of ZP_1 and XP_1
% delta_1 is the angle between ZP_1 and XP_1 projections on
diffraction
% gamma_1 is the angle between XP_1 and XR on diffraction pattern
% For consistancy angles must be measured clockwise to avoid
negatives
% D_1 is the distance measured on the diffraction pattern between
the
% direct beam and the pole center
XP_1 =input('Enter kikuchi band vector for grain 1 seperate by
commas, ex. [1,1,1]:');
ZP_1 =input('Enter pole axis for grain 1 seperated by commas, ex.
[1,1,1]:');
YP_1 =cross(ZP_1, XP_1);
CP_1 =[ XP_1 /norm( XP_1); YP_1 /norm(YP_1);ZP_1/norm(ZP_1)];
delta_1 =((pi/180)*input('Enter delta angle for grain 1 in degrees:'));
gamma_1 =((pi/180)*input('Enter gamma angle for grain 1 in degrees:'));
D_1 =input('Enter distance from pole center to direct beam for grain
1:');
% Second Grain Information
XP_2 =input('Enter kikuchi band vector for grain 2 seperate by
commas, ex. [1,1,1]:');
ZP_2 =input('Enter pole axis for grain 2 seperated by commas, ex.
[1,1,1]:');
YP_2 =cross(ZP_2, XP_2);
CP_2 =[ XP_2 /norm( XP_2); YP_2 /norm(YP_2);ZP_2/norm(ZP_2)];
delta_2 =((pi/180)*input('Enter delta angle for grain 2 in degrees:'));
gamma_2 =((pi/180)*input('Enter gamma angle for grain 2 in degrees:'));
D_2 =input('Enter distance from pole center to direct beam for grain
2:');
% Alpha and beta calculation for grain 1
alpha_1 =asin((D_1*sin(delta_1))/((D_1.^2+L^2).^0.5));
beta_1 =atan((D_1*cos(delta_1))/L);
% Alpha and beta calculation for grian 2
alpha_2 =asin((D_2*sin(delta_2))/((D_2.^2+L^2).^0.5));
beta_2=atan((D_2*cos(delta_2))/L);
% Calculation of [A], [B], [C] for grian 1
```

234
A_1=[1,0,0; 0,\cos(\alpha_1), -\sin(\alpha_1); 0,\sin(\alpha_1), \cos(\alpha_1)];
B_1=[\cos(\beta_1), 0,\sin(\beta_1); 0,1,0; -\sin(\beta_1), 0,\cos(\beta_1)];
C_1=[\cos(\gamma_1), -\sin(\gamma_1), 0; \sin(\gamma_1), \cos(\gamma_1), 0; 0,0,1];
% Calculation of \([A], [B], [C]\) for grain 2
A_2=[1,0,0; 0,\cos(\alpha_2), -\sin(\alpha_2); 0,\sin(\alpha_2), \cos(\alpha_2)];
B_2=[\cos(\beta_2), 0,\sin(\beta_2); 0,1,0; -\sin(\beta_2), 0,\cos(\beta_2)];
C_2=[\cos(\gamma_2), -\sin(\gamma_2), 0; \sin(\gamma_2), \cos(\gamma_2), 0; 0,0,1];
% Calculation of rotation matrix \([PR]\), rotation from pattern to ref
PR_1=A_1*B_1*C_1;
PR_2=A_2*B_2*C_2;
% Calculation of rotation matrix \([CR]\), rotation from crystal to ref
CR_1 =PR_1*CP_1;
CR_2 =PR_2*CP_2;
% Calculation of missorientation matrix \([M12]\)
M12 =CR_2/CR_1;
% Define possible rotations for cubic system in 3-D array
rot_(:,:,1)=[1,0,0; 0,1,0; 0,0,1];
rot_(:,:,2)=[0,0,-1; 0,-1,0; -1,0,0];
rot_(:,:,3)=[0,0,1; 0,1,0; 1,0,0];
rot_(:,:,4)=[0,0,1; 1,0,0; 0,-1,0];
rot_(:,:,5)=[0,1,0; 0,0,1; 1,0,0];
rot_(:,:,6)=[0,0,1; 0,1,0; -1,0,0];
rot_(:,:,7)=[0,-1,0; 0,0,1; 1,0,0];
rot_(:,:,8)=[0,0,-1; 0,1,0; 1,0,0];
rot_(:,:,9)=[0,-1,0; 0,0,1; -1,0,0];
rot_(:,:,10)=[1,0,0; 0,0,1; 0,-1,0];
rot_(:,:,11)=[0,1,0; 0,-1,0; 1,0,0];
rot_(:,:,12)=[1,0,0; 0,-1,0; 0,1,0];
rot_(:,:,13)=[0,0,-1; 1,0,0; 0,-1,0];
rot_(:,:,14)=[1,0,0; 0,0,1; 0,-1,0];
rot_(:,:,15)=[0,0,-1; -1,0,0; 0,1,0];
rot_(:,:,16)=[-1,0,0; 0,0,1; 0,-1,0];
rot_(:,:,17)=[0,0,1; -1,0,0; 0,-1,0];
rot_(:,:,18)=[0,-1,0; -1,0,0; 0,0,-1];
rot_(:,:,19)=[-1,0,0; 0,1,0; 0,-1,0];
rot_(:,:,20)=[0,1,0; -1,0,0; 0,0,1];
rot_(:,:,21)=[-1,0,0; -1,0,0; 0,0,1];
rot_(:,:,22)=[0,1,0; 1,0,0; 0,0,-1];
rot_(:,:,23)=[1,0,0; 0,-1,0; 0,0,-1];
rot_(:,:,24)=[0,-1,0; 1,0,0; 0,0,1];
% Perform calculations involving M12 and rotation matrices
% Outputs are all possible rotation matrices, chi values,
eigenvalues and
% eigenvectors. eigenvectors are possible rotation axes associated
with
% a particular chi misorientation angle
for i=(1:24)
M12_(:,:,i)=rot_(:,:,i)*M12;
chi_(:,:,i)=(180/pi)*acos((trace(M12_(:,:,i))-1)/2);
[eigenvectors_(:,:,i),eigenvalues_(:,:,i)]=eig(M12_(:,:,i));
% fprintf('%n misorientation matrix 
');
M12_(:,:,i); % output off right now
fprintf('misorientation angle \n');
chi_(:,:,i); % output off right now
fprintf('Eigen Values for possible misorientaiton axes \n');
eigenvalues_(:,:,i); % output off right now
fprintf('Eigen Vecotrs representing misorientation axes \n');
eigenvectors_(:,:,i); % output off right now
end
10. Vita:

C. Austin Wade was born to Charles and Kay Wade in New Brunswick, NJ on July, 21st 1987. He was raised in Hopkinton, MA alongside his Jenifer, his sister. Austin attended Hopkinton High School for 4 years prior to graduating and enrolling in Lehigh University’s P.C. Rossin College of Engineering in the 2005 fall semester. After graduating with honors and receiving a B.S. degree in materials science and engineering in the spring of 2009 Austin began work toward a Ph.D. in materials science and engineering under the advisement of Professor Masashi Watanabe.