EFFECTS OF MICRO- AND NANO-STRUCTURE ON THE DEFORMATION RESPONSE OF A $\text{Ag}_{60}\text{Cu}_{40}$ LAMELLAR AND ROD-IN-MATRIX EUTECTIC ALLOY

BY

OWEN THOMAS KINGSTEDT

DISSERTATION

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Doctoral Committee:

Professor John Lambros, Chair
Dean Ian M. Robertson, University of Wisconsin - Madison
Professor Ioannis Chasiotis
Assistant Professor Huck Beng Chew
Assistant Professor Shen Dillon
Abstract

The presented work investigates the mechanical response of the silver-copper eutectic system (Ag$_{60}$Cu$_{40}$, subscripts indicating atomic percent) linking material deformation to microstructural properties. The Ag$_{60}$Cu$_{40}$ material system can be produced as either a multidirectional lamellar or unidirectional reinforcement-in-matrix micro-structure. Specimens of each micro-structure type were studied under quasi-static and dynamic loading conditions.

The first part of this work focuses on the study of the material with a multidirectional lamellar structure. Materials produced with this structure primarily consist of eutectic colonies of alternating layers of silver and copper with layer thicknesses between 35 nm – 200 nm. The orientations of the eutectic colonies are randomly distributed throughout the material resulting in the formation of boundaries between neighboring eutectic colonies which have different orientations with respect to each other. The strength of this material is shown to be strain rate insensitive over the strain rates studied ($10^{-3}$ s$^{-1}$ to $10^{3}$ s$^{-1}$). Comparisons are made between the Ag-Cu stress-strain response and literature stress-strain responses of nano-structured silver and nano-structured copper demonstrating the high strength of the multidirectional Ag-Cu system. Three primary deformation mechanisms that occur at increasing levels of strain at the specimen radial surface are identified: kinking, brooming, and interfacial delamination. At the specimen interior kinking is the only mechanism observed.

The second portion of this work examines the unidirectional reinforcement in matrix structure again for Ag$_{60}$Cu$_{40}$. This structure has a common (101) crystallographic direction matching the axial direction of the cast material. From a single casting specimens are machined such that loading along three directions oriented 1) parallel to, 2) at 45° to and 3) perpendicular
to the \{101\} can occur using dynamic loading. Through alterations in the solidification rate of the unidirectional cast material the micro-structure nominal feature size can be regulated obtaining castings with either 200 nm, 500 nm, 800 nm or 1.2 \( \mu \)m thick reinforcements. For each loading orientation the dynamic material response is presented with the observed internal and external deformation mechanisms. Comparisons of the recorded elastic modulus, yield strength, and strain hardening exponent are made over the loading orientations and nominal micro-structure feature sizes. Crystal anisotropy is used to account for variation in the observed elastic modulus of each loading orientation. Dislocation deformation mechanisms are used to explain the differences in the yield strength and strain hardening. The mechanical properties of the multidirectional lamellar structure are compared to the unidirectional material structure. The multidirectional material is shown to have a higher yield strength. The unidirectional material is shown to have greater strain hardening when microstructure features sizes are greater than 500 nm under certain loading directions.
To my parents:

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Chapter 1: Introduction

Current technologies require the development of materials that are capable of satisfying the stringent design requirements necessary for functionality in extreme environments. Extreme environments in the present context can be thought of as those that are characterized as having one or more of the following conditions: (i) high temperatures, (ii) corrosion, (iii) elevated radiation exposure, (iv) impact or shock loading. Examples of structures operating in extreme environments include the next generation nuclear reactors, spacecraft, orbiting satellites, and ballistic armor. The incremental improvements to material properties achieved through traditional strengthening techniques (e.g., precipitate hardening, alloying, micro-structure refinement) may not be sufficient for producing materials that meet the strict requirements of demanding extreme environment applications. Recent efforts by researchers at Los Alamos National Labs (LANL) [e.g., Misra and Kung 2001, Mara et al. 2008, Hoagland et al. 2004, Beyerlein et al. 2012, Wang and Misra 2011] on the study of nano- (<100 nm) and ultra-fine (100-500 nm) structured bi-phase multilayered materials has provided a starting point for the investigation of bi-phase material systems that possess a high density of heterogeneous interfaces.
as candidates for materials exhibiting far superior strength than traditional alloys. A specific focus of their work has been the understanding of relationship between material micro-structure and mechanical properties. The material systems studied at LANL will also be studied here as they provide promising candidates towards the development of materials for use in extreme environments. This introduction begins with a brief history of work on single phase nano- and ultra-fine structured materials that are precursory to the study of bi-phase nano-/ultra-fine structured materials.

1.1 Single phase nano-structured and ultra-fine grained materials

Nano-structured (NS) materials are defined as having at least one microstructural feature in the nano-scale (<100 nm) range. Depending on the dimension(s) that is on the nano-length scale there are four classifications of NS materials, (i) nano-particle reinforced, (ii) lamellar structures (iii) fibrous structures, and (iv) bulk nano-structured materials [Seigel 1994]. Ultra-fine grained (UFG) materials can be classified similarly with the smallest dimension between 100 nm and 500 nm. Of particular interest to the present work are the lamellar and the fibrous structures. A lamellar structure consists of alternating layers that have a thickness at the nano/ultra-fine length scale, but much greater layer length and width. A fibrous structure consists of rods or platelets with two dimensions on the nano-/ultra-fine length scale surrounded by a continuous matrix.

Nano-structured materials became of interest after the initial work of Gleiter [1981] on inert gas consolidated nano-structured materials which demonstrated nano-structured materials can possess dramatically different mechanical properties compared to their coarse grained counterparts [Gleiter 1989]. Since their inception active research has been conducted in synthesis
techniques, characterization, and understanding the relationship between nano-structure and material properties. The following is a limited summary of the work conducted on single phase nano-/ultrafine grained materials that relates to the present effort.

1.1.1 Synthesis techniques of NS and UFG materials

Production methods for nano-/ultra-fine structured materials can be classified into “bottom up” techniques where materials are built up from assembly of atoms into nano-scale groupings that require subsequent consolidation through mechanical means or deposition, or “top-down” methods that start with a bulk solid material and through mechanical loading or phase transition obtain the appropriately structured material [Zehetbauer and Zhu 2009].

Commonly used “bottom up” techniques that do not require consolidation include electrochemical synthesis (e.g., aqueous electrodeposition) and vapor phase processing (e.g., physical vapor deposition (PVD)). In aqueous electrodeposition a current is applied to a plating system consisting of a conductive substrate submerged in a solution containing metal ions. The applied current causes deposition of a pure metal or alloy on the cathode (substrate). With careful control over the bath composition, pH, temperature, and current density nano-structured materials can be deposited on the substrate [Erb 1995]. Physical vapor deposition techniques such as sputtering occur in a vacuum chamber and rely on magnetron assisted energetic collisions of Argon plasma with a solid metallic target. The high energy collisions result in the ejection of atoms from the target material surface. The target material atoms then deposit on a substrate [Madou 1997]. By controlling the processing parameters, such as substrate heating [Banerjee 2007], deposition angle, or gas pressure [Karabacak et al. 2004] nano-structured films can be produced. Bottom up techniques satisfy the need to have fine control over the produced
nano-structure, but are difficult to scale up for the production of bulk materials. Materials produced are typically limited to thin film coatings on the order of microns.

The relevant “top down” techniques used to produce single phase nano-/ultra-fine grained materials are severe plastic deformation (SPD) techniques. The underlying micro-structure of materials is refined by severe plastic deformation imparting large values of strain, on the order of single digits, to the material [Zehetbauer and Zhu 2009]. In equal-channel angular pressing (ECAP) [Segal 1981] a billet of material is forced through a die with two intersecting channels at a specific angle, typically 90 degrees. The material billet is passed through the die multiple times with a ¼ or ½ rotation of the material after each pass. After a sufficient number of passes the micro-structure of the material is refined to the ultra-fine grained scale 200-300 nm [Valiev 2000]. In high pressure torsion (HPT) [Smirnova et al. 1986] a thin material disk is held in compression between two platens, one of which can rotate. By applying compression and torsional rotation large values of strain are imparted on the specimen from surface friction forces. The applied strain is non-uniform over the radius of the material and increases continually radially, with zero strain applied at the center [Zhilyaev and Langdon 2008]. HPT is capable of refining single phase metals to grain sizes of ~100 nm [Valiev 2000]. The final obtained micro-structure depends on the SPD method used (ECAP vs. HPT), the processing regimes, material composition, and initial micro-structure [Valiev 2000]. Each material will have a unique micro-structure including high dislocation density, non-equilibrium (intragranular) grain boundaries and dislocation cells [Zhu et al. 2001]. As a result of their refined structure SPD produced specimens have higher strength and improved ductility over those produced using the initial compaction methods employed by Gleiter [Zehenter and Zhu 2009].
1.1.2 Properties of NS and UFG materials

The material micro-structure at any length scale, whether coarse grained, UFG, or nano-grained, influences material response to loading. The refined nano-/ultra-fine grained structure causes the material micro-structure to have a high density of interfaces. Interfaces occur as grain boundaries, phase boundaries or surfaces. The response of nano-structured materials is dominated by the high density of interfaces leading to extraordinary properties that far exceed those of their coarse grained counter parts [Beyerlein et al. 2012]. Properties that have seen such improvement are corrosion resistance [Kim et al. 2003], diffusivity [Wang et al. 1997], hardness [Gleiter 1989], and strength [Gleiter 1989].

Of the properties that have shown improvement with refined micro-structure the one of principle interest to the present work is mechanical strength. As the material grain size is reduced to the nano-scale there is essentially a continuous increase in the observed mechanical strength, the Hall-Petch behavior [Hall 1951, Petch 1953]. The Hall-Petch behavior is attributed to the interaction of dislocation pile-ups with grain boundaries which provide increased resistance to plastic flow. The continuous increase in mechanical strength with decreasing grain size has been experimentally observed to break down at length scales below ~10 nm - 20 nm [Chokski et al. 1989, Seigel 1994]. Below these length scales the mechanical strength decreases with decreasing grain size and therefore the Hall-Petch slope of strength vs. (grain size)^{-1/2} becomes negative.

The softening that is seen at such small grain sizes is thought to be caused by the greater fraction of atoms at grain boundaries in nano-structured compared to coarse grained materials. This softening ultimately imposes a limit on how strong nano-crystalline metals may become [Schiotz et al. 1998].
1.1.3 Changes in deformation mechanisms at the NS/UFG length scale

The NS/UFG material property improvements arise from deformation mechanisms that differ from those of coarse grained materials. In general for larger NS grains (50 nm - 100 nm) dislocation processes dominate deformation. As the grain size of NS FCC metals decreases dislocation slip may become less significant and other deformation mechanisms may become more significant, such as partial dislocation slip and deformation twinning. Deformation twinning results in the local rotation of the crystal orientation where dislocation slip does not. The deformation twins that form provide additional barriers to dislocation slip since the rotated crystal structure within the twinned region no longer has slip systems that coincide with the non-twinned region. Copper is a prime example of a material that exhibits a change in the dislocation deformation mechanisms with decreasing microstructural length scale. It is well established that coarse gained copper does not deform by twinning [Hansen and Ralph 1982] due to multiple slip systems which can be activated [Hirth and Lothe 1992], except for cases of very high strain rate loading [Gray et al. 1989, Cao et al. 2010, Meyers et al. 1995] or low temperature loading [Blewitt et al. 1957]. Conversely NS copper deforms via twinning [Chen et al. 2003, Wang et al. 2002, Wang and Huang 2004], with an ideal grain size to promote twinning of 80 nm [Zhang et al. 2010].

At grain sizes less than ~30 nm grain boundary based deformation processes dominate leading to the reversal of the Hall-Petch strengthening effect [Wolf et al. 2005]. There still exists some debate over the active deformation mechanism at this length scale. Grain boundary diffusion creep has been supported by experimental [Gertsma et al. 1994, Masamura et al. 1998] and simulation studies [Yakamov et al. 2002a]. Alternatively, it has been proposed that grain
boundary sliding is responsible for the reversal in the Hall-Petch strengthening effect [Siegel 1997, Schiotz et al. 1998, Swygenhoven 2002].

1.1.4 Limitations

While single-phase nano-structured materials provide an interesting class of materials that shows promise for utilization in the design of materials for extreme environment applications they inherently have limitations because of their refined micro-structure and synthesis techniques. Pure NS metals have been observed to exhibit decreased ductility [Zhu and Liao 2004, Zhao et al. 2006] and reduced strain hardening rates [Dieter 1986]. They occur as a result of the lack of accumulation of dislocations at the grain interior when grain sizes are less than 100 nm, or through saturated dislocation densities in grains above 100 nm in size [Zehetbauer and Zhu 2009]. Of principle concern in terms of widespread use of such materials is the fact that micro-structures of NS and UFG materials are unstable at room temperature [Hegedus et al. 2011] and above [Ma 2003, Koch 2003, Sanders 1997, Weertman et al. 1999] leading to a relaxation of the observed beneficial mechanical properties. It is in part for these reasons that the present work focuses on the study of a specialized subclass of nano-scale materials: metallic nano-/ultra-fine composites.

1.2 Nano-/ultra-fine composite materials

In pursuit of the design of a stronger solid material Koehler [1970] suggested using alternating layers of materials with high and low elastic constants. Through this combination of materials it was demonstrated that high stress is required to drive deformation from one layer to another. The principle requirement of the Koehler-proposed layered arrangement is that the
thickness of each layer must be sufficiently thin, on the order of 100 atomic layers thick or less, such that dislocation generation does not occur. Through this formulation Koehler provided a theoretical basis for the design of multilayered metallic nano-composite materials.

Nano-/UFG composites (UFGC) combine multiple materials in a variety of forms, two of which are directly related to the present work: (i) lamellar and (ii) rod-in-matrix. Since the micro-structure features are at or below the ultra-fine length scale these composites possess a high interface density. Instead of the interfaces primarily occurring in the form of grain boundaries, as in single-phase NS and single-phase UFG materials, they occur as bi-phase interfaces. The principal benefit of studying UFGCs originates in the ability to tailor the bi-phase interface. Through careful selection of materials and synthesis techniques the bi-phase interface can be designed to optimize bulk composite materials to withstand severe environments. Design goals of bi-phase interfaces include the hindering of dislocation motion and the ability to absorb/eliminate defects at the interface providing a healing mechanism to the composite [Beyerlein et al. 2012].

Nano-composite materials can be produced in bulk or non-bulk forms through a number of synthesis techniques. For brevity only those pertaining to relevant previous studies and the current work are covered. Bulk synthesis routes of interest are accumulative roll bonding (ARB) and direct solidification from a eutectic composition melt. The non-bulk techniques are primarily PVD based such as magnetron assisted sputtering.

Accumulative roll bonding [Saito et al. 1999, Tsuji et al. 2002] is a SPD technique in which two material plates are stacked and then rolled to a reduced thickness initiating bonding between the layers. The material is then sectioned, stacked, and rerolled. This process is repeated until the desired layer thickness is achieved. The interfaces that exist between the materials are
mechanically driven allowing for the formation of non-energetically favorable interfaces to form [Demkowicz and Thilly 2011, Kang et al. 2012]. ARB is capable of producing large sheets of material permitting testing of bulk material properties of nano-layered solids.

Direct solidification of material to form composites was first realized by Kraft [1964]. In this process materials at the eutectic composition are melted, generally under vacuum, and then solidified either rapidly through quenching or gradually by the Bridgman technique [Bridgman 1925]. Under rapid solidification conditions the silver-copper system forms a lamellar eutectic with a cellular structure [Shen et al. 2005]. Each eutectic cell consists of alternating phase layers with thicknesses of 35 nm - 200 nm. The randomness of the solidification process initiation leads to the eutectic cells occurring with random orientations across the material. During solidification the eutectic cells meet resulting in a complex hierarchically structured material. Gradual solidification of the silver-copper system leads to the development of a reinforcement-in-matrix structure with a \{101\} crystal growth direction aligned to the rod axis [Cline and Stein 1969]. The lamellar spacing and the rod diameter can be controlled in a limited fashion through the rate at which the melt is removed from the furnace with greater removal rates generating finer material micro-structure sizes. The bi-phase interfaces of the directional solidified materials are well characterized [Eftink 2014].

Non-bulk nano-layered materials can be deposited as a multilayer thin film. The most popular technique for this is magnetron sputtering using multiple source target materials. A shutter system is used to prevent the deposition of both targets simultaneously allowing for the deposition of alternating material layers by alternating opening and closing of shutters. Sputtering allows for the greatest control over the layer thickness, with the trade-off of only being able to create composites with thicknesses of a few microns. The bi-phase interfaces that
exist in sputtered multilayer materials can match those obtained by solidification techniques. Due to the high level of control of layer thicknesses and the number of materials that can be deposited sputtering has been used extensively to create multilayer materials for study.

1.3 Previous Multilayered Ultra-fine/Nano-composites Studies

During plastic deformation interfaces can act as sources of defects, barriers to dislocation motion, and sites that consume dislocations through absorption, or decimation. There has been significant research effort in understanding the relationship between the spacing and atomic scale structure of bi-phase interfaces to parent composite material properties. These studies have looked to move beyond the initial phenomenological treatment of interfaces [Hirth 1972], such as in the Hall-Petch scaling law where interface spacing is related to strength without accounting for the interface structure.

1.3.1 Dislocation mechanisms at reduced length scales

A number of material systems have been studied using nanoindentation [Oliver and Pharr 1992, Oliver and Pharr 2004] to probe hardness changes of multilayer PVD deposited systems with respect to decreasing layer thicknesses, see Figure 1.1 [Misra et al. 2002]. Hardness measurements obtained by nanoindentation provide a measure of the resistance to permanent shape change. Using the Tabor relation \( \sigma_y \approx H/3 \) the measured hardness \( H \) values can indirectly be related to yield stress \( \sigma_y \) [Tabor 1951]. For each of the material systems presented in Figure 1.1 there is an increase in the measured hardness as the layer thickness decreases with a maximum strength occurring at layer thicknesses of a few nano-meters [Misra and Kung 2001]. The solid lines with continuous slope shown for thicknesses down to \( \sim 50 \) nano-
meters are the Hall-Petch trends for each material system. Below a thickness of the ~50 nm the Hall-Petch response no longer provides an accurate estimate of the material hardness. Misra et al. [2005] proposed dislocation-based mechanisms that depend on individual layer thickness, segmented into three distinct regimes that are responsible for the observed strength increase as layer thickness decreases, see Figure 1.2.

**Figure 1.1**: The nanoindentation measured hardness of copper-X (X = Cr, Nb, Ni, or Ag) multilayer systems at decreasing layer thicknesses [Misra et al. 2002].
Figure 1.2: Proposed dislocation deformation mechanisms of multilayered materials at decreasing length scales [Misra et al. 2005].

In the micron to sub-micron regime, the dislocation pile-up based Hall-Petch relation adequately predicts the strength response as a function of layer height (\( \sigma \propto h^{-1/2} \)). In the Hall-Petch model dislocations gather at bi-phase interfaces until the summation of the applied stress and the stress concentration caused by the dislocation pile-up exceed the barrier strength of the interface. Once the barrier strength is exceeded transmission of dislocation slip across the interface takes place. As the layer thickness decreases, the number of pile-up dislocations decreases resulting in a lower stress concentration [Hoagland et al. 2004] necessitating higher applied stresses for the transmission of slip across the bi-phase interface.

At layer thicknesses of a few tens of nano-meters to a few nano-meters the Hall-Petch model over predicts material strength. Over this regime dislocation pile-ups do not form and therefore the dislocation mechanism proposed involves the glide of single loop dislocations within individual layers parallel to the bi-phase interface termed confined layer slip (CLS).
Dislocations primarily originate from the bi-phase interface [Anderson et al. 1999] since the grain boundaries within layers are spaced multiple layer thicknesses apart [Beyerlein et al. 2012]. CLS models have been refined, now fitting observed strengths over layer thicknesses of 5 nm–100 nm [Misra et al. 2005]. CLS models breakdown below thicknesses of ~5 nm predicting strengths that deviate from those experimentally observed indicating a transition to interface crossing of individual dislocations.

At layer thicknesses between 2 nm–5 nm multilayer materials exhibit maximum strength. The peak stress of a multilayer material is determined by the stress required to transmit a single dislocation across the bi-phase interface [Misra et al. 2005]. Dislocation transmission across an interface requires alignment of the slip systems on each side of the interface. Interfaces that are weak in shear are more difficult for dislocations to cross. When a dislocation approaches an interface weak in shear it dissipates energy by shearing the interface and the dislocation gets absorbed. Conversely, if the interface is strong in shear, dislocations will cross the interface due to the reduced core spreading that occurs at the interface [Beyerlein et al. 2012].

The proposed dislocation mechanisms illustrated in Figure 1.2 are generic and may not fully capture factors that could be important to different structured multilayered material systems. For example it has been observed that the single loop dislocations in confined layer slip may span multiple layers [Philips et al. 2003]. Differences in elastic modulus between neighboring layers [Embury and Hirth 1994], residual stresses inherent to material production [Misra et al. 2000], and the structure of the bi-phase interface are also not considered.
1.3.2 Bimetallic interface structures

The structure of the bi-phase interface dictates how dislocations interact with them influencing propagation and nucleation at the interface. Such differences in dislocation mechanisms lead to differences in the mechanical responses of multilayered material systems. Bi-metallic systems are classified into two different interface types: incoherent and coherent. Incoherent systems have larger lattice parameter mismatch and different crystal structures resulting in discontinuous slip systems across the interface. Coherent systems have smaller lattice parameter mismatch with the same crystal structures resulting in continuous slip systems across the interface.

The copper-niobium (Cu-Nb) fcc/bcc nano-structured material system is an example of a material system with incoherent interfaces. It exhibits high strength [Clemens et al. 1999, Aydiner et al. 2009], improved ductility [Mara et al. 2008], and shock resistance [Han et al. 2011] greater than each of its components. The fcc/bcc interface of the Cu-Nb system has the Kurdjumov-Sachs (K-S) orientation [Mitchell et al. 1997]. Atomistic modeling of the Cu-Nb system has shown that the interface can locally shear in response to the interaction of a glide dislocation stress field with the interface [Hoagland et al. 2004]. The localized shear of the interface in response to the glide dislocation stress field attracts the glide dislocation into the interface plane. However, the shear strength of the Cu-Nb interface was found to be lower than the theoretical estimates of the shear strengths of perfect Cu or Nb crystals [Wang and Misra 2011]. The lack of shear strength of the Cu/Nb interface causes an increased resistance to the transmission of dislocations at the interface. As dislocations approach the interface they shear the interface instead of crossing it. Discontinuity of slip systems across the fcc/bcc interface increases the stresses necessary for the transmission of slip. When a dislocation transmits from...
the interface into the other phase it bows out onto the exiting slip plane in a process which is aided by thermal activation [Beyerlein et al. 2012]. Atomistic simulations of the transmission of slip from Cu to Nb determined an applied tensile stresses >4.5 GPa was necessary for slip transfer [Hoagland et al. 2004]. The Hoagland et al. [2004] simulation occurs at 0 K, therefore it is likely that the stress level required for transmission at higher temperatures (e.g., room temperature) is reduced because of thermal activation.

The coherent fcc/fcc Ag-Cu material system is capable of having the cube-on-cube interface orientation. Unlike the K-S orientation the slip systems in the cube-on-cube orientation are nearly aligned. Despite the positive alignment of slip systems across the interface, dislocation motion is suppressed because of a number of factors. Image (Koehler) forces are present due to the differences in the elastic modulus of silver and copper. The difference in the lattice spacing of copper and silver (3.610 Å and 4.090 Å respectively [Megaw 1932]) causes misfit dislocations and coherency strains at the interface between phases. Coherency strains may be tensile or compressive and are typically large compared to the strain at yield for bulk forms of the multilayer composite constituent materials [Hoagland et al. 2004]. Results from atomistic simulations of Cu/Ag, and similar Cu/Ni, systems indicate that coherency strains have the greatest influence on observed strength response of fcc/fcc material systems [Hoagland et al. 2002, Rao and Hazzledine 2000]. The increased strength occurs because of coherency strain forces hindering the motion of glide dislocations near/through the interface. While the interfaces in a coherent system are strong they can still be crossed by dislocations. As a result coherent systems exhibit ductility [Mastorakos et al. 2009].
1.4 The Ag-Cu eutectic system

The Ag-Cu material system, which this dissertation focuses on is suitable to study for several reasons. The mechanical and elastic properties of copper [Carreker 1957] and silver [Carreker and Hibbard 1953] are known over a wide range of temperatures. Silver and copper have low miscibility allowing for a cast material system that has distinct interfaces with limited phase mixing [Subramanian and Perepezko 1993]. The eutectic micro-structure is stable to elevated temperatures near the eutectic melting point [Carreker and Hibbard 1953, Bayles et al. 1697]. Depending on the production technique utilized the material micro-structure can have either a lamellar [Shen 2008] or rod-in-matrix [Cline and Stein 1969] structure with features on the nano- and ultra-fine length scale. Both copper and silver have the face-centered-cubic (fcc) crystallographic structure [Cooksey et al. 1962]. The Ag-Cu material system can be generated such that the silver-copper interface has either a cube-on-cube or twin orientation relationship [Liu et al. 2008].

1.5 Objectives

Previous work of bi-metallic nano-/ultra-fine composite systems has focused on the study of thin film multilayered materials with coherent or incoherent interfaces. The limited thin film thicknesses obtainable have resulted in most experimental studies relying on nanoindentation to probe material properties. Nanoindentation results have shown improved hardness of bi-metallic composite materials [e.g., Misra and Kung 2001, Misra et al. 2002, Misra et al. 2005] but the nanoindentation technique is unable to provide measures of yielding, work hardening, or fracture behavior. Therefore it is desirable to study bulk materials such as the Ag-Cu eutectic system. The silver-copper system can be produced in two different morphologies (i.e., multidirectional
hierarchical multilayered system or unidirectional reinforcement-in-matrix system) that can be controlled to have matching micro-structure feature sizes. Previous studies of the bi-phase multilayered material system subjected to rolling at room temperature have demonstrated that deformation mechanisms within the copper phase can include deformation twining, a result which differs from the dislocation slip seen in similarly structured single-phase copper [Wang et al. 2011]. The change in the observed dislocation mechanisms in the silver-copper eutectic system indicates the interface influences the deformation response of the material. The objectives of this study of the bulk Ag-Cu eutectic material system are the following:

1. Capture the mechanical response of the multidirectional material and the unidirectional material at different loading orientations with the same nominal micro-structure feature sizes. This will provide a comparison of the deformation response of materials with similar micro-structure spacing but with different interface orientations.

2. Determine the effect that loading orientation with respect to a specified crystallographic direction on the deformation response of the Ag-Cu material system. Specific focus is placed on relating the observed mechanical properties, such as yield strength and strain hardening index, to the dislocations mechanisms observed at each orientation.

3. Identify the effect of decreasing micro-structure reinforcement size and spacing within the unidirectional material has the measured yield strength and hardening response.
Changes in the spacing between reinforcements allow for the determination of whether or not deformation mechanisms change as length scales are reduced.

To satisfy the outlined objectives, the work conducted is inherently highly interdisciplinary requiring close collaboration with Mr. Ben Eftink of the Material Science and Engineering Dept. of the University of Illinois and Dean Ian Robertson of the University of Wisconsin-Madison. Their vital contributions to the present work are indicated were applicable throughout the document.

1.6 Dissertation Overview

Chapter 2 of this dissertation describes the copper-silver eutectic material system itself and the experimental techniques utilized here to study the mechanical properties of the Ag-Cu system. Quasi-static loading was conducted at strain rates of $10^{-3} \text{s}^{-1}$ using servo-hydraulic loading frames. Load frame applied load-displacement data was sometimes supplemented by Digital Image Correlation (DIC) and/or mounted strain gauges. Dynamic loading at strain rates of $10^{3} \text{s}^{-1}$ was accomplished using a split-Hopkinson pressure bar. The elastic modulus of specimens was determined using ultrasonic testing of the longitudinal wave speed. These techniques provided measures of the elastic modulus, yield stress and strain hardening index of deformed specimen.

A multidirectional material (i.e., with nano-layer colonies orientated randomly) produced using rapid solidifications conditions is presented in detail Chapter 3. The quasi-static and dynamic deformation responses are compared and illustrates a lack of strain rate sensitivity of the material in the strain rate regime investigated here (at strain rates of $10^{-3} \text{s}^{-1}$ to at strain rates
of $10^3$ s$^{-1})$. Experimental results of the Ag-Cu system are compared to NS silver and NS copper highlighting the high strength of the silver-copper multidirectional material. Three observed deformation mechanisms (kinking, brooming, and interfacial delamination) are observed and discussed.

Chapter 4 covers the deformation response of a unidirectional material that is produced using the Bridgman solidification technique [Bridgman 1925]. Material produced using three different furnace removal rates resulted in micro-structure features sizes ranging between 200 nm and 1.2 µm. From a single casting, specimens of three different loading orientations were machined for investigation: 1) parallel to the growth direction 2) at 45° to the growth direction and 3) perpendicular to the growth direction. A comparison of the observed macroscopic deformation, elastic modulus, yield strength, and strain hardening rate of each furnace removal rate and orientation are presented. Additional comparison is made between the mechanical properties of the multidirectional and unidirectional materials. Finally, conclusions of this study and suggested future work are presented in chapter 5.
Chapter 2: Experimental Techniques

The silver-copper ultra-fine grained materials we focus on here were produced in bulk form cast rods with initial dimensions of ~10 mm diameter by 50 mm length. From the cast material cylindrical specimens were machined for examination quasi-statically using servo-hydraulic load frame loading, dynamically using split-Hopkinson pressure bar loading, and through nondestructive ultrasonic methods. A typical bulk specimen is shown in Figure 2.1. Bulk material properties obtained using these techniques include elastic modulus \(E\), compressive yield strength \(\sigma_y\), and strain hardening exponent \(n\).

Figure 2.1: A typical bulk nano-/ultra-fine structured Ag-Cu specimen
2.1 The binary silver-copper material system

The silver-copper material used in this study denoted as Ag$_{60}$Cu$_{40}$ has a eutectic composition, 60 atomic percent (71.9 weight %) silver and 40 atomic percent (28.1 weight %) copper. At the eutectic composition (point $E$ in the silver-copper material phase diagram in Figure 2.2) the binary material has the lowest melting point at 779.1 °C. When solidified from a liquid melt ($L$) the resulting solid will consist of two solid phases ($\alpha + \beta$), see Figure 2.2. The limited solubility of silver and copper results in a material with defined interfaces and limited alloying within the phases [Subramarian and Pezepeko 1993]. The casting of the materials used in this study was done by Mr. Ben Eftink and Dr. Doug Safarik at Los Alamos National Laboratory.

![Figure 2.2: The phase diagram for the binary silver-copper material. [Massalski, T. B. and H. Okamoto 1990].](image-url)
Depending on solidification conditions, this binary eutectic material can take on two different morphologies. Under high cooling rate conditions, typically obtained by quenching, the solidified material has a hierarchical structure consisting primarily of eutectic colonies [Shen et al. 2005]. Eutectic colonies are regions of parallel alternating material layers of Ag and Cu, each layer on the order of 35 nm - 200 nm in thickness. Eutectic colonies start forming at initiation sites throughout the material but grow with different layer orientations resulting in a multidirectional ultra-fine-structured material lacking a favored growth direction. The solidification fronts of the eutectic colonies meet forming boundaries between colonies. The observed eutectic colonies range in size between tens of microns to a few millimeters with larger colonies forming near the periphery of the solidified material and smaller colonies (“grains”) forming at the center. Materials of this randomly oriented colony layering morphology will be referred to as “multidirectional”. Specific details on the initial as-cast micro-structure and the macroscopic deformation response of the multidirectional material are presented in Chapter 3, Sections 3.2 and 3.3 respectively.

If lower solidification rates are used the Ag₆₀Cu₄₀ material can be produced with a unidirectional morphology. Using the Bridgman technique [Bridgman 1925] the eutectic silver-copper melt is slowly removed from a furnace at a constant rate. The solidified structure consists of copper reinforcements (i.e., rods and platelets) in a silver matrix. The growth direction of the copper reinforcements and the silver matrix has been observed to match the axial direction of the rod in the 101 crystallographic direction [Eftink et al. 2014]. By changing the rate at which the melt is removed from the furnace the reinforcement thickness can be controlled. Removal rates of 73 mm/hr, 7 mm/hr, and 0.46 mm/hr were used in this study producing material with copper reinforcement with thicknesses of 200 nm, 500 nm and 800 nm – 1.2 µm respectively. An in-
depth study of the micro-structure of the unidirectional material and its material response with respect to compressive loading orientation are presented in Chapter 4.

2.2 Characterization techniques

The initial as-cast material structure and the deformed material structures of both Ag$_{60}$Cu$_{40}$ morphologies were characterized using scanning electron microscopy (SEM) and stylus profilometry. Scanning electron microscopy was conducted on a JOEL 6060LV at the Fredrick-Seitz Materials Research Laboratory (MRL) using secondary electron imaging (SEI) and backscattered electron composition (BEC) modes. High resolution images of the initial material micro-structure were captured using the SEI mode. Under SEI conditions defects such as voids or delaminated regions can be difficult to discern, therefore BEC imaging was also used to study deformed material micro-structure. BEC images capture the ratio of the atomic numbers of the material phases providing images where regions of high atomic number are brighter than those with lower atomic numbers [Lloyd 1987]. The difference of the atomic numbers of silver (47) and copper (29) yields images with silver appearing as the bright phase, and copper as the dark phase. Defects such as voids or delaminations appear as black regions which are discernable from the darker copper phase. Thus BEC images are particularly useful when studying the deformed Ag$_{60}$Cu$_{40}$ material micro-structure. SEM images of the initial and deformed material micro-structure can be found in Chapter 3.1 for the multidirectional material and in Chapter 4.1 for the unidirectional material.

Deformed specimens were studied at the meso- (1 µm – 1 mm) and macro-scale (>1 mm) (using a KLA Tencor P-6 profilometer at the Beckman Imaging Technology Group (IGT). A stylus Profilometer provides a line scan of a surface by moving a stylus, with a 2 µm diameter,
along a surface of interest measuring the horizontal and vertical displacement of the stylus with submicron resolution. Numerous line scans separated by ten microns were combined to obtain a three-dimensional profile of deformed Ag$_{60}$Cu$_{40}$ material features over regions as large as 5 mm by 5 mm. The surface of the as-cast and deformed multidirectional materials can be found in Chapter 3. For unidirectional materials profilometry surface scans of the deformed material subjected to different loading orientations can be found in Chapter 4.

2.3 Quasi-static loading

One of the most commonly utilized methods to determine the mechanical properties of materials is quasi-static loading, i.e., the application of a mechanical load (tension, compression, shear, or multiaxial loading) at time scales considerably longer that the inertial response times of the material. Because of the limited amount of material available for this study, only compressive loading was conducted in order to minimize material machining and waste. In compressive quasi-static loading a specimen is held between two hardened platens, one of which moves during loading, with lubrication at the contact surfaces. The motion of the platen is maintained at a constant rate while the applied load is recorded. Here, load-displacement data were corrected for machine compliance [Kalidindi 1997] then reduced to stress-strain data prior to determining material properties. Quasi-static compressive loading was conducted at strain rates of $10^{-2}$ s$^{-1}$ and $10^{-3}$ s$^{-1}$. A smaller table top MTS RT-30 load frame was limited to capturing the material response below 5% strain having a maximum load cell capacity of 22,000 N. For experiments requiring greater load cell capacity a servo-hydraulic Instron 8800 load frame with 100,000 N capacity load cell in the Advanced Materials Testing and Evaluation Lab (AMTEL) was used.
The $\text{Ag}_{60}\text{Cu}_{40}$ material elastic modulus and yield strength were determined using the MTS servo-hydraulic load frame.

For the far field load ($F$) and monitored displacement, a correction of the recorded data for machine compliance becomes necessary. The assumption that a load frame behaves as a linear elastic spring is an oversimplification and can lead to significant errors in evaluating mechanical properties of materials when using the simple compression mode of testing [Kalidindi 1997]. In particular, this assumption has been shown to lead to non-unique values for the machine compliance factor, which depend on the type of material being tested and the geometry of the sample’s used, leading to erroneous stress-strain material responses.

Following Kalidindi [1997] machine displacement ($\delta_c$) is defined as the measured displacement without the presence of a specimen. A curve fit is applied to the $F - \delta_c$ data obtaining an expression for the machine displacement at all applied loads. Then from the recorded applied load - displacement ($\delta_R$) of each specimen the curve fit of the $F - \delta_c$ data is subtracted to obtain the applied load - specimen displacement ($\delta_S$) data set. Figure 2.3 (a) shows the effect of the compliance correction on recorded ($F - \delta_R$) data, to specimen ($F - \delta_S$) data for a Ag-Cu specimen with a known elastic modulus. The compliance corrected stress-strain response is compared to the recorded response as shown in Figure 2.3 (b). The dashed lines indicate the material elastic modulus. The slope of the blue dashed line matches the known elastic modulus of the Ag-Cu specimen, 96.5 GPa, determined using ultrasonic methods. The slope of the non-corrected recorded trace is 23.3 GPa, which falls well below the corrected data demonstrating the necessity of applying a compliance correction to recorded far field data. The yield stress ($\sigma_y$) of compliance corrected stress-strain data was determined using the 0.02%
strain offset. Strain hardening exponent \( n \) was calculated from the slope of plastic region of \( \ln(\sigma) \) vs. \( \ln(\varepsilon) \) data.

![Figure 2.3](image.png)

**Figure 2.3**: (a) Comparison of machine \( \delta_C \), recorded \( \delta_R \) and compliance \( \delta_S \) corrected load-displacement traces of the same compression experiment of Ag-Cu specimen conducted at a strain rate of \( 10^{-3} \). (b) The compliance corrected stress-strain curve of the load-displacement curves shown in (a). Dashed lines are used to indicate the slope of the elastic region.

Supplementing load frame load-displacement data in some cases were, mounted strain gauges (Micro-measurements C2A-13-250LW-350) and real time imaging combined with digital image correlation [Sutton 2009] to quantify the material response to compressive loading. Strain gauge measurements are limited to only capturing the initial 2-3\% strain of the material response. The displacements measured by strain gauges were primarily used to determine the elastic modulus of the multidirectional material.

In general quasi-static testing requires specimens with length to diameter ratios between 1.5 and 3.0 [ASTM E9-09]. With the limited amount of material available for this study the number of quasi-static tests conducted was limited. Dynamic testing techniques require less material with aspect ratio of about 0.5 [Ramesh 2008], thus dynamic experiments were conducted in greater numbers than quasi-static experiments. The silver-copper eutectic material
system has been observed by others to be strain-rate independent [Cline and Stein 1969], and was also confirmed to be so in this study for the multidirectional lamellar micro-structure (see Chapter 3, section 3.3.2.) For the unidirectional material a limited study of the quasi-static deformation response was conducted which indicated that when loading parallel to the growth direction the material is strain-rate sensitive. Other loading orientations were not examined.

2.4 Split-Hopkinson pressure bar

A split-Hopkinson pressure bar (SHPB), also widely known as a Kolsky [1949] bar is an experimental apparatus used for the characterization, through the use of propagating stress pulses, of the mechanical response of materials deforming at high strain rates (\(10^2 - 10^4\) s\(^{-1}\)) [e.g., Nicholas and Rajendran 1990, Walley and Field 1994, Ravichandran and Subhash 1995, Jia et al. 2003]. John Hopkinson [1872] revealed the propagation of stress pulses through the study of thin rods of iron under drop weight loading. It was observed that regardless of the weight used failure was localized at the ends of the tested rods. Stress pulses were investigated by Bertram Hopkinson [1914] to measure the pressure-time history produced by explosives and high speed ballistic impact. Kolsky [1949] was the first to extend the techniques developed by Hopkinson [1914] and Davies [1948] to measure the stress-strain response of a material under impact loading.

In the SHPB, a cylindrical specimen of the material under investigation is sandwiched between two elastic bars of the same known material, the incident bar and the transmitted bar. In Figure 2.4 shows a photo of the SHPB used for specimen testing along with an inset of a specimen held between the two elastic bars. A schematic of the SHPB apparatus and a \(x-t\) diagram of the stress pulses that propagate during a typical SHPB experiment are shown in
Figure 2.5. A compressive stress pulse is initiated by launching a projectile (the striker bar), made of the same material as the incident and transmitted bars, by gas gun into the incident bar, see the solid blue line in Figure 2.5. A momentum trap (Nemat-Nasser et al. 1991, Nemat-Nasser 2000), not shown in Figure 2.5, was mounted to the incident bar to ensure the application of only one loading pulse onto the specimen from the impact of the striker bar. The compressive stress pulse travels through the incident bar reaching the incident bar/specimen interface. At the incident bar/specimen interface a portion of the stress pulse is reflected back towards the impacted end of the incident bar as a tensile pulse shown as blue dashed lines in Figure 2.5. The remaining portion passes through to the specimen as a compressive pulse. The compressive stress pulse continues through the specimen reaching the specimen/transmitted bar interface. At this interface a portion of the compressive stress pulse is reflected back into the specimen with the remainder passing through to the transmitted bar, shown as green lines in Figure 2.5.

Figure 2.4: A photograph of the SHPB system used to conduct dynamic compression experiments. The inset shows a specimen held between the two elastic bars.
The design of the SHPB where the incident bar/specimen and specimen/transmitted bar interface have an acoustic impedance mismatch, along with the short specimen length, causes the compressive pulse reflected from the specimen/transmitted bar interface to reverberate quickly within the specimen, see Figure 2.5. The reverberations of the stress pulse in the specimen occurs over a much shorter time than the temporal width of the compressive pulse resulting in the stress state quickly becoming homogeneous throughout the specimen. Strain gauges are mounted on the surface of the incident and transmitted bars to measure the propagating stress pulses. Typical recorded strain gauge signals are shown in Figure 2.6. To account for possible bending pulses on the measured signals we mount two strain gauges diametrically opposite each other on both the incident and transmitted bars, then average the two strain gauge signals prior to analysis.

**Figure 2.5**: A schematic representation of the SHPB and $x-t$ diagram of the propagation of stress pulses during a typical experiment.
Through careful design of the SHPB experiment one-dimensional elastic wave theory can be applied to the recorded strain gauge signals to calculate the engineering stress ($\sigma_{\text{eng}}$), engineering strain ($\varepsilon_{\text{eng}}$) and engineering strain rate ($\dot{\varepsilon}_{\text{eng}}$) of the specimen during a typical experiment. For one-dimensional elastic wave theory to be valid the incident, transmitted, and striker bar must be constructed of a material that remains elastic during loading. The dimensions of the incident and transmitted bars must have a length ($L_{\text{bar}}$) to diameter ($D_{\text{bar}}$) ratio greater than twenty, but typically on the order of one-hundred. To limit size effects the bar diameter ($D_{\text{bar}}$) to specimen diameter ($D_s$) ratio is kept at approximately two. For homogenization of the reverberating compressive stress wave within the specimen the specimen length ($L_s$) to diameter ($D_s$) ratio is held at one-half [Gray 2000]. Finally the specimen surfaces are lubricated thus limiting the in-plane friction effects allowing for uniaxial stress conditions to be established [Bell 1966, Bertholf and Karnes 1975].

Typical non-smoothed bending compensated raw signals captured by the strain gauges mounted on the incident and transmitted bars are shown in Figure 2.6 (a) with the incident strain ($\varepsilon_I$), reflected strain ($\varepsilon_R$) and transmitted strain ($\varepsilon_T$) signals indicated. With the strains known in each of the elastic bars the forces at the specimen/bar interfaces are calculated from

$$P_1 = E(\varepsilon_I + \varepsilon_R)A_b$$  \hspace{1cm} (2.1)

$$P_2 = E\varepsilon_T A_b$$  \hspace{1cm} (2.2)

where $E$ and $A_b$ are the elastic modulus, and cross-sectional area of the incident and transmitted bars. The force at the incident bar/specimen interface is $P_1$ and the force at the specimen/transmitted bar is $P_2$. If the forces at the interfaces are equal ($P_1 = P_2$) then the force,
and therefore stress, measured from the transmitted bar represents the average force (stress) experienced by the specimen [Gary 2000]. The equilibrium of the forces of the raw data recorded in Figure 2.6 (a) and processed using Equations (2.1 and 2.2) is shown in Figure 2.6 (b) with ‘Force In’ representing the stress at the incident bar/specimen interface \((P_i)\) and ‘Force Out’ representing the stress at the specimen transmitted bar interface \((P_s)\). Additionally, force equilibrium implies that the sum of the strain gauge signals in the incident bar match those of the transmitted bar (i.e., \(\varepsilon_i + \varepsilon_R = \varepsilon_T\)). The engineering stress \((\sigma_{s,\text{eng}})\), engineering strain \((\varepsilon_{s,\text{eng}})\) and engineering strain rate \((\dot{\varepsilon}_{s,\text{eng}})\) are then calculated using [Kolsky 1949]

\[
\sigma_{s,\text{eng}}(t) = E \left( \frac{A_s}{A_b} \right) \varepsilon_T , \quad (2.3)
\]

\[
\varepsilon_{s,\text{eng}}(t) = -\frac{2c_0}{L_s} \int_0^t \varepsilon_R d\tau , \quad (2.4)
\]

\[
\dot{\varepsilon}_{s,\text{eng}}(t) = -\frac{2c_0}{L_s} \varepsilon_R , \quad (2.5)
\]

where \(c_0\), \(E\) and \(A_b\) are the elastic bar wave velocity, Young’s modulus, and cross-sectional area of the incident and transmitted bars; and \(L_s\) and \(A_s\) are the initial length and cross-sectional area of the specimen. Assuming volume conservation during plastic flow the true stress \((\sigma_{s,\text{true}})\), true strain \((\varepsilon_{s,\text{true}})\), and true strain rate \((\dot{\varepsilon}_{s,\text{true}})\) are given by [Ramesh 2008]

\[
\sigma_{s,\text{true}}(t) = \sigma_{s,\text{eng}}(t)(1 - \varepsilon_{s,\text{eng}}(t)) , \quad (2.6)
\]

\[
\varepsilon_{s,\text{true}}(t) = -\ln(1 - \varepsilon_{s,\text{eng}}(t)) , \quad (2.7)
\]

\[
\dot{\varepsilon}_{s,\text{true}}(t) = -\frac{\dot{\varepsilon}_{s,\text{eng}}(t)}{1 - \varepsilon_{s,\text{eng}}(t)} . \quad (2.8)
\]
The engineering stress-strain and true stress-strain material response determined from the raw data signals displayed in Figure 2.6 (a) are shown in Figure 2.6 (c).

![Figure 2.6](image)

**Figure 2.6**: Split-Hopkinson pressure bar data obtained from a typical dynamic compressive loading experiment: (a) recorded raw strain gauge signals of the propagating stress pulses, (b) force balance demonstrating dynamic stress equilibrium, (c) the calculated engineering and true stress-strain material response.

### 2.5 Ultrasonic Testing

Ultrasonic testing of solid materials uses high frequency acoustic energy to characterize material properties and to detect the presence of internal flaws. Sokolov [1929] first proposed the
use of a through-transmission technique of acoustic waves for the detection of flaws in solids [Bergmann 1954]. Muhlhauser followed with the first patent [1931] for the use of ultrasonic nondestructive testing [Graff 1982]. Since the 1950’s the field of ultrasonics has expanded rapidly and is commonly used in biomedical and nondestructive testing applications.

The through-transmission technique of Sokolov uses a transducer mounted to one side of a material with a known thickness \( h \) to initiate an acoustic pulse. A second transducer is mounted opposite the first and acts as a “listener” of the acoustic pulse. A material free of flaws (e.g., voids, cracks) will have a fixed transmission time \( t_0 \) between the initiation of the acoustic pulse from the first transducer and the receiving of the pulse by the second transducer. There the density of specimens was determined prior to testing to determine if large scale voids existed. Post-mortem specimens were imaged under SEM to check for porosity at reduced length scales. Specimens used in testing had densities matching theoretical values without visible porosity under SEM; they are considered them to be free of flaws. Therefore the obtained data during ultrasonic testing is a measure of the longitudinal wave speed \( c_d = h/t_0 \) of the material.

The ultrasonic testing apparatus used in our work consists of a JSR Ultrasonics P35 pulser/receiver, two Ultran WRD12-5 transducers, and a TekTronics 420A oscilloscope. The pulser/receiver generates electrical pulses that are converted to ultrasonic pulses by the first “active” transducer which is coupled using vacuum grease to the material being examined. The second transducer coupled on the opposite side of the material “listens” for the ultrasonic pulse which is then recorded by the oscilloscope. Fixed delay plastic contacts were used with the transducers to limit the signal to noise ratio and provide a known material transmission time. As a result of using the plastic pieces reflections occur at the interfaces between the plastic contacts.
and the metallic specimen. The oscilloscope was set to record the initial arrival of the ultrasonic pulse and subsequent acoustic wave reflections with in the sample.

Using wave propagation theory the uniaxial elastic modulus ($E$) of the material through which the ultrasonic acoustic pulse passes through can be calculated. The longitudinal wave speed is related to material properties through [Meyers 1994].

\[
c_d = \frac{E}{\sqrt{\rho}}, \quad (2.9)
\]

where $\rho$ is the material density. Specimen dimensions and density were determined prior to testing. The uniaxial strain modulus can be expressed as $\bar{E} = E(1-\nu/((1+\nu)(1-2\nu)))$ with $E$ and $\nu$ being the elastic modulus and Poisson’s ratio respectively. A rule of mixtures estimate was applied to determine the material’s effective Poisson’s ratio ($\nu \approx 0.366$).

An overlay of two ultrasonic tests as recorded by the oscilloscope is shown in Figure 2.7 (a). The green trace is a record of the ultrasonic pulse transmission of the two plastic contacts with a fixed transmission time of 7,124 ns. The blue trace is a record of the ultrasonic pulses initial arrival and the subsequent reflections through a silver specimen. The subsequent reflections have a similar shape with each reflection having decreased amplitude. The abscissa is time shifted such that time zero is the initial arrival time of the acoustic pulse passing through the plastic contacts. Vertical dashed red lines are superimposed over the traces indicating the leading edge of the traveling acoustic wave arrival at the “listening” transducer. The timing between the first two dashed lines divided by the specimen thickness provides the material longitudinal wave speed. For the reflected acoustic waves the timing between the vertical red dashed lines is divided by twice the thickness to obtain the longitudinal wave speed. The calculated elastic modulus ($E$) from the initial and reflected wave arrivals are shown in Figure 2.7 (b) as circles.
for silver of a number of specimens with different thicknesses confirming the accuracy of the technique in determining the elastic modulus of materials. The average calculated elastic modulus for each sample thickness is shown in Figure 2.7 (b) as a solid circle and the elastic modulus of silver is shown as a solid blue line.

![Graph](image)

**Figure 2.7**: Ultrasonic testing of silver specimens (a) An overlay of the recorded acoustic wave signals for the fixed delay plastic contacts (green) and silver specimen (blue). (b) The calculated elastic modulus of silver specimens of multiple thicknesses. Open circles indicate values obtained from the initial arrival timing, and reflected waves arrivals at the listening transducer. The average elastic calculated elastic modulus for each thickness is shown as a solid circle. For reference the elastic modulus of silver ($E = 83$ GPa) is provided as a solid horizontal line.
Chapter 3: Bulk multidirectional lamellar silver-copper eutectic material

Multidirectional material produced directly from a binary (silver-copper) eutectic composition melt was examined under quasi-static and dynamic loading conditions. Under these conditions macroscopic mechanical properties including elastic modulus ($E$), yield strength ($\sigma_y$), and strain hardening exponent ($n$) were determined. Analysis of the macroscopic deformation of the material system was investigated with stylus profilometry and optical microscopy. Deformation at the micro scale was investigated using SEM which revealed two dominant deformation modes occurring at increasing levels of strain.

3.1 Material production

The multidirectional material was produced at Los Alamos National Laboratory by Mr. Ben Eftink and Dr. Doug Safarik. Silver and copper pellets, 99.99% and 99.9% purity respectively, with boron trioxide ($B_2O_3$) flux were added to a ~10 mm inner diameter fused silica tube. The boron trioxide flux is present to remove impurities in the melt which would act as undesired nucleation points of anomalous micro-structure. The removal of impurities also aids in
undercooling by reducing the temperature at which solidification initiates, thus enabling the production of a material with ultra-fine scale (100 nm - 500 nm) features [Biloni and Boettinger 1996]. The fused silica tube was then heated to 1250 °C, melting the three components. When the melt reached 1250°C the silica tube was evacuated and held under vacuum until the gas evolution ceased, then backfilled with argon gas and quenched in water [Shen et al. 2005, Shen et al. 2007]. The rapid cooling provided by quenching and the undercooling from purification of the melt results in the appropriate solidification conditions for multiple eutectic colonies consisting of alternating layers of Ag and Cu to form throughout the material.

3.2 Multidirectional material characterization before loading

From the cast material cylindrical specimens were cut using electrical discharge machining (EDM) to dimensions such that their length to diameter ratio was 0.5. Initial characterization of the as-cast material was conducted across the nano- (<100 nm), micro- (100 nm - 1000 nm) and mesoscale (> 1 µm) to capture the hierarchical micro-structure. Cross-section specimens were polished in preparation for examination using SEM and transmission electron microscopy (TEM), with additional cryo-cooled ion milling to electron transparency for TEM samples. TEM characterization, conducted by Mr. Ben Eftink, showed alternating layers of Ag and Cu with thicknesses ranging between 40 nm and 200 nm with well-defined interfaces between layers, as seen in Figure 3.1 (a). The average copper and silver layer thicknesses were measured from SEM micrographs at 46 nm and 88 nm respectively. The individual layer thickness of copper comprises 34.3% of the total silver-copper bi-layer thickness (134 nm) closely matching values predicted by the volume percent of copper in the Ag$_{60}$Cu$_{40}$ material. Work by Shen et al. [2005] predicted the average crystallite size of silver and copper using the
Scherrer equation [Guinier 1963] finding both phases have average crystalline sizes of 45 nm for a Ag$_{60}$Cu$_{40}$ cast eutectic produced using the same method as the material of this study. The white arrows in Figure 3.1 (a) indicate the position of interfaces between layers. The structure of the interface has been studied revealing that the cube-on-cube and hetero-twin orientation relationships occur at the interface [Tian and Zhang 2012, Liu et al. 2008] in this case. In the cube-on-cube interface orientation relationship the cubic axes of the materials are parallel thus the slip planes and slip directions are nearly continuous across the interface [Hoagland et al. 2004]. In the hetero-twin orientation Ag and Cu have matching $\{111\}$ planes ($\{111\}_Cu \parallel \{111\}_Ag$) with symmetry of the atomic structure across the interface [Liu et al. 2008]. Misfit dislocations occur in both interface orientation relationships to accommodate the lattice spacing mismatch of 11.8% between Cu and Ag [Mara et al. 2012].

SEM and optical microscopy images, Figure 3.1 (b,c,d) capture the Ag-Cu material structure at higher length scales. Eutectic colonies, with an average diameter of 198 µm, form containing parallel alternating metallic layers. These colonies occur primarily at the interior of the specimen and are of different orientations as shown in the SEM image presented in Figure 3.1 (b), which illustrates the region near a boundary between two such colonies. Larger anomalous growth regions primarily near the exterior of the cylinder with an average diameter of 920 µm, have a structure consisting of a central region, Figure 3.1 (c), from which alternating layers emanate in a radial pattern, Figure 3.1 (d). At low undercooling a mixture of eutectic colonies and anomalous micro-structures develop from a radial solidification around a single nucleation point [Zhao et al. 2009a, 2009b]. Since the melt is purified, the likely cause of the nucleation points of the anomalous micro-structure is from sharp regions (e.g., surface cracks or burs) on the fused silica tube used during casting [Clopet et al. 2013]. SEM imaging of the
anomalous radial structure revealed that there is a transition from the anomalous structure shown in Figure 3.1 (c) to the normal eutectic structure of alternating material layers. Optical micrographs were taken of the cross-section after etching it in a solution of 5 g FeCl$_3$ + 12 ml HCl + 40 ml H$_2$O for 5 seconds [Shen 2005]. The large scale anomalous growth structure, Figure 3.1 (d), with the initial growth site located at the center of each grain and the radiating layer structure become visible. From Figures 3.1 (b) through 3.1 (d) we can deduce that the Ag-Cu system forms a structural hierarchy with the smallest feature, nano-scale individual layers, grouped together to form microscale colonies and anomalous growth regions, which in turn can be grouped into mesoscale collections of colonies or anomalous growth regions.
Figure 3.1: Characterization of multidirectional silver–copper cast eutectic material: (a) TEM micrograph (courtesy of B. Eftink) showing defined layer interfaces between silver and copper, the white arrows indicate the position of the interface, (b) SEM micrograph showing an interface between eutectic colonies with different orientations, (c) SEM micrograph showing the center of an anomalous growth region, and (d) optical micrograph showing the mesoscale collection of colonies and anomalous growth regions and the defined boundaries between them.

3.3 Multidirectional material response to compressive loading

Multidirectional cylindrical specimens were mechanically loaded under quasi-static and dynamic conditions. For details on the testing methods used see Chapter 2.

3.3.1 Quasi-static material response

Stress-strain curves obtained from three separate quasi-static experiments (two at $10^2$ s$^{-1}$, one at $10^3$ s$^{-1}$) of multidirectional Ag$_{60}$Cu$_{40}$ specimens are compared to the response of work-
hardened coarse grained copper (strain rate $10^{-2}$ s$^{-1}$), well-annealed coarse-grain copper (strain rate $4 \times 10^{-4}$ s$^{-1}$) [Jia et al. 2001] and well-annealed coarse grain silver [Hegedus et al. 2011] in Figure 3.2 (a). The red curve in Figure 3.2 (a), strain rate of $10^{-2}$ s$^{-1}$, shows the unloading response of the Ag$_{60}$Cu$_{40}$ material the strain for which was measured via a strain gauge mounted on the sample. The elastic region of the three silver-copper quasi-static stress-strain curves is shown in Figure 3.2 (b) with a dashed line indicating the slope of the elastic region.

![Figure 3.2](image)

**Figure 3.2**: (a) Quasi-static response of bulk multilayered Ag$_{60}$Cu$_{40}$ cast eutectic silver-copper, work hardened copper, well annealed coarse grain copper [Jia et al. 2001], and well annealed silver [Hegedus et al. 2011], with (b) zoomed in elastic region.

Under quasi-static loading the multidirectional silver-copper material exhibits compressive yield strength greater than that of well-annealed [Jia et al. 2001] and work-hardened coarse-grain copper. Work conducted on a swaged nano-grained Ag$_{60}$Cu$_{40}$ eutectic material [Cai and Bellon 2013] has exhibited yield strength approximately twice that of the Ag$_{60}$Cu$_{40}$ hierarchical material shown in Figure 3.2 (a). The higher yield strength is likely due to the pre-straining imparted on the nano-grained Ag$_{60}$Cu$_{40}$ material during swaging, while the material for this study has a limited numbers of dislocations in the as-cast state.
The work hardening rate of the multidirectional silver-copper material is greater than that of copper. The higher work hardening of the silver-copper material can be interpreted as being a result of inhomogeneous deformation of the material. Initially both phases deform elastically up to the macroscopic yield point, at which point the softer phase (silver) deforms plastically while the harder phase (copper) deforms elastically, resulting in the apparent strain hardening. Assuming a work hardening power law relationship $\sigma = K\varepsilon^n$, where $n$ is the strain hardening exponent and $K$ is the strength coefficient, the strain hardening exponent was calculated from the slope of $\ln(\sigma)$ vs. $\ln(\varepsilon)$ plastic response of the multidirectional Ag$_{60}$Cu$_{40}$ stress-strain curves shown in Figure 3.2 (a) to be $n = 0.24$.

The elastic modulus of the silver-copper material was measured as 71 GPa (see Figure 3.2 (b)), a value which falls below the rule of mixtures estimate of polycrystalline Ag$_{60}$Cu$_{40}$, 97.8 GPa. Multilayer film Ag-Cu materials produced by alternating PVD of silver and copper have also shown reduced elastic modulus, approximately 20% lower than the rule of mixtures estimate [Verdier et al. 2006, Huang and Spaepen 2000]. The source of the reduced modulus in the deposited films was attributed to cracking within each of the layers between the columnar grains composing them [Huang and Spaepen 2000]. In our case however, the cast multidirectional material layers do not have a columnar structure; hence the observed modulus reduction cannot be attributed to intergranular cracking.

Another possible reason for the modulus reduction would be the presence of internal porosity/voids generated during material production. Voids have been observed in the as-cast material near the ends of the cast rod material, but these sections of the material were removed and discarded. Following the formulation of Eshelby [1957] for predicting the volume fraction of non-interacting spherical voids in an isotropic medium, the necessary volume fraction of voids to
account for the reduction of the elastic modulus is 11%. Characterization of the initial as-cast multidirectional material across the nano-, micro- and mesoscale did not indicated the presence of voids. Furthermore the density of the specimens matched the predicted rule of mixture density values indicating the studied materials are essentially fully dense.

The exact reason for the decreased elastic modulus is still under study for nano-structured alloy material systems similar to the Ag$_{60}$Cu$_{40}$ material focused on herein. The reduced elastic modulus when compared to a rule of mixtures estimate was observed under all loading conditions. Machine compliance corrected far field displacements and displacements measured directly from mounted strain gauges from quasi-static loading obtained the same reduced elastic modulus. Dynamic testing although not the most accurate method to obtain elastic properties also captured a reduced elastic modulus response when comparing the multidirectional material response to copper and silver.

3.3.2 Dynamic material response

The dynamic responses of the silver-copper cast eutectic, coarse grain copper and coarse grain silver are compared to each other and to the quasi-static silver-copper material response in Figure 3.3. Over the strain rates tested ($10^{-3}$ s$^{-1}$ to $10^{3}$ s$^{-1}$), the response of the bulk Ag-Cu eutectic material remains consistent without displaying noticeable strain rate effects. Strain rate insensitivity was also reported by Cline and Stein [1969] in the tensile response of a silver-copper eutectic. However, they used a directionally solidified alloy with lamellae aligned with the axial direction, whereas the as-cast material exhibits randomly orientated colonies of parallel lamella. This lack of rate sensitivity in Ag-Cu alloys with different micro-structures suggests this binary eutectic system is rate insensitive. This result is perhaps unexpected as nano-structured
copper exhibits noticeable strain rate dependence over this range [Jia et al. 2001]. As in the static case, Figure 3.2 (a), the work-hardened coarse-grain copper and silver show material responses with flow stresses well below those of the silver-copper cast eutectic material in the dynamic regime investigated (2500 - 6000 s⁻¹), indicating the strengthening effect of the hierarchical layered structure.

**Figure 3.3:** A comparison of the dynamic response of the bulk silver-copper cast eutectic, coarse grain copper and coarse grain silver from specimens prepared for this study.

The results reported in Figure 3.3 are compared with ones in the literature for bulk nano-structured and ultra-fine grained materials. Included in Figure 3.4 are stress-strain curves for bulk ultrafine grained (100 nm - 500 nm) and nano-structured (<100 nm) copper materials that were produced using the following methods high pressure torsion (HPT) [Ziling et al. 2008], equal channel angular pressing (ECAP) [Suo et al. 2010, Suo et al. 2011] and electrodeposition (ED) [Jia et al. 2001, Li et al. 2004], nano-structured silver produced using ECAP [Hegedus et al. 2011] as well as eutectic Ag-Cu alloys [Shen et al. 2007]. HPT and ECAP are both severe plastic deformation techniques that impart large strains on materials to refine their micro-
structure to the nano-scale and ultra-fine scale. ED is a bottom-up processing technique where nano-structured materials produced by way of depositing dissolved metal cations on an electrode. For additional details on HPT, ECAP, and ED see Chapter 1. The hierarchical silver-copper material system, from this work and from the work conducted by Shen [2007], demonstrates a strength that is higher than the single material nano- and ultrafine-grained systems. Therefore the presence of alternating material layers with submicron thicknesses, has been shown to improve the silver-copper macroscopic strength response of the material across a wide range of strain rates using direct measurement techniques.

Figure 3.4: Static and dynamic compressive stress strain curves for case eutectic silver copper, and bulk NS and UFG grained copper and silver.

3.3.3 Macroscopic surface deformation

An optical investigation of the specimen surface was conducted after loading. Specimens were mounted on a rotating post under a stereo microscope and images of the specimen radial cylindrical surface at rotation increments of two degrees were captured. The collection of images was stitched [Preibisch et al. 2009] together for a specimen subjected to 15% strain under
dynamic compression and are shown in Figure 3.5. This post deformation result shows the resultant macroscale deformation on the radial surface. The micro-structure at the radial surface is a combination of regular eutectic growth (i.e., alternating layers) and anomalous growth regions that originate from a central nucleation point radiating outwards. As shown in Figure 3.1 (c) the nucleation point does not have the ordered alternating layered micro-structure and instead has a chaotic non-ordered micro-structure. In response to loading, the nucleation point of each of the radial grains protrudes from the radial surface with a plateau like morphology. The formation of these protrusions is of interest since it differs from the normal uniform surface roughening commonly seen in the deformation of pure metals. Previous studies have demonstrated that the alternating layered structure is stronger than a non-ordered structure [Misra and Kung 2001, Misra et al. 2005]. As a result the weaker regions will selectively deform first to loading leading to the formation of the observed protrusions.

**Figure 3.5:** Stitched stereo microscope images of the radial surface of a specimen deformed to 15% compressive strain. The image strip is spliced into two segments with white arrows indicating the position of the overlap.
A surface topography study was conducted on the radial surface using a KLA Tenor stylus profilometer. Stereo microscope images of the scanned regions, as indicated by a white box, of the as-cast surface and the surface of a specimen deformed to 15% compressive strain dynamically are shown in Figures 3.6 (a) and 3.6 (c) respectively. The surface topography of the scanned region is shown in Figures 3.6 (b) and 3.6 (d) for the as-cast and deformed surfaces, respectively. In the initial surface scan the surface is smooth and does not indicate that there is noticeable surface roughness at nucleation points of the radial structure. Post deformation the position of the nucleation point protrusions is readily apparent. Of interest is the appearance of the onset of shear banding, indicated by black arrows, from the nucleation point protrusions in Figures 3.6 (b) and 3.6 (d). The shear banding is of greatest height closest to the nucleation point and diminishes towards the boundary of the radial structure. The diminishing of shear banding in the alternating layered structure reinforces the observation that the ordered layered structure has superior strength to a chaotic non-ordered structure and that the Ag-Cu interface of the layered structured is resistant to shear.
Figure 3.6: Surface topography comparison of an as-cast radial surface of a multidirectional specimen to a specimen deformed to 15% compressive strain. White boxes in (a) and (c) indicate the scanned surface region. Black arrows in (d) indicate the presence of shear banding. (a) Optical micrograph of the as-cast radial surface, (b) corresponding contour image of the profiled region indicated in (a), (c) Optical micrograph of the 15% compressive strain surface, and (c) corresponding contour image of the profiled region indicated in (c).

3.4 Deformation mechanisms observed at increasing levels of compressive strain

Interrupted loading of specimens was conducted to analyze the deformation mechanisms at increasing levels of strain on the specimen surface. Specimens were subjected to dynamic loading then imaged under SEM at a specific location, then reloaded and reimaged at the same location. Through SEM characterization of the outer surface at higher magnifications than those shown above, two deformation mechanisms were discovered to be dominant: layer kinking, and interfacial failure, each occurring in different regions of the colonies and grains of the specimen. Geometrically layer kinking and interfacial failure both resemble comparable failure mechanisms to those exhibited in fiber reinforced composites [Budiansky and Fleck 1993]. At the boundary between two eutectic grains where layers of different orientations meet, brooming occurs with
longitudinal splitting between neighboring layers [Weaver and Williams 1975]. Away from the grain boundary, interfacial delamination occurs where layers separate from each other causing microbuckling between neighboring layers [Evans and Adler 1978].

These deformation mechanisms become active at increasing levels of strain as indicated in Figure 3.7, which shows SEM micrographs from an experiment interrupted at various applied strains. At 5% strain the layer orientation appears unchanged from their initial state. This observation is made by comparing the layering shown in Figure 3.7 (a) for a specimen that has been deformed to 5%, to Figure 3.1 (b), the as-cast layer orientation. Both Figures 3.1 (b) and 3.7 (a) show straight aligned layers. Above 15% the first deformation mechanism, layer kinking, becomes apparent, see Figure 3.7 (b). At strain levels above 25%, the presence of layer brooming at boundaries and interfacial delamination between layers away from the boundaries between the regular eutectic growth regions of neighboring anomalous growth regions becomes evident. The loading direction for all following SEM images is in the vertical direction.
Figure 3.7: Stress-strain curve of a silver-copper specimen where the deformation occurs in steps. After each loading step SEM images were captured of the surface deformation at increasing levels of strain. At low levels of strain ≤5% (a) the layers remain straight. The dominant deformation mechanisms discovered at higher levels of strain and are (b) layer kinking (c) interfacial brooming and (d) interfacial delamination. The loading direction is vertical in all images.

3.4.1 Layer Kinking

For the specimen to accommodate deformation above 5% the layers visible on the specimen surface undergo a rearrangement where the layers transform from a parallel orientation to one that has significant curvature, as shown in Figure 3.7 (b) and 3.7 (c). This layer kinking is analogous to the microbuckling phenomenon in fiber composites where neighboring fibers with the same parallel orientation buckle as a result of compressive loading forming a band of
material with fibers with the same angle reorientation. To understand the evolution of the kinking deformation mechanism as a function of strain, SEM images of the same grain boundary position on a specimen surface were captured at increasing levels of dynamic strain, see Figure 3.8 (a) 5% strain, Figure 3.8 (b) 15% strain, and Figure 3.8 (c) 25% strain. Comparing the three images of Figure 3.8, the kinking angle of layers increases as the global strain increases. Additionally, once kinking occurs in a region, further deformation of the specimen is localized to the weakened kinked region with non-kinked regions retaining straight aligned layers, as present in the initial state.

The complexity of the hierarchical structure loaded in compression results in a non-uniform stress and strain state throughout the material. To obtain an understanding of the local strain with respect to increasing global strain two pairs of layers (each pair having a layer above and below the grain boundary) are labeled in Figure 3.8 (a,b,c). Each labeled pair consists of two layers that meet at the boundary between neighboring grains. The traced layer pair positions for the dashed line pair and the solid line pair (from Figure 3.8 (a,b,c)) are shown in Figure 3.9 (a) and 3.9 (c) respectively. Along each pair of layers a spline was fit and the local slope was determined and used to measure the local shear strain at that point. It is assumed that far from the boundary (i.e., near the top and bottom of the images in Figure 3.8) the layers experience very little shear strain because they remain unchanged with increasing global strain. The measured shear strain as a function of the position along the layer (position being defined as the total arc length along each layer) for the three global applied strain levels is presented in Figure 3.9 (b) for the dashed line pair and in Figure 3.9 (d) for the solid line pair. The markers in Figure 3.9 (b,d) correspond to the position of the markers shown in Figure 3.9 (a,c).
Figure 3.8: Kinking of layers of specimens at increasing levels of strain (a) 5% dynamic strain (b) 15% dynamic strain (c) 25% dynamic strain. Two pairs of layers are traced, one pair as dashed lines, the other as solid lines. Each layer pair consists of two layers that meet at the boundary between two neighboring grains.
Figure 3.9: Position and shear strain evolution of the dashed line and solid line pairs from Figure 3.8 (a,b,c). The dashed line pair (a) position and (b) shear strain, solid line pair (c) position and (d) shear strain, at increasing levels of global strain.

At 5% global strain the local shear strain, present in the layers above and below the boundary interface is nearly zero – the boundary is indicated by the vertical dashed line and the position of zero shear strain is indicated by the horizontal dashed line in Figures 3.9 (b) and (d). The local shear strain that exists in the layers below the boundary (to the left of the dashed
vertical line) increases as the global strain increases. Once a region has started to kink, the layer reorientation makes it weaker relative to other areas of the specimen that have not kinked, thus further deformation of the specimen leads to an increase in the kinking angle. For an applied global strain of 5%, the local shear strain can reach 10% and increases to over 30% for an applied global 25% strain. The shear strain that exists near the boundary can be positive (see Figure 3.9 (b)) or negative (see Figure (3.9 (d)). The positive sign of the dashed line pair below the boundary is a result of the traced layer curving downwards closer to the boundary. The negative sign of the solid line pair is a result of the traced layer curving upwards near the boundary. The difference in sign of the shear strain is a precursor to failure in the form of brooming, where two neighboring layers split apart from each other (see next section). As the applied loading increases the shear strain increase appears to be concentrated in a region of 10 μm length directly below the boundary. While the layers below the interface deform quite readily those above the boundary (to the right of the dashed vertical line) experience little shear strain. The examination of quasi-static and dynamic specimens yielded a similar kinking response of the layers. Thus, this deformation mechanism appears to be strain-rate independent.

3.4.2 Interfacial failure between layers

Once specimens reach a level of strain greater than ~25%, brooming of the nano-layers at the boundary between grains begins to occur. The presence of brooming indicates that due to previous kinking there has been a reduction in the lateral confinement provided by neighboring layers. The amplitude of the brooming delaminations in the multidirectional material are small, typically on the order of less than two layer thicknesses as seen in Figure 3.10 (a). Brooming was
most commonly observed in regions that had initial layer orientations that were within 15 degrees of the loading direction.

At higher levels of strain (>25%), away from the boundary between grains, the dominant deformation mechanism is interfacial delamination between the layers, as shown in Figure 3.10 (b). Similarly to kinking and brooming, the initial orientation of the layers prior to deformation facilitates occurrence of the delaminations. As the strain level increases the number of delaminations and their amplitude increase. At high levels of strain, around 50%, single layers that span the opening created by the delaminations may remain fully intact. The single layers that span delamination openings provide an opportunity to study the failure region which allows for interfacial delamination to occur. Using a focused ion beam (FIB) the single spanning layer can be preferentially sectioned from the sample and prepared for TEM imaging to determine the position of failure. Additionally work is necessary to determine the failure position as it is unknown if it is occurring at the interface between layers or very near the interface within one of the material layers. Energy-dispersive x-ray spectroscopy (EDS) provided inconclusive results of the composition of the spanning single layer due to their limited thickness.
Figure 3.10: Dominant deformation mechanisms that occur at strains greater than 25% strain, (a) brooming for nano-scale layers at the boundary between two eutectic regions and (b) interfacial delamination between layers.

At the specimen exterior surface there is little radial constraint present. The center of grains readily deform forming protrusions from the surface. Near the boundary between surface grains there is some level of in-plane constraint (though normal deformation out-of-plane still has little constraint) thus the material deforms through in-plane kinking and brooming. The openings created during brooming are limited because of the presence of neighboring layers. Kinking is established near the boundary and increases with increasing strain. Analysis of the layer kinking highlights the presence of a non-uniform stress state with some regions of the specimen showing layer reorientations while others show very little change from their initial state. Further from the boundary the constraints from the grain boundary diminish allowing for larger openings between layers to form, thus interfacial delaminations exist. As the specimen deformation increases the amplitude of the interfacial delaminations increase, occasionally with single layers spanning the openings created.
3.4.3 Orientation dependence

The occurrence of the observed deformation mechanisms is dependent on the initial orientation of the layer structure to the loading orientation. From SEM studies it was found that the angle between layers and the loading direction that most favored the occurrence of kinking was between 15° and 45°. Angles of \( \leq 15° \) were most favored for interfacial delamination. When the angle is greater than 45° the above discussed deformation mechanisms were not observed. Regions of the specimen with layers perpendicular to the loading orientation appear to be unchanged from the as-cast state. Figure 3.11 presents a region of the specimen with layers showing interfacial delamination that are closely aligned to the loading direction and nearby layers that are perpendicular to the loading direction showing negligible deformation.

![Figure 3.11: SEM micrograph showing the preferential deformation of layers aligned to the loading direction.](image)
3.5 Internal deformation mechanisms at increasing levels of strain

Globally the specimen is loaded in uniaxial compression, but locally there are variations of the stress state, because of microstructural effects and the differing constraints at the interior and exterior of the specimen. Examination of SEM micrographs of deformed specimen cross-sections revealed that the exterior and interior deformation is indeed different, although there are some commonalities. For example at 15% applied strain the internal structure of the eutectic colonies appears similar to that of the as-cast state, having straight aligned layers; compare Figure 3.12 (a) with Figure 3.7 (a). Kinking of internal layers does also occur, but at higher strains as shown in Figure 3.12 (b) and 3.12 (c), for a specimen loaded to 25% strain, regions of kinking are indicated by arrows. However, this kinking differs from that seen on the exterior surface: it occurs throughout the entire eutectic colonies whereas at the surface kinking was limited to occurring to within 10 µm of the boundary. This is attributed to the highly constrained nature of deformation at the specimen interior. At the specimen surface the grain structure is free to deform normally (i.e., out-of-plane), which has been seen in the formation of protrusions, resulting in a localization of compression at the boundaries between grains, which then leads to kinking and brooming at the boundary. At 50% global strain, Figure 3.12 (c) internal layers continue to kink (see arrows in Figure 3.12 (c) with increasing prevalence without developing delaminations between layers, again a direct result of the constraint at the specimen interior which is not present on the surface. Additionally, the kink band widths at the specimen interior are much smaller than those on the specimen exterior, having a width of approximately one micron.
Figure 3.12: SEM micrographs of the internal deformation at increasing strain levels, (a) 15%, (b) 25%, and (c) 50%. As the strain level increases kinking positions indicated with white arrows becomes prevalent with kink band widths smaller than those observed on the specimen surface.

3.6 Dislocation deformation mechanisms

To capture the deformation mechanisms on the nano-scale a limited TEM study of the specimen interior was conducted by Mr. Ben Eftink. This TEM study revealed the presence of dislocations at the interfaces between material layers as indicated by the contrast due to dislocations at the interface, in Figure 3.13 (a). Despite the interface having the cube-on-cube orientation relationship with aligned slip systems dislocation motion between silver and copper is restricted. The lack of dislocation motion is primarily a result of the alternating compression-to-tension coherency strains which enable the matching of the different lattice parameters of silver
and copper at the interface. The coherency strains are typically quite large when compared to the elastic strain at yield. Image forces [Head 1953] also aid in resisting dislocation motion at the interface. Image forces occur on dislocations as they pass from a region of low elastic modulus (i.e., silver) to a region of high elastic modulus (i.e., copper) as a result of the increase in strain energy associated with the dislocation because of the elastic modulus change [Cline and Stein 1969]. The inability of the dislocations to easily glide through the bi-material interface contributes to the increase in strength seen in the material responses shown in Figures 3.2, 3.3 and 3.4.

Additionally this TEM study revealed the presence of deformation twins seen in Figure 3.13 (b) as horizontal lines in both the copper and silver material layers. In Figure 3.13 (b) the dotted line indicates the position of the bi-material interface, and the white arrows indicate crystallographic directions showing twinning is present on the \{111\} plane. The presence and alignment of the deformation twins suggests that there is communication between the layers across the Ag-Cu interface.

Figure 3.13: TEM micrographs of nano-scale deformation mechanisms of compressively loaded Ag-Cu (a) dislocations indicated by the contrast region at material interfaces and (b) deformation twins (horizontal lines) in both copper and silver. The white arrows indicate crystallographic direction, with twinning present on the \{111\} plane. Images are courtesy of Mr. Ben Eftink.
Deformation twinning in the Ag-Cu material system has been reported previously in simulations [Hoagland et al. 2002, Wang et al. 2011] and experimental studies [Beyerlein et al. 2011] when layer thicknesses are similar to those in this study, ~200 nm – 400 nm. At the same time, TEM analysis of the deformation of other multilayered copper systems, such as copper-niobium, have not shown twinning in the copper system up to peak load values of 2.5 GPa [Wang and Misra 2011]. The presence of twinning in the copper layers is of interest because materials with low stacking fault energy such as silver twin readily [Tadmor and Bernstein 2004, Suzuki and Barrett 1958], where materials with medium stacking energy such as copper [Carter and Ray 1977, Hirth and Lothe 1982], tend not to twin particularly under room-temperature quasi-static loading [Beyerlein et al. 2011]. Since twinning has been observed in the Ag-Cu system (see Figure 3.13 (b)) with ultra-fine length scale micro-structure, but has not in the Cu-Nb system or pure copper systems of the same length scale, the interface must play a role in the transfer of deformation to the copper layer. Using atomistic studies the deformation twinning in copper has been observed to occur by emission of twinning partials from silver to copper. Since silver twins readily it provides a source of twinning partials to sustain twinning in copper under deformation [Beyerlein et al. 2011]. The presence of twinning adds additional barriers to dislocation motion as the slip systems are no longer continuous across the layer [Wang and Huang 2006, Anderoglu et al. 2010]. For a single dislocation to cross the twin interface a high resolved shear stress is necessary therefore twinning strengthens the multidirectional material [Aganasyev and Sansoz 2007, Lu et al. 2009]. More details of study at the nano- length scale can be found in the PhD dissertation of Mr. Ben Eftink – in preparation.
3.7 Concluding remarks

In the past the presence of a high density of interfaces in a material in the form of bi-phase interfaces has been shown to increase overall material strength. This strength increase has been examined in the submicron scale and has been attributed to interfacial resistance of strain transfer due to the following dislocation mechanisms: Hall-Petch relation, confined layer slip, and single dislocations crossing through bi-material interfaces. Herein we have studied and directly shown for bulk material the increased static and dynamic strength of a hierarchical structured Ag$_{60}$Cu$_{40}$ material. The hierarchical structure, consisting of two layered arrangements: eutectic colonies and radiating structure, was shown to play a role in the observed deformation mechanisms. Due to the random orientation of the eutectic colonies and grain layers, some layers are oriented favorably to the loading direction allowing deformation mechanisms in the form of kinking, brooming, and interfacial delamination to occur. The initial orientation with respect to the loading direction influences the presence of deformation mechanisms seen on the surface. A system that is highly ordered would provide a simplified system that may allow for a more targeted study of the effect of micro-structure on the material response. A unidirectional silver-copper material is discussed in Chapter 4.
Chapter 4: Directional solidified rod-in-matrix silver-copper eutectic material

A unidirectional Ag$_{60}$Cu$_{40}$ cast eutectic material was produced with a favored crystallographic growth direction matching the cast rod axial direction. Through variation of the casting parameters it was possible to obtain four different micro-structure sizes, as described subsequently. The mechanical response of each micro-structure size was examined under three different compressive loading orientations: 1) loading parallel to the axial growth direction (0˚), 2) loading applied at 45˚ to the growth direction, and 3) loading perpendicular to the growth direction (90˚). As before, non-destructive ultrasonic testing, profilometry and SEM imaging were employed to characterize the deformed material structure with emphasis on identifying the deformation mechanisms that occur in each of the loading orientations and their relation to nominal micro-structure feature sizes.

4.1 Material production

The unidirectional material was cast at Los Alamos National Laboratory by Mr. Ben Eftink and Dr. Doug Safarik. The seed material of the cast unidirectional rods is the undeformed
Ag$_{60}$Cu$_{40}$ multidirectional material presented in Section 3.1. Once the procedure described there is followed to obtain a randomly oriented Ag$_{60}$Cu$_{40}$ rod, this seed material is placed in a fused silica tube and sealed under vacuum. The fused silica tube is then heated to 1223 K in a furnace. Using the Bridgman technique [Bridgman 1925] the fused silica tube is removed from the furnace at a constant rate promoting directional solidification of the silver and copper phases. Three removal rates were used in this study, namely 0.46 mm/hr, 7.3 mm/hr and 73 mm/hr, to control the size scale of the micro-structure that eventually forms. Note that the solidification rate of the unidirectional material is slow compared to the rapid solidification rate by quenching used when producing the multidirectional material (Section 3.1). The combination of removing the melt from the furnace at a prescribed rate and the low solidification rate results in a material with discontinuous copper reinforcements (i.e., rods and platelets) elongated in the axial direction within a silver matrix. The Ag and Cu phases grow with a common $\langle 101 \rangle$ direction parallel to the rod axis [Stein and Cline 1969, Eftink et al. 2014]. Post solidification the cast material is annealed at 673 K for 4 hours at $10^{-6}$ torr to reduce the solid solution solubility of Ag in Cu approaching values on the order of 0.5 atomic percent [He et al. 2006]. The annealing treatment of the unidirectional Ag$_{60}$Cu$_{40}$ material was not observed to change the micro-structure feature size or morphology.

4.2 Unidirectional material characterization before loading

Specimens were cut from the unidirectional cast material using EDM. From a single rod specimens were cut to allow for different orientations of the growth direction (i.e., copper reinforcement direction) with respect to the loading direction. As shown in Figure 4.1 specimens were cut such that the growth direction will be parallel to the specimen axial direction (0°), at 45°
Characterization of the material was conducted at the nano- (<100 nm) and microscale (100 nm -1000 nm) along viewing directions parallel and perpendicular to the growth direction. Specimens were prepared for SEM imaging using mechanical polishing with a final step using 0.3 µm Al₂O₃ slurry. Figures 4.2 (a,c,e,g), in the left hand column, show the unidirectional material structure observed viewing down the axial growth direction for three different removal rates, and at two different magnifications for the slowest rate. Copper reinforcements, the dark areas in the micrographs, are observed to have either circular or elongated cross-sections and are distributed across the Ag matrix material, the lighter area in the micrographs. Two rods were created using the slowest furnace removal rate (0.46 mm/hr) possessing micro-structures with uniform reinforcement thickness of either 1.2 µm (Figure 4.2 (a)) or 800 nm (Figure 4.2 (c)). A previous study of the solidification rates of the unidirectional Ag₆₀Cu₄₀ eutectic material system [Cooksey et al. 1964] indicated feature sizes of 1 µm occurring at rates of 21 µm/s. In our work,
the intermediate removal rate (7.3 mm/hr) resulted in a micro-structure with reinforcement thicknesses of 500 nm (Figure 4.2 (e)) and the highest removal rate (73 mm/hr) had thicknesses of 200 nm (Figure 4.2 (g)). Through comparison of Figures 4.2 (a) and 4.2 (g) it can be seen that the material micro-structure transitions from a rod-in-matrix to platelet-in-matrix micro-structure. Figures 4.2 (b,d,f,h), the right hand column in Figure 4.2, show the unidirectional material structure viewed parallel to the growth direction illustrating the discontinuous nature of the copper reinforcements, i.e., the copper rods/platelets do not extend the entire length of a sample.

Additional specimen preparation involving cryogenic ion milling was conducted by Mr. Ben Eftink for electron backscatter diffraction (EBSD) and TEM imaging. Electron backscatter diffraction provides a color map of material crystallographic orientation. An EBSD map of the crystallographic direction along the cast material axial direction is shown in Figure 4.3 (a) illustrating the uniformity of the \(\langle101\rangle\) axial growth direction. Figure 4.3 (b) presents an EBSD map of crystallographic orientations perpendicular to the axial direction for the same region shown in Figure 4.3 (a) The non-uniformity of the crystallographic orientation perpendicular to the growth direction indicates that the silver and copper phases solidified with crystallographic rotations about the \(\langle101\rangle\) growth direction.
Figure 4.2: SEM characterization of the unidirectional material at solidification rates of (a,b) 0.46 mm/hr (c,d) 0.46 mm/hr, and (e,f) 7.3 mm/hr and (g,h) 73 mm/hr. Images (a,c,e,g) view in the axial growth direction. Images (b,d,f,h) view perpendicular to the growth direction. As the furnace removal rate increases the copper reinforcement thickness decreases. The length of the copper reinforcements is not dependent on the furnace removal rate.
Figure 4.3: An EBSD color map of the unidirectional material (a) with the crystallographic reference direction out of the page highlighting the $\{101\}$ axial growth direction. (b) An EBSD color map of the same region shown in (a) viewing the crystallographic orientations $90^\circ$ to that of (a). Images shown in Figure 4.3 were obtained by Mr. Ben Eftink [Eftink et al. 2014].

A TEM study of the unidirectional material revealed low dislocation density in both Ag and Cu, with Ag exhibiting an initial dislocation density higher than Cu, see Figure 4.4 (a). Dislocations are indicated by arrow heads and elastic distortions by full arrows. High resolution TEM (HRTEM) conducted by Mr. Ben Eftink found that the Ag-Cu interface is $\{111\}$ cube-on cube with irregularly spaced $\{111\}$ steps [Eftink et al. 2014], see Figure 4.4 (b). The previously observed twin-orientation in the multidirectional material was found to occur unidirectional material when solidified using the fastest removal rate 73 mm/hr was used but not at the 0.46
mm/hr rate. The rapid solidification rates necessary to produce the multidirectional material are more favorable to the formation of this twinning interface orientation relationship [Han et al. 1998, Tian and Zhang 2012] when compared to the low solidification rates utilized when casting the 0.46 mm/hr unidirectional material. The steps at the interface indicated by a zig-zag white line in Figure 4.4 (b) can be either a single plane of atoms or multiple planes and account for the observed interface curvature at greater length scales. Misfit dislocations, occurring as extra planes in the Cu phase, at the interface are found from Fourier transformation of the HRTEM images. The misfit dislocation spacing was found to vary between 8-11 planes and are marked in Figure 4.4 (b) with black circles. The spacing of the misfit dislocations matches that found for cube-on-cube orientation relationship in the multidirectional material [Liu et al. 2008]. More details of the material characterization at this length scale can be found in Eftink et al. [2014] and Eftink [2014].

Figure 4.4: TEM images of the unidirectional material. (a) Low dislocation density of the solidified material with higher dislocation density in the silver phase. (b) HRTEM image showing {111} interface steps which are responsible for interface curvature and the position of misfit dislocations as indicated by black circles. Images courtesy of Mr. Ben Eftink [Eftink et al. 2014].
4.3 Loading parallel to reinforcement

Unidirectional cylindrical specimens produced at each of the furnace removal rates with the \(\{101\}\) growth direction matching the loading direction were subjected to mechanical compressive loading under dynamic conditions using a SHPB. Quasi-static loading coupled with digital image correlation was also performed, though it was limited to two experiments because of the large specimen dimensions necessary and the limited material availability. For additional details on the experimental techniques used see Chapter 2.

4.3.1 Dynamic material response

The dynamic material response of specimens loaded parallel to the \(\{101\}\) growth direction produced using each of the furnace removal rates are presented in Figure 4.5. Two castings were done at the 0.46 mm/hr and 73 mm/hr furnace removal rates. The different colors used in Figure 4.5 indicate specimens from separate castings. The furnace removal rate, microstructure feature size and strain rate for each experiment are indicated in the legend. As the micro-structure size is refined the material strength increases with the 200 nm size (73 mm/hr) showing the greatest strength and the 1.2 µm size (0.46 mm/hr) demonstrating the least strength. Table 4.1 provides the yield strength of each curve presented in Figure 4.5. Yield strengths vary slightly due to small changes in the micro-structure size of the length of a casting. These micro-structure size variations are inherent to the casting process.
Figure 4.5: The dynamic stress-strain curves of the 0° loading orientation for each of the furnace removal rates. The dimension of the copper reinforcements and strain rates of each experiment are indicated in the legend.

<table>
<thead>
<tr>
<th>Furnace removal rate (mm/hr)</th>
<th>Nominal feature size</th>
<th>Yield stress $\sigma_y$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.46</td>
<td>1.2 μm</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>800 nm</td>
<td>174</td>
</tr>
<tr>
<td>7.3</td>
<td>500 nm</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td></td>
<td>193</td>
</tr>
<tr>
<td>73</td>
<td>200 nm</td>
<td>207</td>
</tr>
<tr>
<td></td>
<td></td>
<td>347</td>
</tr>
<tr>
<td></td>
<td></td>
<td>331</td>
</tr>
</tbody>
</table>

Table 4.1: Yield strength of materials loaded parallel to the growth direction with micro-structure size and furnace removal rate indicated.

Plastic strain recovery

Under dynamic loading conditions unidirectional specimens loaded parallel to the growth direction with the finest micro-structure (200 nm - 73 mm/hr) exhibited strain recovery upon unloading much greater than can be solely attributed to elastic recovery, perhaps indicating that a secondary recovery mechanism such as plastic recovery may be active. Figure 4.6 shows the initial loading of one specimen (solid cyan line) and the repeated loading of another (dashed line).
lines). The short lines with circles along the top horizontal axis indicate the strain measured using a micrometer after SHPB loading. The short lines with squares along the bottom horizontal axis indicate the strain calculated from SHPB strain gauge signals analyzed with 1-D assumptions, see Chapter 2.2. Two separate specimens (solid cyan and dashed blue) were initially loaded to ~10%. When measured after loading the specimens exhibit strains nearly 4% less than calculated using 1-D assumptions. The elastic modulus of each of the specimens was determined prior to loading using non-destructive ultrasonic testing at 71 GPa. Using this measured elastic modulus and the maximum loads of the cyan and blue curves in Figure 4.6, the predicted elastic recovery is 0.57%, much lower than the nearly 4% difference in the calculated and measured strains. Under subsequent SHPB loading, shown in Figure 4.6, this strain recovery continues to occur though at continually diminishing amounts, until about 22% total strain, at which point strain recovery is almost entirely elastic. This plastic strain recovery was not observed in any other experiments other than the 0° case and then only for the smallest microstructural size scale (200 nm reinforcement size).
Plastic recovery of the Ag-Cu material system has been seen in recent molecular dynamics (MD) simulations [Li and Chew 2014] from the reversal of deformation twinning. In their simulations a multilayer Ag-Cu system with 4 nm thick layers consisting of 40 nm grains was subjected to uniaxial tensile loading normal to the bi-phase interface. Under loading, the intra-layer columnar boundaries act as sources for twinning partials facilitating growth of deformation twins. The twins grow crossing multiple interfaces. Unloading is performed by reversing the loading direction. Once unloaded to below $\varepsilon = 0.01$ the deformation twins retract rapidly to the columnar boundary, thus recovering the plastic strain. The reasoning for the observed recovery is due to the alternating coherency stresses of alternating sign that occur because of the large lattice misfit of silver and copper. There are a number of differences between the MD simulation of Li and Chew [2014] and the unidirectional material used here:
The experimentally observed plastic recovery here occurs under compressive loading, whereas the MD simulation reports recovery under tensile loading. The MD simulation lamellar structure has individual layers that are more than an order of magnitude smaller than the copper reinforcement thicknesses. Despite these differences there is the possibility that the predicted reversal of twinning is the mechanism that causes plastic recovery in both. In the case of the Ag-Cu material system anomalous deformation twins have been reported in the unidirectional material with 1.2 μm micro-structure feature size loaded parallel to the \(101\) crystallographic direction [Eftink et al. 2014].

Other fcc nano-crystalline systems (e.g., aluminum and gold [Rajagopalan et al. 2007, Li et al. 2009]) have also shown plastic recovery over prolonged periods of time at room temperature. The rate of plastic recovery was also found to increase with increasing annealing temperature. Under SHPB loading specimens undergo rapid plastic deformation resulting in specimen heating which could act similarly to the post deformation annealing that accelerated recovery in the nanocrystalline aluminum and gold materials used by Rajagopalan et al. [2007]. Therefore it is possible that thermal energy is necessary to activate the mechanisms responsible for plastic strain recovery. The ability of two fcc nano-structured materials (i.e., aluminum and gold) to recovery plastically suggests that plastic strain recovery may be a feature of other fcc metals such as silver or copper.

Another possible mechanism for strain recovery at this scale can be attributed to the nature of the interfaces separating the Cu and Ag. Although the twin reversal discussed above could explain a partial recovery of plastic strain, it would necessitate nearly perfect reversal of the complex mechanisms of twin formation, including any interactions that had occurred between the twin and the Cu-Ag interface. An alternate reversible deformation mechanism at this
length scale could be dislocation based and associated with the ability of the Cu-Ag interface to absorb dislocations. Upon unloading dislocations previously “stored” at the Cu-Ag interface may be released thus producing a global strain recovery. The ability of the boundary to store and release dislocations would depend on boundary type, on dimensions such as the inter-boundary spacing (linked to the microstructure feature size), and on the local stress state, thus explaining why this recovery is visible only for the smallest microstructural feature and only for 0° loading. Of course determining which one(s) of these mechanisms occurs requires additional TEM microscopy studies beyond the scope of the present document.

Another alternative mechanism, but at a somewhat higher length scale than those discussed above, for the observed plastic recovery could be driven by residual internal stresses due to inhomogeneous loading according to Rajagopalan et al. [2007]. During the initial phase of the deformation the material deforms elastically. At some critical stress favorably oriented regions of the specimen deform plastically while other non-favorably oriented regions continue to deform elastically. The non-homogeneous deformation causes localized internal stresses to build in the specimen. Eventually under additional loading all regions of the specimen deform plastically resulting in a constant stress-strain slope. Total specimen strain is composed of recoverable elastic strain, permanent non-recoverable plastic strain from all specimen regions deforming plastically, and recoverable plastic deformation from the non-homogeneous deformation. The recovery of the plastic deformation from the non-homogeneous deformation is driven by internal residual stresses. The ends of dislocations that occur within either the copper or silver phase can be pinned at the Ag-Cu interface. Under load these dislocations propagate within the interior of the layer overcoming barriers because of the additional energy from loading. During unloading the dislocations retreat back towards the Ag-Cu interface due to
residual internal stresses and thermal assisted depinning. Residual internal stresses are present in the silver-copper eutectic system in the form of coherency stress which occur as a result of the lattice mismatch between silver and copper. The experimentally observed, temperature dependent plastic recovery suggests thermally assisted depinning of dislocations could possibly be the responsible mechanism.

4.3.2 Quasi-static material response

Further investigation of the plastic recovery seen in the 200 nm unidirectional micro-structured material was conducted under quasi-static loading conditions. Additional quasi-static experiments were selected because the far field applied load displacement data can be supplemented with digital image correlation (DIC). Through using DIC a mapping of the local deformation over nearly the entire sample can be captured. If plastic strain recovery were to occur locally or over an entire specimen at the levels shown in under dynamic loading it would be resolvable using DIC. Digital image correlation uses sets of images captured in succession of a speckled specimen surface during deformation. The speckled surface provides a non-uniform pixel intensity over the surface. Selecting subsets of pixels from the captured digital images, correlation methods track the motion of subsets by matching average intensity of the subsets before and after deformation. From the correlation methods used the specimen deformation can be monitored in 2-D using one camera, or in 3-D using two cameras capturing images simultaneously. In our case since we wish to image curved cylindrical surfaces so, 3-D stereo DIC was conducted using two Allied Vision Tech Prosilica GX cameras with frame rates of 10 Hz. The captured image sets were analyzed using a commercial package, Vic-3D from
Correlated Solutions Inc., with a pixel subset size of 51, a spatial resolution of 16 µm/pixel, and a correlation interval of 7 pixels. A typical speckle pattern of a cylindrical specimen is shown in Figure 4.7 (a). A contour map of the strain in the loading direction (vertical) obtained using 3-D DIC is shown in Figure 4.7 (b).

![Figure 4.7](a) A typical surface speckle pattern of a specimen used for three-dimensional digital image correlation, (b) a contour map of the vertical strain determined using 3-D DIC.

Quasi-static compressive loading was conducted on two specimens with growth directions matching the loading direction and with micro-structure feature sizes of 200 nm. Both specimens were prepared from the same casting using EDM machining with final dimensions of 7.90 mm diameter by 8 mm length for the first and 7.94 mm diameter by 16 mm length for the second. The flat surfaces of each cylindrical specimen were mechanically polished with a final
step using a 3 micron diamond suspension. Speckle patterns necessary for DIC were applied to
the radial surface of each specimen as shown in Figure 4.7 (a).

An Instron 8800 servo-hydraulic load frame with 100 kN load cell was used to apply
mechanical loading at a strain rate of $10^{-3}$ s$^{-1}$. To limit the effect of friction during loading
lubrication was applied to the specimen/platen contact surfaces. Deformation of the 8 mm long
specimen was conducted by first deforming the material to 3% strain, followed by unloading.
This process was repeated using ~3% strain increments up to 12% strain. The 8 mm length
specimen stress-strain material response, corrected for machine compliance, is presented in
Figure 4.8. Each of the ~3% compression increments and the corresponding unload curves are
shown in matching colors. The elastic modulus ($E$) of the 8 mm length specimen measured from
the initial linear portion of the stress strain curve was 94 GPa and the initial yield stress ($\sigma_y$)
found using a 0.2% strain offset from the blue curve in Figure 4.8 is 192 MPa. The strain
hardening exponent ($n$) of the 8 mm length specimen determined from the slope of the natural
log of the stress and strain ($\ln(\sigma)$ vs $\ln(\varepsilon)$) in the plastic region was 0.28.

The 16 mm length specimen was deformed to 4% compressive strain then unloaded, see
Figure 4.9. The specimen elastic modulus ($E$) of 97 GPa, offset yield strength ($\sigma_y$) of 219 MPa,
and strain hardening exponent ($n$) 0.31 were determined from the stress-strain response. The
colored short tick marks along the top horizontal axis of Figures 4.8 and 4.9 indicate the strain
measured with a micrometer after each deformation increment. In this case, unlike the SHPB
results earlier, the engineering strain measured after each loading increment is in good agreement
with the load frame compliance corrected engineering strain. Due to limitations of the Instron
8800 load frame used there was a time delay between the finishing of the loading increment and
the initiation of the unloading resulting in the gap in data seen between the loading and unloading curves of the same color in Figures 4.8 and 4.9.

**Figure 4.8**: The stress-strain response of an 8 mm long 7.90 mm diameter unidirectional Ag-Cu specimen loaded parallel to the material growth direction. Loading was conducted in ~3% strain increments followed by unloading. Tick marks along the top horizontal axis indicate the measured compressive strain of the specimen after each loading increment.

**Figure 4.9**: The stress-strain response of a 16 mm long 7.94 mm diameter...
unidirectional AgCu specimen loaded parallel to the material growth direction. The tick mark along the top horizontal axis indicates the compressive strain of the specimen measured via micrometer after loading.

In Figures 4.8 and 4.9 the only observed recovery occurs elastically with the unloading curve matching the elastic modulus of the loading curve. To ensure that if plastic recovery were to occur but was not resolved by the load cell or load frame displacement 3-D DIC was conducted during the unloading portion of each of the quasi-static experiments. Shown in Figure 4.10 (a) is the unloading curve of the 16 mm specimen. Recorded strains from 3-D DIC are presented at four points along the unloading curve 1) at the initiation of unloading, 2) at half of the load of point 1, 3) the point at which the load frame no longer measures an applied load, and 4) after the specimen is unloaded and a visible gap appears between the compression platens and specimen. These points were chosen such that if plastic recovery were to occur it would appear between points 3) and 4). Points 1) and 2) are chosen to demonstrate the accuracy and capability of the 3D DIC measurements to measure small strains. The DIC calculated strain in the axial loading direction is presented for each of the four points mentioned above in Figures 4.10 (b,c,d,e). The DIC obtained average strain fields closely match the strain values of the stress strain curve. The color bar shown in Figure 4.10 spans the minimum and maximum strains calculated via 3D DIC. The discrepancy in the sign of the strains between Figure 4.10 (a) and Figures 4.10 (b,c,d,e) is due to DIC interpreting the specimen motion as a tensile experiment not the unloading of a compressed specimen. The observed strains in Figure 4.10 (d) and Figure 4.10 (e) are constant and do not show strain recovery. To determine if plastic strain recovery occurred locally and is not visible in Figures 4.10 (b,c,d,e) due to only showing 16 color contours, the vertical strain (\( \varepsilon_{yy} \)) at heights of 3.5 mm, 0 mm, and -3.5 mm are given in Figures 4.11 (a), 4.11
(b) and 4.11 (c) respectively. The vertical strain in the vertical direction is presented in Figure 4.11 (d).

Form each of the plots in Figures 4.10 and 4.11 it can be seen that local plastic recovery does not occur under quasi-static conditions. If the active deformation mechanism that allows for plastic strain recovery is twinning it could be possible that high strain rate loading is necessary to cause the formation of deformation twins and more specifically twins in the copper layer. It is well established that copper does not exhibit deformation twinning unless loaded under specific conditions such as low temperature deformation [Blewitt et al. 1957] or if the micro-structure is refined to the ultra-fine or nano-scale [Meyers et al. 1995]. Perhaps the quasi-static loading does not occur at high enough of strain rate to cause twinning in the copper layer.

TEM study of a unidirectional Ag-Cu material with the 1.2 micro-structure feature size has shown deformation twinning in the copper layer due to silver supplying dislocation partials. If the micro-structure is refined to the 200 nm scale it could be possible that a greater number of twins to be present in copper since the micro-structure would be more favorable for them to occur. Of greatest interest to further the understanding of the observed plastic recovery is additional TEM study of quasi-statically and dynamically deformed specimens, but this has not taken place at this time.
Figure 4.10: 3D DIC study of plastic recovery of 73 mm/hr specimens under quasi-static loading. (a) The compliance corrected unloading curve of the 16 mm long specimen (b,c,d,e) 3D-DIC calculated strains in the axial loading direction at the points indicated in (a). Point (e) occurs after a visible separation between the compression platens and specimen appears.
Figure 4.11: The 3D DIC strain in the vertical direction. Values in x direction height positions of (a) 3.5 mm, (b) 0 mm, and (c) -3.5 mm. Values in the y direction along x=0 are given in (d).

Following deformation, specimens were imaged under a stereo microscope. For the 0° loading orientation striations appear at compressive strains above 10% on the specimen radial surface as indicated by white arrows in Figure 4.12 (a). The striations match the direction of the copper reinforcements and run the entire specimen height. The radial deformation of specimens was observed to be non-uniform at strains above 10%. To highlight this point a dashed circle of
the initial specimen diameter has been overlaid in Figure 4.12 (b). The position of the striation shown in Figure 4.12 (a) is indicated with a white arrow in the top view Figure 4.12 (b).

![Figure 4.12](image.png)

**Figure 4.12**: Macroscopic deformation of a parallel loading orientation specimen. (a) The radial surface of a specimen loaded parallel to the growth direction to 12% compressive strain. White arrows indicate the position of a vertical striation that match the copper reinforcement direction. (b) The top view of the same specimen shown in (a) highlighting the non-uniform deformation in all radial directions. The position of the striation shown in (a) is indicated in (b) with a white arrow.

### 4.3.3 Deformation mechanisms

**Microstructure Deformation**

Deformed specimens were prepared for SEM imaging of their internal deformation structure by cutting along the axial direction using EDM. The two specimen halves were then mounted in a conductive epoxy (Beuhler) for ease of handling during polishing. Mechanical polishing with a final step using a 0.3 µm Al₂O₃ slurry was conducted to prepare surfaces for imaging. SEM images of the interior of a 0° specimen deformed to 16 % are shown in Figure 4.13 (a) and 4.13 (b). The loading direction in both images and throughout this chapter is in the vertical direction. At the length scales observable with SEM the deformed specimen microstructure at the center of the specimen does not show noticeable deviation from the initial as-cast
structure – compare Figure 4.13 (a) to Figure 4.1 (d). The constraint provided by neighboring material is high enough to suppress microscale deformation mechanisms. Near the radial surface where the material is less constrained, kinking of the copper reinforcements becomes apparent at compressive strains greater than 10%, see Figure 4.13 (b). Material near the kinked region is preferentially forced outwards radially and is what appears on the specimen radial surface as vertical striations (see Figure 4.8) matching the copper reinforcement direction.

Dislocation deformation mechanisms

TEM study of deformed specimens produced using a furnace removal rate 0.46 mm/hr with 1.2 μm feature sizes did find that dislocation slip is the primary deformation mechanism [Eftink et al. 2014]. Twinning was not observed to occur in either the copper or silver phase. Additional TEM study is necessary to distinguish the deformation mechanisms occurring as the microstructure is refined to the ultra-fine scale.

4.4 Loading at 45° to reinforcement

The machining of specimens with 45° reinforcement orientation to the loading direction results in significant waste material. In order to be as efficient as possible with the limited
material available to this study, a reduced number of experiments at this orientation were conducted for each of the furnace removal rates. For quasi-static testing the necessary specimen dimensions were simply not obtainable because of the initial dimensions of the directionally solidified rod. Dynamic SHPB loading requires a smaller specimen geometry that can be more easily machined from the initial directionally solidified material. Therefore only dynamic SHPB loading was conducted in this case.

4.4.1 Dynamic material response

The dynamic material responses of specimens produced from the cast material with the copper reinforcement (growth) direction at 45° to the loading direction are presented in Figure 4.14. The furnace removal rate, micro-structure sizes and strain rates are indicated in the legend for each trace. As was observed with the parallel loading orientation there is a yield strength dependence on the micro-structure feature size. Specimens with the finest structure of 200 nm (73 mm/hr) possessed the greatest yield strength of 176 MPa and 197 MPa. Specimens produced from furnace removal rates below 73 mm/hr had similar yield strengths between 88 MPa and 120 MPa.
Figure 4.14: The dynamic stress-strain curves of the 45° loading orientation for each of the furnace removal rates. The dimension of the copper reinforcements and strain rates of each experiment are indicated in the legend.

4.4.2 Macroscopic deformation

Stereo microscope images of the resulting macroscopic deformation were captured following deformation. On the radial surface diagonal shear bands occur that match the direction of the copper reinforcements, see Figure 4.15 (a). The positions of shear banding in Figure 4.15 (a) are indicated by white arrows. When observed from above the non-uniform deformation that results from the preferential shear along the copper reinforcement direction (out of the page and to the left) becomes apparent, see Figure 4.15 (b). A dashed circle overlay of the initial specimen diameter highlights the elliptical cross-section with results from deformation.
Figure 4.15: Macroscopic deformation of a 45° loading orientation specimen. (a) The side view of a specimen deformed to 20% compressive strain with arrows indicating the position of shear banding with matches the direction of the copper reinforcements. (b) The top view of the same specimen shown in (a) highlighting the non-uniform deformation which preferentially occurs along the direction of the copper reinforcements is the operative deformation mechanism.

Stylus profilometry was conducted to study the shear banding observed on the specimen radial surface to obtain band spacing with respect to the micro-structure feature size. Deformed specimens were cut in half along the semi-major axis in the axial direction using EDM, then cast in PDMS (Sylagaard 184) to securely hold them preventing motion during scanning. Line contour images of scans conducted with 10 µm offsets of a 0.46 mm/hr specimen deformed to 28% strain and of a 73 mm/hr specimen deformed to 20% strain are shown in Figure 4.16 (a) and 4.16 (b), respectively. The reinforcement orientation in Figure 4.16 (a) is up and to the right, and in Figure 4.16 (b) is down and the right. The positions of a few prevalent shear bands are indicated with black arrows. The shear band spacing was found to be dependent on the micro-structure feature size. The shear band spacing of a 0.46 mm/hr specimen with 800 nm micro-structure feature size was measured at 295 µm. The 73 mm/hr specimen with the finest micro-structure feature size has an average shear band spacing of 95 µm. Although the contours shown are for specimens deformed to different levels of strain they show the observed trend that finer micro-structured specimens showed smaller spacing of shear bands and coarser structured materials showing greater spacing.
Figure 4.16: Contour profile images obtained from stylus profilometry scans of the radial surface of 45° loading orientations specimens. (a) A specimen produced using furnace removal rate of 0.46 mm/hr with a 800 nm micro-structure feature size with the orientation of the reinforcements horizontally up and to the right (b) A specimen produced using a furnace removal rate of 73 mm/hr with a 200 nm micro-structure feature size with the orientation of the reinforcements horizontally down and to the right. The positions of prominent shear bands are indicated with black arrows.

4.4.3 Deformation mechanisms

To investigate the deformation along the direction of greatest lateral strain the deformed specimen was cut using EDM in the axial direction along the cross-section semi-major axis. The resulting pieces were then mounted in a conductive epoxy followed by mechanical polishing in manner identical to the 0° specimens, see Section 4.3. SEM images of the internal deformation structure of a 0.46 mm/hr specimen with 1.2 µm feature size are shown in Figures 4.17 (a), 4.17 (b) and 4.17 (c) at increasing magnifications. An image of a 73 mm/hr specimen with 200 nm feature size is shown in Figure 4.17 (d). SEM imaging conducted over the specimen interior
revealed a uniform structure with copper reinforcements at 45° to the vertical loading direction. Previously observed microscale deformation mechanisms such as interfacial delamination or kinking were not observed. In response to the compressive deformation there are changes observed in the copper reinforcements at high levels of magnification, see Figures 4.17 (b) and 4.17 (c). The silver-copper interface is straight in the as-cast orientation but becomes wavy under deformation. The waviness indicates that deformation is occurring concurrently in the silver matrix and the copper reinforcements primarily in the form of shear. If deformation were only occurring in the Ag matrix or the Cu reinforcements separations would appear at the terminations of the reinforcements. At micro-structure feature sizes below 1.2 µm waviness of the silver-copper interface was not observed at this scale as shown in Figure 4.17 (d).

![Figure 4.17: SEM micrographs of the internal deformation of the 45° fiber orientation to loading of at increasing magnifications (a,b,c) of a 0.46 mm/hr removal rate specimen. Internal deformation of 73 mm/hr removal rate specimen is shown in (d). Waviness of the silver-copper interface was observed in deformed specimens with micro-structure features sizes greater than 800 nm.](image-url)
The dislocation deformation mechanisms present when loading at 45° to the growth direction differ from those in the 0° case. Dislocation slip occurs, as in the 0° case, with additional abundant twinning in both silver and copper phases. Twinning has been viewed in silver terminating at the Ag-Cu interface as well as crossing the interface from silver to copper. In regions where deformation twins do not cross the interface dislocation emission into the copper phase has been observed [Eftink et al. 2014].

4.5 Loading perpendicular to reinforcement

As with the 45° orientation specimens the production of specimens with reinforcement orientation perpendicular to the specimen axial direction creates significant waste material. Therefore the material response of the 90° orientation was only investigated dynamically followed by sectioning and SEM imaging of internal deformation.

4.5.1 Dynamic material response

The stress-strain response of specimens loaded at 90° to the growth direction is presented in Figure 4.18. As was shown in the 0° and 45° case the finest micro-structure feature size exhibits the greatest strength response with a value of 273 MPa. The response of the 7.3 mm/hr and 0.46 mm/hr specimens are similar falling between 100 MPa and 154 MPa.
Figure 4.18: The dynamic stress-strain curves of the 90° loading orientation for each of the furnace removal rates. The dimension of the copper reinforcements and strain rates of each experiment are indicated in the legend.

4.5.2 Macroscopic deformation

In response to loading the deformation of the 90° orientation specimens showed the high levels of anisotropy expanding greatly in the direction perpendicular the copper reinforcements see Figure 4.19 (a). An overlay of the initial specimen diameter prior to deformation is included for comparison. The presence of the copper reinforcements constrains deformation in the vertical direction of Figure 4.19 (a). To accommodate compressive deformation the specimen expands readily perpendicular to the reinforcement direction (i.e., in the horizontal direction of Figure 4.19 (a)). On the loading surface striations similar in appearance to shallow notches become apparent matching the direction of the reinforcements in the deformed specimen. These striations occurred in each of the 90° orientation specimens. Crossing shear bands are visible on the specimen radial surface when looking down the growth direction, see Figure 4.19 (b). The position of the shear bands are highlighted by white arrows.
**Figure 4.19**: Macroscopic deformation of a 90° loading orientation specimen. (a) The top view of a typical specimen response highlighting the preferential deformation in the direction perpendicular to vertical fiber direction. The dashed white circle indicates the initial specimen diameter. (b) The side view of a specimen deformed to 20% compressive strain with arrows indicating the position of crossing shear bands.

4.5.3 Deformation mechanisms

*Deformation along the reinforcement growth direction*

From Figure 4.19 (a) we see that there is limited macroscopic deformation along the reinforcement direction of the material. The typical measured strain in the growth direction of the 90° loading orientation for specimens was less than 5% of the initial diameter. SEM images of the internal micro-structure of a 73 mm/hr specimen viewed perpendicularly to the growth direction show intact copper reinforcements, see Figure 4.20. The lack of deformation in the growth direction indicates that the silver-copper interface is resistant to shear deformation. Studies of fcc-fcc coherent interfaces [Anderson and Carpenter 2010] have shown that the coherent interface is relatively strong in shear compared to the fcc-bcc incoherent interface [Bellou et al. 2011].
Figure 4.20: SEM micrograph of the deformation in the growth direction of a 90° loading orientation specimen.

Surface striations

The striations on the deformed specimen loading surfaces were studied using stylus profilometry obtaining a 3-D profile of the observed striations. Figure 4.21 shows a profilometry scan of the loading surface of a 0.46 mm/hr specimen deformed to 25% strain. The growth direction of the copper reinforcements matches the horizontal direction in Figure 4.21. The depth of the notches on the surface varies from relatively shallow notches of just a few microns to deep notches up to 50 microns deep.
An SEM study was performed with focus placed on studying the localized deformation that exists near the surface striations, particularly those with a $v$-notch shape. An example of $v$-notch shape is shown in blue near the bottom of the profiled region in Figure 4.20. Specimens were cut via EDM and polished in the same fashion as previously described. The selected SEM viewing direction is coincidental to the growth direction of the copper reinforcements. SEM images of regions near surface notches are presented in Figures 4.22 and 4.23. The first step of the formation of the surface notches is shown in Figure 4.22. A white arrow is used to indicate the position of a colony boundary between eutectic regions that solidified concurrently. As the specimen was subjected to compressive loading the deformation along the reinforcement
direction was limited resulting in tensile loading perpendicular to the fiber direction, horizontal in Figure 4.22. After reaching a critical value, the tensile loading in the lateral direction caused slipping at the boundary between neighboring colonies resulting in a shallow depression forming at the loading surface as shown in Figure 4.22. A contour matching the depression shape is presented to highlight profile of the shallow depression presence.

![Depression contour](image)

**Figure 4.22:** The shallow surface depression that takes place as a result of the sliding of neighboring eutectic colonies near the at the specimen surface. This is the first step in the formation of the notching seen on the loading surface. Viewing direction is coincidental to the axial growth direction.

After the formation of the shallow depression, continued sliding at the colony boundary resulted in the formation of v-notch resembling a blunted crack tip. The tensile loading perpendicular to the reinforcement direction acts to load the notch in mode I. Specimen dimensions in the direction of the notch allow for plane strain assumptions. SEM images of the region near a notch that has opened a short distance are presented in Figure 4.23 (a) with a zoomed in image near the notch tip shown in Figure 4.23 (b). The vertical dashed white line
indicates the notch plane. A general shape of the plastic zone around a notch in plane strain conditions has elliptical shaped lobes that extend perpendicularly from the plane. This generalized shape of a plane strain plastic zone is superimposed over Figure 4.23 (a) as a means of aiding in the explanation of the deformation regions observed near the notch tip and is not intended to portray the actual plastic zone. In the “wake zone” of the notch significant thinning of the copper reinforcements has occurred as a result of the high localized stresses on either side of the notch tip. Within the general area of the conceptual plastic zone significant reductions in the reinforcement thickness are also observed. The zoomed in region presented in Figure 4.23 (b) shows the significant reduction in the micro-structure feature size. Reinforcements that have initial thicknesses of 1 µm - 2 µm just ahead of the notch tip are reduced in thickness to just a few tens of nano-meters. Even under the severe reduction in thickness (see Figure 4.23 (b)) separation between the silver matrix and copper reinforcements is not observed under SEM imaging conditions pointing again to the strength of the interface to shear loading.
Figure 4.23: Deformation near surface notching seen in the 90° loading orientation. (a) A zoomed out view showing the size of the deformed micro-structure region occurring because of the stress concentration caused by a v-notch. The white dashed line indicates the notch plane, and the red elliptical lobed shape is the generalized shape of the plastic zone of a plane strain notch. (b) A zoomed in region of the micro-structure near the notch tip showing the significant reduction of the micro-structure feature size.
**Shear banding**

Shear banding is a non-crystallographic band-like region of concentrated plastic deformation which occurs in practically all bulk metals subjected to plastic deformation [Duggan et al. 1978, Tvergaard and Needleman 1993, Hirsch and Lucke 1988]. Shear banding is a localized mechanism that takes place when dislocation or twinning deformation is hindered or requires very high levels of stress [Wagner et al. 2007, Hong et al. 2010]. It starts at or within individual gains and may proceed across multiple interfaces without substantially altering morphological features [Paul et al. 2009, Duckman et al. 2001]. Crystal plasticity finite element (CPFE) models of a 2-D plane strain Cu-Ag layered material system with layer thicknesses selected to mimic the eutectic composition (3:6.5) loaded under compression have shown a crystal orientation dependence on the propagation of shear banding across multiple Ag-Cu interfaces [Jia et al. 2013]. Shear banding in single phase copper and single phase silver is favored in the $(\{112\},\{11\overline{1}\})$ orientation and suppressed in the $(011),(0\overline{1}0)$ orientation. Shear banding can occur in the layer with the most favorable orientation and then due to the stress concentration at the phase boundary (i.e., silver-copper interface) communicate across multiple layers. Over the layer orientations examined in the CPFE model [Jia et al. 2013] shear bands were communicated by stress concentrations at the phase boundaries under similar levels of strain as those used to deform the specimen shown in Figure 4.19 (b). Shear banding in the unidirectional material loaded transversely to the growth direction results in severe thickness reductions of the copper and silver phases as shown in Figure 4.24. The shear bands observed extend through the thickness of the deformed specimen. Unlike kinking, brooming and interfacial delamination shear banding is a deformation mechanism that does not directly depend on the micro-structure of the material.
**Figure 4.24**: SEM micrograph of a region of shear banding through multiple silver-copper interfaces. Severe reductions in thickness occur over the width of the shear band.

**Dislocation deformation mechanisms**

Unlike loading the 0° and 45° loading orientations the 90° orientation has crystallographic orientation dependent dislocation deformation mechanisms. From rotations of the crystallographic structure of the material phases about the growth direction along the cast material length different orientations perpendicular to the \( \langle 10\bar{1} \rangle \) direction are possible. The two local loading orientations \([10\bar{1}]\) and \([11\bar{1}]\) have been studied [Eftink et al. 2014]. In the \([10\bar{1}]\) orientation dislocation slip is the dominant deformation mechanism. In the \([11\bar{1}]\) orientation both twinning and dislocation slip occur.
4.6 Unidirectional material response comparisons

4.6.1 Specimen axial elastic modulus

The elastic modulus of each specimen was found using non-destructive ultrasonic testing prior to deformation. A summary of the measured axial elastic modulus of specimens is presented in Figure 4.25 with the rule of mixtures predicted isotropic elastic modulus \( E_{ROM} \) and the isotropic modulus of bulk pure copper \( E_{Cu} \) and pure silver \( E_{Ag} \). Furnace removal rates of 0.46 mm/hr and 7.3 mm/hr exhibit elastic moduli similar to the isotropic rule of mixtures estimate. The unidirectional material produced at a removal rate of 73 mm/hr displayed an axial elastic modulus below the isotropic modulus of silver. In general the elastic modulus along the growth direction (0° orientation) was the greatest. The elastic modulus of the 45° and 90° orientation were observed to be similar over all micro-structure feature sizes examined.

![Figure 4.25](image)

**Figure 4.25:** The elastic modulus of unidirectional materials with different solidification rates and fiber orientations determined through non-destructive ultrasonic testing.
As was shown in Section 4.2 the unidirectional material has a preferred \(\langle 101\rangle\) axial growth direction. To account for the variation in elastic modulus with respect to the loading direction crystal anisotropy was investigated. Both silver and copper have cubic symmetry and thus there are only three independent stiffness elastic constants \((C_{11}, C_{12}, \text{ and } C_{44})\) necessary to describe their elastic response. The elastic constants of each material are provided in Table 4.2. In the case of uniaxial tension or compression the elastic modulus in the direction of applied load can be calculated for cubic crystals using the following [Nye 1985]

\[
\frac{1}{E_{hkl}} = S_{11} - 2 \left( S_{11} - S_{12} \right) \frac{1}{2} S_{44} \left( m^2 n^2 + n^2 p^2 + m^2 p^2 \right),
\]

(4.1)

where \(hkl\) indicates the crystallographic direction of the elastic modulus being solved for, \(S_{11}, S_{12}, \text{ and } S_{44}\) are the elastic compliance values of the material determined from the inverse of the fourth order stiffness tensor \(S_{ijkl} = C_{ijkl}^{-1}\), and \(m, n, p\) are the direction cosines of the angle between the direction of interest \([hkl]\) and the \(x, y, z\) \(\langle 100\rangle\) directions. The value of the direction cosines contribution of Equation 4.1 is zero for the \(\langle 100\rangle\) crystal directions and is at a maximum of 1/3 for the \(\langle 111\rangle\) direction.

| \(\text{Table 4.2: Elastic constants of silver and copper cubic crystals. } C_{11} \text{ corresponds to the } \langle 100\rangle \text{ crystal direction. [Radwan 2011]}\) |
|-----------------|-----------------|-----------------|
| \(C_{11}\)      | Silver (GPa)    | Copper (GPa)    |
| 122.2           | 169             |
| \(C_{12}\)      | 91.8            | 122             |
| \(C_{44}\)      | 46.1            | 75.3            |

For the loading case parallel to the fiber (i.e., growth) direction the crystallographic loading orientation is along the \(\langle 101\rangle\) direction. When loading at 45° to the growth direction the
possible crystallographic loading orientations include the \langle 100 \rangle and \langle 001 \rangle directions. The loading at 90° to growth case leads to the possibility of any of the following crystallographic orientations, \langle 010 \rangle, \langle 101 \rangle, \langle 10 \overline{1} \rangle, \langle 11 \overline{1} \rangle, \langle 1 \overline{1} 1 \rangle, \langle 1 \overline{1} 1 \rangle and \langle 11 \overline{1} \rangle. The increased number of crystallographic orientation that are possible is a result of the rotation of the crystal structure about the growth direction as was demonstrated to occur in the unidirectional Ag_{60}Cu_{40} material system, see Figure 4.3(b). Equation (4.1) simplifies for the 0°, 45°, and 90° loading cases into the three following equations of interest. The low crystal indices of \langle 111 \rangle and \langle 100 \rangle provide the respective maximum and minimum elastic moduli for materials with cubic symmetry [Hopcroft et al. 2010]:

\[
\frac{1}{E_{100}} = S_{11}, \quad (4.2)
\]

\[
\frac{1}{E_{101}} = S_{11} - \frac{1}{2} \left( S_{11} - S_{22} \right) - \frac{1}{2} S_{44}, \quad (4.3)
\]

\[
\frac{1}{E_{111}} = S_{11} - \frac{2}{3} \left( S_{11} - S_{12} \right) - \frac{1}{2} S_{44}, \quad (4.4)
\]

The calculated elastic modulus in each of the directions for silver and copper and a simple rule of mixtures estimate are given in Table 4.3. The silver and copper estimates shown in Table 4.3 are used as the limiting bounds for describing the range of possible elastic moduli that could be accounted for with crystal anisotropy when measuring the elastic moduli of unidirectional materials. These bounds are indicated in Figure 4.26 as short horizontal lines with the crystal direction indicated next to them. The plotted range of Figure 4.26 does not include the elastic modulus of \langle 111 \rangle copper or the \langle 111 \rangle rule of mixtures estimate as they far exceed the ultrasonically measured elastic moduli.
Table 4.3: Calculated elastic constants of silver, copper, and simple rule of mixtures estimate (ROM) from equations (4.2-4.4).

<table>
<thead>
<tr>
<th></th>
<th>Silver (GPa)</th>
<th>Copper (GPa)</th>
<th>ROM (GPa)</th>
</tr>
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<tbody>
<tr>
<td>$E_{100}$</td>
<td>43</td>
<td>66</td>
<td>52</td>
</tr>
<tr>
<td>$E_{101}$</td>
<td>83.</td>
<td>130</td>
<td>102</td>
</tr>
<tr>
<td>$E_{111}$</td>
<td>120</td>
<td>191</td>
<td>148</td>
</tr>
</tbody>
</table>

Figure 4.26: Comparison of crystal anisotropy elastic bounds with the ultrasonically measured elastic moduli of each of the three loading orientations.

The elastic moduli calculated using Equations (4.2), (4.3), and (4.4) differ from those measured ultrasonically. The rotations about the $(101)$ direction are not accounted for in the above calculations nor are higher index directions. Therefore the calculated elastic modulus upper bound of the $45^\circ$ orientation may be greater, encompassing the measured values of the $0.46$ mm/hr and $7.3$ mm/hr removal rate materials. Additionally, the above formulation does not account for the presence of an interface between the silver and copper. At the interface the
presence of coherency strains may cause elastic modulus deviations from the theoretical predicted values since the copper phase is under tension and the silver phase is under compression.

As with the multidirectional material system the reasoning for the decreased elastic modulus is still under study. The reduced elastic modulus was measured by non-destructive ultrasonic testing, quasi-static loading, and dynamic loading. The presence of the increased number of silver-copper interfaces leads to an atypical material response in the elastic region.

4.6.2 Yield stress

The dynamic testing conducted captured a strength dependence on the micro-structure feature size and loading orientation. Dynamic stress strain curves initially presented in Figures 4.5, 4.14, and 4.18 are now presented in Figures 4.27 (a,b,c,d) organized by micro-structure feature size from largest to smallest respectively. In Figure 4.27 (d) the quasi-static stress-strain is also included showing that the 0° loading orientation of the finest micro-structure may be mildly strain-rate sensitive between $10^{-3}$ s$^{-1}$ and $10^{3}$ s$^{-1}$. Additional quasi-static testing for each furnace removal rate and loading orientation should be conducted to more accurately capture strain-rate sensitivity.
Figure 4.27: Comparison of the material response to loading for each orientation for specimens with (a) 1.2 µm, (b) 800 nm, (c) 500 nm, and (d) 200 nm. Both quasi-static and dynamic curves of the 0° loading orientation for the 200 nm micro-structure are shown in (d).

For each of the solidification conditions it was seen that the 0° fiber orientation had the greatest yield strength followed by the 90° orientation with the 45° orientation having the least strength. Figure 4.28 shows the yield strength of each of the loading orientations with respect to the inverse root of the dimension ($h^{-1/2}$) of the copper reinforcement. For the coarser micro-structures there is relatively small change in the yield strength of the material with respect to
loading direction. Finer micro-structures exhibit greater difference in the strength of each of the loading orientations. Linear fits were applied to each of the loading orientations and are included in Figure 4.28. Additionally the yield strength of the multidirectional material is included as a horizontal black line.

![Figure 4.28](image)

**Figure 4.28:** A comparison of the unidirectional material yield strength of each fiber orientation with respect to micro-structure feature size.

The Hall-Petch strength relationship is explained as occurring due to the pile-up of dislocations at interfaces. The differences in the slopes of the three loading orientations are attributed to the dislocation mechanisms that occur in each orientation. The dislocation deformation mechanism active in the 0° orientation is dislocation slip. The coherent Ag-Cu interface hinders the transmission of slip through the interface because of the alternating coherency strains, image forces due to modulus mismatch [Hoagland et al. 2004]. An increase in the number of interfaces decreases the distance that dislocations can travel before encountering an interface. The reduced propagation distance and resistance to slip transmission leads to an
increased material strength response with decreasing micro-structure length scale. In the 45° orientation the twinning is the primary deformation mechanism and dislocation slip is the secondary deformation mechanism. Deformation twins in silver provide ample supply of twinning partials to copper facilitating anomalous twinning [Wang et al. 2011]. The increase in the number of interfaces will not directly affect the occurrence of twinning. The secondary dislocation slip causes the resulting increase in the observed strength as the micro-structure is refined as interfaces and twinned regions. The observed dislocation deformation mechanisms in the 90° loading orientation were found to be dependent on the crystallographic loading orientation. Both dislocation slip and deformation twinning were seen. The presence of additional interfaces and orientation dependent twinning cause the deformation response of the 90° orientation to fall between the dislocation slip dominated response (0°) and the twinning dominated response (45°).

4.6.3 Stress-strain response

The response of the two representative uniaxial compressive stress-strain curves of the multidirectional material, one quasi static and one dynamic, are compared to the unidirectional material response, see Figure 4.29. The multidirectional material exhibits greater strength than any of unidirectional materials. The 200 nm unidirectional material (shown as cyan curves without distinction between the three loading angles 0°, 45° and 90°) has microstructure reinforcements that are similar in size to the largest layer thicknesses in the multidirectional material (blue and black traces). A direct comparison is difficult between the two material systems due to the complexity of their structures at the micro- and nanoscale. At the microscale, for the multidirectional material at the radial surface, it was observed that once failure initiates in
a region it continues with increasing compressive strain while neighboring regions located across
the boundary between eutectic colonies did not show deformation. The presence of the boundary
between colonies of different orientations has an effect on the local material response limiting
the communication of microscopic deformation. The internal deformation of the multidirectional
material only showed kinking of the layers without interfacial failure taking place. At the
specimen interior the boundaries between the eutectic colonies “pin” the layers constraining
deformation. The increased strength response of the multidirectional material could be attributed
to the additional constraint at the eutectic colony boundaries since these boundaries were not
observed to hinder the deformation response of the unidirectional material. At the nanoscale, the
interface type between the silver and copper phases changes with the solidification rate. In the
multidirectional material the dominant interface type occurs in the twin orientation. In the
unidirectional material as the reinforcement size decreases the interface type transitions from
cube-on-cube to the twin orientation. The difference in the interface type needs further attention
as one may be a stronger barrier to dislocation motion between the copper and silver. TEM
studies of the finest microstructure unidirectional material have yet to be conducted therefore it is
unknown if the dislocation mechanisms (i.e., dislocation slip vs. twinning) change with respect
to the interface type for each of the different loading orientations.
Figure 4.29: Comparison of the stress-strain response of the multidirectional to the unidirectional materials of each nominal feature size.

4.6.4 Strain hardening

The strain hardening index of each of the dynamic stress-strain curves shown in Figure 4.29 was determined from the slope of the plastic region of the ln(σ) vs ln(ε) curve. Strain hardening occurs as a result of dislocation motion in response to plastic deformation. For most metals the strain hardening index is between 0.2 and 0.5. At the solidification rate of 0.46 mm/hr the strain hardening index was the same for both thicknesses (i.e., 800 nm and 1.2 µm) and similar for each of the reinforcement orientations. At solidification rates of 7.3 mm/hr and 73 mm/hr the strain hardening index differs significantly between the loading orientations with the 45° and 90° orientations showing similar strain hardening and the 0° orientation showing a reduced strain hardening index. Deformation twinning provides boundaries to dislocation slip and additional twinning similar to grain boundaries. The twinning observed in the 45° and 90° specimens would therefore cause additional barriers to dislocation motion resulting in increased work hardening [Mahajan and Chin 1973] compared to the work hardening of the 0° orientation.
As the micro-structure feature size is refined the strain hardening rate decreases for each orientation. Strain hardening is reduced at smaller micro-structures because of the difficulty of dislocation accumulation at the grain interior [Deiter 1986]. The strain hardening rate of the multidirectional material is provided as a solid horizontal black line.

![Graph showing strain hardening index with respect to reinforcement dimensions.](image)

**Figure 4.30**: Strain hardening index of each of the unidirectional loading orientations with respect to reinforcement dimensions.

### 4.6.5 Lateral strains

The macroscopic compressive loading response of the unidirectional material was unique for each loading orientation, as was summarized in Figures 4.12, 4.15, and 4.19. The post-deformation lateral specimen strains in the greatest (circles) and least (square) directions are shown for the 0° (blue), 45° (green) and 90° orientations (red) in Figure 4.30. The colored solid lines indicate the isotropic radial strain predicted for each specimen based on volume conservation from their initial dimensions. The deformation of the 0° loading orientation follows...
the isotropic prediction up to 10 percent compressive strain. Above 10% strain the material deformation no longer exhibits uniformity with regions of the specimen exhibiting non-uniform radial deformations as a result of kinking near the radial surface. In the 45° specimen the direction of greatest lateral strain coincides with the direction of shearing along the growth direction. For the 90° case the direction of least strain coincides with the reinforcement (growth) direction. The greatest lateral strain occurs perpendicular to the growth direction. Two mechanisms permit the lateral straining perpendicular to the growth direction. The first mechanism initiates as sliding at eutectic colony boundaries which transitions to the formation of surface cracks visible on the specimen loading surfaces. The second mechanism is crossing shear bands.
Figure 4.31: Macroscopic deformed dimension change for each of the three loading orientations. The 0° orientation shown in blue, 45° orientation in green and 90° orientation in red. The greatest deformed specimen lateral strain is represented by circles and the smallest lateral strain is represented by squares.

4.7 Concluding remarks

The unidirectional Ag-Cu material system provided the opportunity to examine specific loading orientations with respect to the materials crystallographic orientation. It has been shown that the three loading orientations have mechanical responses that depend on the deformation mechanisms of the micro-structure and the dislocation mechanisms taking place.

The effect of the orientation of the copper reinforcements to the loading direction appears in the macroscopic deformation. In the 0° loading orientation internal kinking near the radial surface results in striations appearing the on the radial surface. In the 45° orientation specimens
preferentially shear along the direction of the copper reinforcements elongating more in one lateral direction more than the other. The 90° orientation deforms preferentially perpendicular to the fiber orientation. Along the fiber direction very little deformation occurs.

The two active deformation mechanisms of dislocation slip and deformation twinning determine each loading orientation’s response to loading. When twinning occurs, as it does in the 45° and 90° orientation, the observed strain hardening rate is increased compared to the 0° orientation where dislocation slip is the dominant deformation mechanism. The yield strength is also attributed to the dislocation mechanisms and Ag-Cu interface. The Ag-Cu interface is resistant to the transmission of dislocation slip thus the 0° which does not show twinning exhibits the greatest strength. In the 45° and 90° loading orientations deformation twins are communicated across the interface resulting in yield strengths below the 0° orientation.

The recorded elastic modulus of unidirectional materials produced at furnace removal rates of 0.46 mm/hr and 7.3 mm/hr are similar to the isotropic rule of mixtures estimate of a Ag₆₀Cu₄₀ system. As with the multidirectional material the 200 nm micro-structured unidirectional material exhibited a suppressed elastic modulus. The suppressed elastic modulus was measured under three conditions 1) quasi-static loading 2) dynamic loading and 3) ultrasonic testing.
Chapter 5: Conclusions and Future Work

This work provided an investigation of the response of a silver-copper eutectic material with two different morphologies, a multidirectional alternating multilayer hierarchical structure and a copper reinforcement in silver matrix structure. Processing parameters were varied to capture the effect that micro-structure feature size and spacing of the reinforced matrix material have on the material mechanical response to compressive loading. The conclusions and future work presented here are divided into three sections. The first section covers the multidirectional material, the second covers the unidirectional material and the third provides possible avenues of future work for the Ag-Cu material system.

5.1 Multidirectional Ag-Cu material system

The multidirectional material, introduced in Chapter 3, consists of eutectic colonies of alternating parallel layers of silver and copper with thicknesses between 25 nm and 200 nm (average Cu layer thickness: 46 nm, average Ag layer thickness: 88 nm). The eutectic colonies have random orientations scattered throughout the material system. Near the surface anomalous
solidification was observed which is typical of materials cast at high solidification rates with low undercooling. Multidirectional materials were subjected to quasi-static and dynamic compressive loading. The material was observed to be strain rate insensitive with mechanical properties such as yield strength and hardening rate being similar over the range of strain rates used, between $10^{-3}$ s$^{-1}$ and $10^{3}$ s$^{-1}$.

Post deformation specimen radial surfaces were analyzed using stereo microscopy, stylus profilometry and scanning electron microscopy. Stereo microscopy and stylus profilometry captured the specimen surface deformation finding that the center anomalous growth regions preferentially deforms forming a plateau like region from which localized shear bands form within the eutectic colonies.

SEM microscopy was conducted on the radial surface and at the specimen interior at increasing levels of strain. Interrupted specimen loading followed by SEM imaging captured the three dominant deformation mechanisms that occur at the micro-scale, layer kinking, brooming and interfacial delamination. Layer kinking was observed to occur when the initial orientation of the layers was within $15^\circ$-$45^\circ$ of the loading orientation. Images captured of the same region of a specimen at compressive strains of 5%, 15% and 25% had layer pairs traced on them. The local shear strain along each of the layers highlighted the concentration of kinking within the first ~10 µm of the interface between colonies. Shear strain was not observed to transfer between the boundaries between neighboring colonies. Kinking is the mechanism that precedes brooming as was seen with layers in close proximity showing opposite signs of shear strain. Interfacial failure in the form of brooming and interfacial delamination typically occurred with $15^\circ$ of the loading direction. At the specimen interior the high level of constraint prevents separations between layers therefore brooming and interfacial delaminations are suppressed, although kinking was
observed in the interior, but becomes active at strains greater than when first occurring on the surface. Also, the width of kink bands seen at the specimen interior are smaller than those at the surface.

The observed dominant deformation mechanisms appear to be independent of strain rate with specimens deformed to the global strain level showing similar presence of kinking and interfacial delamination.

The fundamental contribution of this part of the work is to demonstrate the substantial strengthening in metallic multilayer nano-structures but at a bulk scale. Although some nanoindentation experimental evidence existed of nano-layered material strengthening through indentation of layered sputtered or rolled micro-structures, there has been limited study showing such strengthening in bulk nano-layered solids. The eutectic solidification allowed for the casting of bulk samples. Our experiments not only capture the strengthening in bulk nano-layer materials but also illustrated that there exists a hierarchical structure, not present in sputter small scale nano-layered samples, that also influences in different ways the hardening response of the nano-layers at larger strains (through the processes of kinking/brooming and delamination). Therefore the results can be used as a guide for more detailed material design of novel bulk nano-layered systems.

5.2 Unidirectional Ag-Cu material system

The as-cast state of the unidirectional material, presented in Chapter 4, consists of discontinuous copper reinforcements elongated along the axial direction in a silver matrix. The material has a preferred $\langle 101 \rangle$ crystallographic growth direction which matches the direction of the copper reinforcements. Through the application of different furnace removal rates the
microstructural feature size of the cast material can be controlled. The furnace removal rates used in this study were 0.46 mm/hr, 7.3 mm/hr and 73 mm/hr and resulted in features sizes of 800 nm or 1.2 µm for the slowest rate, 500 nm for the intermediate rate, and 200 nm for the fastest rate. Specimens were machined from the as-cast rods such that three different loading orientation could be studied 1) loading parallel to the growth direction, 2) at 45° to the growth direction and 3) at 90° to the growth direction.

Under dynamic loading conditions the unidirectional material exhibited increasing yield strengths with decreasing feature size. An orientation effect on the measured strength was also observed with the parallel (0°) loading orientation showing the greatest strength followed by the 90° loading orientation, and then the 45° orientation. The observed strength relationships are accounted for by the dislocation mechanisms captured by a companion TEM study [Eftink et al. 2014]. In the 0° loading orientation the dominant deformation mechanism is dislocation slip which leads to dislocation pile-ups at the interface. As the micro-structure size decreases the number of dislocations in the pile-up decreases resulting in a smaller stress concentration at the interface requiring higher applied stresses for deformation to proceed across the interface. In the 45° specimen profuse deformation twinning was observed in both the copper and silver phases. Typically copper does not twin readily but in this case silver provides twinning partials to the copper phase allowing for communication of twinning across the Ag-Cu interface. Since twinning is not directly dependent on the micro-structure feature spacing the 45° loading orientation shows the lowest slope in a yield stress vs. inverse feature size. The 90° orientation was observed to have both twinning and dislocation slip occurring in both phases. For this case twinning was also seen to depend on the local crystallographic orientation with some orientations showing twinning while others did not.
The 0° orientation material response for the 200 nm micro-structure exhibited possible plastic strain recovery under dynamic loading but not under quasi-static loading. MD simulations have pointed to plastic recovery of the Ag-Cu system occurring though the reversal of deformation twins. The lack of plastic strain recovery in the quasi-statically loaded specimen could be attributed to the insufficient conditions for twinning to communicate across the Ag-Cu interface or due to the specialized conditions (e.g., nano-structured [Chen et al. 2003, Wang et al. 2002, Wang and Huang 2004, Zhang et al. 2010], high strain rate [Gray et al. 1989, Cao et al. 2010, Meyers et al. 1995]) necessary for the twinning of copper.

The complexity of the hierarchical structure causes difficulties when interpreting the mechanisms that contribute to the captured high strength response. The unidirectional system on the other hand provides a system with a well-defined structure at the micro- and nano-scale. The work presented here contributes to solidifying links between material deformation mechanisms and observed mechanical properties of material systems with a high density of bi-phase interfaces. The experiments has shown that the mechanical response of the unidirectional system depends dependent on the loading orientation and the underlying micro-structure feature size, particularly as the feature size is reduce. Above 500 nm feature sizes the 45° and 90° orientation yield strength responses are similar but start to diverge at smaller feature sizes. The strain hardening was shown to be higher for the 45° and 90° orientations than the 0° orientation. The results shown here for the Ag-Cu unidirectional material system will aid future design of other material systems that need high strength and ductility.
5.3 Future work

In the work presented in this document only compressive loading was used to study mechanical properties due to smaller specimen dimension requirements than tensile testing. Experimental studies by Cline and Stein [1969] have pointed to the mechanical properties of the directionally solidified material being similar when deformed under tension for the 0° and 45° orientations. It was clearly seen in this study that the 45° orientation was significantly weaker than the 0° orientation. This indicates that the deformation mechanisms occurring at the micro- and nano-scales in compression and tension loading likely differ. For example kinking is a deformation mechanism that occurs in compression only and is not expected under tension. Simulations by Li and Chew [2014] have shown the plastic recovery under tensile conditions with loading orientation similar to the 0° loading orientation of this work. Therefore it is of interest to probe the Ag-Cu unidirectional material under quasi-static and dynamic tensile conditions also to determine if plastic recovery does occur there and under what conditions.

Another route of examination of the Ag-Cu material system is through the use of the laser spallation technique. In the laser spallation technique a high powered laser is used to load thin film materials mounted on a substrate. Strain rates of $\sim 10^7$ s$^{-1}$ are achievable using this technique. Thus far most of the studies of incoherent and coherent material systems outlined in section 1.3 have focused on the use of nanoindentation measuring film hardness. Nanoindentation, while a valuable measurement method, does not provide details of the actual strength of the interface between the two material systems. Using the traditional laser-spallation technique loading normal to the interface plane occurs. Through incrementally increasing the amplitude of the propagating stress wave a measure of the tensile strength of the Ag-Cu material...
interface could be obtained. Furthermore the laser spallation technique can be modified such that the loading of the multilayer film interfaces are in shear.
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