

EFFECTS OF PLASTIC DEFORMATION FROM ULTRASONIC ADDITIVE MANUFACTURING

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ABSTRACT

Nuclear energy technology can be exponentially advanced using advanced manufacturing, which can drastically transform how materials, structures, and designs can be built. Ultrasonic Additive Manufacturing (UAM) represents one of the four main additive manufacturing methods, although it is also the newest. As UAM technology and applications develop, a fundamental understanding of the bonding mechanism is crucial to fully realize its potential. Currently UAM bonding is considered to occur through breaking down surface asperities and removing surface oxides. Plastic deformation occurs although its role is currently unclear. This research analyzes material configurations in a variety of geometries, with similar and dissimilar material interfaces, and with pure metals and complex engineered materials. A variety of characterization techniques were used to develop a general description that UAM bonding requires plastic deformation.

First, we analyzed various dissimilar material interfaces created between UAM foils and the coating of embedded optical fibers. Enhanced interdiffusion of elements was found beyond that expected from the thermal profile experienced during bonding. This interdiffusion was rationalized based on enhanced point defect vacancies creating additional diffusion pathways. Following on this study, we analyzed the local strengthening at one of these interfaces. These interfaces strengthened through a complex interaction dominated by dislocation forest hardening, reduced grain sizes, and vacancy clusters created by the agglomeration of vacancies. UAM bonding of pre-treated Al 6061 was also performed and analyzed using multi-length scale characterization. Macroscale strengthening was observed as well as foil-foil interface strengthening. This was a result of dynamic recrystallization, dynamic recovery, adiabatic heating, and precipitate dissolution (as the vacancies allowed enhanced diffusion of elements). Finally, UAM bonding of titanium was analyzed. The HCP phase of titanium significantly resisted plastic deformation, which resulted in a phase transformation to the BCC phase, which was stabilized by the introduction of certain stabilizing elements. The strain induced phase transformation and enhanced vacancy driven interdiffusion were utilized to demonstrate a viable method of improving UAM bonding by focusing on the plastic deformation requirement. The phenomena outlined in this research demonstrates an improvement in our understanding of the fundamental bonding requirements of UAM, and deformation induced vacancy formation.

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CHAPTER 1

INTRODUCTION

Advancing nuclear energy technology is one of the grand challenges of the 21st century. Metal additive manufacturing (AM) provides a very promising method of accelerating the growth of nuclear power through creating new materials, structural designs, and active health and process monitoring. Although fascinating advances in technology can be realized through AM, the fundamental understanding of how certain processes occur is still unclear. Through studying the physical and mechanical metallurgy of materials created through AM, our knowledge of material science is expanded, which is complementary to the readiness of these related advanced applications.

One of the core additive manufacturing technologies is the Ultrasonic Additive Manufacturing (UAM) method. This differs from other AM techniques in that it bonds using a solid-state means, rather than melting and solidifying materials. The UAM method provides significant advantages because it can join dissimilar metals, and it can create valuable multi-material composites including embedding fragile materials.

The metallurgical bonding process of UAM has been thoroughly studied using a variety of techniques, and several key components of bonding have been identified (i.e. collapse of surface asperities, dispersal of oxides, and the creation of atomically clean surfaces). It is well recognized that during UAM bonding, significant plastic deformation occurs. The role of this plastic deformation is currently unclear, as some researchers suggest the plastic deformation is a by-product of creating clean surfaces, while others hint that plastic deformation is a requirement of bonding.

If plastic deformation is a requirement of UAM bonding, it would represent a significant shift in the scientific and technical perspective of approaching UAM. This could provide a better fundamental understanding of how materials move during plastic deformation from ultrasonic shear forces. Additionally, UAM bonding techniques could be altered with the design approach of promoting more plastic deformation thereby improving the bonding of extremely difficult or impossible to weld materials.

The purpose of this dissertation is to understand the effects of plastic deformation on the microstructure of materials bonded through UAM. An emphasis will be placed on understanding the metallurgical components involved in UAM bonding as well as describing the movement of atoms, evolution of the microstructure, and potential phase formation. A short brief of each of the following chapters covered in this dissertation is described below.

Chapter 2: A motivation and overview of published literature on Metal Additive Manufacturing and Ultrasonic Additive Manufacturing is presented. A review of the physical and mechanical metallurgy of analogous solid-state bonding processes and the effects from severe plastic deformation is discussed. A review is provided about the role of lattice defects in severe plastic deformation and the initial evidence of this in ultrasonic bonding.

Chapter 3: Several UAM bonded dissimilar metal interfaces between a foil and an embedded optical fiber coating are explored. Interdiffusion of elements is observed at rates faster than equilibrium processes could predict. The enhanced elemental migration is correlated with elevated concentrations of lattice defect vacancies at the interfaces creating short circuit diffusion pathways.

Chapter 4: Mechanical properties across a nickel-gold interface (one of the same from Chapter 3) are explored. Strengthening is observed and is correlated to the microstructure evolution that occurred. The significant features include a refined grain structure, elevated dislocation densities, and vacancy clusters. The vacancy clusters are compared to the point defect vacancies created during the interdiffusion of elements. A sensitivity analysis of the various strengthening effects is performed, as well as a superposition principle to describe their interaction.

Chapter 5: UAM bonding was performed on pre-treated aluminum (Al6061 in the quenched and annealed condition). Following bonding, multiscale characterization was performed demonstrating strengthening occurred in the entire build, and local foil-foil interfaces became stronger. The microstructure evolution of the aluminum resulted from dynamic recrystallization, dynamic recovery, adiabatic heating, and precipitate dissolution.

Chapter 6: UAM bonding was performed on commercially pure titanium and the Ti-6Al-4V alloy. Successful bonding occurred as the titanium's hexagonal close packed (HCP, α) crystal structure transformed into a body centered cubic (BCC, β) crystal structure from the UAM plastic deformation. The phase transformation was supported by the introduction of BCC stabilizing elements through lattice defect vacancies, and the transformed material's microvoids are rationalized based on the $\alpha \rightarrow \beta$ phase transformation and plastic deformation. Bonding can be improved by focusing on the plastic deformation requirement of UAM, and examples are shown of this.

Chapter 7: The effect of surface roughness on plastic deformation of UAM was considered. Variation of work hardening is likely present throughout UAM interfaces although accurate characterization of this effect is not trivial and outside the scope of reasonable work here.

Chapter 8: The conclusions and significance from this work are discussed along with proposed future work. Due to that variety of materials and geometries explored in this dissertation, a general assertion can be made that plastic deformation is a requirement for UAM bonding. By utilizing plastic deformation, significant advances can be made in UAM bonding. ***update** Additionally, future scientific studies such as the mechanism for strain induced phase transformation and stabilization would greatly improve our materials science understanding.

CHAPTER 2

LITERATURE REVIEW

2.1 Motivation: Developing Nuclear Energy Through Advanced Materials and Manufacturing

Displacing traditional fossil fired energy sources with nuclear energy is critical for providing economic and environmentally sustainable energy to the United States, as well as creating energy independence and security. Nuclear energy is a carbon free energy source, which can avoid the 470,000,000 metric tons of carbon production each year currently produced. Nuclear energy currently adds \$6 billion to the U.S. gross domestic product, and it provides 500,000 jobs per year with salaries approximately thirty percent higher than local average, while also creating twice as many jobs per power plant than fossil fueled plants can provide ¹.

Although nuclear energy can provide clean sustainable power, it currently supplies only 20% of the U.S. energy. Limitations include the high capital costs of building power plants, public perception, and operation safety. Additionally, most advanced reactor designs require materials capable of withstanding higher operating temperatures and irradiation damage. All current nuclear power plants in the U.S. are large light water reactors (LWR), which can provide over 700 MW electric of power. These large power plants often take over a decade to be built and licensed, and construction costs often become overbudget ².

An advanced reactor design with strong potential to mitigate these issues is the small modular reactor (SMR). Although SMRs produce less power than an LWR, up to 300 MW electric, their small design reduces capital costs, simplifies the reactor design, creates intrinsic safety, and provides production scalability for licensing a fleet of reactors ². The compact design of the SMR also provides the opportunity to reimagine how reactors are designed and created using techniques such as additive manufacturing. For example, additive manufacturing allows for the creation of advanced materials and new structural and neutronic designs to be rapidly prototyped and evaluated. Designs are no longer limited by what conventional manufacturing can create; therefore, reactor components and configurations can be optimized for their specific application. Additive manufacturing also provides the ability to create complex three-dimensional components, such as embedding sensors into critical structures to enable health monitoring and autonomy ^{3,4}.

The national priority of creating advanced nuclear reactors via additive manufacturing can be exemplified through programs such as the Department of Energy Transformational Challenge Reactor ⁵. The commercial, economic, and environment viability is also demonstrated through the investments by the Tennessee Valley Authority[®] ⁶, Dominion Energy[®] ⁷, BWXT[®] ⁸, Ultra Safe Nuclear[®] ⁹, Terrapower[®] ¹⁰, Hyperion[®] ¹¹, Holtec[®] ¹², and NuScale[®] ¹³ to name a few. As mentioned above, the development of materials, processing, and technologies is a vital component of transitioning to nuclear energy. The development of relevant materials and advanced manufacturing through metal additive manufacturing is demonstrated in the sections below.

2.2 Introduction to Metal Additive Manufacturing

Metal additive manufacturing (AM) is a popular and relatively new manufacturing method for creating near net shaped three-dimensional components all at one time. This allows for the application of new materials, shapes, and devices previously impossible with traditional manufacturing methods. The development of metal AM is complementary to the materials science understanding from these AM techniques. Per the ASTM F42 process terminology on Additive Manufacturing there are seven standard categories of AM. Four of these categories relate to metal AM. Three of the categories are solidification bonding (Powder Bed Fusion, Direct Energy Deposition, and Binder Jet), and one is solid-state bonding (Sheet Lamination) ¹⁴.

2.2.1 Solidification Bonding

The three solidification-bonding additive manufacturing methods (i.e. Powder Bed Fusion, Direct Energy Deposition, and Binder Jet) are briefly described below. Powder Bed Fusion (PBF), as shown in Figure 2.1a, uses a focused energy beam (laser or electron beam) to selectively melt or sinter the top layer of a metal powder bed. The metal powder bed then has a new layer of powder raked on top and the process is repeated. Once the part is created, the excess powder can be removed and recycled. In this way a three-dimensional part can be created. Typical build volumes below 0.03 m³ can be achieved ¹⁵. Although PBF is a straightforward technique and provides parts with high precision and complexity (layer thickness ~10-50 μm), warpage and defects resulting from closed internal features and lack of fusion can occur ^{16,17}.

The direct energy deposition (DED) process, as shown in Figure 2.1b, creates a metal part by depositing feedstock directly onto a molten pool, as opposed to melting a powder bed. The DED process uses a laser, arc, or electron beam as a heat source, and the feedstock can be either a powder or a wire. The origin of DED can be traced to traditional welding technology where a material is deposited onto a melt pool and a shield gas is flowed over the melt pool ¹⁸⁻²¹. The build set-up can be quite larger than powder bed fusion and can utilize a 3-axis or 5-axis setup to create complex geometries ²². Although DED has a rougher surface finish and requires post-processing, it is a powerful tool for repairing damage ²³.

The binder jet process, as shown in Figure 2.1c, differs from PBF and DED in that each layer of deposited material is not melted or sintered to bond with the layer beneath. Instead, the binder jet process deposits a liquid binder on the metal powder, then cures the binder which holds the material together. After the part has been created in this layerwise process, the consolidated green body part is sintered. This removes the binder, creating the final part. Binder jetting also allows for a secondary metal to be infiltrated into the part, achieving a high final density ²⁴⁻²⁶. The main challenges with this process include difficulty in controlling the porosity and shrinkage during sintering ²².

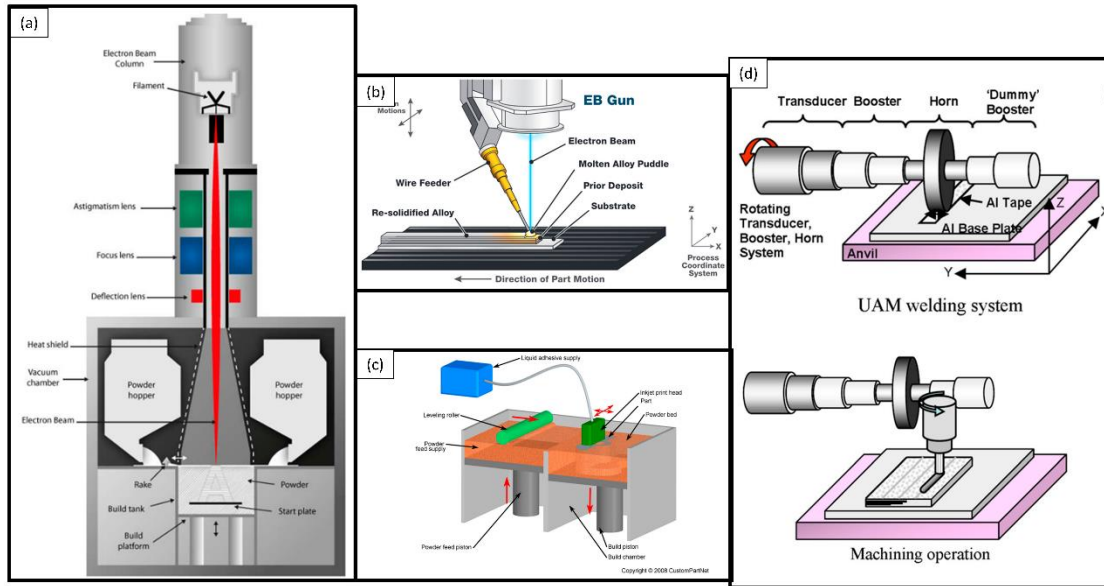


Figure 2.1. Four types of metal AM manufacturing. a) Powder Bed Fusion ²⁷, b) Direct Energy Deposition ²⁸, c) Binder Jet ²⁹, d) Sheet Lamination ³⁰

2.2.2 Solid-State Bonding

Sheet lamination is unique from the previous three metal additive manufacturing processes in that melting or sintering of the layers is not required to join the material. Instead, the materials are joined while they remain in the solid form. Sheet lamination uses precisely cut thin foils stacked on top of each other to create a three-dimensional part. Sheet lamination provides low geometric distortion, relatively good surface finish, low costs, and relatively low bonding temperatures, although several disadvantages are also present. Sheet lamination suffers from mechanical property degradation in the z-direction (build height), and the difficulty of creating overhang features. The most popular sheet lamination process for additive manufacturing is Ultrasonic Additive Manufacturing (UAM). In the UAM process, a rolling horn, known as a *sonotrode*, applies the bonding force, while alternating machining operations remove unwanted material. This is shown in Figure 2.1d. A thorough description of the UAM process is described below (Section 2.3).

An introduction to various solid state bonding processes can help provide context, advantages, and limitations of UAM. The following sections will first briefly discuss other solid state bonding processes (i.e. accumulated roll bonding, diffusion bonding, friction bonding, and explosive bonding) before discussing ultrasonic bonding.

Layered materials can be created through an accumulated roll bonding process (ARB), shown in Figure 2.2a, in which similar or dissimilar sheets or foils are rolled together. Bonding is achieved when the deformation reduction between the materials reaches a threshold value. The surface conditions of the materials to be joined are critical to achieve bonding, therefore scratch brushing and degreasing are often used. Once the surface contaminants are removed, the materials are passed through a rolling mill which reduces the thickness of the materials through creating significant plastic deformation³¹. As bonding creates severe plastic deformation ($\dot{\epsilon}$ up to 10^4 s^{-1} ³²), the surface oxides are fractured. Heat can sometimes be applied to reduce the yield stress and to require less reduction of thickness to create bonding. FCC materials such as aluminum, copper, gold, and silver can be easily joined using roll bonding, while HCP materials have much more difficulty in roll bonding. The reason for this is suggested that the oxide films on the HCP metals break up independently of each other, while the oxide films on FCC materials break up coherently with each other. This can create a larger area for the materials to join. Additionally HCP materials can work harden and fracture in locations besides the interface, as compared to FCC materials which do not³³.

Diffusion bonding occurs when materials are brought into intimate contact under an applied pressure ($\dot{\epsilon}$ up to 10^{-4} s^{-1} ^{34,35}) at an elevated temperature. This is shown in Figure 2.2b. The bonding occurs through the interdiffusion of elements across the joint interface. Rougher surfaces typically create superior strength and a more bonded interface, and the most well bonded interfaces typically require long holding times over an hour. Lack of bonding is typically due to air entrapment at the interfaces³⁶.

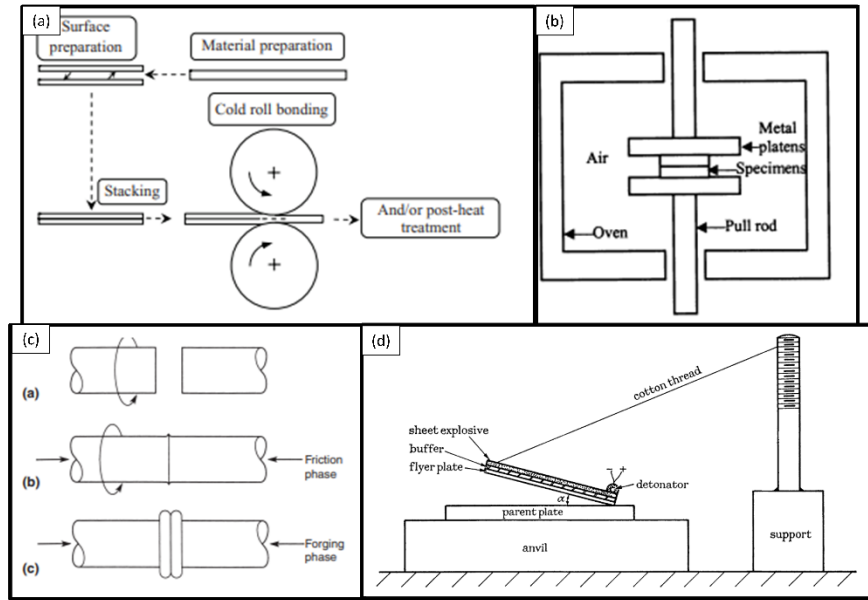


Figure 2.2. Additional solid-state bonding processes. a) Accumulated roll bonding, b) Diffusion bonding, c) Explosive bonding, d) Friction bonding

Diffusion bonding is achieved through the following process: (i) asperity contact, (ii) asperity deformation, (iii) grain boundary migration, recrystallization, and pore size reduction, and (iv) bulk diffusion, oxide and contaminated dissolution, and pore elimination³⁷. Although diffusion bonding allows large areas to be joined together without distortion, the bonding requires temperatures above $0.75 T_m$. This can allow surface oxidation and intermetallic formation which can be detrimental to the materials³⁸.

Friction bonding, as shown in Figure 2.2c, occurs through the heat generation produced by the relative motion between interfaces being joined. Friction bonding relies on the direct conversion of mechanical energy to thermal energy to form the weld. Typically, friction bonding occurs as one rotating part contacts another stationary part. As the pressure between parts increases, the interfacial temperature increases and lowers the yield strength. This continues until the welding temperature is reached. Once the materials reach the plastic temperature range, welding can occur. There are several variations of friction welding including linear friction welding, friction stud welding, friction stir welding, and friction stir additive manufacturing. Although there are geometry restrictions for friction welding, surface preparation and oxide removal are not necessary³⁹. The effective strain rate created in the material due to the high rotational velocities could exceed 10^3 s^{-1} ⁴⁰.

Explosive welding, as shown in Figure 2.2d, occurs when an explosive device is used to create an accelerated oblique impact between a sheet of material (flyer plate) and another base plate (parent plate). As the materials crash into each other, severe plastic deformation occurs. The severe plastic deformation removes a thin surface layer of material ($< 50 \mu\text{m}$), and creates a metallurgical bond⁴¹. The bonded interface has a characteristic wavy shape. This is likely due to the material jetting which scours the surfaces clean during impact. Estimates of the plastic strain rate created during explosive welding can exceed 10^7 s^{-1} ⁴².

The solid-state bonding processes, as described above, have demonstrated that surface contact is important for bonding, as well as severe plastic deformation and induced heat through material contact.

2.3 Mechanism of Ultrasonic Additive Manufacturing (UAM) Bonding: Known & Unknown

2.3.1 Overview

Ultrasonic Additive Manufacturing (UAM), initially developed by White^{43,44}, is a method in which three dimensional metallic components can be fabricated through cyclic additive and subtractive operations. During additive operations, foil tape layers ($\sim 150 \mu\text{m}$ thick) are bonded to each other and to a substrate through a solid-state process that relies on high strain rate ($\sim 10^5 \text{ s}^{-1}$ ^{45,46}) ultrasonic oscillations (20 kHz) without melting

the materials. The ultrasonic vibrations are applied using a rolling cylindrical horn called a *sonotrode*. The sonotrode simultaneously applies a downward force on the foil (in the z-direction) and laterally scrubs (in the y-direction) as it traverses forward (in the x-direction). The additive bonding process can be alternated with subtractive machining (such as computer numerical control or laser machining) to create an intricate three-dimensional component. A diagram of the two-part UAM process is displayed in Figure 2.1d.

The bonding system consists of an ultrasonic transducer, a booster, the sonotrode welding horn, and a secondary 'dummy' booster. The ultrasonic vibrations are sent through the sonotrode as it rolls in the x-direction bonding the material. The ultrasonic transducer operates at a vibration frequency of 20 kHz, and the power can vary from 1.5 kW to 9 kW. The higher power system, termed Very High Power UAM, with a dual transducer is a more recent update to the design of UAM systems. This was introduced to allow bonding of more difficult to weld materials ⁴⁷.

The UAM process is unique because it is a low temperature ^{48–51} process that can bond dissimilar and difficult to weld materials, while allowing for the creation of complex three-dimensional components ^{22,52–54}. A few of the unique and advantageous materials created using UAM include bonds of copper ⁵⁵, steel-nickel ⁵⁶, steel-tantalum ⁵⁷, titanium-aluminum ^{58–62}, aluminum-copper ^{63–65}, nickel-gold ^{65,66}, aluminum-carbon fiber reinforced polymer ⁶⁷, zirconium ⁶⁸, nickel-titanium wires ⁶⁹, embedded sensors ^{66,70,71}, actuators ⁷², parts for thermal management ^{30,73} or cooling channels ⁷⁴, chemical microflow reactor ⁷⁵, magnetic fields ^{53,76,77}, neutron poison systems ^{78–80}, and embedding fragile materials such as SiC ceramics ^{81–83} or sensors ^{70,71,84,85}. The readers are referred to the review article by Wolcott ⁵³ thoroughly describing current applications of the UAM process. UAM processing relies on good metallurgical bonding between the materials. Therefore, the mechanical and physical metallurgy relating to UAM bonding must be well understood. This forms the basis for the current dissertation.

2.3.2 Current Understanding of Bonding Mechanism

The intense ultrasonic oscillations from the sonotrode (20 kHz) lead to cyclic displacement of surfaces at the foil-sonotrode and at foil-foil interfaces. This cyclic displacement leads to the dispersal of surface oxides and collapse of surface asperities, key requirements for solid-state bonding ⁸⁶. Once the surfaces are broken down, atomically surfaces are exposed to each other. Following this, the materials bond, well below their respective melting temperatures ^{86,87}.

The role of surface oxide removal during UAM has been studied by Johnson et al. ⁸⁸. Using ion beam microscopy, the author observed features directly outside the faying surfaces corresponding to the dispersed surface oxides (Figure 2.3a). This demonstrates that the UAM process removes prior oxides on the surface of materials to enable bonding. Fuji et al. ⁸⁹ also studied UAM bonding and demonstrated how surface

asperities yield and collapse during bonding (Figure 2.3b). All materials have microasperities rather than being perfectly flat surfaces. This allows only a small fraction of the material surfaces brought together to truly be in contact^{90,91}. When a normal load is applied on two metal surfaces, the microasperities can yield, forming a joint. Additionally shear loading of two metal surfaces has been proven to create stronger bonds than just normal loading⁹². This is due to the increased area of contact when asperities are more effectively collapsed^{91,92}. This is the bases of using a normal and shear force to bond UAM materials. When Lu et al.⁹³ placed oxide-free room temperature atomically flat gold nanowires in contact, the materials could be joined. Although these are very thin wires (~2 nm wide), this initially suggests that when metal surfaces are in nascent contact without surface asperities or oxides present, they can bond at negligible temperatures.

The removal of the asperities and roughness are key requirements for UAM bonding, but there is also high strain and strain-rate (10^5 s^{-1} ⁴⁶) plastic deformation that occurs, which prepares the surfaces. The plastic deformation at the faying interfaces typically results in significant grain refinement, associated with a dynamic recrystallization event. The grains undergo severe plastic deformation causing the crystal structure to reorient and form grains in a lower energy state. This was first rationalized by Dehoff & Babu⁹⁴ in which foils exhibited a strong rolling direction prior to UAM bonding (observed in the bulk foil regions) and while small equiaxed grains were observed at the bonded regions (Figure 2.3c). Typically the refined grain structure is confined to a local region (10-15 μm) near the interface while the remaining bulk material is unaffected^{45,55,57,94,95}. Although grain recrystallization events is commonly observed^{62,96-98}, it does not always happen. When metal surfaces are not in perfect contact, they do not bond. This results in a large void between the foils, and the lack of grain refinement⁹⁸ (Figure 2.3d).

Although external temperature is typically not applied, local temperature rises have been observed during UAM bonding. Accurate temperature measurements are difficult to obtain due to the rapid nature of the process, although temperature profiles of 150-200°C have been recorded in soft FCC interfaces^{99,100}, while higher values have been suggested in difficult to weld materials^{50,68}. The measured thermal cycles are typically less than 0.5 seconds, which includes the ramp up and down in temperature^{55,99,100}. Other factors such as welding power, normal force, and amplitude can also affect the local temperature rise (Figure 2.3e). The cause of the temperature rise is due to the adiabatic heating from the plastic deformation of the material during bonding. The readers are referred to the ASM handbook for more details of the current understanding of the metallurgy of the UAM process⁸⁷.

As described above, the current understand of UAM bonding is that the mating surfaces must be clean of oxides and roughness for bonding to occur. Plastic deformation occurs as a by-product of creating clean atomic surfaces. Currently literature is split on this role, as some preliminary indications suggest that instead, plastic deformation is a requirement of bonding.

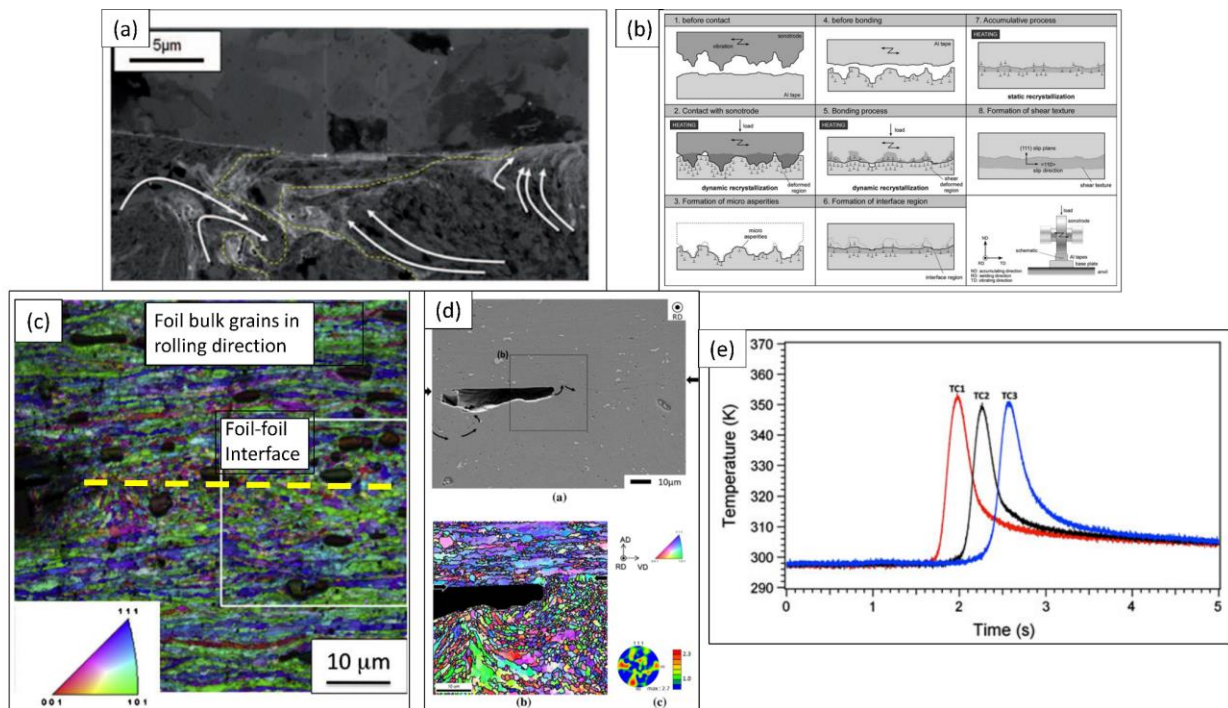


Figure 2.3. Effects from UAM severe plastic deformation: a) Oxide dispersion at faying interfaces ⁸⁸, b) Asperities collapse ⁸⁹, c) Dynamic recrystallized grains at interface ⁹⁴, d) Lack of bonding void without grain refinement ⁹⁸, e) Temperature rises during bonding

2.3.3 Knowledge Gap

The role of plastic deformation in UAM bonding is currently unclear. It could be a by-product of bonding, or it could be a requirement. As mentioned previously, some studies indicate that bonding occurs once atomically clean surfaces are created⁹³, while other studies suggest that plastic deformation increases bonding¹⁰¹. Furthermore, most of the bonding techniques described in Section 2.1 require atomic motion to some degree during bonding. Therefore, a logical question to address is: what is the role of plastic deformation during UAM bonding?

To analyze this knowledge gap further, other processes that use high strain rate severe plastic deformation (SPD) can be considered. During plastic deformation of metals, the materials microstructure gets harder due to work hardening, dislocation generation, and lattice defect formation¹⁰². During low temperatures ($<0.5 T_m$) high strain rate SPD high concentrations of lattice defects including vacancies have been postulated as being created¹⁰³. There are only a small number of reports of deformation induced vacancies. These include SPD processes such as the accumulated roll bonding (ARB)^{104–106}, equal-channel angular pressing (ECAP)^{107,108}, and high-pressure torsion (HPT)^{109,110} processes. During lower temperatures, higher strains and strain rates, higher concentrations of lattice defects are reported^{104–107,111}. These defects can cause vacancy cluster defects^{104–106} and accelerated atomic migration including precipitation and diffusion. Vacancies concentrations has high at 10^{-4} have been reported in some cases^{108,110}.

Lattice defect formation during plastic deformation dislocation movement has been postulated to occur in several ways. Screw dislocations intersecting on oblique planes could result in one dislocation bowing around the other one, eventually pinching off in a similar fashion to a Taylor-Orowan obstacle. This results in pinching off edge dislocation on neighboring planes. As these annihilate, they can leave behind rows of vacant lattice sites or interstitial sites. Another manner of vacancy formation occurs as mixed character dislocations have a jog that gets caught by an obstacle. It can wrap around the impediment, and as the loop meets the jog, it can leave behind a trail of defects¹¹². Furthermore, as edge dislocations climb over obstacles and multiple jogged screw dislocations interact, they can form vacancies. The intersecting dislocations migrate in a non-conservative manner, leaving a trail of vacancies or interstitial atoms behind¹¹³. Formation of vacancies typically dominates over the formation of interstitials because of the lower vacancy formation energy. Additionally, vacancies that are created in a string relatively close together can lead to more vacancy agglomeration into clusters, which are more easily observed. The production rate of vacancy formation is related to the stress and strain rate experienced by the material^{114,115}; therefore, it is not surprising that the higher flow stress and work induced on a material during high strain rate deformation processing would create more vacancies.

Initial evidence of enhanced atomic movement has been observed in UAM, although the kinetics has yet to be understood. Using atom probe tomography, Sridharan et al.

observed enhanced atomic migration of oxygen and magnesium in a UAM interface of Al6061 ¹¹⁶ and iron-Al6061 ¹¹⁷ (Figure 2.4a). Grain boundary segregation and non-equilibrium oxide formation were suggested as potential mechanisms, although the exact mechanism of the atomic kinetics was outside the scope of the study. The results demonstrate initial evidence of plastic deformation resulting in atomic motion and non-equilibrium defect formation.

Ultrasonic spot welding can also provide initial guidance of enhanced atomic movement and lattice defect formation. Chen et al. ¹¹⁸ found a heat affected zone (HAZ) and a thermo-mechanically affected zone (TMAZ) during welding of Al 6111 T4. Surprisingly, the aluminum aged faster than expected and even beyond the parent material. Transmission electron microscopy showed precipitate growth over an 8-month period (Figure 2.4b), which hardness testing also confirmed. The accelerated natural aging of the HAZ corresponded to an excess vacancy concentration of at least 100 times larger than that expected in the quenched material, although the authors conceded their vacancy calculations were unrealistically large. The results suggest accelerated post weld natural aging caused the dissolution of solute clusters and Guinier-Preston zones (GPZ) ¹¹⁸, which are often associated with excess vacancy concentrations ¹¹⁹. As described above, there have been a small number of ultrasonic bonding studies in which surprising material changes have been observed. An in-depth analysis has not yet been performed of the effect of plastic deformation on UAM bonding and the corresponding non-equilibrium lattice defects and vacancies. This deficiency will be addressed with this dissertation.

2.4 Scientific and Technical Approach

2.4.1 Underlying problem statement

Ultrasonic additive manufacturing (UAM) is a relatively new additive manufacturing process, and the fundamentals of the bonding mechanism are relatively unclear. Although clearly the surface asperities and oxides must be removed prior to bonding, the effect of plastic deformation on bonding is unknown. Several previous studies have demonstrated that severe plastic deformation occurs on the faying surfaces, but the important question remains: is the plastic deformation a by-product of bonding, or is it a requirement? A comprehensive understanding of the effects of plastic deformation is not yet realized. An understanding of these effects and the kinetics of the deformation induced lattice defects created by UAM is required to further implement this science and technology.

A preliminary examination of expected atomic motion can further illustrate the problem statement. Consider the classical diffusion expressions such as the Arrhenius equation $D = D_0 \exp\left(\frac{-Q}{kT}\right)$ and Fick's 2nd law $x \sim \sqrt{Dt}$, where, D is the diffusivity, D_0 is the pre-exponential constant, Q is the activation energy for diffusion, k is Boltzmann's constant, T is temperature, x is the diffusion distance and t is time.

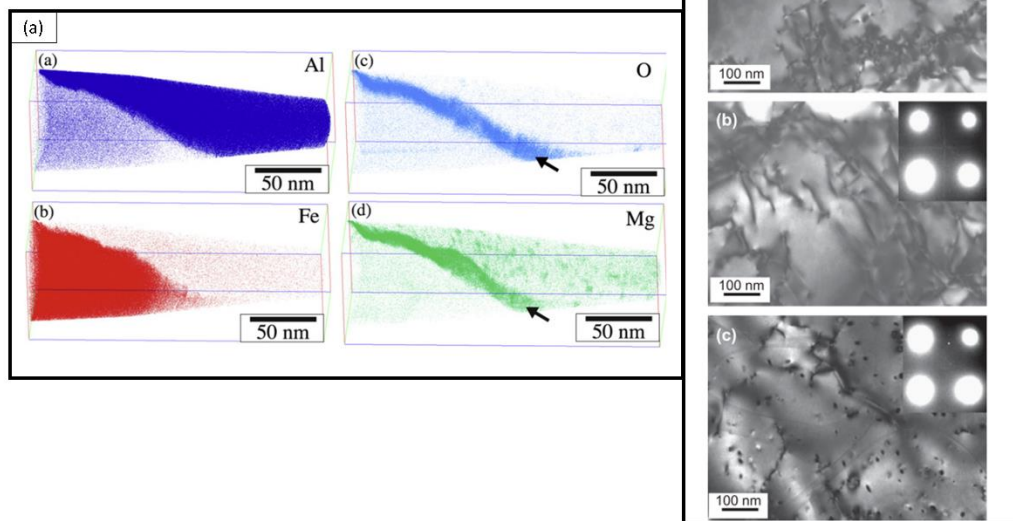


Figure 2.4. Initial evidence of lattice defects during UAM: a) Atomic migration of Mg and O ¹¹⁷, b) Accelerated post weld natural aging of Al 6111 ¹¹⁸

Since the UAM process is a low time and temperature bonding process, these expressions predict that the expected diffusion of atoms should be negligible during UAM. Contrary to this, recent experiments have suggested that significant elemental segregation and accelerated material aging could occur. This discrepancy requires further attention to understand the processes occurring during UAM plastic deformation, and this is our current motivation.

2.4.2 Hypothesis for this study

The hypothesis is that plastic deformation is a requirement for UAM bonding, and this plastic deformation can create significant crystalline lattice defects. Towards this end, UAM bonding will be performed, experimental observations and computational thermodynamic calculations will be performed, and physical and mechanical metallurgy analysis will be used to rationalize the results. The microstructure evolution will be evaluated to determine the role of plastic deformation and the potential of enhanced crystal lattice defect formation.

Evaluations will be performed on a variety of UAM materials and geometric configurations to generalize the results. This study will analyze asymmetric interface geometries between a foil and optical fiber coating, and symmetric geometries between two foils. UAM bonded interfaces will be evaluated using commercially pure metals, as well as interfaces with complicated engineered materials. To isolate individual mechanisms related to plastic deformation bonding, small interlayers are applied to certain difficult-to-weld materials. Prior to experimental bonding, the composition of the interlayer with respect to the bonding material is evaluated using computational thermodynamics. The composition is selectively identified to promote UAM bonding by improving plastic slip and/or lattice defect vacancy formation.

2.4.3 Tools Used for Capturing this Effect

UAM bonding to create these materials was performed at Fabrisonic®, Ohio State University, and Oak Ridge National Laboratory (ORNL). Metallography preparation and analysis is performed at the University of Tennessee, Knoxville (UTK) Institute for Advanced Materials and Manufacturing (IAMM), the National Institute for Materials Science (NIMS), Oak Ridge National Laboratory (ORNL), the Manufacturing Demonstration Facility (MDF) at ORNL, KLA®, and the 11-BM beamline at Argonne National Laboratory (ANL). Computational thermodynamics was performed using the Thermo-calc® software. Experimental characterization of materials before and after UAM bonding was performed using optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Electron microscopy is coupled with energy dispersive spectroscopy (EDS) to determine the elemental composition of the materials and interfaces. Nanoindentation was used to determine microstructural strengthening properties. Electron back scatter diffraction (EBSD), x-ray diffraction

(XRD), and convergent beam electron diffraction (CBED) were also used to characterize the crystalline structure of the materials.

CHAPTER 3

INTERDIFFUSION OF ELEMENTS DURING

ULTRASONIC ADDITIVE

MANUFACTURING

Abstract

This paper reports evidence for enhanced elemental interdiffusion during ultrasonic additive manufacturing (UAM) across metal boundaries of copper-aluminum, nickel-gold, and nickel-gold-aluminum. The high solute interdiffusion measured by energy dispersive x-ray spectroscopy line scans is rationalized with calculated vacancy concentrations orders of magnitude larger than thermal equilibrium values. The above estimates are supported by existing knowledge related to defect physics and UAM thermal cycles. The observation of pronounced elemental mixing are evidence for the presence of enhanced nonequilibrium immiscible metal interdiffusion during UAM processing.

3.1 Introduction

This research was motivated by the unexpected experimental observation of pronounced interdiffusion during the routine characterization of metallized fiber optics to create smart structures for nuclear reactor applications¹²⁰. These smart structures were produced by embedding optical fibers using ultrasonic additive manufacturing (UAM).

A broad introduction to the UAM process is described in Section 2.3, and a detailed literature review is provided below for context to this study. The UAM process can be used to embed fragile materials such as optical fiber strain sensors by interrupting the alternating additive and subtractive operations, as shown in Figure 3.1a below.

The ultrasonic vibrations from the sonotrode cause the localized surface asperities to deform plastically and the surface oxides at the interface of the foils to break down. This operation creates two atomically clean surfaces that bond at temperatures significantly below their respective melting temperatures⁸⁶. This is shown below in Figure 3.1b. The additive layering operations are alternated with subtractive operations using a computer numerical controlled (CNC) mill to remove unwanted material. In this way, a near net shape 3D component can be fabricated^{22,52,81,89,94}. Optical fiber strain sensors can be embedded through exploiting the alternating additive and subtracting operations in the following manner. The additive process is paused after several foil layers have been added to the substrate, then the CNC mill is used to cut an optical fiber optic sized channel (straight or curved) into the top foil. The optical fiber can then be placed into this channel and the additive process is resumed adding more foil layers on top of the now embedded optical fiber^{70,120,121}. This is shown below in Figure 3.1c.

UAM is similar to other solid-state welding techniques in the sense that it relies on plastic deformation to achieve oxide dispersion and bring about nascent metal contact which are necessary conditions for solid state welding to occur^{55,62,94}.

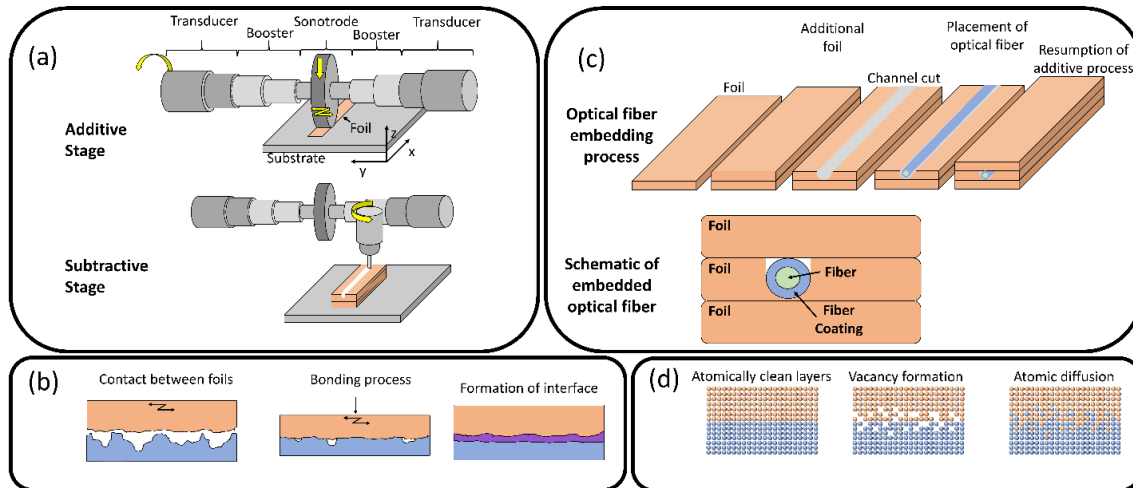


Figure 3.1 Schematic of UAM process. (a) Overview of the additive and subtractive stages, (b) Optical fiber embedding process, (c) Micrometer level bonding process, (d) Atomic level bonding process

However, it remains unclear whether this joining process occurs with significant macroscopic heat generation, as is the case with friction welding and friction stir welding. This is primarily due to the difficulties in conducting measurements at the time scales involved in UAM ^{99,100}. However, recent theoretical calculations have shown that the interface temperatures may exceed the recrystallization temperature (i.e., 50% melting point temperature in kelvin). These observations have been confirmed with detailed microscopy of the weld interfaces which show grain refinement corresponding to a dynamic recrystallization ^{49,50,118,122,123}. However, literature also postulates that during joining of dissimilar metals, high strain rate deformation through UAM may affect elemental interdiffusion through elevated concentrations of vacancies ¹²⁴. This hypothesis is also illustrated schematically in Figure 3.1d.

Additionally, the microscopic interface interactions between the UAM foils and fiber optic metal coatings have received limited attention in lieu of the technical demonstrability of the fiber optic embedding process. The full technical implementation of embedded fiber optics for nuclear applications mandates a scientific understanding of the material interactions during the embedding process.

Embedding fiber-optic sensors with UAM is intriguing because the sensors can be used for spatially distributed strain monitoring for various applications ^{66,70,125–129}. Although fiber optic mechanisms are not this paper's focus, several fundamentals are briefly reviewed for context. The conventional polymer coatings of fiber optics could survive the UAM embedding process ¹³⁰, although they are unsuitable for performance in harsh environments, such as high-temperature, high-radiation fluence, and chemically reactive environments limiting the end use. Thus, optical fibers embedded into structural materials in these demanding environments must have the polymer coating stripped away and replaced with a metal coating ^{70,121}. The process of coating an optical fiber (*metallization*) can be performed through electroplating (for copper or gold coatings) or through electroless deposition (for nickel coatings) ^{66,131,132}. Since the UAM process allows dissimilar metals to bond, the optical fiber can be coated with any metal required for its specific application. The exact mechanisms of dissimilar metal welding under these geometrical constraints are not clear.

Previous UAM work has shown that similar metals ^{89,98}, and dissimilar metals undergo intense plastic deformation at the interface to induce bond formation ^{56,57,62}. Almost all literature show that the plastic deformation is localized almost entirely in the softer metal ^{56,57,60,62}. However, whether the extensive plastic deformation could contribute to enhanced interdiffusion is still not clear. Previous multi-scale characterization of high strain rate solid-state impact welds made with steel and aluminum showed extensive interdiffusion of elements due to localized diffusion promoted by melting ¹³³. However, similar studies performed on UAM samples did not show any significant interdiffusion ¹¹⁷. One can rationalize these differences based on differences in the extent of adiabatic heating between these two processes.

In the case of high strains induced during accumulative roll bonding (ARB) where two metal sheets are joined in the solid state by cold rolling, significant interdiffusion has

been documented. The unique results observed in ARB refinement include remarkable deviation from thermodynamic equilibrium. In composite structures, such as Cu-Nb layers, mechanical alloying of the immiscible phases was found. The previously sharp interface boundary between the copper and niobium widened as both elements appear intermixed. Although research is still underway in this field, the models used to explain this phenomenon include ballistic mixing and other nonequilibrium diffusion processes, such as plasticity-driven mechanical mixing and severe plastic deformation (SPD) ^{134,135}. While the overall strains may be comparable to the UAM process, the ARB strain rate at which the deformation occurs is over 3 orders of magnitude lower.

Gunduz et al. ¹²⁴ investigated the possibility of interdiffusion in ultrasonic welding using an aluminum and zinc dissimilar metal pair. The authors performed Energy Dispersive X-ray Spectroscopy (EDS) analyses in a Scanning Electron Microscope (SEM) and showed the presence of a micron scale interdiffusion zone. Interestingly, Gunduz et al. assumed there was no temperature increase during bonding and concluded that the diffusion profile must be linked to a strain rate-induced vacancy concentration of up to 0.07 atomic fraction. This assumption would lower the local melting temperature and increase the interdiffusivity by a factor of 10^5 . Currently, researchers in the field disagree on the mechanism of interdiffusion seen across UAM interfaces. Chen et al. ¹¹⁸ accepted the Gunduz et al. claim that an increased vacancy concentration and associated diffusivity could exist for their alloy system even though their experiment had higher welding temperature. With an increase in temperature the vacancy annihilation rate could also be enhanced. Fujii et al. ⁵⁰ used the Gunduz et al. claim of an elevated vacancy concentration to rationalize how recrystallization could occur at lower temperatures. However, Fujii et al. could not calculate a vacancy concentration as high as Gunduz et al. Ward et al. ⁹⁵ criticized the Gunduz et al. assumption of the absence of a temperature rise and the extremely high vacancy concentration ($\sim 10^{-1}$) citing that it would destabilize the crystalline lattice. Instead, Ward et al. modeled the UAM interface using elevated temperatures and thermodynamically equilibrium vacancy concentrations. Sietins et al. ⁶⁴ used high resolution transmission electron microscopy (TEM) EDS techniques to observe UAM interfaces. Based on these measurements, the authors attributed the interdiffusion to bulk diffusion without invoking elevated vacancy concentration arguments. Other low-resolution SEM observations of UAM interfaces ^{58,59,62,69} have also conceded that due to the spatial resolution of the equipment being used, significant diffusion could not be resolved. Based on this literature review, one can conclude that there are disagreements in the community with regard to interdiffusion occurring across UAM interfaces.

Therefore, the scope of this research study pertains to interdiffusion of elements from the coatings of the fiber optic strain gauges into the foils during UAM and rationalization of the same using physics of interdiffusion.

3.2 Experimental Procedure

3.2.1 Introduction to Fibers and Coatings

Three sets of samples were evaluated: the Al-Cu sample, the Ni-Au sample, and the Al-Au-Ni sample. The Al-Cu sample configuration was based on an optical fiber electroplated with copper ($20\text{ }\mu\text{m} \pm 5\text{ }\mu\text{m}$) (CU1300 fiber from IVG Fiber), embedded into Al-6061 foils using UAM. Two interfaces from the Al-Cu samples were analyzed. In addition, an optical fiber with electroplated copper before the embedding process, called the *copper baseline sample*, was also considered as a baseline. The cross-sectional areas of the electroplated copper regions were characterized before and after the embedding process. The Ni-Au sample configuration was based on an optical fiber electroplated with gold ($15\text{ }\mu\text{m} \pm 5\text{ }\mu\text{m}$) (ASI9.0/125/155G fiber from Fiberguide Industries), which was then embedded into Ni-200 foils using UAM. An optical fiber with electroplated gold, called the *gold baseline sample*, was also considered as a baseline for comparison before the embedding process. The Al-Au-Ni sample configuration had an optical fiber coated with nickel ($1.5\text{--}5\text{ }\mu\text{m}$) through an electroless process, then immersed in gold (ENIG) ($0.15\text{--}0.20\text{ }\mu\text{m}$) (3896 fiber from OZ Optics), and then embedded into Al-6061 foils using UAM. Two bilayer interface combinations (i.e., Al-Cu and Ni-Au) and one tri-layer interface combination (i.e., Al-Au-Ni) were explored. All the SEM images from the interface regions were analyzed using Image-J software.

3.2.2 UAM Processing Conditions

All samples were produced using a 9kW UAM machine at Fabrisonic LLC (Columbus, OH) using $150\text{ }\mu\text{m}$ thick $\times$ 25.4 mm wide foils. During UAM processing of the Al-Cu and the Al-Au-Ni samples, the sonotrode horn exerted a downward force (in the z-direction) of 4,000 N and traveled forward (in the x-direction) at a speed of 0.033 m/s with a horizontal oscillation amplitude (in the y-direction) of $28\text{ }\mu\text{m}$. For the Ni-Au sample, the sonotrode horn exerted a downward force of 7,000 N and traveled forward at a speed of 0.022 m/s with a horizontal oscillation amplitude of $38\text{ }\mu\text{m}$. During all the above experiments, the sonotrode vibrations were set at a frequency of 20 kHz. The estimated temperature profile was extracted from the non-dimensional data published by Sririman et al.⁹⁹ using WebPlotDigitizer software¹³⁶. Fifty data points were extracted and extrapolated by setting the maximum temperature as described in section 3.4 and setting the room temperature at 298K. After the fabrication process, samples were cut in different sections, cold mounted in epoxy, and polished to a $0.05\text{ }\mu\text{m}$ finish using standard metallography techniques.

3.2.3 Optical and Electron Microscopy

For the optical microscopy, a Zeiss AxioCam 30.5 was used. The microstructures were recorded using bright-field (BF) imaging and extended depth-of-focus corrections.

For the scanning electron microscopy (SEM) analysis, the field emission Hitachi S4800 was used. The samples were carbon coated to reduce electrostatic charging effects. A working distance of 8.8 mm was used with an acceleration voltage of 20 keV and a probe current of 10 μ A with an equipped electron dispersive X-ray spectroscopy (EDS) detector. The SEM-EDS analysis used the quantitative ZAF correction technique.

Samples for transmission electron microscopy (TEM) analysis were extracted from metallic foil-fiber coating interfaces and baseline fiber coatings. To prepare for TEM analysis, the cold-mounted samples were milled into thin foils using a Ga⁺ focused ion beam (FIB), Hitachi NB5000. The energy of the Ga⁺ ions progressively decreased from 30 keV to 5 keV to create the thin foils with approximate dimensions 3000x6000x50 nm. The thin foils were welded onto molybdenum grids and stored in a Ted Pella vacuum chamber. Molybdenum grids were used instead of standard copper grids to mitigate potential fluorescence effects from the grids during analysis.

For the TEM analysis, a field emission Talos F200X was used with an acceleration voltage of 200 kV and a probe current of ~1,000 pA with an equipped EDS detector. Scanning transmission electron microscope images of the BF, dark field (DF), and high-angle annular DF (HAADF) were collected at angles of 9 mrad, 12-20 mrad, and 61-200 mrad respectively. The TEM EDS analysis was performed using a standardless semi quantitative analysis on Bruker ESPRIT 1.9 software that used Cliff-Lorimer corrections. Every EDS spectrum and line scan were taken at three locations on the sample with three repetitions at each location to improve statistical significance. The EDS line scans plotted below represent the average of the three-line scans taken across each interface with errors bars representing the range of the collected data equally spaced for visual clarity.

3.3 Results

3.3.1 Baseline Samples

As mentioned earlier, the optical fibers were examined before embedding. The baseline copper-coated fiber and the baseline gold-coated fiber were imaged, and their elemental compositions were quantified. The EDS spectra for the coatings were taken in high-magnification windows encompassing solely the metal coating. The images and EDS spectra are shown below in Figure 3.2. The arrows in Figure 3.2a show the slight charging effects present in the image. Figure 3.2a shows the copper-coated optical fiber, and its corresponding EDS spectrum is shown in Figure 3.2c.

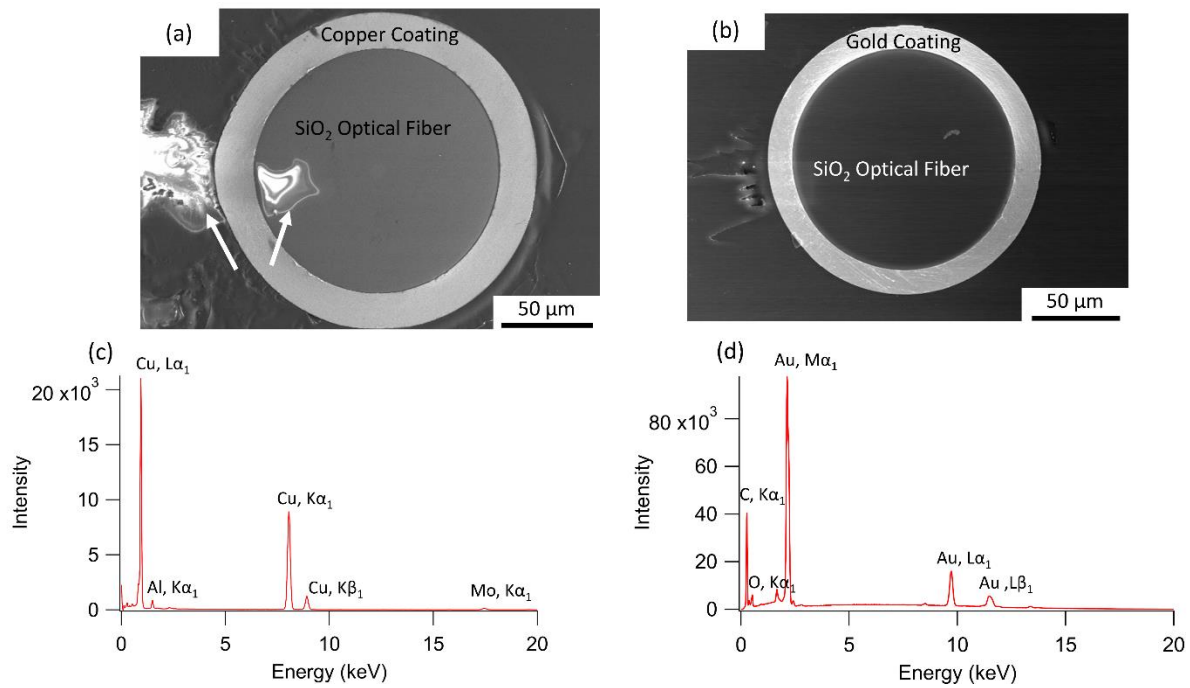


Figure 3.2 Baseline coated fiber images and EDS scans. (a) SEM image of copper-coated fiber, (b) SEM image of gold-coated fiber, (c) TEM EDS spectrum of copper-coated fiber, and (d) SEM EDS spectrum of gold-coated fiber

Figure 3.2b shows the gold-coated optical fiber, and its corresponding EDS spectrum is shown in Figure 3.2d. From the SEM image of the baseline copper sample, the cross-sectional area of the electroplated copper is $9110 \mu\text{m}^2$. The EDS spectra were analyzed using the procedure described above to create the elemental composition results, as shown in Table 3.1 and Table 3.2. To perform the TEM EDS characterization of the baseline copper-coated fiber (Table 3.1), the FIB sample was welded to a molybdenum grid. Although molybdenum appears in the EDS spectrum, the elemental composition deconvoluted the contribution of the molybdenum to the overall composition. This resulted in the copper-coated baseline fiber having a majority of copper with approximately 4.5 at. % aluminum impurity. In the SEM EDS characterization of the baseline gold-coated fiber (Table 3.2), the carbon and oxygen found in the spectrum were also deconvoluted from the elemental composition. This resulted in the gold-coated sample having 100% gold.

3.3.2 Bi-layer Interfaces

This section describes the results pertaining to the *bi-layer interface* between the two different metals. The Al-Cu sample was examined at two different interface locations, and the Ni-Au sample was examined at one interface location. Two different interface locations of the Al-Cu sample were analyzed because the interfaces appeared significantly different with an open boundary (i.e. not good joint) appearing in the first Al-Cu interface and a tight boundary (i.e. good joint) appearing in the second Al-Cu interface. Since the focus of this paper is related to interdiffusion across the interfaces that have been joined, the analysis primarily focused on the tight boundaries including the second Al-Cu interface and the Ni-Au interface. The data from the 2nd Al-Cu interface is also used in the diffusion calculations to be described later. Once the calculations are calibrated for these conditions, these calculations were extended to the other interfaces to obtain the final diffusivity and vacancy concentration values.

The first Al-Cu interface is shown in Figure 3.3. Figure 3.3a and Figure 3.3b show an optical micrograph and SEM overview of the embedded metallized optical fiber. The aluminum foil, copper coating, and SiO₂ optical fiber are shown. The halo (indicated by an arrow in Figure 3.3b) is caused by charging effects in the electron microscope. Figure 3.3c, Figure 3.3d, and Figure 3.3e show high-magnification TEM images of the interface between the copper and aluminum. There are many nano-scale voids, porosities, and open spaces between the two metals, as indicated by the circles in Figure 3.3c, Figure 3.3d, and Figure 3.3e. From the TEM images, the interface region is roughly 250 nm wide. From the SEM image of the embedded electroplated copper, the cross-sectional area is $9878 \pm 17 \mu\text{m}^2$. The elemental concentration variation across the first Al-Cu interface is shown in Figure 3.4. Copper, aluminum, oxygen, carbon, silicon, and magnesium are shown. The interface region between the copper and the aluminum region is highlighted. Large amounts of oxygen and carbon are present in this region, as well as minor amounts of silicon and magnesium. From the TEM EDS data, the interface region is concluded to be approximately 300 nm wide.

Table 3.1 TEM EDS results of baseline copper-coated fiber.

Element	Carbon	Oxygen	Aluminum	Silicon	Copper	Molybdenum
At. %	7.2	2.1	4.5	0.1	86.1	0

Table 3.2 SEM EDS results of baseline gold-coated fiber.

Element	Carbon	Oxygen	Gold
At. %	0	0	100

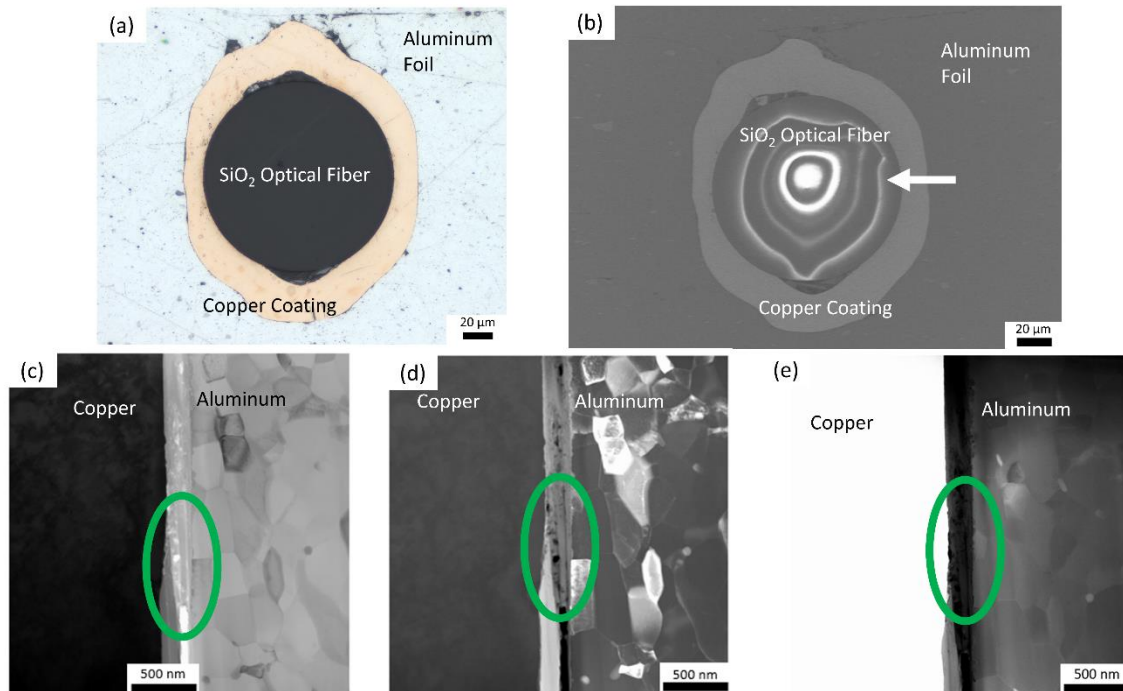


Figure 3.3 First Al-Cu interface images: (a) optical, (b) SEM, (c) BF, (d) DF, and (e) HAADF. The interface is normal to the beam direction

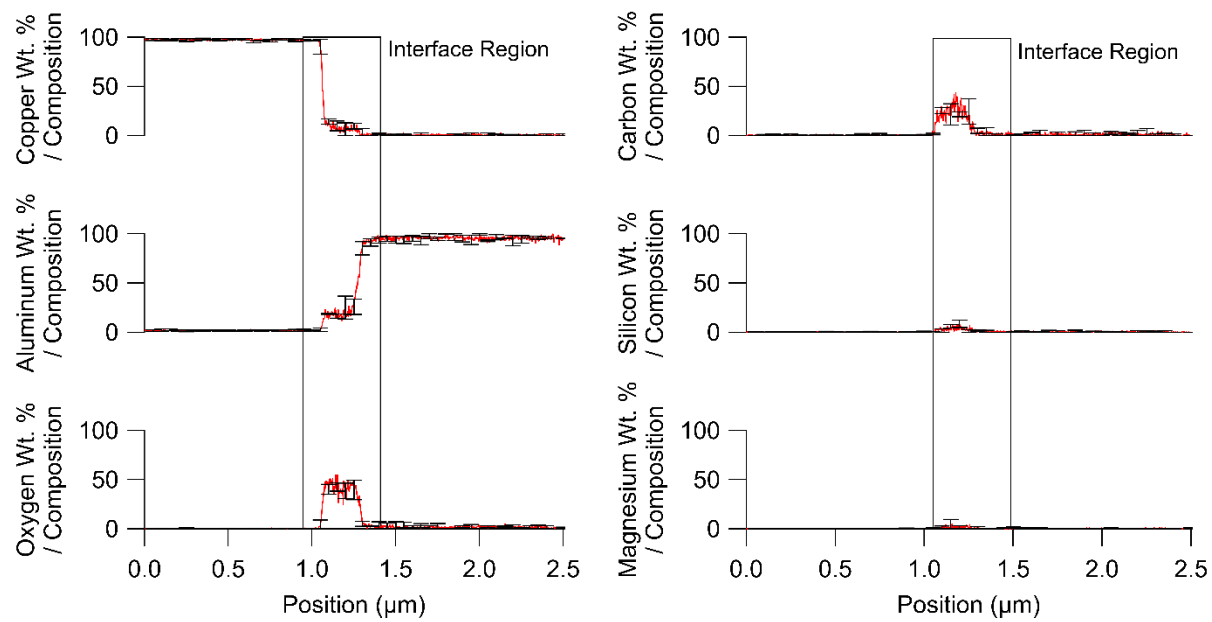


Figure 3.4 TEM EDS line-scan profiles of the first Al-Cu interface.

The second Al-Cu interface is shown in Figure 3.5. The high-magnification TEM images shown in Figure 3.5 are from the same original sample shown in Figure 3.3a and Figure 3.3b; thus, the optical micrograph and SEM overview images are not repeated in Figure 3.5. The highlighted circles indicate the part of the interface region between the metals. Although some open regions could exist, there are fewer voids, porosities, and open regions than in the first Al-Cu interface (Figure 3.3). From the TEM images, there appears to be some type of intermixing between the aluminum and copper in this region. This region is measured to be ~40 nm wide.

The elemental spectrum across the second Al-Cu interface is shown in Figure 3.6. Copper, aluminum, oxygen, carbon, silicon, and magnesium are shown. The interface region between the copper and the aluminum region is highlighted. The interface region of the second Al-Cu interface (Figure 3.5 and Figure 3.6) is significantly different than first Al-Cu interface (Figure 3.2 and Figure 3.3). In the second interface region, a combination of copper, aluminum, and oxygen comprise the majority of the interface region. Other elements—such as carbon, silicon, and magnesium—comprise nearly insignificant portions of the interface. Over half the interface region is a combination of aluminum and oxygen, suggesting that an aluminum oxide is present. From the TEM EDS data, the interface region is measured to be ~70 nm wide.

The Ni-Au interface images are shown in Figure 3.7. Figure 3.7a and Figure 3.7b show an optical micrograph and SEM overview of the embedded metallized optical fiber. The nickel foil, gold coating, and SiO₂ fiber are shown. The particles indicated by the arrow in Figure 3.7b could be from carbon particles deposited onto the SEM surface to reduce charging effects. The particles could also be impurities caught in the open region between the coating and the film before imaging that escaped during the microscopy vacuum process. Figure 3.7c, Figure 3.7d, and Figure 3.7e show the high-magnification TEM images of the interface between the gold and nickel. The interface between the two metals is highlighted with circles. From the TEM images, the interface region is roughly 40 nm wide. Additionally, there is a small void on the left side of the highlighted gold-nickel interface seen in the TEM images. This void appears bright in the BF image in Figure 3.7c and dark in the HAADF image in Figure 3.7e. The SEM image of Figure 3.7b has gold coating in the upper right corner, but the optical image of Figure 3.7a does not. Although the samples are the same, the optical image was taken after re-polishing after the FIB-TEM sample preparation, resulting in an optical image roughly 20 μ m below the surface of the SEM image.

The elemental spectrum across the Ni-Au interface is shown in Figure 3.8. Gold, nickel, iron, aluminum, and oxygen are shown. The interface region between the gold and nickel region is highlighted. In this interface region, gold and nickel are present simultaneously with very minor contributions by other elements, such as iron, aluminum, and oxygen. Since gold and nickel are immiscible metals, the presence of both metals in the same region is very surprising and unusual. From the TEM EDS data, the interface region is measured to be ~50 nm wide.

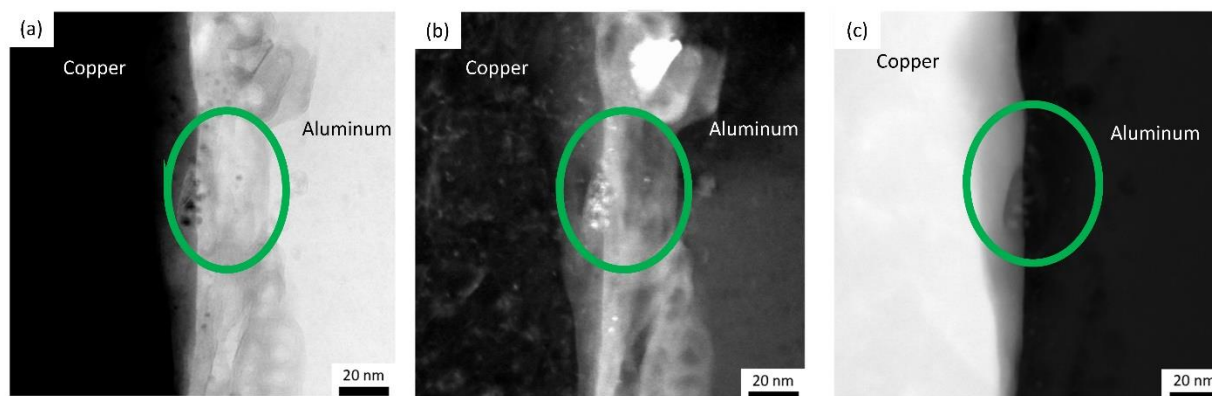


Figure 3.5 Second Al-Cu interface images: (a) BF, (b) DF, and (c) HAADF. The interface is normal to the beam direction

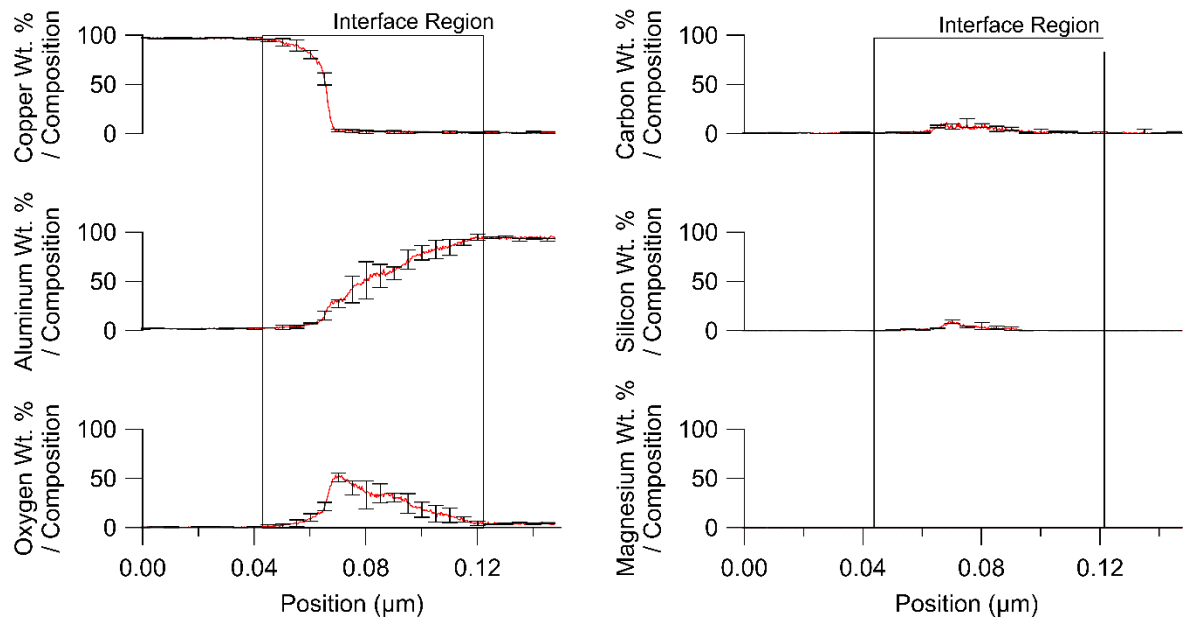


Figure 3.6 TEM EDS line-scan profile of the second Al-Cu interface.

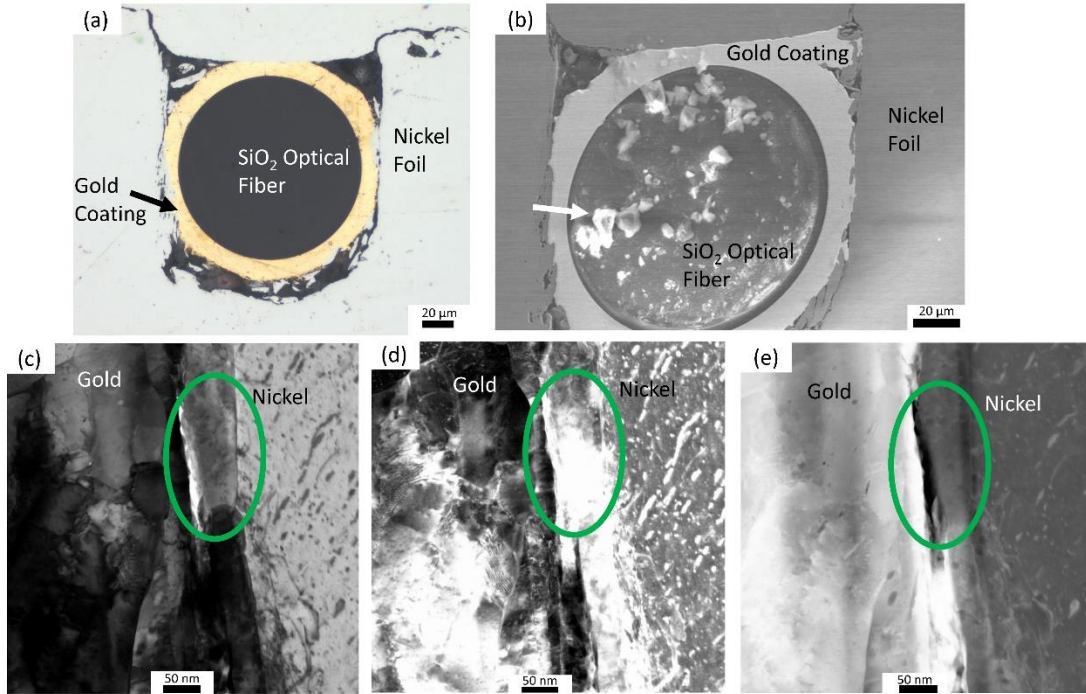


Figure 3.7 Ni-Au interface images: (a) optical, (b) SEM, (c) BF, (d) DF and (e) HAADF. The interface is normal to the beam direction.

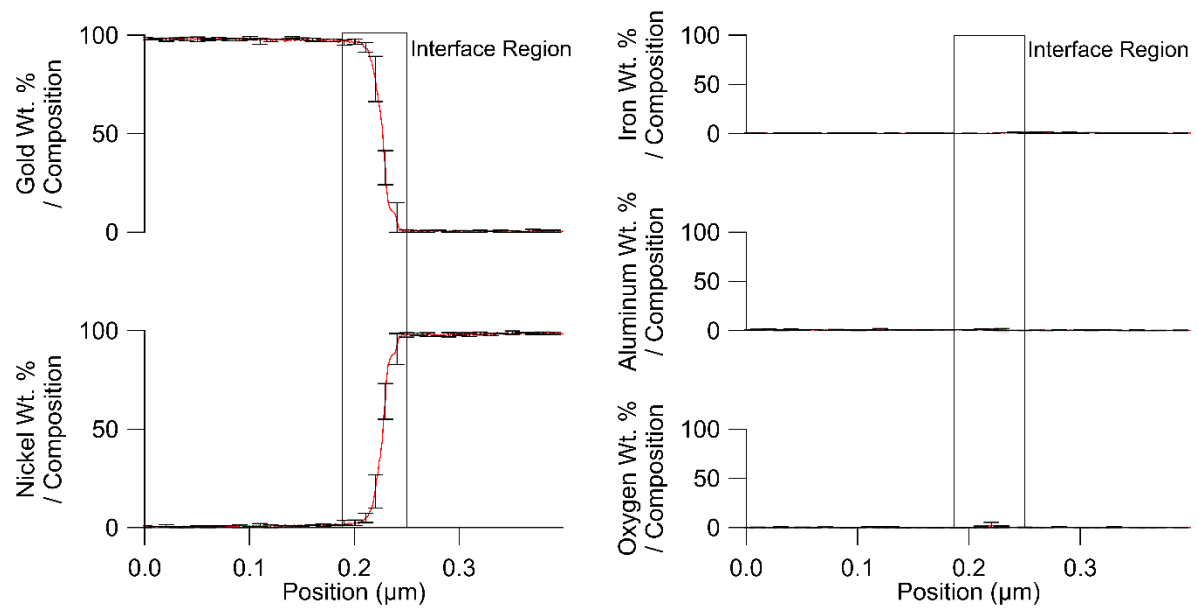


Figure 3.8 TEM EDS line-scan profiles of the Ni-Au interface.

3.3.1 Tri-Layer Interfaces

The *tri-layer interface* across three different metals was explored in the Al-Au-Ni sample, as shown in Figure 3.9 and Figure 3.10. The Al-Au-Ni interface images are shown in Figure 3.9. Figure 3.9a and Figure 3.9b show an optical micrograph and SEM overview of the embedded metallized optical fiber. The aluminum foil, nickel coating, and optical fiber are shown in these overview images. The gold monolayer is not apparent in these low-magnification images. Figure 3.9c, Figure 3.9d, and Figure 3.9e show the high-magnification TEM images of the tri-layer interface. The nickel is on the left, the aluminum is on the right, and the gold monolayer is in the middle. This small gold layer is highlighted with circles. From the TEM images, the width of the gold monolayer is measured to be 90 nm wide.

Figure 3.10 shows the elemental spectrum across the Al-Au-Ni interface. Nickel, gold, aluminum, oxygen, and phosphorous are shown in this highlighted interface. The gold monolayer between the nickel and aluminum can be clearly seen. There is a relatively broad boundary interface between the nickel and the gold and a relatively sharp boundary interface between the gold and the aluminum UAM foil. Additionally, there is a significant rise in oxygen content on the aluminum side of the interface, which suggests that an aluminum oxide combination could be present at that interface. According to the TEM EDS data, the interface region of the nickel and gold is ~90 nm wide, and the interface between the gold and the aluminum foil is less than ~5 nm wide.

3.3.1 Measured Solute Diffusion

In Figure 3.10, the total interface distance between the gold monolayer and the aluminum foil is less than ~5 nm, which is near the resolvable limit of the TEM EDS analysis after considering beam broadening effects and possible slight tilting and twisting of the interface relative to the incident electron beam. Therefore, the gold monolayer on the outside of the nickel-coated fiber could have prevented any significant interdiffusion in the tri-layer Al-Au-Ni sample. Figure 3.4, Figure 3.6, Figure 3.8, show that there is interdiffusion across the bi-layer metal interface after the UAM embedding process.

To quantitatively interpret interdiffusion across the bi-layer interfaces, a time and temperature profile that the samples experienced must be estimated, although it was not directly measured in this study. The temperature profile during ultrasonic consolidation (UC) can be affected by several factors including power from the sonotrode, normal force, metal-metal contact area, sonotrode speed, and oscillation frequency. The temperature contribution from these factors has been experimentally measured during UAM bonding^{99,100} and ultrasonic spot welding (USW)^{49,50,118,122,123} using type K thermocouples and thermal imaging cameras. A term of energy per unit area (J/mm^2) is typically used to normalize the UC welding parameters.

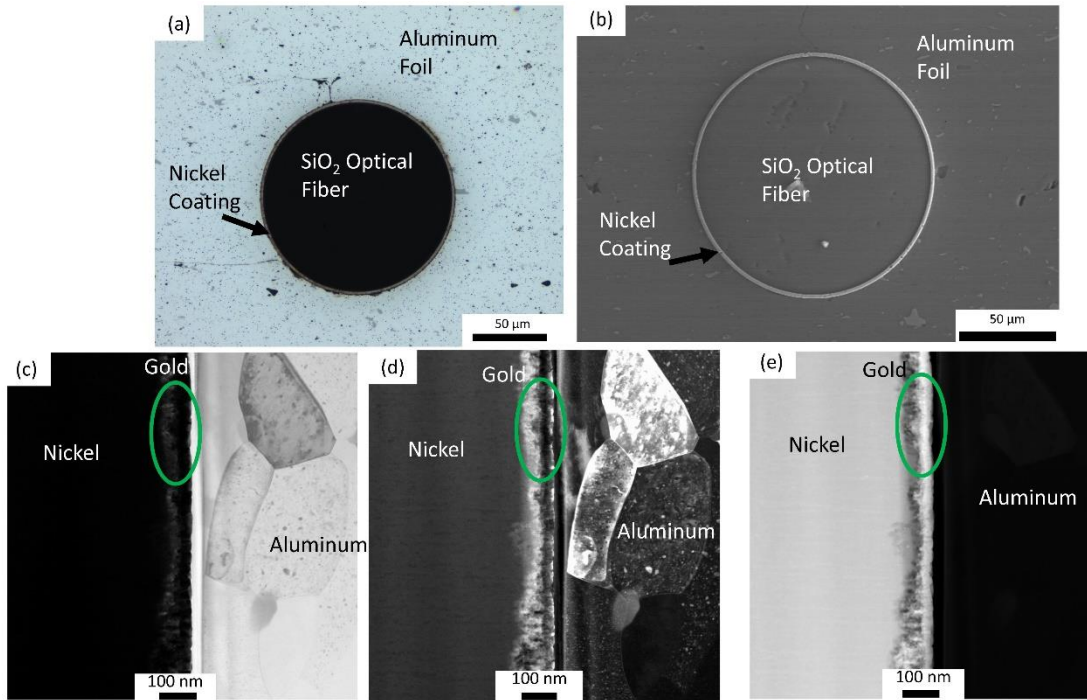


Figure 3.9 Al-Au-Ni interface images: (a) optical, (b) SEM, (c) BF, (d) DF, and (e) HAADF. The interface is normal to the beam direction.

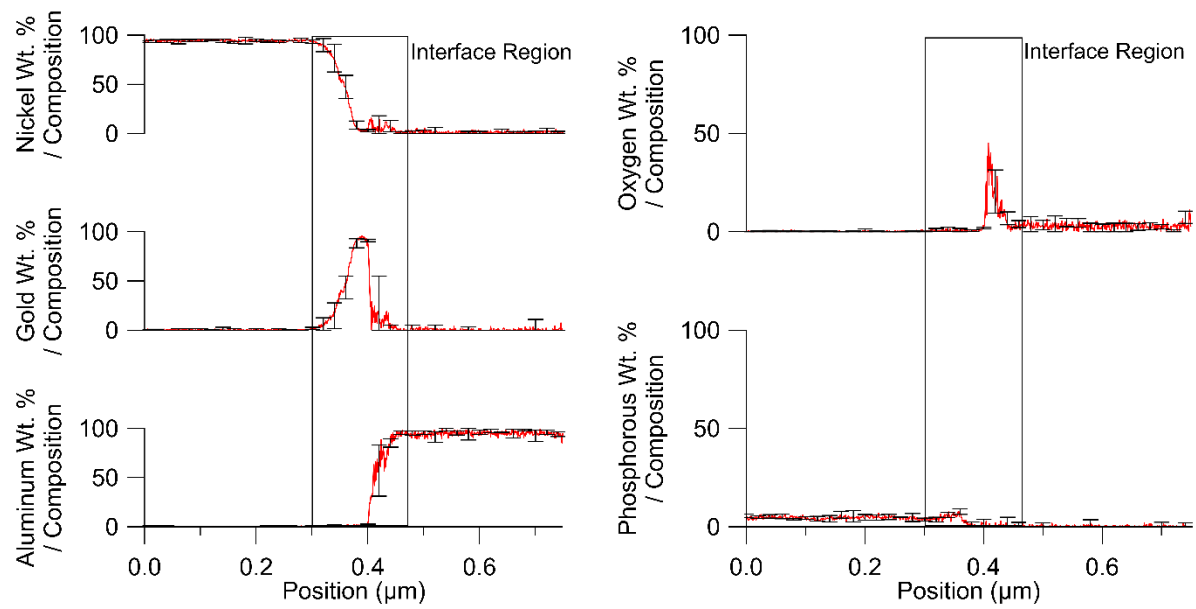


Figure 3.10 TEM EDS line-scan profiles of the Al-Au-Ni interface.

Using a simple derivation described by Sriraman et al.¹⁰⁰, the energy per unit area experienced by the samples in this study is $10\text{-}16\text{ J/mm}^2$, which according to previous studies^{49,50,99,100,118,122,123} corresponds to a peak temperature between $115\text{ - }400^\circ\text{C}$. The oscillation amplitude and frequency could also adjust the mean temperature value by 20°C ⁹⁹, although these are relatively minor factors compared to the 275°C temperature variation found throughout literature. The large range of the potential peak temperatures is strongly affected by the large experimental errors which exist in UAM temperature measurements. As mentioned above, the applied ultrasonic frequency is 20 kHz . Therefore, the time resolution required to accurately measure temperature from each back-and-forth pass of the sonotrode must be below 0.05 ms ($1/20\text{ kHz}$).

UAM thermal measurement studies have recognized this and maximized their thermocouple sampling rate to $10,000$ per second while using an unsheathed $70\text{ }\mu\text{m}$ diameter Type K thermocouple to minimize the thermocouple time constant. This corresponds to receiving a signal from the thermocouple every 0.1 ms ^{99,100}. The time constant of the thermocouple should also be considered. The time constant is the time required for the sensor to respond to at least 63.2% of its total output signal when subjected to a step change in temperature. This is a function of the thermal heat capacity and mass of the thermocouple^{137–139}. For an unsheathed $70\text{ }\mu\text{m}$ Type K thermocouple at room temperature, the time constant is approximately $135\text{-}150\text{ ms}$ ^{140–143}. This means although a rapid signal was recorded from the thermocouple every 0.1 ms , the thermocouple could only respond to temperature changes at most every 135 ms . Therefore, the true magnitude of the temperature spike due to UAM bonding could be missed while using these thermocouples. Additionally, the non-contact thermal imaging cameras used in the above studies cannot access a direct line of site with the internal weld, and the emissivity of metals allows only a fraction of the radiative heat to be detected¹⁴⁴.

Considering these factors of the UC normalization term, the previous experimental research, and the experimental uncertainty of the temperature measurements, an approximate peak temperature value of 225°C (498K) is assumed for the diffusivity calculations below. Using the arbitrary temperature profile from Sriraman et al.⁹⁹ and this approximate peak temperature, an estimated thermal profile can be created for the welding parameters used in this study. This is shown below in Figure 3.11. The estimated thermal profile is used since no temperature measurements were taken in this experiment.

Additionally the phenomenological equation for thermal interdiffusivity $\tilde{D}$ between aluminum and copper, derived by Matsuno et al.¹⁴⁵ using the Boltzmann-Matano method, can be considered here. The interdiffusivity across the temperature profile in Figure 3.11 can be calculated using the values of atomic fraction of aluminum in copper N_{Al} from the baseline copper fiber ($\sim 4.5\text{ at. \%}$) and the gas constant R of $8.314\text{ J/(K}\cdot\text{mole)}$. Also note that the term $\tilde{D}$ simply denotes interdiffusivity between an A-B alloy, while the term D typically denotes diffusivity of a sole solute atom in an otherwise homogenous solid solvent solution. The former is considered in this study.

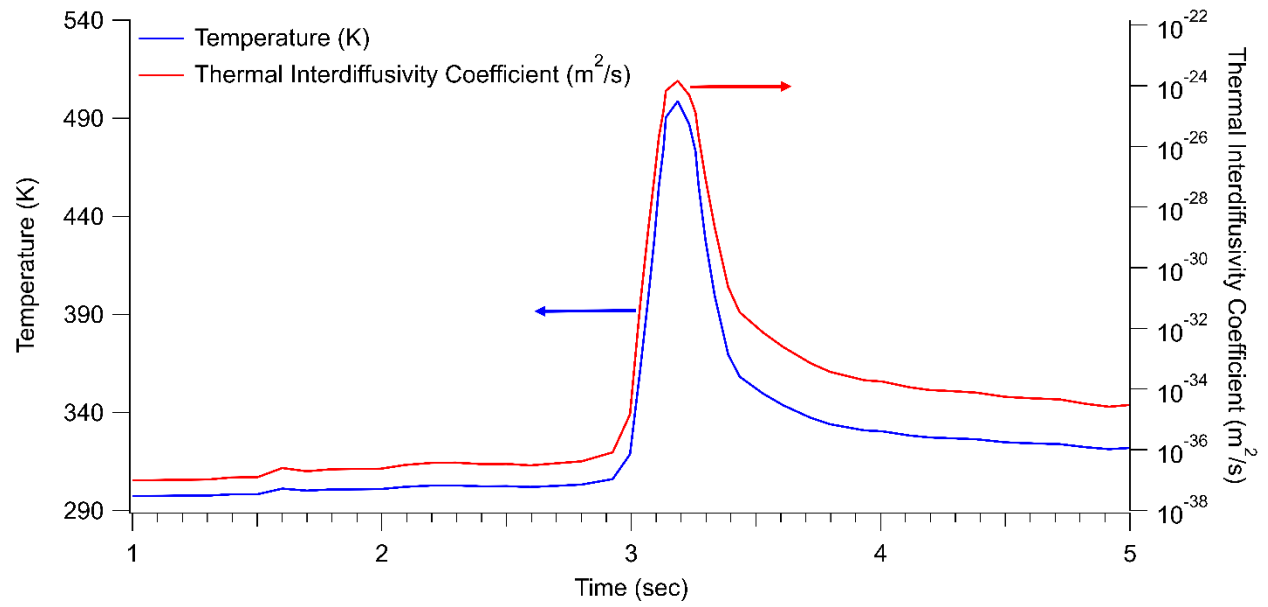


Figure 3.11 Estimated thermal profile from Sriraman et al. ⁹⁹ and interdiffusion coefficient assuming only thermal contributions

$$\tilde{D}(N_{Al}) = 0.43 \times 10^{-4} \cdot \exp \left\{ -\frac{(194000 - 180000N_{Al})}{RT} \right\} \quad \text{Equation 3.1}$$

The method commonly used for determining any diffusivity during heating up and cooling down time is considered. In this case the solution for the diffusivity for each time t interval is replaced by the averaged product $\overline{Dt}$ by the equation $\overline{Dt} = \int_0^t D(t) dt$ ¹⁴⁶. Using this method the interdiffusivity during the interface temperature profile, also shown below in Figure 3.11, demonstrates the heating up and cooling down time provide a negligible contribution to the total time-integrated interdiffusivity. Therefore, only the time (0.2 sec) at peak temperature will be used for the experimental diffusivity equations below.

Considering the diffusion couple profile method^{146,147} from the second Al-Cu interface shown in Figure 3.6, the distance, x , at which the aluminum concentration reaches 50% of the maximum aluminum concentration is 0.035 μm from the edge of the interface. Using Fick's second law approximation, the experimental interdiffusivity during a time interval of 0.2 s is $6.1 \times 10^{-15} \text{ m}^2/\text{s}$.

$$x \sim \sqrt{\tilde{D}t} \quad \text{Equation 3.2}$$

Significant discrepancy is found when comparing between the expected interdiffusivity value from the thermal approach by Matsuno et al. and the experimentally estimated interdiffusivity value from the EDS measurements of solute diffusion ($10^{-24} \text{ m}^2/\text{s}$ vs $10^{-15} \text{ m}^2/\text{s}$ respectively). The small residence time and minimal homologous temperature rise ($\sim 0.4 T/T_m$) prevents thermal equilibrium diffusion from being a viable explanation of the observed atomic motion (roughly 9 orders of magnitude discrepancy). Thus, alternative diffusion mechanisms must be operational.

Finally, it should be noted that the energy normalizing term (J/mm^2) could be an incomplete description for the thermal profile experienced at the interfaces in this study due to the unique geometries present. The thermal profiles were created for UAM *foil-foil* bonding in which each foil has the same ratio of cross-sectional area of 1:1, whereas the present experiment investigated the *foil-fiber coating* interface where the cross-sectional area between the two bonded geometries is not equal. In fact, using the foil width of 25.4 mm, foil thickness of 0.15 mm, and the electroplated copper cross sectional area of $9110 \mu\text{m}^2$, the ratio of the foil-fiber coating cross sectional area is 1:0.0024. It is possible the disproportional geometries create a unique situation unlike what would be observed with two equally proportional geometries. Further analysis is needed to determine the potential impact of this unequal cross-sectional area.

3.4 Discussion

3.4.1 Rationalization of the Interdiffusion

The phenomenological approach to diffusion using Fick's laws and thermal equilibrium diffusion, as described above, clearly does not provide a complete description of the atomic motion during UAM. Therefore, the atomistic approach to diffusion can be considered. The interdiffusion equation is shown below where f is the correlation factor, a_0 is the lattice constant, ν is the Debye frequency of atomic vibration on its lattice site, E_m is the vacancy migration energy, k is the Boltzmann constant of 8.617×10^{-5} eV/K, and T is the absolute temperature^{146–152}. For the dissimilar FCC metal interfaces explored here, in which the vacancy-atom exchange ratio is not known, a nominal value of 0.78 is used for the correlation factor^{153–160}.

$$\tilde{D} = f a_0^2 X_v \nu \cdot \exp\left(-\frac{E_m}{kT}\right) \quad \text{Equation 3.3}$$

The material constants that are needed to obtain the interdiffusion coefficients from Equation 3.3 for the elemental concentration profiles of the Al-Cu interfaces and the Ni-Au interface are shown in Table 3.3 below.

Using the material constants for copper and gold shown in Table 3.3, the vacancy concentration needed for interdiffusion across each interface can be calculated. Table 3.4 shows the values for each interface and the calculated interdiffusivity using Fick's second law approximation. To illustrate the magnitude of the elevated vacancy concentrations estimated in Table 3.4, thermal equilibrium vacancy concentrations can be calculated as shown below in Table 3.5. The similarities and differences between the two Al-Cu interfaces should be discussed further. Both interfaces demonstrate the presence of voids and porosity as shown as white dots in the BF images in Figure 3.3d and Figure 3.5a, and black dots in the DF images in Figure 3.3e and Figure 3.5b. It is hypothesized that these voids resulted from the accumulation of vacancies migrating towards the interfaces. Clearly the main difference between the two interfaces is the presence of the ellipsoidal gap between the metals. The first Al-Cu interface in Figure 3.3 has a ~100 nm gap between the Al and Cu, while the second Al-Cu interface in Figure 3.5 does not have an gap between the metals. Since solutes are observed on opposite sides of the gap in Figure 3.3, it is believed that the Al and Cu likely separated after interdiffusion of these elements. The subtle difference between the interfaces is attributed to non-uniform thermo-mechanical conditions at the interface during the ultrasonic metal welding process¹⁷⁵. This is expected to result in non-uniform distribution of plastic strains¹⁷⁶. As a result, some of the interfaces that had joined may be torn apart with the high magnitude of plastic strain (e.g. 1st Al-Cu interface, Figure 3.3) while others remained intact (2nd Al-Cu interface, Figure 3.5). It is important to note that any solid-

state or resistance spot welding geometries exhibit non-uniform stress distribution due to the inherent geometry effects ¹⁷⁷.

The interdiffusion physics described above uses the entire interface width including the gap. Since the first Al-Cu interface has a gap in the middle of the interface region, the total distance used for the interdiffusion equation is larger than it otherwise would be. This creates an even larger vacancy concentration as shown in Table 3.4. The second Al-Cu interface did not exhibit separation; therefore, it was chosen to illustrate the interdiffusion physics due to the absence of the potentially convoluting gap.

From an atomistic point of view, the mobility of large solute atoms (Al, Cu, Ni, Au) require vacancies to be present since their movement depends on the substitutional diffusion mechanism (i.e. there must be an open lattice location for a solute atom to jump into) ^{153,161,178}. However, the mobility of A and B atoms in an A-B metal interface is typically not equal, as Kirkendall's experiments have demonstrated ^{150,151}. As hinted at earlier, the interdiffusion is typically compositionally dependent, although a simplified interface interdiffusion value was created to demonstrate the physics present in this study.

Although major solute atoms require vacancy point defects to migrate, traditional interstitial impurity atoms (C, O) do not require vacancies to migrate. This simpler migration pattern is described as interstitial diffusion (in contrast to substitutional diffusion) in which the impurity solute atoms, being much smaller in atomic diameter than the bulk solvent atomic diameter, diffuse from one interstitial site to another. In the FCC matrix, these are the octahedral and tetragonal lattice sites in between the host FCC lattice ^{153,161,178}.

for the estimated thermal profile maximum and the melting temperature. If the vacancy concentration corresponds to thermodynamic equilibrium at a given temperature, then it is determined by the vacancy formation energy E_f and the absolute temperature ^{102,161,162}.

This analysis demonstrates that the estimated vacancy concentrations across the sample interfaces necessary to explain the observed solute diffusion are quite large. The vacancy concentrations are much larger than thermal equilibrium levels at the estimated maximum temperature and even at the metals' respective melting temperatures. These values would be quite alarming if they are correct because they begin to reach the critical vacancy concentration hypothesized by Johnson ¹⁶³ based on the defect-induced shear catastrophe ^{164,165}. This limit describes the lattice defect concentrations that are required to raise a metallic material's free energy to the point that it loses its crystallinity and becomes amorphous. Other examples of a material briefly losing its crystallinity include irradiation damage cascades ^{166–169} and ARB mechanical alloying, as mentioned below.

Table 3.3 Material constants for interdiffusion expression.

Material	E_m (eV) ¹⁷⁰	ν (s ⁻¹) ¹⁷¹	a_0 (Å) ¹⁷²
Copper	0.70	7.98×10^{13}	3.6
Gold	0.71	4.92×10^{13}	4.1

Table 3.4 Interdiffusivity and vacancy concentration of each interface.

Sample	$\tilde{D}$ (m ² /s)	X _v (at fraction)
First Al-Cu interface	5.0×10^{-14}	7.5×10^{-2}
Second Al-Cu interface	6.1×10^{-15}	9.2×10^{-3}
Ni-Au interface	3.1×10^{-15}	7.4×10^{-3}

Table 3.5 Thermal equilibrium vacancy concentrations

Material	E_f (eV) ¹⁷⁰	T_m (K)	X_v (at fraction) at 225°C	X_v (at fraction) at T_m
Copper	1.28	1358	1.12×10^{-13}	1.78×10^{-5}
Gold	0.93	1337	3.90×10^{-10}	3.13×10^{-4}

$$X_v = \exp\left(-\frac{E_f}{kT}\right) \quad \text{Equation 3.4}$$

However, as mentioned previously, there are various measurement uncertainties and alternative possibilities beyond just an elevated vacancy concentration that could explain the interdiffusion. Therefore, these vacancy concentration values should be considered as upper bounds rather than exact values.

The elemental concentrations in the various interfaces can be briefly compared. In the first Al-Cu interface (Figure 3.4), the main elements of aluminum and copper experienced interdiffusion, but non-trivial fractions of the minor solute atoms carbon, oxygen, and silicon were also observed in the open boundary interface. In contrast, in the second Al-Cu interface (Figure 3.6) only oxygen was observed as an interface impurity element. If an ordered crystal were created near this interface, a thin intermetallic of aluminum and copper and/or an aluminum oxide could have been present. Finally the Ni-Au interface (Figure 3.8) appears to have nickel and gold present in the same region although the equilibrium phase diagram and thermodynamic assessments of this system suggest limited mutual miscibility at low temperatures^{173,174}. This is surprising although the mechanical mixing of immiscible metals has also been found in other bonding processes, such as the ARB process, as discussed later.

The similarities and differences between the two Al-Cu interfaces should be discussed further. Both interfaces demonstrate the presence of voids and porosity as shown as white dots in the BF images in Figure 3.3d and Figure 3.5a, and black dots in the DF images in Figure 3.3e and Figure 3.5b. It is hypothesized that these voids resulted from the accumulation of vacancies migrating towards the interfaces. Clearly the main difference between the two interfaces is the presence of the ellipsoidal gap between the metals. The first Al-Cu interface in Figure 3.3 has a ~100 nm gap between the Al and Cu, while the second Al-Cu interface in Figure 3.5 does not have a gap between the metals. Since solutes are observed on opposite sides of the gap in Figure 3.3, it is believed that the Al and Cu likely separated after interdiffusion of these elements. The subtle difference between the interfaces is attributed to non-uniform thermo-mechanical conditions at the interface during the ultrasonic metal welding process¹⁷⁵. This is expected to result in non-uniform distribution of plastic strains¹⁷⁶. As a result, some of the interfaces that had joined may be torn apart with the high magnitude of plastic strain (e.g. 1st Al-Cu interface, Figure 3.3) while others remained intact (2nd Al-Cu interface, Figure 3.5). It is important to note that any solid-state or resistance spot welding geometries exhibit non-uniform stress distribution due to the inherent geometry effects¹⁷⁷.

The interdiffusion physics described above uses the entire interface width including the gap. Since the first Al-Cu interface has a gap in the middle of the interface region, the total distance used for the interdiffusion equation is larger than it otherwise would be. This creates an even larger vacancy concentration as shown in Table 3.4. The second

Al-Cu interface did not exhibit separation; therefore, it was chosen to illustrate the interdiffusion physics due to the absence of the potentially convoluting gap.

From an atomistic point of view, the mobility of large solute atoms (Al, Cu, Ni, Au) require vacancies to be present since their movement depends on the substitutional diffusion mechanism (i.e. there must be an open lattice location for a solute atom to jump into) ^{153,161,178}. However, the mobility of A and B atoms in an A-B metal interface is typically not equal, as Kirkendall's experiments have demonstrated ^{150,151}. As hinted at earlier, the interdiffusion is typically compositionally dependent, although a simplified interface interdiffusion value was created to demonstrate the physics present in this study.

Although major solute atoms require vacancy point defects to migrate, traditional interstitial impurity atoms (C, O) do not require vacancies to migrate. This simpler migration pattern is described as interstitial diffusion (in contrast to substitutional diffusion) in which the impurity solute atoms, being much smaller in atomic diameter than the bulk solvent atomic diameter, diffuse from one interstitial site to another. In the FCC matrix, these are the octahedral and tetragonal lattice sites in between the host FCC lattice ^{153,161,178}.

The large mobility of the oxygen atoms migrating towards the interface in the Al-Cu system is likely due to this interstitial diffusion mechanism. This mechanism can also help describe the small atom dispersion that others have observed in UAM interfaces ¹¹⁷. Although carbon is often described as an interstitial atom for typical metals such as BCC iron ^{153,161,178}, carbon has extremely low solubility in aluminum, typically less than 0.1 ppm at and below 750°C ¹⁷⁹⁻¹⁸². This makes the detected carbon x-rays shown in Figure 3.3 quite curious. Since the TEM EDS in this study used a field emission electron source in an ultra-high vacuum, the carbon x-rays have likely originated directly from the sample. Further research including atom probe tomography is needed to understand the mechanisms.

For a complete understanding of the defect physics, vacancy migration must be considered in addition to the major and minor solute migration. Consider first that when bonding was initiated, there were two atomically clean planes of atoms in contact. Then due to the elevated vacancy concentration, there was a flux of atoms outward from this flat plane towards the opposite bulk region. This created an interface region 50 nm or more. For this outward flux of atoms to occur (from the initially clean interface towards the bulk), there must also have been an inward flux of vacancies to support it (from the bulk towards the center of the interface region).

Although this flux of vacancies and solute atoms could have occurred solely through the bulk lattice, the material was not a single crystal. Although detailed electron backscatter diffraction (EBSD) analysis, for microstructural characteristics, was not performed in these samples due to limited size. Many other UAM interface analyses have shown elevated dislocation densities, severe grain refinement, large concentrations of high

angle grain boundaries (HAGB), and migrating grain boundaries towards the foil interfaces likely due to a process analogous to dynamic recrystallization (DRX)^{57,60,62,94,99,100,116,183–187}. During the DRX process a crystal releases internal stored energy from accumulated plastic strains. New essentially strain free crystals grow at the expense of the deformed crystals. The material is swept by HAGB, perhaps more than once, as the material realigns atoms into crystals with lower free energy^{161,188,189}. Some have postulated that the migrating grain boundaries not only sweep through each side of a UAM foil interface, but even across foil interface boundaries⁵⁵. Nevertheless, this phenomenon is less likely with dissimilar foil interfaces due to the decreased grain boundary mobility while carrying solute atoms^{188,190}.

Although sweeping grain boundaries may not rapidly carry solute atoms, stationary grain boundaries could offer short circuit solute diffusion pathways in addition to or instead of vacancies¹⁵³. Grain boundary diffusion of vacancies and interstitials occurs primarily through the relatively open space between grains. The defects migrate by jumping from the lattice, into the grain boundary, traveling through the grain boundary, then jumping back out into the lattice. Both vacancies and interstitials can move in grain boundaries with single atom exchanges or with collective jumps, although most often the motion involves two or more atoms. There is no clear consensus on the relative strength of the different types of point defects on grain boundary diffusion in metals, but there is clear evidence that both contribute to the diffusivity^{153,188,191–193}. Of course, if grain boundary interdiffusion significantly contributes to the major solute interdiffusion in this study, then the vacancy concentration required for the interdiffusion, as predicted in Table 3.4, could be lower than estimated.

3.4.2 Critique of Previous UAM Enhanced Vacancy Concentration Analyses

As shown in Table 3.4, the atomic fraction of vacancies across the three different interdiffusion boundaries is on the order of 10^{-3} , although as discussed, grain boundary interdiffusion could contribute to lowering this value. This extreme vacancy concentration is still several orders of magnitude lower than the vacancy concentration of 10^{-1} proposed by Gunduz et al. Several factors could have caused the significant difference between these vacancy concentrations. Gunduz et al. did not consider the classical random walk diffusion physics^{146–152}, nor did Gunduz et al. consider any thermal cycles or temperature increases. In fact, the published literatures show that the temperature increase at the interface is significant^{49,50,95,99,100,118,122,123,175}.

In addition to the defect physics and temperature profiles overlooked by Gunduz et al., the initial argument of their paper was based on experimental data that did not mention or consider measurement uncertainties. The author's initial argument was based on a single SEM EDS line profile with a 1 μm range of compositionally equivalent material, which the author claims became molten. They did not consider the SEM operating parameters nor the interaction volume convolution^{194,195}, which is larger than the lateral range of the supposed molten materials. The issues outlined above signify that the Gunduz et al. conclusions may not be accurate.

3.4.3 Correlation of the Interdiffusion Observed in ARB Processing

The UAM process is not the only process that can create layered materials driven far from equilibrium. The ARB process can create mechanical alloying of immiscible materials due to SPD, which refines the microstructure as dislocations interact during the repeated severe straining process^{135,196}. The mechanical alloying of different materials has experimentally been found to create layered foils such as aluminum and magnesium with high diffusivities and intermetallic formation^{197,198}. Copper and zirconium have also experienced mechanical alloying with amorphization, which is experimentally observed in extreme cases¹⁹⁹.

The fundamental phenomena causing deformation induced mechanical and chemical mixing from phases that have non-soluble elements is still debated. The common explanations for this mixing include: a purely diffusion-driven mechanism, defect-enhanced diffusion, mechanical mixing (also referred to as shuffling or ballistic mixing), and deformation driven amorphization²⁰⁰.

3.4.4 Postulation Regarding the Vacancy Formation

This work explored the elemental composition profiles across bi-layer metal boundaries and calculated interdiffusivity values across the interfaces that must exist according to the measured data. These interdiffusivity values were rationalized using vacancy concentrations that are several orders of magnitude above thermal equilibrium values. The exact origin of these vacancies is still uncertain and should be explored further.

Introduction of defects such as vacancies increases with applied plastic deformation. There are several methods for describing plastic deformation from externally applied work. A common method for comparing the work done to a metal through traditional cold roll bonding or the ARB process is a reduction of thickness measurement. Typical values for roll bonding processes are ~30-70% reduction of thickness^{201–205}. Comparing the cross-sectional area of the electroplated copper before and after the embedding process demonstrates a negligible -3.2% reduction of thickness. Therefore, only a minor reduction of thickness occurred during the ultrasonic bonding process although a significant number of vacancies were apparently still created.

Additionally, strain measurements were being investigated when the copper-coated fiber and the nickel-coated fiber were embedded into aluminum. These measurements could help in providing insight into the nature of the vacancy formation. The strain across the fiber was measured before and after the embedding process. The difference between these strain measurements is called the *residual strain* in the fiber. Petrie et al. performed these measurements⁶⁶, which are shown in Figure 3.12 and Figure 3.13.

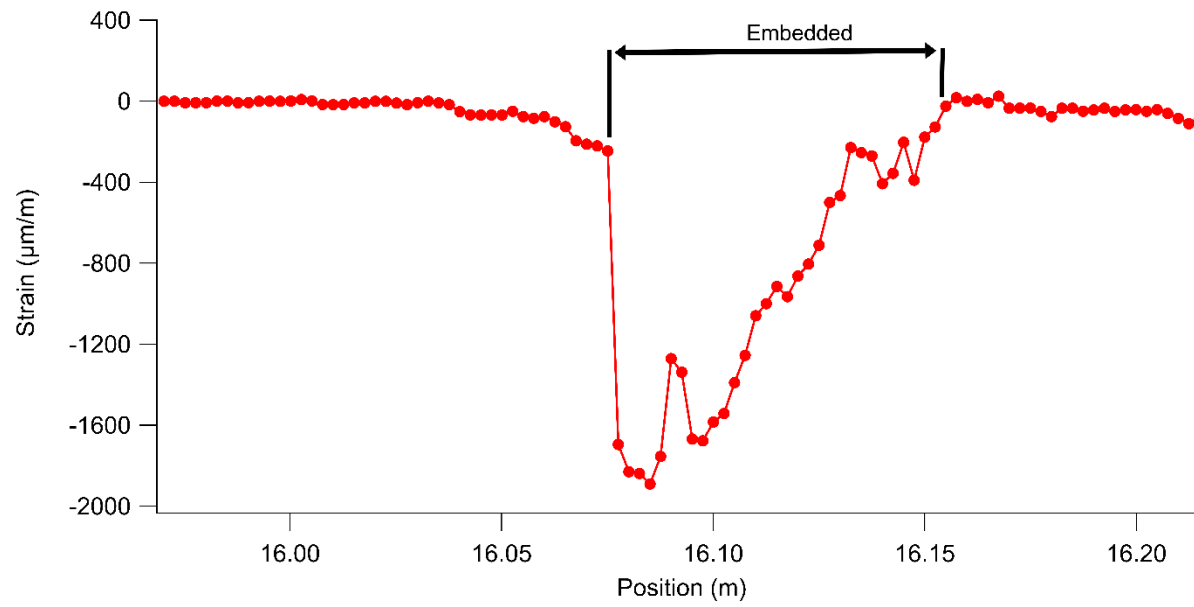


Figure 3.12 Residual strain measurements in the Al-Cu sample. Used with permission from Reference ⁶⁶.

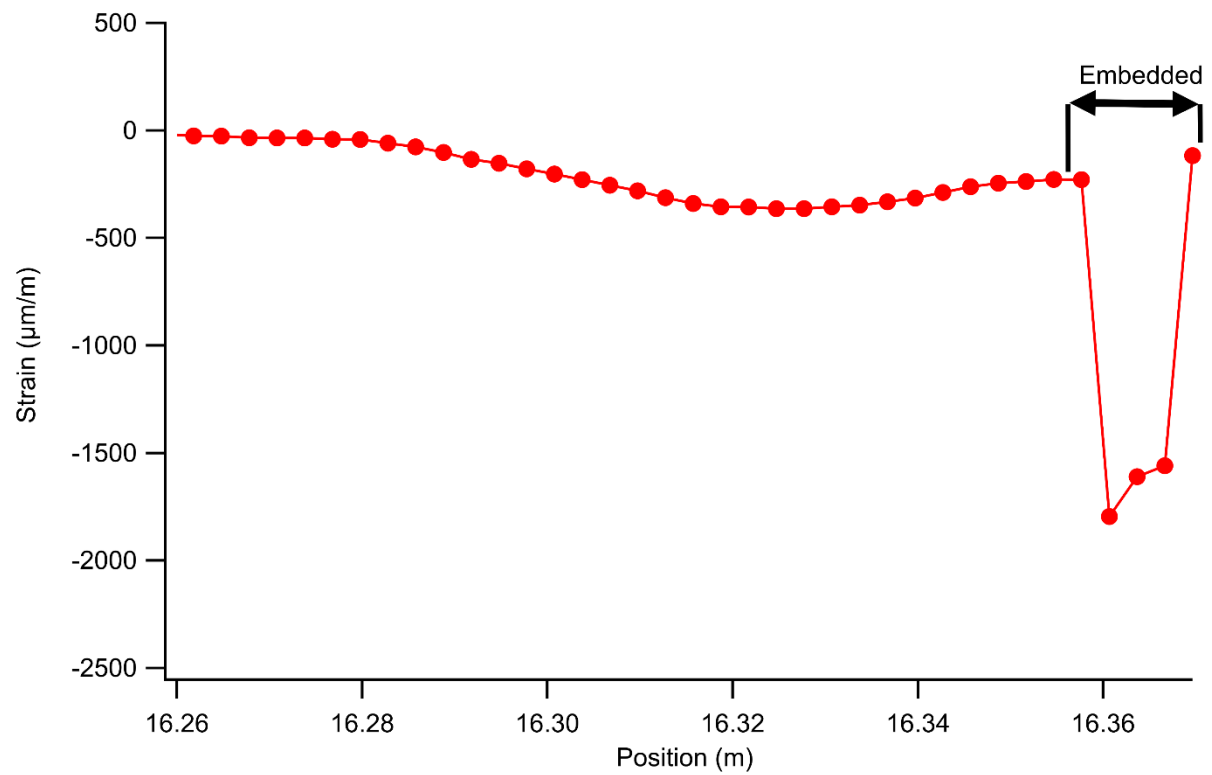


Figure 3.13 Residual strain measurements in the Al-Au-Ni sample. Used with permission from Reference ⁶⁶.

These strains are calculated based on the difference between the optical transmission scans of the fiber before embedding and after embedding. Both the Al-Cu sample and the Al-Au-Ni sample showed significant residual compressive strain. The strain could be related to the enhanced interdiffusivity calculated, elevated vacancy formation, and dynamic recrystallization. However, as mentioned above, the lack of elemental distribution in the Al-Au-Ni sample is likely due to the gold deposited during the nickel coating procedure. In addition, caution must be taken on interpretation of the differences in the magnitude of the strain due to complexities based on variables relevant to ultrasonic additive manufacturing, i.e., channel depth, load profile, and fixturing conditions.

Finally it should be noted that some researchers have postulated elevated vacancy concentrations could be created directly from ultrasonic energy introduced into a material ²⁰⁶. The theories have proposed the ultrasonic energy could be unpinning dislocations, and vacancies could be created as the dislocations jog in a non-conservative manner ¹¹³. Although studies have pointed towards observed increases in electrical resistivity during applied ultrasonic energy, which implies additional lattice defects ²⁰⁷, critics have noted that temperature effects, which are non-trivial during applied ultrasonic frequencies (Section 3.3.4 and Equation 3.4), were not considered in these analyses.

3.5 Acknowledgments

This research is sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory (ORNL), managed by UT-Battelle LLC, for the US Department of Energy. Adam Hehr and Mark Norfolk (Fabrisonic LLC, Columbus, Ohio) fabricated the embedded fiber samples. Dorothy Coffey assisted in TEM lamella fabrication. Metallography and optical microscopy were performed in the ORNL Manufacturing Demonstration Facility (MDF). SEM and EDS Bruker analysis were performed in the ORNL High Temperature Materials Laboratory (HTML). TEM was performed in the ORNL Low Activation Materials Development and Analysis Laboratory (LAMDA).

3.6 Supplementary Materials

3.6.1 Sensitivity Analysis of Vacancy Concentrations and Diffusivity

As Equation 3.3 and Table 3.4 demonstrate, enhanced lattice vacancy concentrations can increase diffusivity even more than elevated temperature can. To illustrate this concept, a sensitivity analysis was performed using Equation 3.3 on copper and gold as shown below in Figure 3.14 and Figure 3.15, respectively.

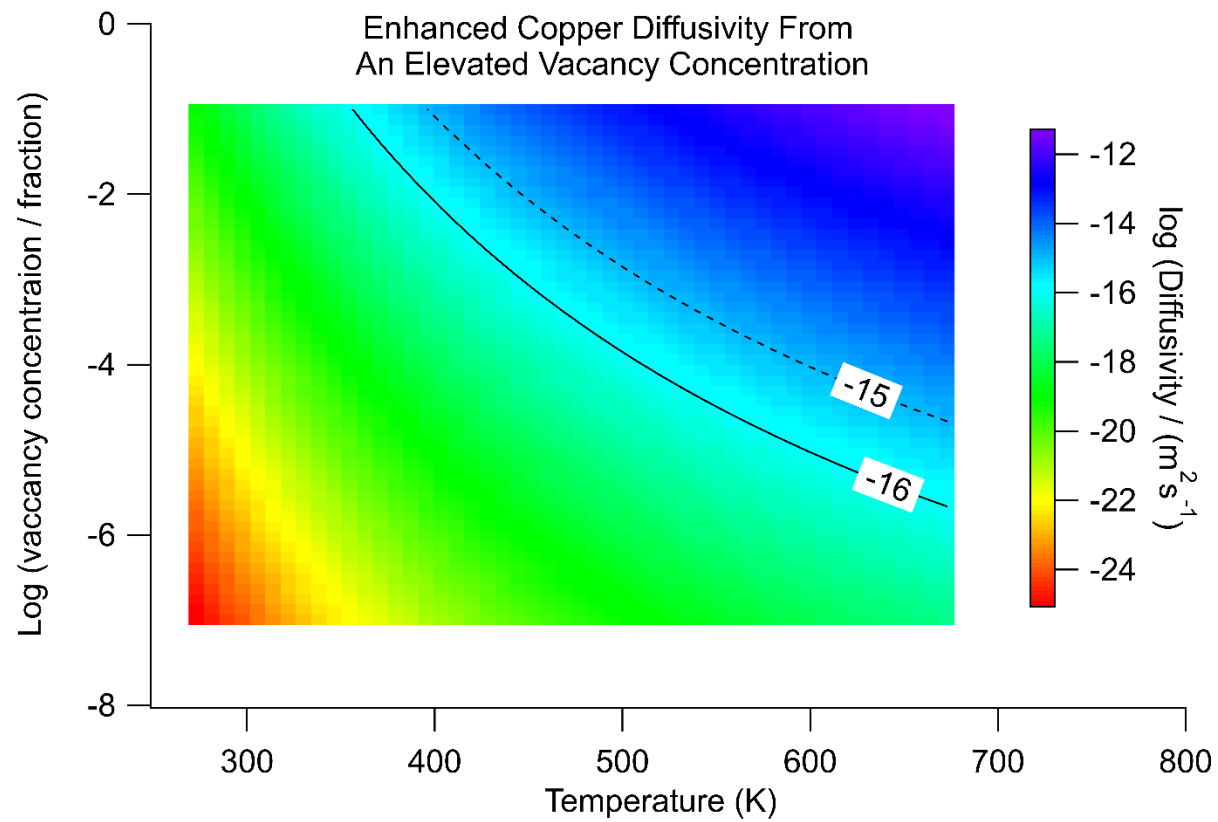


Figure 3.14 Sensitivity analysis for copper diffusivity.

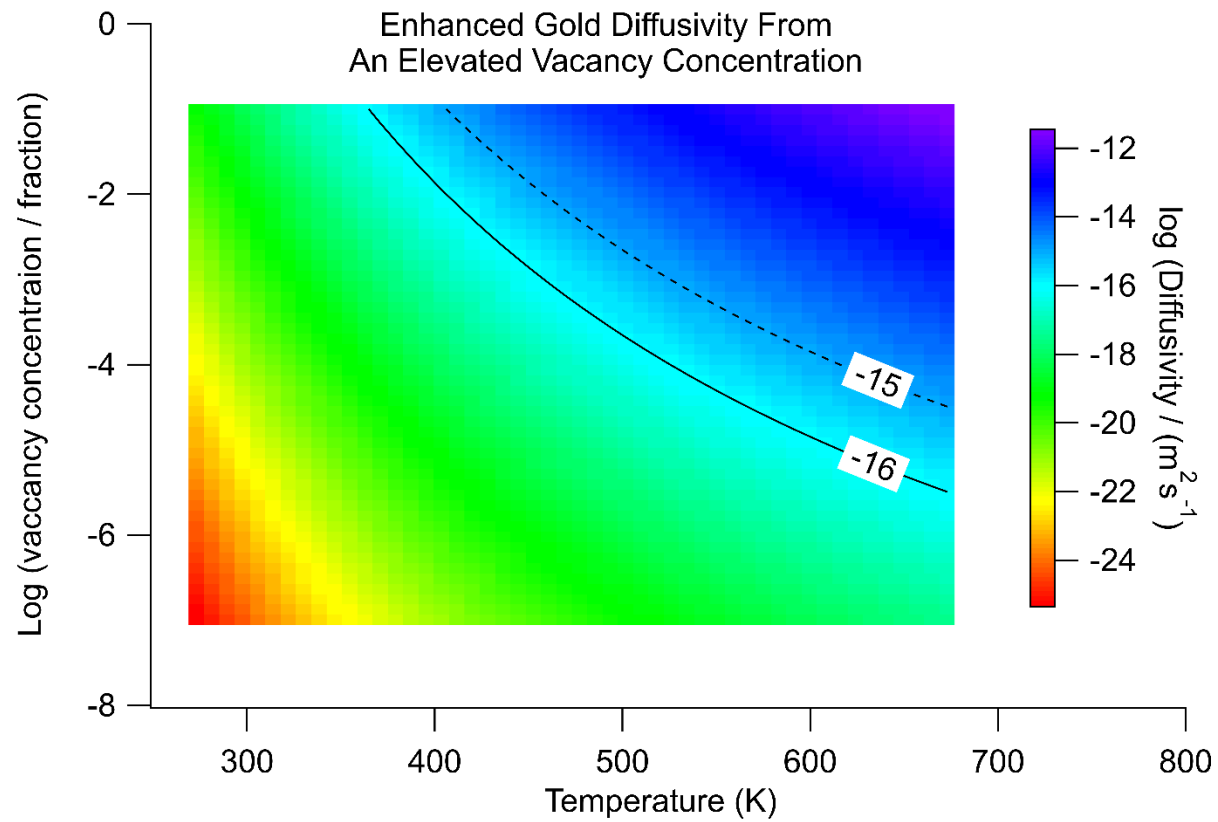


Figure 3.15 Sensitivity analysis for gold diffusivity.

The y-axis (vacancy concentration) is on a logarithmic scale while the x-axis (temperature) is on a linear scale with the heat map and intersecting lines demonstrating the interdiffusivity parameter on a logarithmic scale.

The sensitivity graphs illustrate the huge interdiffusivity increase that can result from lattice structure defects such as vacancies. However, as discussed, vacancies may not be the only contributing factor to the enhanced interdiffusion.

3.6.1 Uncertainty in the EDS Measurement

SEM/TEM EDS techniques are considered standard characterization techniques, but their detection resolution must be considered. The X-rays used for compositional analysis are created from electron interactions in the target material. The spatial resolution of the detected X-rays depends on the volume in which the electrons interact with the material and generate X-rays (i.e., interaction volume). Since the bulk material is probed in the SEM, the spatial resolution can be large, often exceeding $2\text{ }\mu\text{m}^3$. Conventional SEM EDS analysis will not allow observing the diffusion process at the interfaces described here as it may hide the effect. Therefore, higher resolution TEM analysis is required.

When a thin foil is analyzed under TEM, the lateral distance of electron beam spreading is considered, to a first order approximation, as comparable to the transverse thickness of the foil normal to the beam direction. The extrapolated range of the electrons through the foil R_x , in ångströms can be approximated using the method by Cosslett and Thomas²⁰⁸ utilizing a combination of a derivation from the Bethe energy loss law and empirical fitting where k is a constant of 45 for Au and E_c is the energy lost to the material.

$$R_x = kE_c^{1.5} \quad \text{Equation 3.5}$$

An electron beam with an acceleration voltage as low as possible for the equipment (5 keV) was directed normal to the foils. Since the foils were electron transparent at this voltage, the energy loss can be considered as the mean acceleration voltage from the incident beam. The maximum extrapolated range of the electrons through the foils using the three-halves power law from Cosslett and Thomas is approximately 50 nm.

The X-rays detected during EDS analysis are characteristic of the element being examined. Thus, the created EDS spectrum is a direct result of the composition of the material being analyzed. The intensity of the X-rays produced from the sample and detected by the microscope is directly related to the relative amount of that element in the sample. Unfortunately, the characteristic X-rays generated from excited target elements are not the only X-ray source. A continuous distribution of background Bremsstrahlung X-rays can also be created as electrons slow due to the Coulombic forces with the atomic electron shell. Since the EDS detector observes the characteristic

X-rays and the continuous distribution of X-rays, elements that are a less than 1 wt. % of the bulk composition are difficult to confidently detect since they can be masked by the Bremsstrahlung X-rays^{194,209}.

Ultimately, the EDS detection has some degree of uncertainty, but it is considered an accurate method for characterizing the composition of materials, provided that the spatial resolution and compositional resolution are acknowledged. The differing lateral range found in the EDS maps vs. the STEM images is likely a results of this experimental measurement uncertainty.

CHAPTER 4

STRENGTHENING EFFECTS AT

DISSIMILAR METAL INTERFACES

CREATED BY ULTRASONIC ADDITIVE

MANUFACTURING

Abstract

Ultrasonic additive manufacturing (UAM) technology can produce structural materials with complex geometries and embedded sensors. Under UAM processing conditions, complex interfaces are created between these materials due to high strain rate ($> 10^5 \text{ s}^{-1}$) plastic deformation. Fundamental understanding of strengthening mechanisms at these interfaces are needed for engineering deployment. In this research, we correlated the interface microstructure to their strengthening mechanisms using nanoindentation and scanning electron microscopy techniques. Strengthening at interface regions are correlated to microstructural features at different length scales including refined grains (200 nm), increase in vacancy clusters ($10^{16}/\text{cm}^3$), and dislocation networks ($10^{10}/\text{cm}^2$). This conclusion was arrived through superposition principles to describe the combination of many strengthening mechanisms and their respective microstructure feature sensitivity.

4.1 Introduction

A thorough introduction to the Ultrasonic Additive Manufacturing (UAM) process has been described earlier (Chapter 2.3), therefore only a brief introduction is described here as it relates to this study. As mentioned previously, optical fiber strain sensors can be embedded into materials through the UAM process. The optical fibers can be embedded by the following steps: (i) build to a certain height; (ii) stop the UAM process mid-build; (iii) machine a channel; (iv) place the fiber into the channel; and (v) resume the additive process. Embedded optical fiber strain sensors have become a viable approach for spatial and temporal strain monitoring in components destined for harsh environments. The process of embedding these strain sensors has been thoroughly reviewed elsewhere^{65,66,70,81,83,85,120,121,130}. The research presented in this paper was triggered by unusual observation of dissimilar material diffusion at the interface locations⁶⁵. To provide context to the results to be presented in this paper, a brief introduction is provided to the UAM process. A simplified schematic of the UAM process is shown in Figure 4.1. Figure 4.1 illustrates a cylindrical horn, known as a *sonotrode*, and a milling bit which are used to add foils and remove materials, respectively. The optical fiber that can be embedded using UAM is also shown in Figure 4.1.

The details of the microstructural evolution during the UAM process have been the focus of various PhD theses^{63,97}, publications¹⁸⁷ and is relevant to the current paper. However, in contrast to the literature, our specific focus is on strengthening mechanisms at dissimilar material combinations created by UAM which have not been previously explored and rationalized. Recent research has been motivated by specific dissimilar metal combinations that are created by UAM through the embedding of optical fibers with metallic coatings within metal components. The measurements of the chemical concentrations across the interfaces indicated that atomic diffusion occurred at a rate faster than bulk equilibrium matrix- or even non-equilibrium grain boundary-diffusion.

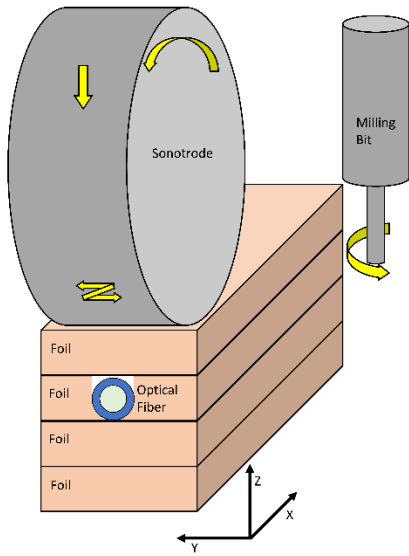


Figure 4.1 UAM schematic overview of the sonotrode bonding foils and embedding an optical fiber

The above puzzling results were rationalized by Pagan et al.⁶⁵ by invoking high concentrations (e.g., 0.0075 to 0.075 atomic fraction) of point-defects, i.e. vacancies. However, the consequences of the enhanced vacancy concentration on the mechanical behaviors were not addressed.

Prior methods of extracting mechanical properties of UAM joints have been through shear^{59,210}, tensile²¹¹, compression, and microhardness measurements⁹⁷. Although the limited size of the interfaces examined here makes these tests not directly useful. In this work, the final hardness at the interface and bulk is related to the initial microstructure. However, the following question remains to be addressed: how can we extract the mechanical properties from these localized sub-micron interfaces and rationalize them based on the underlying microstructure?

Sriraman et al. extracted mechanical properties through microhardness tests and correlated the data to electron backscatter diffraction (EBSD) measurements on UAM interfaces of Al6061¹⁸⁵ and copper⁵⁵. They found an overall decrease in hardness resulting from the UAM process along with an increase/decrease in EBSD image quality near the foil interface. The authors suggested this could be due to dynamic recrystallized grains from the bonding process. Dehoff and Babu⁹⁴ and Schick et al.^{45,46} found elevated dislocation densities and grain refinement at UAM aluminum interfaces also suggesting that a dynamic recrystallization process could be occurring at the interface during the bonding process. Tensile testing of Al6061 UAM interfaces was performed by Sridharan et al.²¹¹ in the build (z) direction and the transverse (x or y) direction, and compared against bulk properties prior to the UAM process. Compared to the bulk properties, they observed a 25% reduction in yield stress in the transverse direction and an 84% reduction in yield stress in the build direction. The anisotropic nature of the UAM samples was attributed to localized strain build-up at the interfaces. The authors suggested that the UAM process could have created adiabatic shear bands and microvoids at the interface. When the interface had a tensile load, the microvoids coalesce, create voids, and propagate cracks along the interface line resulting in brittle failure. However, all the above results suffer from spatial resolution of the indenter or the gauge volume being larger than the interface regions. One of the potential methods to interrogate the mechanical behavior of fine interfaces is through nanoindentation²¹².

Nanoindentation was first used to probe UAM interfaces by Li et al.²¹³ on an SiC fiber and an optical fiber embedded in aluminum. Although the large indent spacing (~ 20 μm) prevented site-specific interfacial structural analysis, the authors compared the harder material near the fiber interfaces with microscopy measurements of grain refinement and sub-grain formation and suggested that grain boundary hardening created the observed work hardening. Sridharan et al.⁵⁷ also performed nanoindentation on UAM interfaces. The preliminary investigation showed that interface regions with voids and without mechanical contact (unbonded) were softer than bulk regions, and regions with mechanical contact (bonded) were harder than bulk regions. Microscopy of the interfaces also observed a refined crystal structure on regions with intimate contact. This led the authors to conclude that bonded regions experienced a

continuous dynamic recrystallization process during bonding. The deformation mechanism of the interface was attributed to a general combination of grain boundary hardening and dislocation strain hardening. The differences in bonded regions vs not bonded regions were attributed to the non-uniform pressure distribution and plastic deformation along the interface. However the above work did not consider the role of vacancy clusters on the mechanical behavior or a large nanoindentation data set ⁶⁵.

There lacks UAM studies of nanoscale mechanical deformation mechanisms that consider the effect of enhanced lattice vacancy concentrations or that consider the specific dissimilar metal interface of an optical fiber coating – foil interface. Therefore, the current research focuses on providing a comprehensive evaluation of the interfaces using nanoindentation as a function of geometric location reference to the embedded sensor geometry.

4.2 Experimentation

UAM Processing

An optical fiber was electroplated in gold (15 +/- 5 μm) (ASI9.0/125/155G fiber from Fiberguide® Industries) and then embedded into Ni-200 foils using UAM procedures. The UAM processing used a 9 kW, 20 kHz UAM machine at Fabrisonic LLC (Columbus, OH) using 150 μm thick x 25.4 mm wide foils. The sonotrode horn exerted a downward force of 7000 N, traveled forward at a speed of 0.022 m/s with a horizontal oscillation amplitude of 38 μm . Using computerized numerically controlled (CNC) milling, a channel was cut at a width of approximately 152 μm . The fiber optic was then placed inside and the rest of the layer-by-layer building was completed. The UAM sample was then cold mounted in epoxy and mechanically polished down to 0.05 μm surface finish using standard metallography procedures.

Nanoindentation

The nanoindentation was performed on a KLA iNano using a Berkovich indentation tip. The continuous stiffness measurements (CSM) used load controlled nanoindentation to a peak load of 30 mN using a 45Hz oscillation frequency, and at a strain rate of 0.005s⁻¹. The CSM indents for the bulk mechanical testing of nickel were performed approximately 2 mm away from the gold fiber in the center of a nickel foil, using a 7x6 array indents with 20 μm interspacing. In the gold coating, only two CSM indents (peak load of 30 mN) were successfully probed. The data below the tapping depth is removed due to the likelihood of the indentation tip losing contact with the surface of the sample during indentation. The tapping depth, as described by Pharr ²¹² is the point at which a large amount of dynamic unloading can occur creating errors in the measured force, displacement, and stiffness. The tapping depth is calculated as 70 nm for gold and 30 nm for nickel. The tapping depth is not an issue for the shallow depth indentation method since it uses a controlled load-unload method.

For the shallow depth indentations, the KLA nanoblitz method was used. The nanoblitz method for the left side Ni-Au interface (2500 indents), and the right side Ni-Au interface (1200 indents) was performed with a peak load of 0.5 mN to a depth of ~ 100 nm with indents spaced 1 micron apart. For the top Ni-Au interface (6400 indents), the nanoblitz method was performed with a peak load of 0.25 mN to a depth of ~ 60 nm and indent spacing of 0.5 μm apart. The nanoblitz depth to spacing parameters were chosen to maximize the mechanical property spatial resolution while preventing overlap of each indentation's strength distribution below the surface ²¹⁴.

Microstructural Characterization

Optical microscopy was performed using a Nikon Eclipse MA200 using Nomarski bright field (BF) imaging. The Scanning Electron Microscopy (SEM) imaging was performed on a Zeiss EVO at 20 keV using a tungsten filament source. The Electron Backscatter Diffraction (EBSD) patterns were performed using a JEOL JSM-7000F with TSL EBSD. The electron filament source is single crystal tungsten <100> with a zirconium oxide coating.

Samples for Scanning Transmission Electron Microscopy (STEM) and conventional Transmission Electron Microscopy (TEM) were extracted from the foil – fiber coating interface using a Ga^+ Focused Ion Beam (FIB) Hitachi NB5000. An overview of the sample locations are outlined in Figure 4.2. The energy of the Ga^+ ions progressively decreased from 30 kV, 8 nA to 5 kV, 10 pA to create thin foils with approximate dimensions 3000 x 6000 x 50 nm. The STEM images were taken on a field emission Talos F200X using an acceleration voltage of 200 kV and a probe current of ~1000 pA. The BF and high angle annular dark field (HAADF) image was collected at an angle of 9 mrad and 61 to 200 mrad respectively. The TEM images were taken on a 200 kV Schottky JEOL JEM-2100F and a 200 kV field emission Zeiss Libra MC.

The grain size from the STEM image was calculated using the Heyn's line intercept method ²¹⁵. Both the transverse and longitudinal grain size were measured on the first lamella sample as noted. One standard deviation of the transverse grain size distribution and the longitudinal grain size distribution were calculated, then averaged for the average grain size standard deviation. The grain aspect ratios were calculated using the ratio of the transverse grain size to the longitudinal grain size. The dislocation density (ρ) from the STEM image was calculated using the line-intercept method ²¹⁶ using $\rho = 2N/Lt$, where N is the number of intersections between the dislocations and randomly drawn lines, L is the total length of lines (approximately 3600 nm in this work), and t is the thickness of the thin foil specimen. The dislocation density approximation was performed on the second lamella sample in a bright contrast region as noted.

4.3 Results

Overview of Microstructure

The macro – and microstructures from the gold coated optical fiber embedded in nickel foils are shown in Figure 4.2a and Figure 4.2b. Along with the images is a schematic of the embedded fiber demonstrating the imposed lateral oscillations with respect to the image features. Some variability in the interface regions is evident at different locations around the fiber, good and poor bonding. It is interesting to see that good bonding is observed in locations that are parallel (Region A) and perpendicular (Region B and C) to the direction of the lateral vibrations of the sonotrode. Based on the published literature, one would expect shear deformation only along the interface A, that are parallel to the vibration motion. Therefore, we hypothesize that the heterogeneous plastic deformation of the surfaces, as a function of angular location, occurred in the constrained regions due to decomposition of normal and shear stresses imposed by the sonotrode and the spatial geometry of the fiber, channel, and metallic foils. To validate this hypothesis, we evaluated the crystallographic characteristics using electron back-scattered diffraction (EBSD) imaging.

Figure 4.2c and Figure 4.2d show EBSD inverse orientation map and image quality map of the sample on the right side (Region C) of the nickel-gold interface respectively. The EBSD patterns indicate that the grain sizes in the gold region are below the microscope resolutions. This is indeed expected since the gold is deposited on the optical fiber using electrolytic methods. The EBSD data from the bulk and interface regions of the nickel foil show distinct features. Near the interface the pattern quality is very poor. This suggests that these regions should have a high concentration of lattice defects. Furthermore, the swirl patterns seen in these interface regions suggest recirculatory material flow during UAM processing. Interestingly, such swirl patterns of grains have also been observed in 3xxx series aluminum alloy UAM builds⁸⁸. In contrast the regions in the middle of the nickel foil show relatively good image quality suggesting less plastic deformation. To understand the site-specific variation of mechanical behavior, the three regions (Region A, Region B, and Region C) are characterized in depth. Figure 4.3 shows scanning transmission electron microscopy (STEM) images of the interface between the nickel and gold at the top (Region A) location around the embedded optical fiber, denoted as Region A in Figure 4.3. The image is rotated clockwise 90 degrees so that the nickel is on the right and the gold is on the left. Figure 4.3a is an overview bright field (BF) image of the first thin TEM sample extracted using focused ion beam (FIB) machining. The grain sizes of the highlighted boxes in Figure 4.3a are summarized in Table 4.1. Figure 4.3b and Figure 4.3c are BF and high angle annular dark field (HAADF) images at high magnification of the Ni-Au interface, respectively. This location is indicated by the arrow from Figure 4.3a. The white arrows in Figure 4.3b and Figure 4.3c indicate a region of white speckles in the BF image and dark speckles in the HAADF image. Since HAADF images will appear bright in locations with large Z value, the dark regions are interpreted as nano-scale voids or vacancy clusters in this region near the interface. This is remarkable since these voids are different in size and shape compared with the non-bonded regions.

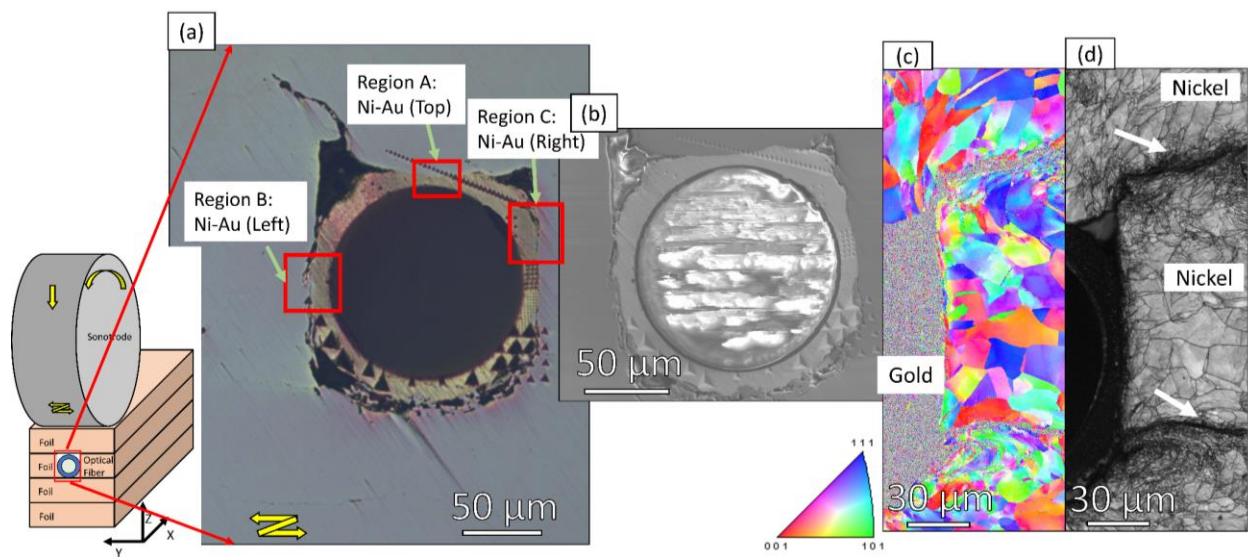


Figure 4.2. Overview of Ni-Au Sample, and interface analysis locations. a) Optical Bright Field, b) SEM, c) Inverse Pole Figure, d) Image Quality

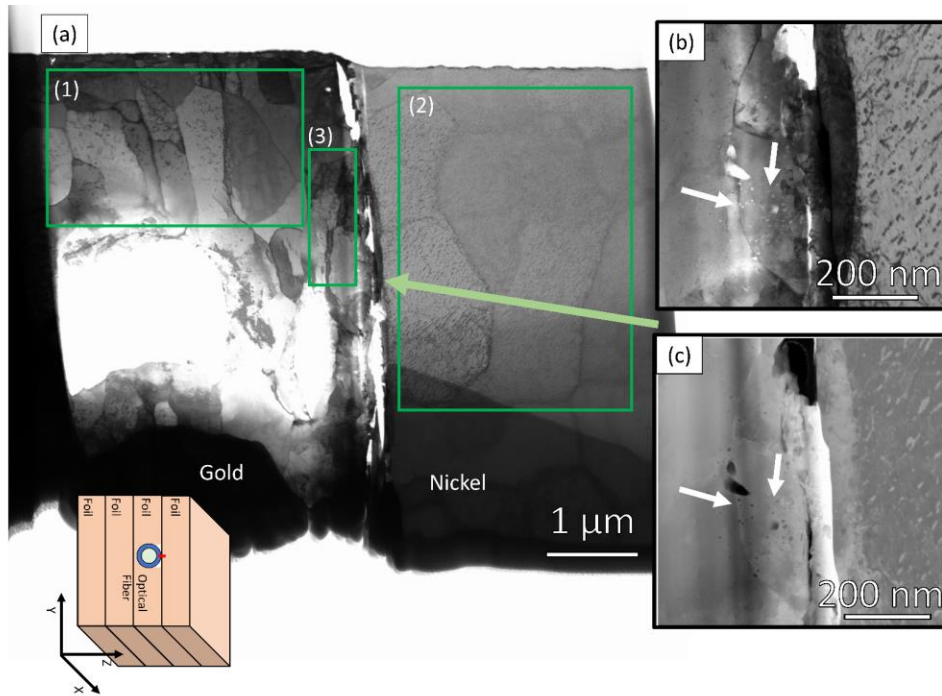


Figure 4.3. STEM image of gold-nickel interface at the top Region A location. a) BF overview image of the first lamella, b) BF magnification of first lamella's interface region, c) HAADF magnification of first lamella's interface region

Table 4.1. Summary of Average Grain Size Measurement at Ni-Au Interface (Region A)

Sections	Transverse (nm)	Longitudinal (nm)	Aspect Ratio	Average (nm) $\pm$ 1 SD
Region 1	369 $\pm$ 229	560 $\pm$ 457	-0.51	464 $\pm$ 343
Region 2	1159 $\pm$ 425	1766 $\pm$ 714	-0.52	1463 $\pm$ 569
Region 3	134 $\pm$ 88	395 $\pm$ 225	-1.95	264 $\pm$ 156

Multiple thin films from Region A were prepared to obtain suitable TEM microstructural details. Dislocations were imaged on the gold side and the nickel side of the interface using a two-beam approximation near the [011] zone axis for both materials Figure 4.5. Although undesirable features are present such as bend contours, contrast from dislocations are also present. The gold side of the interface is shown in Figure 4.5a, b, and c with an average dislocation density of $4.6 \cdot 10^{10} \text{ cm}^{-2}$. The nickel side of the interface is shown in Figure 4.5d, e, and f with an average dislocation density of $4.7 \cdot 10^{10} \text{ cm}^{-2}$. The dislocation densities are comparable to heavily cold worked materials. Results confirm that the gold grains are much smaller than the nickel grains. The small size of the gold grain is also supported by the EBSD data. Additionally, the gold-nickel interface region has smaller-grain size than the base gold region. This suggests that heavy plastic deformation at the interface leads to accumulative grain refinement, in agreement with published papers pertaining to UAM in aluminum alloys^{88,94}. The next fundamental question is whether these microstructures have any effect on the localized strength. The results of the mechanical heterogeneity characterization using nanoindentation techniques are summarized in Figure 4.5.

Figure 4.5 shows the interface region from Region A that is between the nickel foil and the gold coating near the top of the optical fiber. Figure 4.5a and Figure 4.5b are the EBSD inverse pole figure and image quality map of the interface, respectively. Since the EBSD images were taken prior to the nanoindentations, the indent markings are not present. The EBSD images show large grains present in the nickel region (Figure 4.5a), while small grains and regions with poor image quality (Figure 4.5b) are seen in the gold region. It is noteworthy that both gold and nickel have the same crystal structure (FCC) and therefore the intermixing between two elements cannot be determined. Significant solute interdiffusion has already been measured and published earlier⁶⁵. Therefore, in this paper, we focused on strengthening effects at these interfaces.

Nanoindentation Results:

Similar nanoindentation tests and analysis were performed in Region A, Region B, and Region C to contrast the various spatial locations with respect to the imposed oscillations from the sonotrode.

Region A: Figure 4.5c is the SEM image of the interface demonstrating the various sample regions that were probed. The regions containing the nanoblitz indents are highlighted with a box. There were two prior nanoindenter trials also in the interface display. There are 10 large indents in a diagonal line across the image, and there is a larger depth and larger spacing nanoblitz array in the left half of the image. Figure 4.5d and Figure 4.5e show the hardness contour and modulus contour plot from the nanoblitz indent array, respectively. The hardness and modulus data still appear representative even though several prior indentation tests were performed on the sample. The hardness contour plot shows distinct regions of hardness in the various materials probed (nickel, gold, and SiO₂). The gold region with a prior indentation array shows slight variations in the measured hardness.

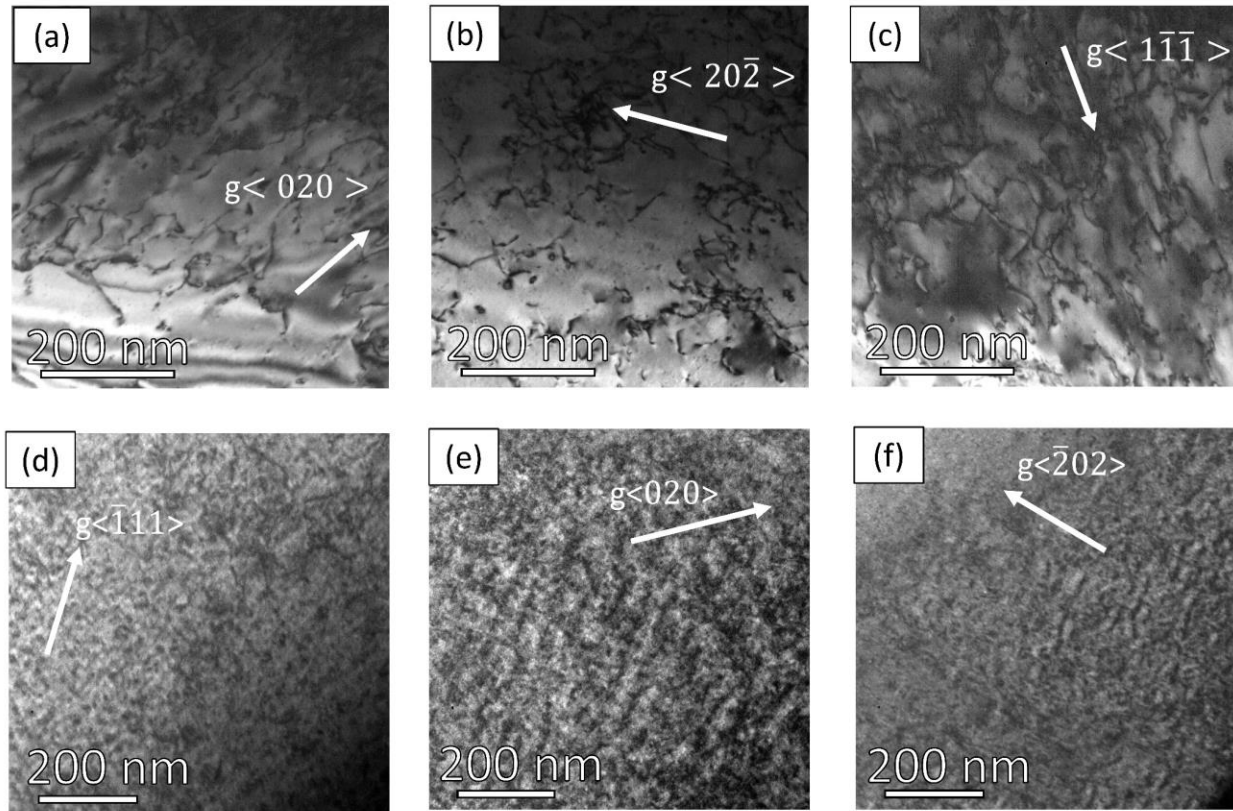


Figure 4.4. Dislocation density at Ni-Au Interfaces using TEM BF two-beam approximation near the $[110]$ zone axis. a) Gold side in $g<020>$ direction, b) Gold side in $g<20\bar{2}>$ direction, c) Gold side in $g<1\bar{1}\bar{1}>$ direction, d) Nickel side in $g<1\bar{1}\bar{1}>$ direction, e) Nickel side in $g<020>$ direction, f) Nickel side in $g<20\bar{2}>$ direction

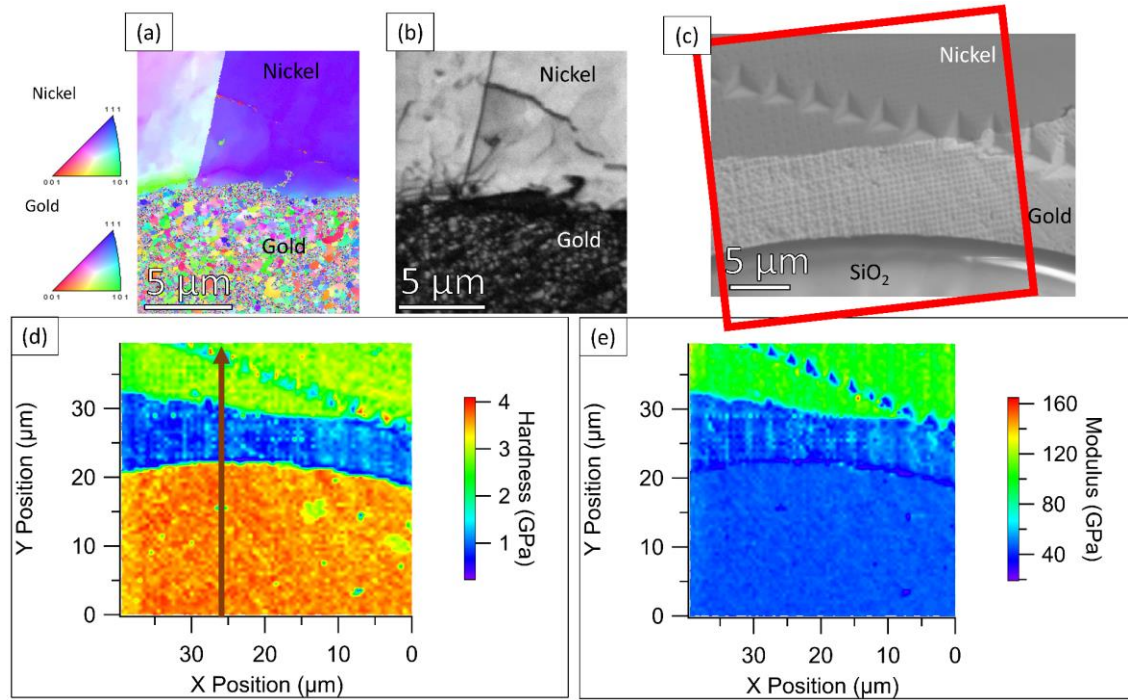


Figure 4.5. Results of Ni-Au Interface in Region A: a) EBSD inverse pole figure, b) EBSD image quality, c) SEM, d) Hardness map across the interface, e) Modulus map across the interface

The nanoindentation data from the regions highlighted in Figure 4.5c is analyzed further and summarized in Figure 4.6. Figure 4.6a is a hardness histogram (using a kernel-density estimate using Gaussian kernels) and shows four distinct regions, i.e. softest gold region (1 GPa), an intermediate-hardness interface between Ni-Au (2 GPa), harder nickel (~3 GPa), and hardest SiO₂ (3.5 GPa) optical fiber (Figure 4.6c). In Figure 4.6a, the hardness distributions appear to be Gaussian for the gold, nickel, and SiO₂ materials. However, the hardness distribution of the SiO₂ is the smallest, while both the both Ni and Au regions show broader distributions. To understand these properties with reference to the overall geometry, all the nanoblitz hardness data is plotted vs the y-axis (Figure 4.6b). For additional clarity of the nanoblitz data, Figure 4.6c shows a subplot of the hardness vs Y position graph for only a single line at X=26.5 μm as shown in Figure 4.5e. In Figure 4.6b and Figure 4.6c, a sharp hardness drop (width < 1 μm) between the SiO₂ and the gold regions was observed. In contrast the interface region between gold and nickel is broader (~ 2 μm). Furthermore, there is a broad hardness distribution between the nickel and the gold. The broad interface can be interpreted as normal errors associated with the indentation sampling volume ²¹⁷. Alternatively, it is possible that this broader interface contains the intermixed solute transition zone region of material in which both nickel and gold are present. This region was created by the UAM bonding. This region is approximately 2 μm in length according to the nanoindentation information. The results suggest that there may be a heterogeneous distribution of micro or nanostructural features that lead to strengthening. This leads to the next fundamental question: will there be similar or different effects on the interfaces that are oriented at different angles to the sonotrode motion? This question is addressed by analyzing similar nanoindentations from regions B and C.

Region B: Figure 4.7 shows the interface region from Region B between the nickel foil and the gold coating near the left side of the optical fiber. This orientation is in a 90-degree counter-clockwise rotation from Region A and is perpendicular to the direction of the sonotrode motion. Figure 4.7a is an SEM image of the indent array with region containing the indents highlighted with a box. Figure 4.7b and Figure 4.7c are the hardness contour and modulus contour plot from the indents, respectively. One large prior nanoindent marker can be seen in the lower middle region of the micrographs. Large cracks can be observed along the upper parts of the interface. Since the crack is observed in the nickel section outside of the interface, it is likely that this region separated after bonding. The hardness contours demonstrate distinct regions of nickel, gold, and SiO₂, although the individual sections do not appear as uniform as those from the Region A interface. Near the interfaces, the hardness increases slightly. The modulus in the SiO₂ very close to the gold decrease significantly in value. This is also observed near the nickel-gold interface where the cracks and open spaces appear.

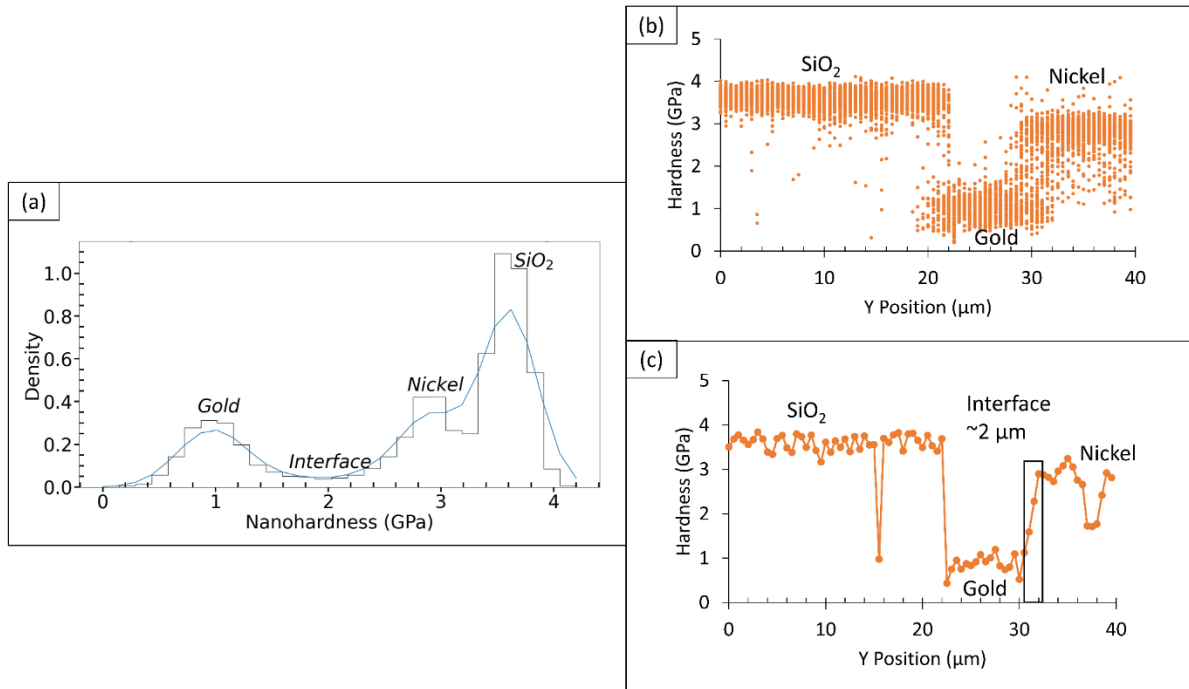


Figure 4.6. Nanoindentation results Ni-Au interface from Region A. a) Histogram and gaussian distribution of the hardness data, b) all hardness results vs Y position, c) Hardness vs Y position for only a single line

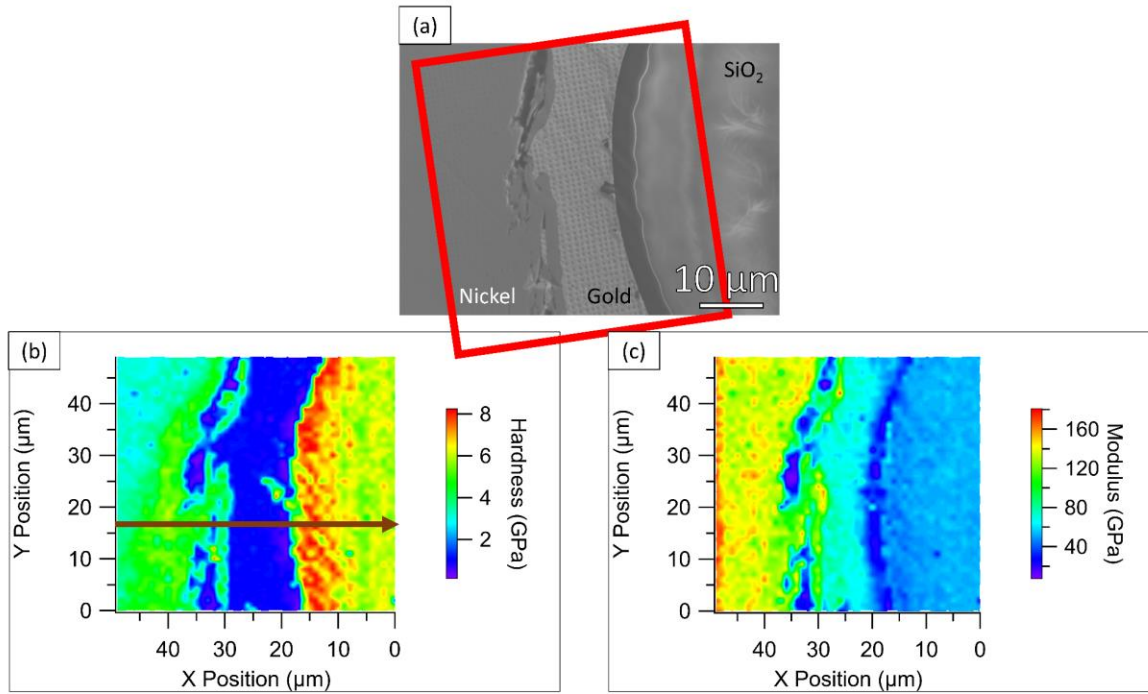


Figure 4.7. Results of Ni-Au Interface in Region B: a) SEM, b) Hardness map across the interface, c) Modulus map across the interface

The hardness data from Region B shown in Figure 4.7 is analyzed further and summarized in Figure 4.8. Figure 4.8a is a hardness histogram demonstrating the various regions probed. The indentation results in Region B demonstrate comparable features to Region A, although the histograms slightly differ. The distribution shows four distinct regions, i.e softest gold region (1 GPa), slightly harder interface region between nickel and gold (2 GPa), harder nickel (3-4 GPa), and hardest SiO₂ (6 GPa) optical fiber. Figure 4.8a suggest gaussian distributions of the gold, nickel, and SiO₂ hardness variations. In the Region B interface, the gold has a sharper distribution of hardness, while the nickel and SiO₂ show large distributions. To evaluate the variation in hardness with respect to the geometry of the optical fiber, all the nanoblitz data is plotted vs the x-axis (Y position during nanoindenter testing) (Figure 4.8b) in the direction from left to right on the micrographs. For additional clarity, Figure 4.8c shows a subplot of the nanohardness data for only the single line shown in Figure 4.7b at the Y=17 μm line. The features in Figure 4.8c mirror the features in Figure 4.6c due to the spatial orientation of Region B.

In Figure 4.8b and Figure 4.8c there is a gradual hardness drop between the nickel and gold interface, while in contrast there is a sharp hardness increase between the gold and the SiO₂. There appears to be a distinct region between the nickel and gold in which the nanohardness corresponds to both materials. According to the nanoindentation data, this interface transition distance could be approximately 4 μm . Additionally, the nickel probed here has a wider hardness distribution than the nickel probed at the top interface (Region A). The nickel appears harder close to the interface boundary of nickel and gold, and softer approximately ten microns away. Cracking is also observed near the interface. This is likely due to a reduction in ductility because of the increased yield strength. While the reduced ductility seen in the top section of the interface in Figure 4.7 could have resulted in the observed cracking and open spaces, the middle and lower sections of this interface could have created additional work hardening due to the tighter compression in these regions brought about by the constraint.

Region C: Figure 4.9 shows the results from the nanoblitz testing of the nickel-gold interface from Region C. This interface is in a direction geometrically perpendicular to the direction of the sonotrode motion. Region C is in a 90-degree clockwise rotation to Region A, although it is closer to the top of the foil-foil interface than that of Region B. Figure 4.9 shows Region C between the nickel foil and the gold coating near the top right corner of the optical fiber. Figure 4.9a and Figure 4.9b are the EBSD inverse pole figure and image quality map of the interface, respectively. The EBSD images were taken prior to the nanoindentations, therefore indent markings are not present. The EBSD images show a decrease in pattern quality near the Ni-Ni interface and the Ni-Au interface indicating significant grain refinement in these areas. Additionally, the gold coating appears unresolvable in the EBSD pattern, indicating these grains are too small for the SEM detector.

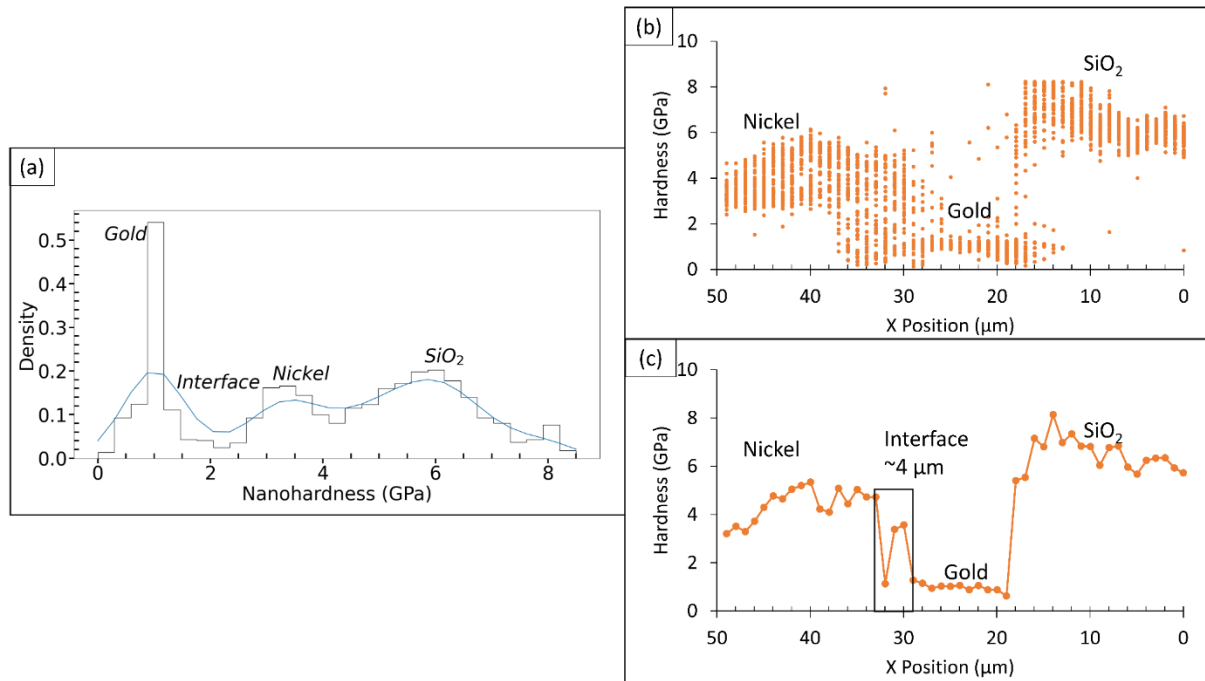


Figure 4.8. Nanoindentation results for the Region B Ni-Au interface. a) Histogram distribution of all the nanoindentation hardness results, b) all hardness data vs X position, c) hardness vs X position for a single line

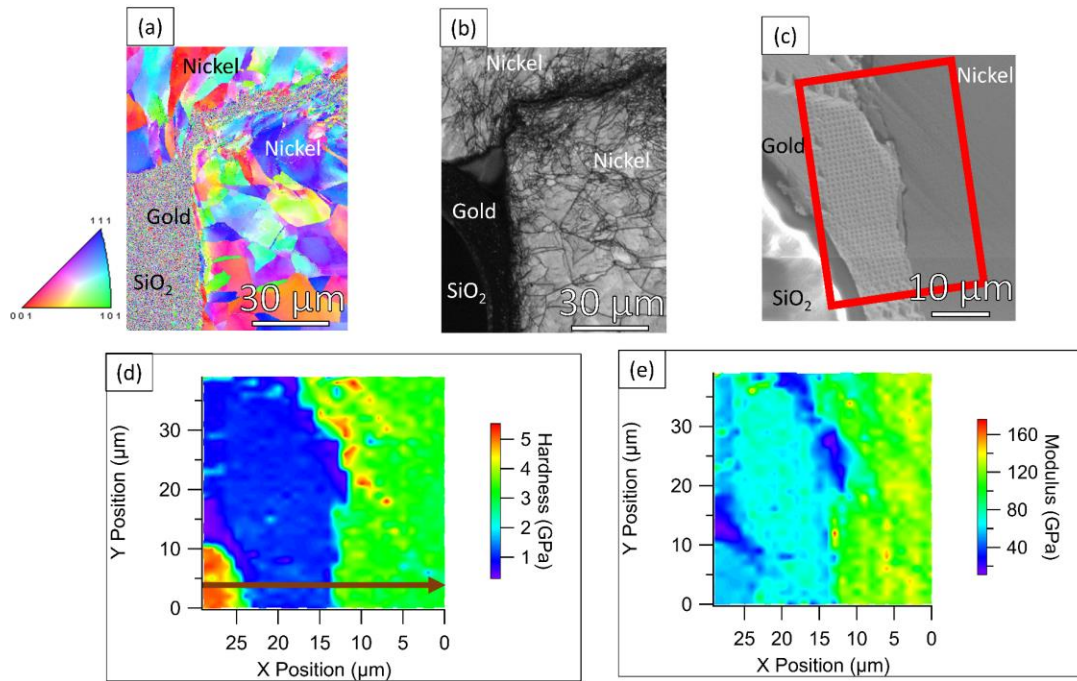


Figure 4.9. Result of Ni-Au Interface in Region C: a) EBSD Inverse Pole Figure, b) EBSD Image Quality, c) SEM, d) Hardness map across the interface, e) Modulus map across the interface

The indented region is shown in Figure 4.9c highlighted with the box. A small crack is evident near this interface, although it is much smaller than the cracks observed in Region C. There are several sets of prior nanoindentations near the outside of the Region C highlighted box. Figure 4.9d and Figure 4.9e are the nanoindentation hardness contour and modulus contour of the interface, respectively. Although the prior indents are close to the highlighted box of Region C, the hardness and modulus of the interface appear largely representative of these regions. The hardness and modulus contours show distinct regions of nickel, gold, and SiO₂. The modulus contour shows several locations of significant decreases which could be incorrect.

Like other analyses, the data from Figure 4.9 is analyzed and summarized in Figure 4.10. Figure 4.10a is a hardness histogram demonstrating the various regions probed. In agreement with previous results, the distributions show the softest gold region, the slightly harder nickel-gold interface, the harder nickel region, and the much harder SiO₂ region. A gaussian distribution is consistent within these measurements also. The gold and nickel have similar hardness distributions while the SiO₂ encompasses only a small fraction of the probed region. To evaluate the variations in hardness with reference to the overall geometry, all the nanoblitz hardness is plotted vs the x-axis (Y position during nanoindenter testing) (Figure 4.10b) in the direction from left to right on the micrographs encompassing each of the materials. Figure 4.10c is a subplot of the nanohardness data for only the single line shown in Figure 4.9f at the X=4 μm position. In Figure 4.10b and Figure 4.10c there is a gradual hardness increase between the nickel and gold, while there is a sharp hardness increase between the gold and SiO₂. This gradual increase in hardness between the nickel and gold extends over approximately 1 μm in length according to the nanoindentation. This is slightly smaller than the interface observed in Region A and Region B.

Regions A, B, and C demonstrate the mechanical properties can vary at various spatial locations around the optical fiber. The next fundamental question is to compare the interfaces and determine the strengthening mechanisms that are operating.

4.4 Discussion

Comparison of Data from Interfaces

The nickel-gold interfaces, (Figure 4.6b and Figure 4.6c, Figure 4.8b and Figure 4.8c, and Figure 4.10b and Figure 4.10c) indicate that the interface transition zone between the nickel and gold has a width between 1 μm and 4 μm . The difference in interface width appears to be dependent on the spatial location of the Ni-Au interface that is probed, relative to the UAM sonotrode position. These spatial differences are likely due to the non-uniform plastic strain distributions induced by the ultrasonic welding process and the geometrical constraints imposed by the embedding¹⁷⁶ and the volumetric dispersion of dissimilar materials. It is well established that the interpretation of any nanohardness data should occur only after evaluating the uncertainties related to the interaction volume under the nanoindenter.

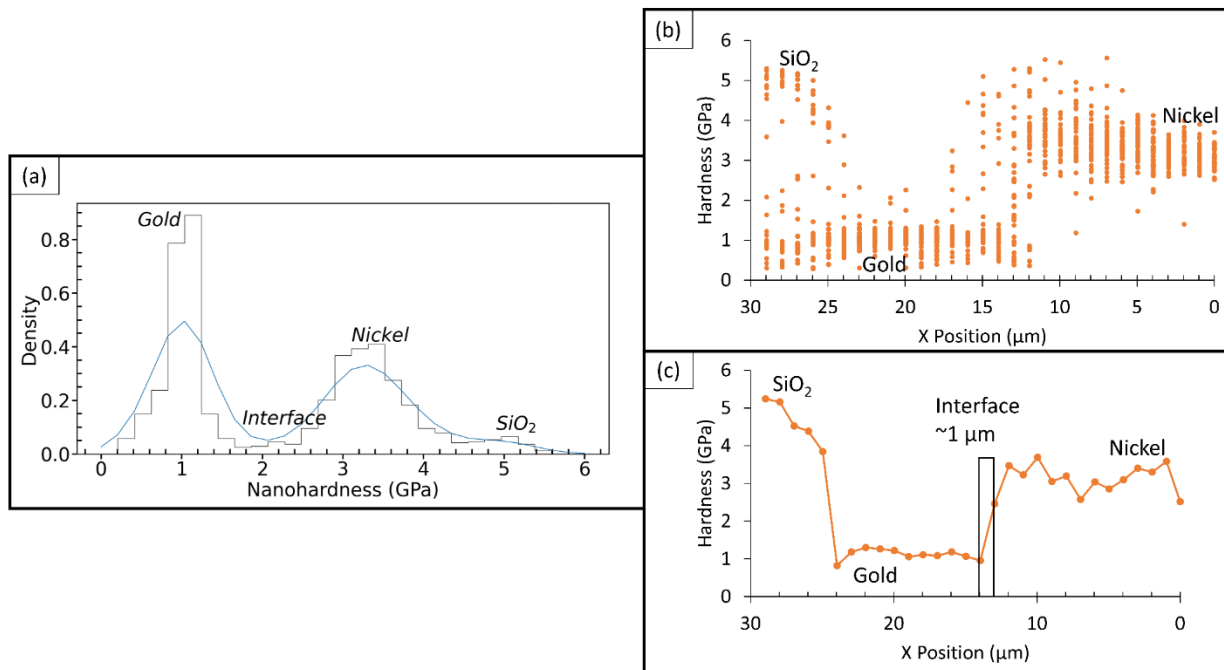


Figure 4.10. Nanoindentation results for Region C. a) Histogram of the hardness from the array, b) All hardness data points vs X position, c) Hardness vs X position for only a single line

The low depth nanohardness values do not represent bulk hardness values as calculated from traditional indentation techniques. This is due to the well-known low depth indentation size effect^{218–224} often seen in which materials that indicate a large hardness value at very low probing depths. The Nix-Gao approximation²²⁵ is the most popular technique for estimating the bulk equivalent hardness from nanoindentation measurements. Although the Nix-Gao technique (Equation 4.1) has received criticism^{226–229}, it is the only tangible estimate that provides some guidance. Therefore, we evaluate our data using this method. The Nix-Gao equation is provided below where H is the hardness at a given depth h , H_0 is the bulk equivalent hardness (or asymptotic hardness), and h^* is the characteristic indentation size effect length scale²²⁵.

$$\frac{H}{H_0} = \sqrt{1 + \frac{h^*}{h}} \quad \text{Equation 4.1}$$

When the hardness squared is plotted against the reciprocal of depth, the intercept of the line created is H_0^2 and the slope is related to h^* . The Nix-Gao approximation for the nickel and gold materials using the CSM indentation technique at locations far away from the interfaces are demonstrated in Figure 4.11a and Figure 4.11b respectively. Using this method, the bulk equivalent hardness of nickel was calculated to be at 1.84 GPa with a characteristic h^* of 385 nm. The bulk equivalent hardness of gold is calculated to be at 0.23 GPa with a characteristic h^* of 147 nm.

These bulk equivalent hardness values are significantly lower than the hardness measured at low depths (Figure 4.11c). Therefore, this additional analysis is necessary. The hardness histograms of Figure 4.6a, Figure 4.8a, and Figure 4.10a can be used to calculate the range and average nanohardness of the nickel and gold. Then these nanohardness values can be compared to the Nix-Gao approximated bulk equivalent hardness values as shown in Figure 4.11c. The interface region observed by the nanohardness is nearly the average of the nickel and gold nanohardness values. Therefore, the bulk equivalent hardness of the interface region is also approximated as the average between the bulk equivalent hardness of the nickel and the gold. From Figure 4.11c, the bulk equivalent hardness of the Ni-Au transition zone is approximately 1.01 GPa. The interface can be described as strengthening of the gold from 0.37 GPa to 1.01 GPa resulting in a change (ΔH_{Ni-Au}) in hardness of 0.64 GPa.

The Tabor relationship of $H \sim 3\sigma_y$ ^{217,230,231} is often used to convert this increase in hardness to an increase in yield strength $\Delta\sigma_y$. Although Zhu et al.²³² recently demonstrated that the Tabor relationship does not consider nanoindentation pileup effects and can overestimate the mechanical strength. Therefore, their relationship of $\Delta\sigma_y^{NI} = 0.285\Delta H_0$ can be used to estimate the nanoindentation yield strength ($\Delta\sigma_y^{NI} = 182 \text{ MPa}$) from the bulk equivalent hardness.

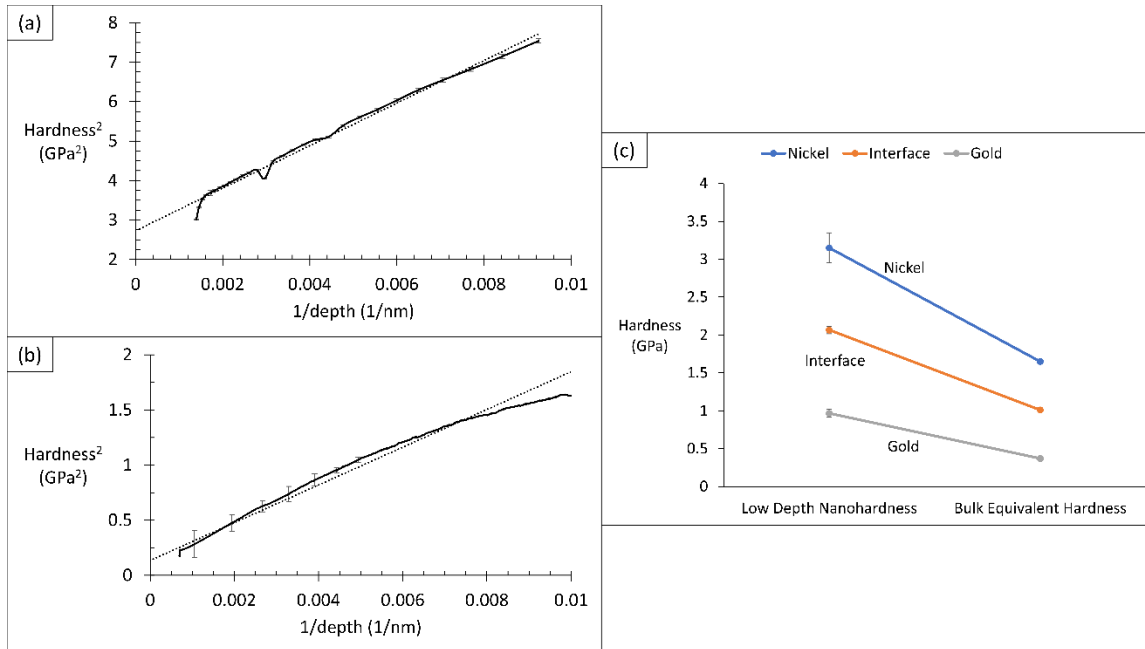


Figure 4.11. Conversion of nanohardness to bulk equivalent hardness. A) Nix-Gao relationship in nickel, B) Nix-Gao relationship in gold, C) comparison of hardness values for strengthening evaluations

This expression of increase in yield strength allows for the nanoscale deformation mechanisms of the interface to be rationalized. The above results also clearly show that the UAM embedding may not lead to uniform strengthening of the materials around the fiber optic sensors. This will be relevant to industrial deployment.

Rationalization of Observed Strengthening: Although we have confirmed that the non-uniformity of hardness extents in the matrix around the periphery of the embedded fiber optic, we need to rationalize this effects with mechanical metallurgy principles¹⁰². The strength of a material is governed by its resistance to the movement of dislocations through the matrix. The most common strengthening mechanisms include solid solution hardening, strain hardening, grain boundary hardening, point defect (i.e. vacancy) hardening, and dispersed barrier hardening¹⁰². These mechanisms are considered to rationalize the observed strengthening of the Ni-Au interface.

Strain Hardening: This is related to the interaction of dislocations as the magnitude of the plastic strain increases. As a dislocation moves in a stress field, it experiences resistance from other dislocations in the same slip planes. This is described in a classic Taylor hardening equation shown in Equation 4.2. In this equation, $\Delta\sigma_{sh}$ is the yield strength increase from strain hardening, M is the Taylor factor (~ 3.06 for equiaxed FCC and BCC materials²³³), $\alpha \sim 0.1$, G is the shear modulus (26 GPa for gold), b is the magnitude of the dislocation Burgers vector, and ρ is the dislocation density¹⁰².

$$\Delta\sigma_{sh} = M\alpha Gb\rho^{1/2} \quad \text{Equation 4.2}$$

The magnitude of the Burgers vector in an FCC crystal structure can be calculated using Equation 4.3. The value of b can be calculated using the lattice parameter of gold, $4.065 \text{ \AA}$ ¹⁷².

$$b = \frac{a_0}{\sqrt{2}} \langle 110 \rangle \quad \text{Equation 4.3}$$

As discussed in the previous section, the dislocation density at this interface is approximately $4.65 \times 10^{10} \text{ cm}^{-2}$. Assuming that strain hardening at the interface occurs through dislocation forest interactions, the strength increase from this dislocation density alone can be calculated to be 49.3 MPa. Previous microstructural analysis of aluminum under UAM deformation^{45,46,94} suggests that a dislocation density could exist between $10^9 - 10^{12} \text{ cm}^{-2}$ which is in agreement with the dislocation density approximated here. This dislocation density corresponds to a cold worked structure in which strengthening is impacted by the elevated dislocation density. An elevated dislocation density can be created through homogenous or heterogeneous nucleation. Homogeneous nucleation occurs in a perfect lattice through the act of a shear stress on dislocations. Heterogenous nucleation of dislocations occurs through dislocations interacting with lattice defects or other lattice impurities. The stress required for heterogeneous nucleation is much lower than for homogenous nucleation. Heterogeneous nucleation can also occur more frequently with more lattice defects¹⁶¹.

Therefore, the other lattice defect strengthening obstacles, as discussed below, could not only cause strengthening through their respective methods, but they could also assist in the formation of more dislocations increasing the strength from strain hardening.

Grain Boundary Strengthening: This factor can be described by Hall²³⁴ and Petch²³⁵, as the resistance of dislocation motion due to the size of grains d and the material specific boundary strength k_y . The grain boundary strength constant of crystals has been thoroughly studied throughout the proceeding decades, as shown by the Cordero et al. review article²³⁶. The Hall-Petch relationship is given by:

$$\Delta\sigma_y = k_y d^{-1/2} \quad \text{Equation 4.4}$$

The interface transition region and grain refinement zone are seen on the gold side of the interface in Figure 4.3. As shown in Table 4.1 above, the average grain size at the interface (Region 3) is 264 nm, and the grain size in the adjacent gold region (Region 1) is 464 nm. Therefore, the grain size strengthening of the transition region can be calculated by subtracting the grain size strengthening in the adjacent gold region (Region 1 grain size with $k_{y, \text{gold}}$: 0.08 MPa m^{1/2}^{237,238}) from the grain size strengthening of the transition region (Region 3 grain size with an average k_y between $k_{y, \text{gold}}$: 0.08 MPa m^{1/2}^{237,238}, and $k_{y, \text{nickel}}$: 0.23 MPa m^{1/2}^{208,239–247}). The approximate increase in strength due to grain boundary refinement, $\Delta\sigma_{gb}$, of the Ni-Au interface is estimated as 184 MPa. The errors in grain size value can be estimated by the standard deviation of measurements at the Ni-Au interface (see Table 4.1).

The small grains observed here leads to a fundamental question on the limits of the Hall-Petch relationship. The Hall-Petch relationship was derived based on dislocation pile-up against the grain boundary. Therefore, the minimum grain size at which this relationship breaks down is when a grain is not large enough to support dislocation pile up, i.e., 10-20 nm²³⁶. Furthermore, the boundary strengthening must also consider the indentation size. The plastic strain field associated with an indent must be large enough to cause dislocations to pile-up against the boundary. For an indent of depth h , the plastic strain field can be approximated to have a size of $7*h$ ^{217,230,248,249}. Therefore, a grain boundary must exist in the plastic strain field to cause a pile-up effect. For the nanoblitz indents to a depth of 50 nm, the plastic strain field extends approximately 350 nm. The grain sizes described at the Ni-Au interface (Region 3 in Figure 4.3a & Table 4.1) are smaller than 350 nm. Therefore, we can conclude that exists a grain boundary within the plastic strain field caused by the indentation. Based on the above discussions, we can conclude that the Hall-Petch strengthening is indeed valid for rationalization of strengthening at Ni-Au interfaces.

Solid Solution Strengthening: Solid solution strengthening occurs when mobile dislocations interact with solute atoms or individual point defects. The individual atoms cause lattice distortions in the crystalline matrix resulting in drag forces on the dislocation. Random solute atoms create small regions which are elastically more or less rigid than the matrix. There has been an experimentally determined square root

relationship between the yield stress increase and the concentration of solute atoms, $\sigma \propto \sqrt{c}$ ^{250–253}, although the power law relationships of linear^{241,254} and 2/3 power^{255–258} have also been observed depending on the material and solute concentration. The proportional constant and mismatch interaction parameter ε_s between them is a function of the lattice and elastic modulus misfit between the solute atom and the solvent atoms^{250,259,260}. As Fleischer²⁵⁰ described, the relationship between the mismatch parameter and the strength increase has a 3/2 slope on a log-log plot. Therefore, the interaction parameter is raised to the 3/2 power in the conventional substitutional solid solution strengthening equation (Equation 4.5). These expressions have been thoroughly discussed in classic mechanical metallurgy textbooks¹⁰².

$$\Delta\sigma_{ss} = 3^{1/2} \cdot \frac{G \cdot \varepsilon_s^{3/2} \cdot c^{1/2}}{700} \quad \text{Equation 4.5}$$

The solid solution strengthening mechanism can be applied to the current nickel-gold interface as following. The lattice misfit parameter can be estimated by assuming a linear relationship between the lattice parameter of pure gold ($a_0 = 4.065 \text{ \AA}$) and pure nickel ($a_0 = 3.499 \text{ \AA}$)¹⁷² as a function of the concentration of solute. In a similar manner, the modulus misfit parameter can be estimated by assuming a linear relationship between the shear modulus of pure gold ($G = 26 \text{ GPa}$) and pure nickel ($G = 72 \text{ GPa}$)²⁶¹ as a function of the concentration of solute. Finally, it becomes a simple function to calculate the interaction parameter and the solid solution strengthening of nickel and gold as a function of solute in the solvent. The maximum solid solution strengthening $\Delta\sigma_{ss}$, calculated as 0.33 MPa, is minimal (~1% effect) as compared to the observed strengthening. Therefore, solid solution strengthening is not considered as a significant contributor for our interface properties.

Point Defect Vacancy Strengthening: Pagan et al.⁶⁵ described the cross diffusion at the Ni-Au interface based on supersaturated concentrations of point defect vacancies. This leads to a question: will a high vacancy concentration lead to observed strengthening? Effects of vacancy hardening were first demonstrated in 1955 by Maddin and Cottrell²⁶². By comparing quenched and furnace cooled aluminum single crystals, they were able to retain higher equilibrium concentrations of vacancies in the aluminum. This increased the critical resolved shear stress from 57 gm/mm² to 518 gm/mm². The yield strength increase was rationalized by the vacancies creating additional drag on the dislocations and by dislocation jogs in the materials. There was additional energy needed to move the dislocation through a field of point defects. This increased the strength of the material. Strengthening from supersaturated vacancies is often considered to have a similar mechanism to solid solution strengthening. This is because individual point defect vacancies can trap and drag the mobile dislocations¹⁰². To consider point defect strengthening using the solid solution expressions (Equation 4.5), the modulus- and the lattice- misfit parameters must be estimated as a function of vacancy concentration to determine the mismatch interaction parameter. Research in low temperature isochronal irradiations was used to evaluate these relationships. This is valid because the point defect physics are similar regardless of the source of these

point defects ²⁶³. The change in modulus as a function of vacancy concentration dG/dc was investigated by Townsend et al. ²⁶⁴ for Cu and W and was estimated to be -13%. Dieckamp and Sosin ²⁶⁵ also found -7% change in copper. Interestingly Robrock and Schilling ²⁶⁶ found an average value of -24% for aluminum along with variations as a function of crystallographic orientation. Using these data, we approximated dG/dc for the Ni-Au interface to be -15%. A change in lattice parameter as a function of lattice defect concentration da/dc can be estimated. For isolated vacancy dilation in copper, Wolfer ¹⁷⁰ recommends a value of da/dc to -0.25. This value is used here. The strengthening factor is also related to the concentration of vacancies (estimated by Pagan et al. ⁶⁵ at the Ni-Au interface to be 7.4×10^{-3}). For this concentration of vacancies, the strength increase, $\Delta\sigma_{vac}$, was calculated to be 4.1 MPa. The above estimates must also be discussed based on defect annihilation kinetics as a function of thermo-mechanical signatures during UAM processing.

Stability and Collapse of Vacancies to Clusters: From the current UAM processing conditions Pagan et al. ⁶⁵ estimated the bonding temperature to be ~498 K (225°C). To evaluate the feasibility of point defect annihilation occurring during UAM processing, the onset temperature for vacancy migration (stage 3 recovery) should be considered. This has been determined from isochronal annealing tests of irradiated materials ^{267,268}. The accepted stage 3 recovery temperature for nickel is 350 K (77 °C) ^{169,269–271}. The UAM processing temperature is clearly above the stage 3 defect annihilation temperature for nickel alloys. Therefore, it can be assumed that the mono-vacancies are mobile and will be able to coalesce into vacancy clusters. Therefore, the original point defect vacancies created during bonding that accelerated interdiffusion are likely to be coalesced into vacancy clusters.

Figure 4.3b and Figure 4.3c, show tentative evidence for vacancy clusters or voids near the interface. These are white dots in the BF image and dark dots in the HAADF image. The clusters appear to have an average diameter of 7 nm ($R_{cluster}$) and a number density ($n_{cluster}$) of $4.8 \times 10^{16} \frac{clusters}{cm^3}$. Since the cluster density is used for strengthening calculations below, the density is estimated using the volume of the nanoindentation plastic strain field to avoid under- or over-estimating their strengthening contributions. The nanoindentation plastic strain field probing width is approximately $7 \times$ the indent depth (h). An approximate nanoindentation probing area is estimated by $\pi r^2/2$, where r is one half the width of the plastic strain field. There are approximately 115 vacancy clusters based on counting from Figure 4.3. If the number of apparent vacancy clusters is divided by the nanoindentation probing area and the TEM lamella foil thickness (50 nm), the vacancy cluster density at the interface is 4.8×10^{16} clusters/cm³. The estimate is validated further with the following theoretical calculations based on the number of individual point defect vacancies necessary to form these clusters. Since there are four atoms in an FCC unit cell, the atomic volume, i.e., Ω , of one empty lattice location (vacancy) is given as $\frac{a_0^3}{4}$. This leads to the following equation.

$$n_{vac} \times \Omega = n_{cluster} \times R_{cluster} \quad \text{Equation 4.6}$$

Using the lattice parameter for gold as $4.065 \text{ \AA}$ ¹⁷², we estimate 10,695 vacancies per cluster. Using the observed cluster density, we estimate there will be $5.8 \times 10^{20} \frac{\text{vacancies}}{\text{cm}^3}$ (n_{vac}) in all the clusters. The number of gold atoms in a unit volume (n_{Au}) can be calculated using the bulk density (ρ), Avogadro's number (N_A), and the molar mass (M) with the following equation.

$$n = \rho \times N_A / M \quad \text{Equation 4.7}$$

We calculate n_{Au} to be $5.9 \times 10^{22} \text{ atoms/cm}^3$. Now using these two estimates, the vacancy concentration ($X_v = n_{vac}/n_{Au}$) was calculated to be 9.8×10^{-3} . The vacancy concentration is in excellent agreement with the vacancy concentration estimated from the cross diffusion kinetics from Pagan et al.⁶⁵, i.e. 7.4×10^{-3} , given the sample experimental uncertainties. Now this leads to the next fundamental question: *Will vacancy clusters lead to strengthening?*

Vacancy Cluster Strengthening: Currently there are two models for dislocation interactions with vacancy clusters. Both are based on dispersed barrier strengthening through dislocation barrier cutting. In the dispersed barrier model by Seeger²⁷² for strong obstacles, dislocations intersect obstacles on their glide plane. The distance between obstacles is determined through classic geometric considerations. The second model for cluster strengthening is the Friedel-Kroupa-Hirsch (FKH) model^{273,274}. In the FKH model obstacles are considered to have greater effective inter-cluster spacing, as compared to their geometric consideration. This creates less extensive dislocation bowing prior to cutting. In both cluster models, the mobile dislocations interact with the clusters through their elastic strain fields. The elastic strain field created by the cluster is due to the volumetric dilation created by the vacancies, which is proportional to the concentration of these defects^{170,272,275–277}. The strengthening described by the Seeger model $\Delta\sigma_{Seeger}$, and the FKH model $\Delta\sigma_{FKH}$ are given in the following equations.

$$\Delta\sigma_{Seeger} = M\alpha\mu b\sqrt{Nd} \quad \text{Equation 4.8}$$

$$\Delta\sigma_{FKH} = \gamma M\mu b d N^{2/3} \quad \text{Equation 4.9}$$

Here M is the Taylor factor (~ 3.06 for equiaxed FCC and BCC materials²³³), α is the Seeger defect cluster barrier strength (~ 0.4 for strong vacancy clusters or voids), μ is the shear modulus (26 GPa for gold), b is the magnitude of the Burgers vector of the gliding dislocation ($\frac{a_0}{\sqrt{2}} <110>$ in gold), N is the cluster density, and d is the cluster

diameter (average of 7 nm), and γ is the FKH obstacle strength coefficient (0.2 for weak barrier vacancy clusters). The hardening factor for clusters acting as dislocation barriers increases as a function of the defect cluster size and type. For vacancy clusters with a diameter of 7 nm, the hardening coefficient could be close to 0.87²⁷⁸. This indicates the vacancy clusters are quite strong obstacles, and the Seeger model is more appropriate here than the FKH model. As discussed above, the vacancy cluster density for the localized region near the interface within the nanoindentation probing volume is 4.8×10^{16} clusters/cm³. An average value for vacancy cluster strengthening is demonstrated through these calculations for the Seeger and FKH models. The effect of clusters on strengthening is further shown in the sensitivity analysis.

$$\Delta\sigma_{Seeger} = 168 \text{ MPa} \quad \text{Equation 4.10}$$

$$\Delta\sigma_{FKH} = 42.3 \text{ MPa} \quad \text{Equation 4.11}$$

Sensitivity Analysis: Based on the above discussions, the observed strengthening cannot be attributed to one or more strengthening obstacles without uncertainty. Therefore, a sensitivity analysis of the strengthening was performed and is shown in Figure 4.12 using a range of physically reasonable values. Figure 4.12a demonstrates that the strengthening from strain hardening is very sensitive to the dislocation density on a logarithmic scale. With an extremely large dislocation density (10^{12} cm⁻²), in our experiments moderate strengthening contributions could be reached. Figure 4.12b shows that the fine grain size contributes greatly to strengthening only when the grain size is below the micron scale. The sensitivity analysis of Figure 4.12c confirms that the solute concentrations only have minimal effect, even when the shear modulus and interaction parameter also depend on the solute concentrations. Figure 4.12d demonstrates that the vacancy strengthening is largely dictated by the concentration of vacancies present in the material. This also results in a relatively small strengthening. Figure 4.12e demonstrates that the strengthening is controlled by the cluster size and density in the Seeger model, and relatively large contributions to the overall strengthening can be achieved for reasonable cluster parameters. Figure 4.12f demonstrates that the FKH strengthening is controlled by cluster size and density. This is similar to the Seeger model, but the magnitude of the strengthening is smaller.

A comparison of the strengthening mechanisms is shown in Figure 4.13. This graph was created using the average and standard deviation from each of the potential microstructural features as shown in the sensitivity analyses in Figure 4.12. The grain size strengthening has the largest contribution followed by the cluster strengthening with the Seeger model, then strain hardening.

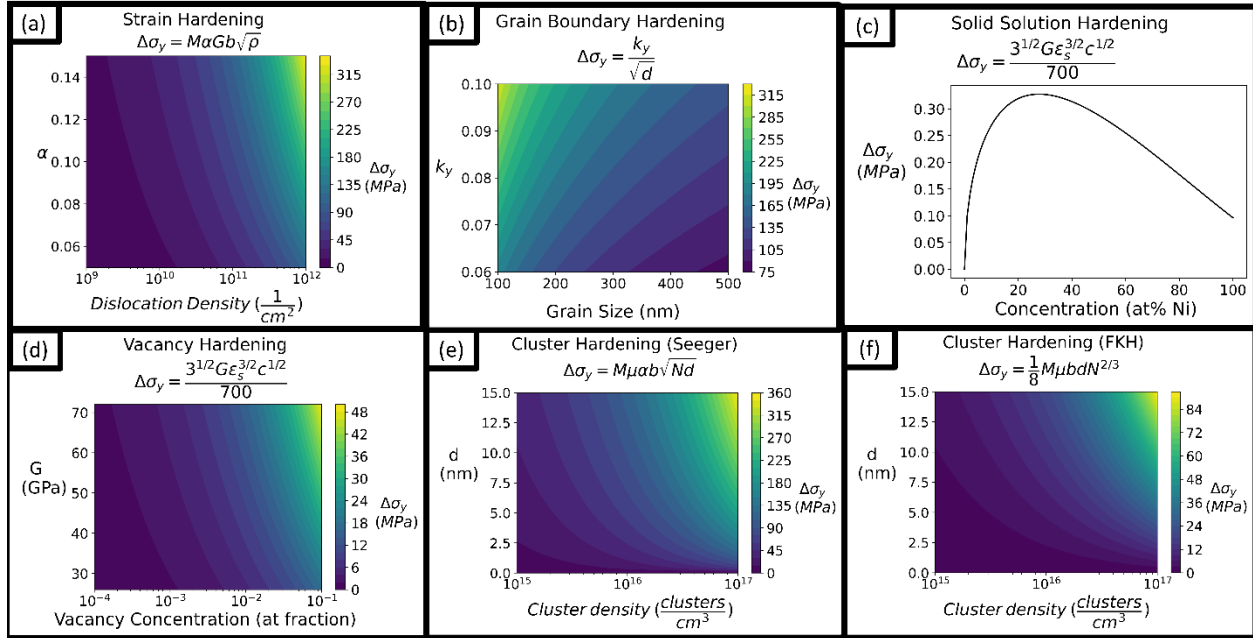


Figure 4.12. Sensitivity analysis of each strengthening mechanism. a) Strain hardening, b) Grain boundary hardening, c) Solid solution hardening, d) Vacancy hardening, e) Cluster hardening using the Seeger model, f) Cluster hardening using the FKH model

Strengthening Mechanism Interaction: The overall total strengthening effect on the Ni-Au interface could most accurately be described as a combination of the above-mentioned strengthening effects due to the various dislocation obstacles present in the material. The hardness superposition principle can be used to approximate the effective combination of these effects ^{279,280}. Dislocation obstacles with comparable strengths ($S = 0$) can be combined through a root mean square addition, and dislocation obstacle combinations of weak and strong strengths ($S = 1$) can be combined through linear superposition.

$$\sigma_{total} = S(\sigma_1 + \sigma_2) + (1 - S)\sqrt{\sigma_1^2 + \sigma_2^2} \quad \text{Equation 4.12}$$

Using the information from Figure 4.13, the relative strengths of the different mechanisms can be assigned. A thorough computational analysis would be necessary to describe the range of relative obstacle strengths. Here a simplification is used in which dislocation obstacles are assigned as being either strong or weak. This should be adequate to describe the strength within a reasonable range of error. Grain boundaries, strain hardening, and vacancy clusters using the Seeger model are assigned as being strong obstacles. Solid solution strengthening, and point defects are assigned as being weak obstacles. The strong obstacles are assigned because migrating dislocations cannot move around these obstacles. Also dislocation entanglement can create additional dislocations through methods such as the Frank-Read source ²⁸¹. The weak obstacles are assigned because migrating dislocations can potentially climb over or cut through these obstacles. Vacancy clusters using the FKH model are not used in this superposition calculation because the strength contribution from these microstructural features are already considered using the Seeger model, and the strengthening coefficient is likely near 0.9. Therefore, the FKH model is not appropriate here. Additionally, grain boundaries and strain hardening are typically considered long-range obstacles while solid solution strengthening, and point defects are considered short-range obstacles ¹⁰². Since the long-range and short-range obstacles are different scales and different mechanisms they should be added linearly. Using these arguments, the hardness superposition principle simplifies to the following equation.

$$\sigma_{total} = \sqrt{\sigma_{gb}^2 + \sigma_{sh}^2 + \sigma_{Seeger}^2} + \sqrt{\sigma_{ss}^2 + \sigma_{vac}^2} \quad \text{Equation 4.13}$$

The total strengthening was calculated using the hardness superposition principle and the calculated average strength for each mechanism as described in the previous sections.

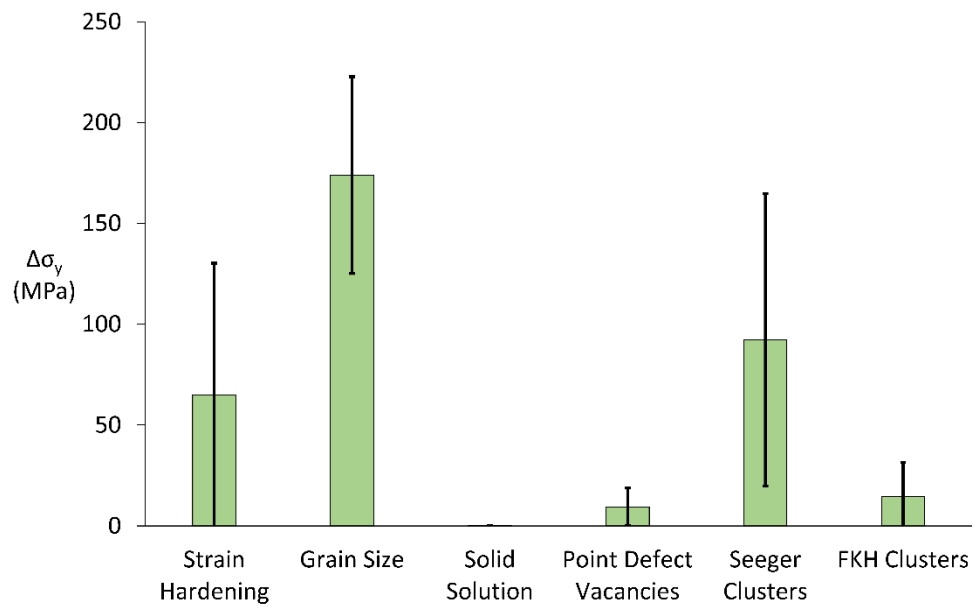


Figure 4.13. Sensitivity and comparison of the strengthening mechanisms. Each strengthening mechanism is shown along with error bars representing with one standard deviation.

$$\sigma_{total} = \sqrt{(184 \text{ MPa})^2 + (49.3 \text{ MPa})^2 + (168 \text{ MPa})^2} + \sqrt{(0.33 \text{ MPa})^2 + (4.1 \text{ MPa})^2} \quad \text{Equation 4.14}$$

Since the observed strengthening from the nanoindentation was approximately 182 MPa, the estimated hardness using superposition methods (Equation 4.14) demonstrates accuracy within ~30 %. Based on the superposition model, we attribute the measured hardening after UAM consolidation to strain hardening, grain boundary refinement, and formation of vacancy clusters.

4.5 Summary and Conclusion

The current research provides unique insight into nano-scale mechanical strengthening processes at the gold-nickel interfaces joined through ultrasonic additive manufacturing. The strengthening effects have been probed using nanoindentation and the net increase in strengthening was estimated to be 182 MPa. These strengthening effects were rationalized using microstructural features observed through electron microscopy. The interface microstructure around the UAM-processed components exhibited significant variations with respect to the spatial position from the sonotrode. The strengthening effects are attributed to a combination of nanoscale grain boundary Hall-Petch hardening, vacancy clusters or voids, and network dislocations. These results are relevant to micron-scale embedding of sensors within structural components.

4.6 Acknowledgements

Christian Petrie supplied the materials for this study. Adam Hehr and Mark Norfolk (Fabrisonic LLC, Columbus, Ohio) fabricated the embedded fiber sample. Nanoindentations were performed at the National Institute for Materials Science (NIMS) at Tsukuba, Japan and at the KLA Corporation in Knoxville, Tennessee. The SEM, EBSD, and optical microscopy were performed at NIMS and in the Institute of Advanced Materials and Manufacturing (IAMM) at the University of Tennessee. STEM microscopy was performed at the Oak Ridge National Laboratory (ORNL) in the Low Activation Materials Development and Analysis Laboratory (LAMDA) by Dr. Donovan Leonard. Conventional TEM microscopy was performed at the LAMDA facility and the IAMM facility. This work was partially performed while M. Pagan was a visiting intern at NIMS. Funding for this research was supported by NIMS and the Governor's Chair Program.

CHAPTER 5

STRENGTHENING OF TEMPERED

ALUMINUM DURING ULTRASONIC

ADDITIVE MANUFACTURING

Abstract

Strengthening effects in materials bonded by Ultrasonic Additive Manufacturing (UAM) were investigated. Aluminum (Al 6061) was pre-treated by tempering and annealing prior to bonding through UAM. Following UAM, multiscale material characterization was performed. Tensile testing in the x-direction demonstrated the material became harder after the UAM process, and nanoindentation demonstrate the foil-foil interfaces became harder than the bulk foil material. The strengthening effects are a result of microstructure changes at the interfaces and in the bulk foil regions which were characterized using x-ray diffraction, scanning electron microscopy, transmission electron microscopy, and energy dispersive spectroscopy. These microstructure changes result from dynamic recrystallization, dynamic recovery, adiabatic heating, and precipitate dissolution.

5.1 Introduction

A thorough introduction to the Ultrasonic Additive Manufacturing (UAM) process has been described earlier (Chapter 2.3), therefore details of applications and bonding mechanisms will not be repeated. The methods of extracting the mechanical properties of UAM components include shear^{59,210}, tensile^{46,211}, microhardness^{55,97,185}, and nanoindentation testing^{57,213,282}. Mechanical testing is often coupled with microscopy or diffraction to understand the mechanical and physical metallurgy of UAM builds. Indentation testing has found that UAM builds typically have a local increase in strength at well bonded foil-foil interfaces⁵⁷ along with a decrease in the pattern quality from electron backscatter diffraction (EBSD)^{55,185}. The decrease in EBSD pattern quality is associated with a dynamic recrystallized structure at the interface. The dynamic recrystallized structure results in reduced grain sizes and elevated dislocation densities^{45,46,94}. Finite element modeling has also suggested the imposed plastic deformation refines the grain structure and increases dislocation density¹⁷⁶. The force from the sonotrode on the top surface of a foil could also increase the dislocation density more as compared to the bottom of a foil¹⁸⁷. Recent studies which observed nanometer sized voids at UAM interfaces^{65,282} could potentially also increase the strength through dispersed dislocation barrier effects²⁷².

Tensile testing of UAM builds from Al6061 H-18 was performed by Sridharan et al.²¹¹. The tensile tests were performed in the build (z) direction, the transverse (x or y) direction, and compared against bulk properties. The authors observed a 25% reduction in yield stress in the transverse direction and an 84% reduction of yield stress in the build direction. The authors suggested that shear bands and microvoids were created at the interfaces. When the interface experiences a tensile load, the microvoids coalesce, create voids, and crack, resulting in brittle failure. Tensile testing of Al 3003 H-18 was also performed by Schick et al.⁴⁶ in the longitudinal and transverse directions. This revealed a decrease in build strength as compared to bulk values. The strength decrease was related to a large fraction of non-contact parabola shaped voids. The voids reduce the load bearing cross-section and increase the stress concentration

intensity factor. Tensile testing in this current study is performed in the rolling (x) direction to compare with the above results. The orientation of the tensile dogbones with respect to the sonotrode and foil-foil interfaces is shown in Figure 5.1.

Additionally, materials created by UAM can create microstructures with significant crystalline lattice defects. Compared with quenched materials, UAM plastic deformation can enhance lattice defect concentrations even further. Chen et al.¹¹⁸ performed ultrasonic welding on a T4 tempered Al 6111 structure. Using modeling, hardness measurements, and electron microscopy, the authors observed a heat affected zone and precipitate structure at the foil-foil interfaces that grew over an 8-month period. The authors noted that the post weld aging occurred much faster than expected, which corresponds to a lattice point defect vacancy concentration over 100 times larger than it should have been. Other authors investigating UAM bonding have noted large vacancy concentrations at the interfaces, which can lead to significant effects such as enhanced elemental interdiffusion and interface strengthening effects^{65,282}. Lattice defect changes during UAM have not yet been associated with large scale mechanical properties such as tensile testing. Additionally, various states of pretreating material prior to UAM have yet to be characterized. These factors lead to the fundamental questions this research attempts to address: how do various pretreatments affect the microstructure of material created by UAM, and how can these microstructure changes affect the built material's mechanical strength?

5.2 Experimental Methods

Aluminum (Al 6061) and UAM Processing

Al 6061 foils were initially received in the H-18 condition, prior to the welding pretreatment. The aluminum was annealed into the O condition by increasing the temperature of the aluminum to 415°C for three hours, then slowly cooling to room temperature (10°C/ hour). This slow cooling allows the aluminum to reach an equilibrium phase distribution at room temperature. Additional samples of the Al 6061 were tempered into the T4 condition. This was done by increasing the temperature to 529°C for one hour followed by quenching in water, which locked the phase distribution at 529°C. These thermal cycles represent standard heat treatment for Al 6061²⁸³.

The pre-treated foils (~150 µm thick) were bonded to an Al 6061 T4 baseplate using a SonicLayer 4000 UAM system, with a vacuum chuck used to secure the weld substrate. Before UAM welding, the baseplate was first recovered using an endmill to ensure a flat build surface and then cleaned with alcohol to remove possible contamination. Texturing was then applied to the baseplate to help improve welding quality by rolling the sonotrode over the surface while applying ultrasonic vibrations without adding a foil. For welding the *O Foils*, the UAM processing parameters were a normal force of 4000 N, a weld speed of 200 inch/min (84.7 mm/sec), an amplitude of 33 µm, and a baseplate temperature of 24°C.

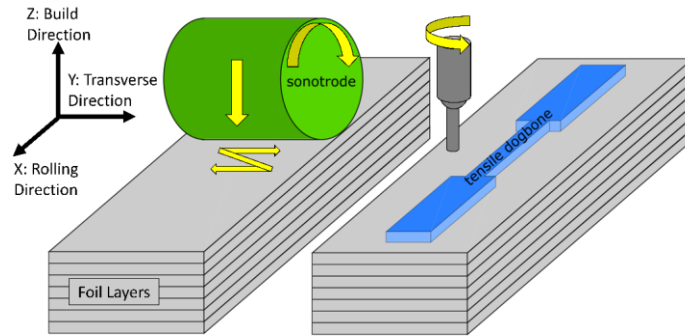


Figure 5.1. Overview of UAM bonding along with the tensile dogbones

For the *T4 Foils*, the UAM processing parameters were a normal force of 4000 N, a weld speed of 100 inch/min (42.3 mm/sec), an amplitude of 36 μm , and a baseplate temperature of 66°C. The *T4 UAM* sample contained twelve bonded *T4 Foils*, and the *O UAM* sample contained fifteen bonded *O Foils*.

The tensile samples were subsize dogbones (gauge length 4") machined out using a 0.125" diameter endmill in the x-direction orientation (Figure 5.1). The specimens were machined out entirely within the bonded foil regions. All tests were performed at room temperature on an MTS C43.504 load frame in conjunction with MTS wedge grips. The load frame was operated in displacement control mode at a crosshead speed of 1.27 mm/min (initial strain rate of 0.75 s⁻¹). The axial load was measured by a 5 kN range load cell. To measure dogbone strain, a Correlated Solutions digital image correlation (DIC) system was used with a virtual extensometer of 1 inch (25.4 mm) surrounding the break. Four tensile samples were used for each case, and the results are shown in Figure 5.2.

Nanoindentation

Nanoindentation experiments between the 1st and 2nd foil layers were performed on a KLA iMicro instrument using a Berkovich indentation tip with the shallow depth nanoblitz method^{284–286}. The nanoindentations used a peak load of 1.15mN. This corresponds to a peak indentation depth of 120-200 nm, depending on the location and hardness in the material. The three-dimensional nanoblitz hardness contour profiles were converted into average hardness line profiles by averaging the measured hardness at regular intervals away from the foil-foil interfaces. The y-error bars on the hardness line profiles represent one standard deviation from the average hardness and the x-error bars represent the indent spacing.

Large depth nanoindentations were performed using the continuous stiffness method (CSM)^{287–289} in the middle of the 1st bonded foil and at the interface between the 1st and 2nd foil. The bulk foil regions had at least twenty-five CSM indents performed, and their average and standard deviation are reported. There was difficulty in accurately indenting on the interface due to its small width. Indent arrays were performed near the interface and the indents with a higher hardness are reported as the interface. The CSM indents were performed approximately six months after the TEM testing, therefore some natural aging of the aluminum might have occurred. All CSM indents were performed using a Berkovich tip to a peak load of 20 mN, using a strain rate of 0.20 s⁻¹, an oscillation frequency of 110 Hz, and an oscillation amplitude of 2 nm. All indents were performed with sufficient spacing between indents to reduce overlap of their plastic strain fields²¹⁴.

Microstructural Characterization

Computational thermodynamics of the materials were performed using the Thermo-Calc® program²⁹⁰. Samples for microscopy analysis were prepared by cold mounting in epoxy followed by mechanical polishing using standard metallography techniques. To reduce charging effects, a thin carbon coat was applied to the surface of the samples.

Scanning electron microscopy (SEM) images were taken using a Zeiss Evo with a LaB₆ filament. For fractography, the SEM working distance was maximized to increase the depth of field (DOF) across the surface ¹⁹⁴.

Samples for x-ray diffraction (XRD) were prepared using a low-speed saw. For the UAM bonded samples, a cross section of approximately five foils was sectioned for analysis. X-ray diffraction was performed at the 11BM beamline at the Advanced Photon Source (APS) ($\lambda = 0.4581$ nm) ^{291,292} using Debye-Scherrer geometry, and analysis of the scans was performed using standard Rietveld Refinement techniques ^{293,294}.

Samples for transmission electron microscopy (TEM) were extracted from the bonded material at interfaces between the first and second foil layers, and at locations distant from any obvious lack of bonding voids. These TEM lamella samples were prepared using a focused ion beam (FIB) / SEM Zeiss Auriga using standard procedures with a gallium-ion beam at voltages from 30 kV to 5 kV and with a beam current progressively decreasing from 2 nA to 50 pA. Finally, the TEM-lamellae were lifted from the sample surface using an OmniProbe and welded to a copper grid for further TEM analysis. The microstructure of the FIB lamellae was analyzed in a Titan 60-300 Scanning Transmission Electron Microscope (STEM) operated at 300 kV. The images were taken with a camera length of 460mm with an HAADF collection angle of 21-126 mrad. A Super-XTM energy dispersive x-ray spectrometer (EDXS) was used to obtain compositional maps. The spectrum images obtained were quantified using the VeloxTM software. The grain size from the STEM image was calculated using the Heyn's line intercept method ²¹⁵, and the dislocation density was determined using the line-cut method ²¹⁶. It should be noted that the TEM analysis was performed approximately two months after other characterizations. Therefore, additional natural aging of the aluminum could have occurred resulting in slightly larger precipitate sizes. Additionally, it should be noted that the TEM samples were not taken directly below the nanoindentations. This means material variations and uncertainties are present, and they should be considered when comparing the results.

5.3 Results

5.3.1 Tensile Testing

This study demonstrates the strengthening that can develop in materials created by ultrasonic additive manufacturing (UAM). Following this introduction of tensile properties, each material will be systematically investigated. As discussed previously, UAM creates structures by bonding foils together. Therefore, material characterized prior to the UAM process will be referred to as foil material. Material characterized after bonding will be referred to as being in the UAM geometry.

Individual tensile stress-strain curves (from the x-direction) are shown in Figure 5.2 for the *O Foil* samples, the *O UAM* samples, the *T4 Foil* samples, and the *T4 UAM* samples. The stress-strain curves demonstrate that the initial Al 6061-T4 material is harder than the initial Al6061-O material. Additionally, the UAM bonding causes an increase in strength for both sets of material. This is in direct contrast to the decrease in strength due to UAM in Al 6061 H-18 material observed by Sridharan et al.²¹¹. The rationalization of the increase in strength after UAM bonding is the focus of this present work.

Mechanical properties from the tensile testing data are summarized in Table 5.1. The average and standard deviation from each set of samples is listed along with standard reference values. Notably, the strain hardening coefficient from the *O UAM* samples and the *T4 UAM* sample, as determined using Considère's criteria²⁹⁵, are quite low. This indicates the materials have near perfect plastic deformation prior to failure. The elastic modulus of the *O UAM* and *T4 UAM* samples are within 10% of the standard values for Al 6061, indicating these tests are valid within reasonable experimental error. The elastic modulus is quite low for the foil samples due to the difficulty in performing those tests. It should be noted that these tensile properties might not have perfect comparison with the published literature of standard Al 6061 temper tensile properties^{296–299}. This is due to several factors including the nature of the subsize tensile bars that were used in this experiment. Additionally, the standards for aluminum temper designations describe that annealing processes should remove all prior heat treatment or cold rolling²⁹⁶. As shown in the sections below, some distinct microstructure features remain from the foil rolling process prior to UAM bonding. However, as noted previously, the purpose of this study is to understand how the mechanical properties of these materials changed due to the UAM process, and to understand the microstructures that created these property changes.

5.3.2 Characterization of Al 6061 O Foil (Before UAM)

The baseline *O Foil* material was analyzed using scanning transmission electron microscopy (STEM). Figure 5.3 is the STEM high angle annular dark field (HAADF) image of the Al 6061 *O Foil*. A dislocation cell structure can be clearly observed having an approximate cell size of 1 μm . The cell wall structure is seen by the higher contrast spaghetti lines (dislocations). The cell walls contain a significant concentration of dislocations, while cell interiors have a low density of dislocations. A dislocation cell structure is often associated with microstructures after significant plastic deformation^{189,300}. The cell wall structure could be present in this sample due to the rolling processing which was required to roll the aluminum into a thin foil ($\sim 150\ \mu\text{m}$). The subsequent annealing process (to create the *O* condition) might not have been sufficient to remove the dislocation network.

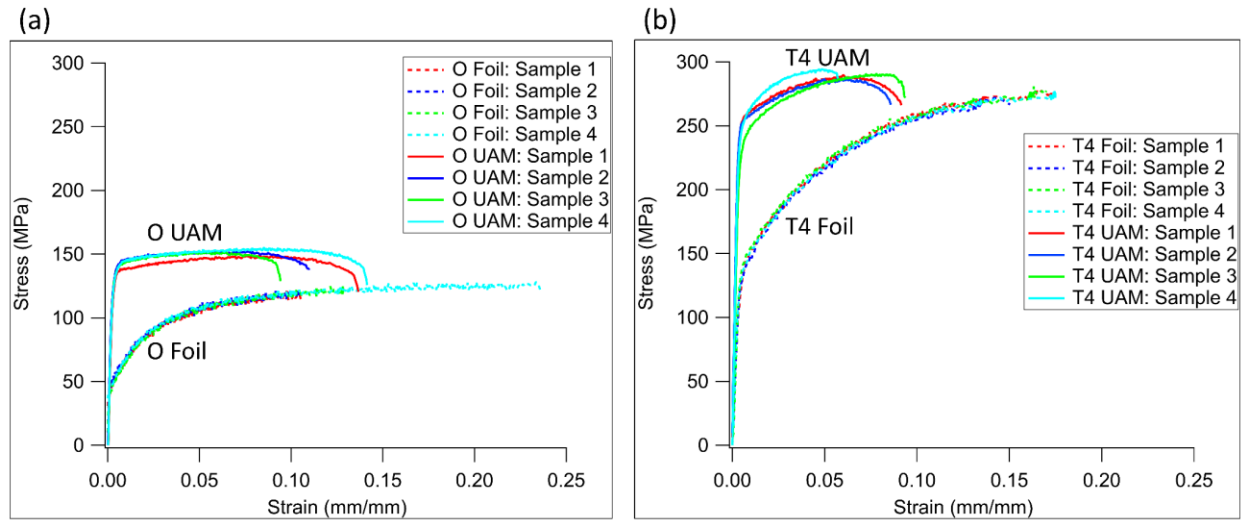


Figure 5.2. Tensile testing results a) Al6061-O, b) Al6061-T4

Table 5.1: Mechanical Properties From Tensile Testing

Sample	Yield Stress (MPa)	Ultimate Tensile Stress (MPa)	n	n^{301}	E (GPa)	E (GPa) ³⁰²
<i>O Foil</i>	46 ± 5.1	126 ± 3.0	0.128	0.158	21.8	68.9
<i>O UAM</i>	127 ± 2.1	150 ± 2.3	0.008		63.6	68.9
<i>T4 Foil</i>	137 ± 1.4	277 ± 1.9	0.071	0.069	32.3	68.9
<i>T4 UAM</i>	210 ± 18.2	270 ± 20.1	0.024		75.0	68.9

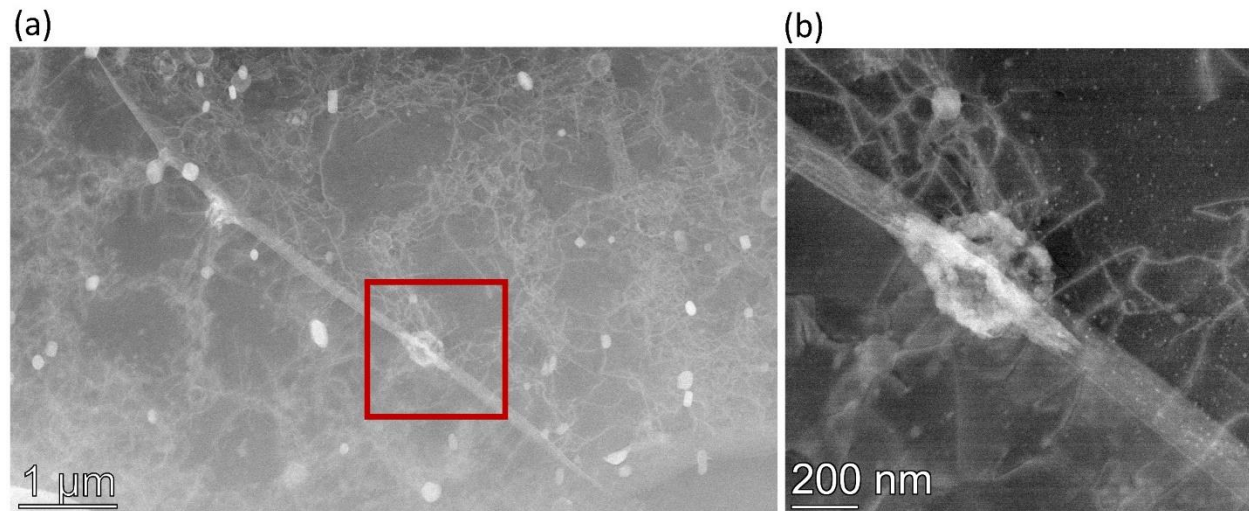


Figure 5.3: STEM HAADF image of the Al 6061 O Foil microstructure. a) Dislocation cell structure, b) Grain boundary/precipitate from highlighted region

From Figure 5.3a, the dislocation density is $1.06 \times 10^{10} \text{ cm}^{-2}$. In addition to the observed dislocation network, precipitates of various sizes and a single grain boundary are observed. In the STEM image (Figure 5.3a), a single grain boundary – from the top left towards the bottom right – can be identified. Since the viewing window is approximately $60 \mu\text{m}^2$, the grain size must be quite large ($\gg 100 \mu\text{m}^2$). The bright high-contrast objects in this HAADF-STEM image are likely the precipitates (with a high combined atomic number of $Z = 38$) in the aluminum matrix (atomic number $Z = 13$). These precipitate objects are mostly located in the center of dislocation cell walls and grain boundaries. Figure 5.3b is a magnification of the central grain boundary, as highlighted in Figure 5.3a. The grain boundary cuts through the center of a large precipitate. To determine the chemical composition of the precipitates, TEM elemental analysis, e.g. energy dispersive X-ray spectroscopy (EDS) analysis, was performed.

Figure 5.4 shows a HAADF-STEM image of the sample and corresponding EDS maps. The EDS images were taken at the same location as described above. In this region of interest, precipitates with various elemental compositions were observed. Some of these precipitates contain magnesium and silicon, suggesting a Mg_2Si precipitate. Other precipitates contain concentrations of iron, manganese, and chromium. The quantified spectrum images indicate that the precipitates pinning dislocation cell walls are Mg_2Si . These precipitates are spherical and ellipsoidal in shape, with a characteristic Feret diameter of approximately 200 nm and an average spacing L of $1.02 \mu\text{m}$. The volume fraction v_f of the precipitates can be approximated as the volume of each precipitate divided by the three-dimensional average spacing between each particle, $v_f = \frac{\frac{4}{3}\pi r^3}{L^3}$. The volume fraction of Mg_2Si precipitates is 0.00396.

5.3.3 Characterization of Al 6061 O UAM

STEM

After UAM bonding of the *O Foils*, the microstructure was significantly altered. A thin lamella of the *O UAM* interface is shown below (Figure 5.5). The interface between two *O Foils* is indicated with the arrow in Figure 5.5a. Although there is pronounced grain refinement within ~ 100 nm of the interface, regions located >200 - 300 nm from the interface show a relatively large grain structure. The microstructure at regions $>0.3 \mu\text{m}$ away from the interface exhibit large grains with an average size of $620 \text{ nm} \pm 299 \text{ nm}$ with large pinning precipitates, mostly at grain boundaries.

The interface microstructure was examined using HAADF-STEM (Figure 5.5b) and TEM bright field (BF) image (Figure 5.5c). The refined grain structure is apparent at the interface. The interface region contains extremely fine grains ($100 \text{ nm} \pm 69 \text{ nm}$) within a region approximately 115 nm to 800 nm in width. The refined grain size is likely the result of a dynamic recrystallization event previously described at UAM interfaces^{45,97,100,303}. In addition to the refined grain structures, there are regions of dark circles in the HAADF image and bright circles in the BF image. These regions could be voids or vacancy clusters.

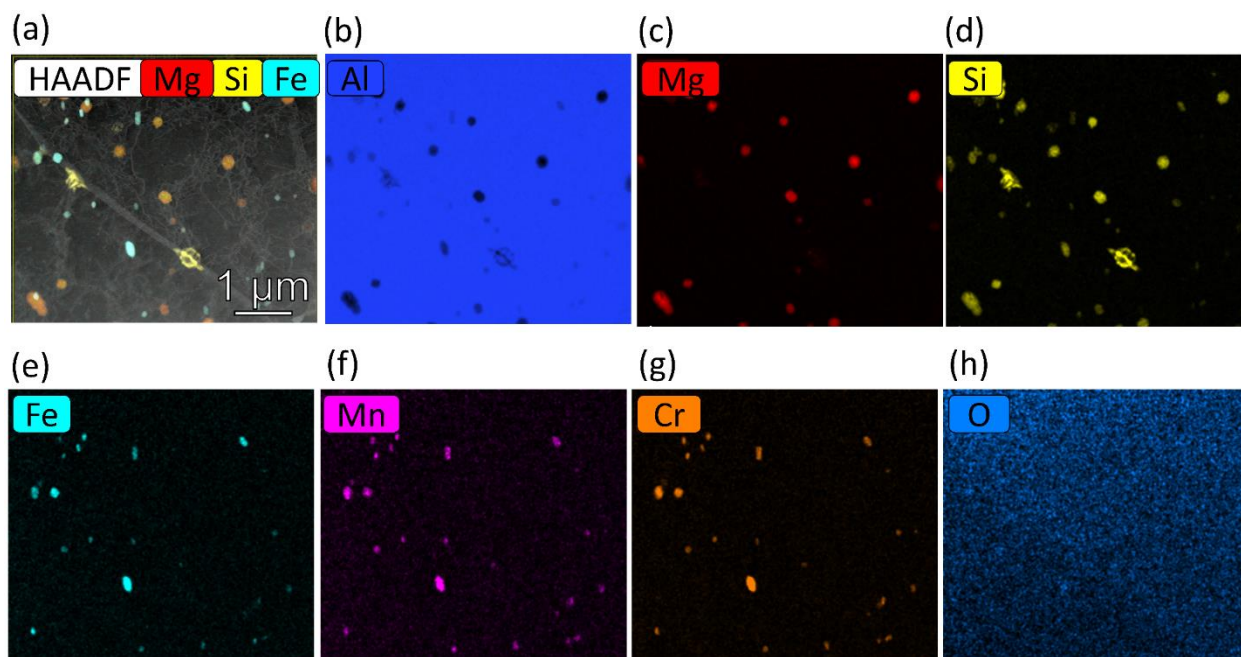


Figure 5.4: STEM/EDS of Al 6061 O Foil. a) HAADF image, b) EDS map of aluminum, b) EDS map of magnesium, c) EDS map of silicon, d) EDS map of iron, f) EDS map of chromium, h) EDS map of oxygen

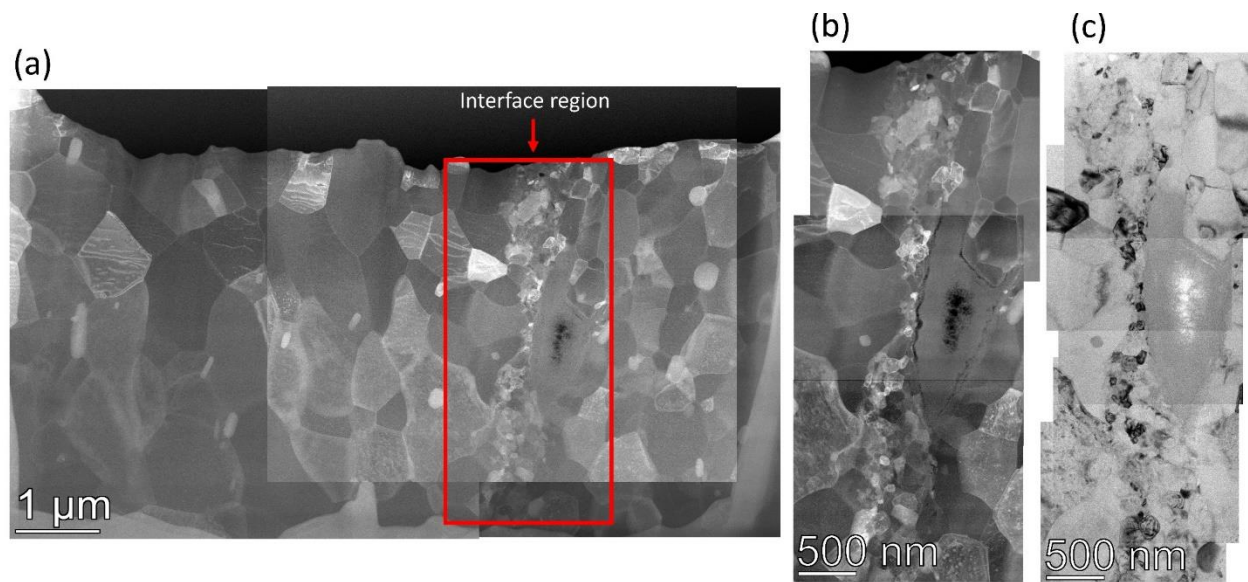


Figure 5.5: STEM/TEM analysis of Al 6061 O UAM microstructure: a) STEM HAADF image of the lamella, b) STEM HAADF of the interface, c) TEM BF of the interface

Vacancy clusters are present at the interface on grain boundaries and inside a large grain on one side of the interface. The vacancy clusters, which are preferential on only one side of the interface, could also be related to the non-uniform hardness increase across the interface observed through nanoindentation (shown below).

It should be noted that the voids present could potentially be explained by the TEM sample preparation by FIB as well. However, the voids are not present far away from the interface region. Additionally, there is elemental migration, as described below. The voids could be associated with excess point defect lattice vacancies, which produced enhanced atomic diffusion, then combined into larger vacancy clusters. Vacancy clusters and accelerated diffusion have been observed as a result of severe plastic deformation^{65,304,305} and radiation effects^{169,268,306}. Therefore, it is highly likely that the voids are associated with the UAM bonding process.

The precipitates have a plate-like morphology, appearing rod-like in the two-dimensional representation shown. The element distribution in these precipitates in the interface region can be identified using EDS, shown in Figure 5.6 and Figure 5.7. EDS maps identify magnesium, silicon, iron, manganese, and chromium content. Figure 5.7a is a combined EDS map of the interface with two EDS line profiles as indicated. Figure 5.7b demonstrates the local concentration of elements at the top right precipitate. This concentration of elements suggests an MgSi or Mg₂Si composition. Magnesium and silica have only a small difference in characteristic x-ray energy, therefore slight overlapping of the tails could occur. This slight energy overlap and x-ray absorption effects could convolute the exact composition²⁰⁹. Since the Mg₂Si structure is the only stable Mg-Si configuration¹⁴⁴, it can be confidently assumed that these precipitates are Mg₂Si. Figure 5.7c demonstrates that the bottom left precipitate has a local concentration of elements that trend towards a configuration of an Al₉Fe₂Si₂ and/or Al₁₃Cr₄Si₄ precipitate. Both these stoichiometries are thermodynamically stable in the Al 6061 O condition²⁹⁰. The intermetallic iron or chromium precipitates are a result from impurities in the aluminum casting process, and they do not significantly contribute to strengthening^{307–309}. Although the non-strengthening precipitates of iron, manganese, and chromium appear mostly unaffected by the UAM process, the Mg₂Si precipitates appear significantly different. There are fewer Mg₂Si precipitates present after bonding, and only one remains within 1 μm of the interface. The magnesium appears broken up and dissolved back into the aluminum at the interface, while several large pockets of silicon remain. This suggests that the magnesium diffused and dissolved more quickly than the silicon.

Fractography

The fracture surface of the O UAM sample (Figure 5.8) can shed more light on the deformation response of this material. The overview image (Figure 5.8a) demonstrates approximately fifteen foils were used in the tensile testing. Further magnifications on the fracture surfaces (Figure 5.8b & Figure 5.8c) show that ductile fracture is present during deformation. Significant reduction of area occurs prior to fracture, and the final fracture appears near the center of the foil.

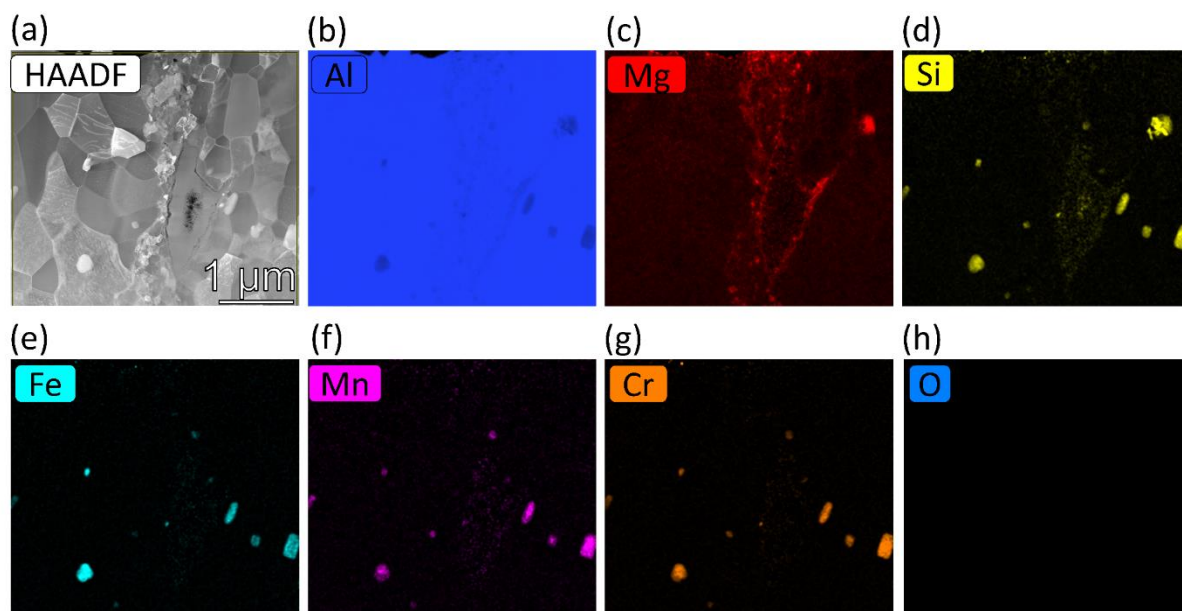


Figure 5.6: STEM / EDS map of the Al 6061 O UAM interface. a) STEM HAADF image, b) EDS map of aluminum, c) EDS map of magnesium, d) EDS map of silicon, e) EDS map of iron, f) EDS map of chromium, h) EDS map of oxygen

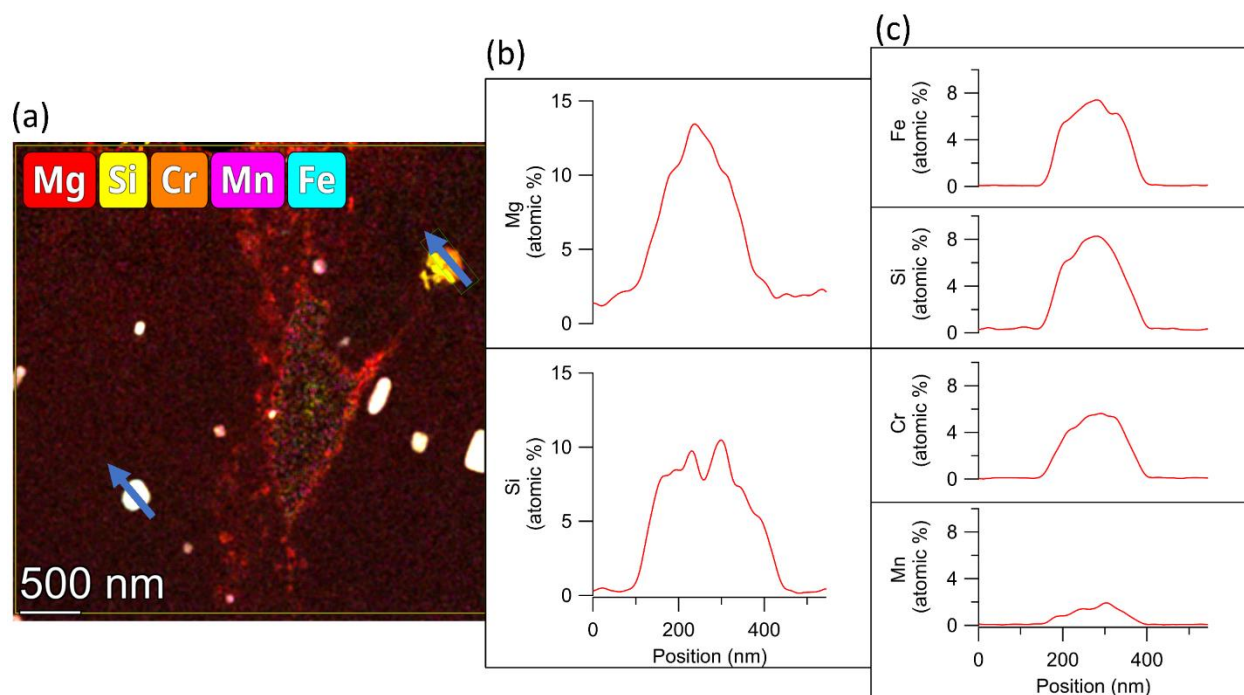


Figure 5.7. STEM / EDS line scan of Al 6061 O UAM interface. a) Combined EDS maps with indicated line scans, b) EDS line scan of top right Mg₂Si precipitate, c) EDS line scan of bottom right Fe-Si-Cr-Mn precipitate

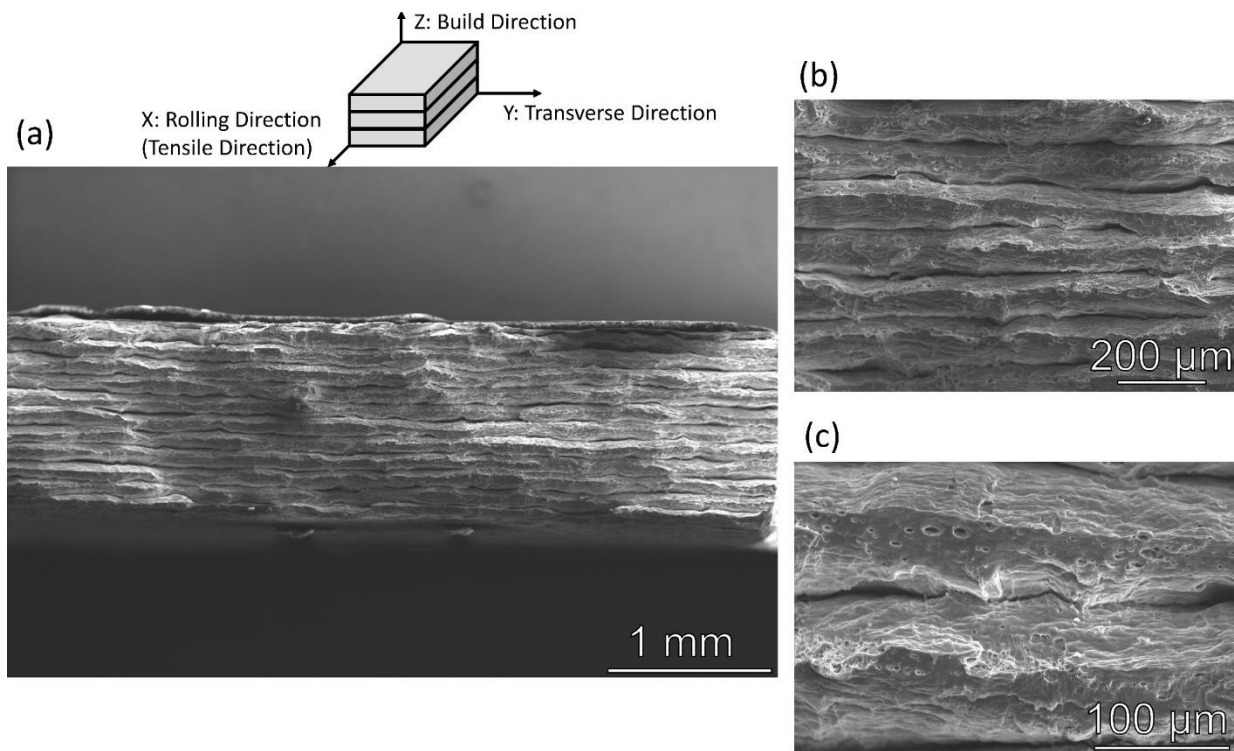


Figure 5.8: Tensile fracture surface of the O UAM sample. a) Overview of the entire fracture surface, b) magnification several foils, c) further magnification of two foils and their interface

The chisel edge/knife edge fracture occurs within each of the fifteen individual original foils. Dimples are present throughout the fracture surfaces, which are typically associated with deformation at precipitates or other inclusions^{310–314}.

As noted in the stress-strain curves, the *O UAM* samples had significant necking prior to failure. Since the middle of the foil necked more than the interfaces, it is likely the interface was harder with reduced ductility. This caused it to fail sooner, then upon further loading the foils continued to deform and neck until they ultimately fractured. Although the interfaces were harder than the middle of the foil, the foils do not appear to have separated from each other. This indicates that although the *O UAM* interfaces became harder than the middle of the foils, the increase in hardness was not significant enough to cause separation.

Nanoindentation

To quantify the local mechanical properties, nanoindentation was performed. The hardness was compared across the interface using a shallow depth nanoblitz array and large depth continuous stiffness mode (CSM) array at the interface and bulk foil region (Figure 5.9). The nanoblitz hardness contour (Figure 5.9a) is rotated for visual aid so that the top of the build is located at the top of the image. The contour demonstrates that the interface is much harder than the bulk foil region. A normalized line of the indents (Figure 5.9b) is provided to demonstrate the average and standard deviation of the hardness. The SEM image of the indent array (Figure 5.9c) is rotated to correspond to the hardness contour plot. The sizes of the indents (from the SEM image) are smaller at the interface as compared to the bulk foil regions. This suggests that the indents should be harder there, although the indent size effect should also be considered. The interface between the foils, as viewed from nanoindentation, appears asymmetric. There is a gradual rise of hardness on the top of the bottom foil, then a sharper decrease in hardness on the bottom of the top foil. The region of the material with the highest hardness is the interface. From the nanoindentation spatial mapping, it has a width of approximately $12\ \mu\text{m} \pm 2\ \mu\text{m}$. The CSM indentations performed on the interface and in the bulk foil regions are shown in Figure 5.9d. Although the interface is harder than the bulk foil region, there is also a depth dependence to the nanoindentation hardness values. Additional analysis must be performed to quantify the hardness difference at the interface and bulk regions. This is discussed further in the section below.

X-ray Diffraction

Crystallographic strain can be understood using x-ray diffraction (XRD). The diffraction patterns comparing the *O Foil* and *O UAM* samples are shown below in Figure 5.10. The aluminum and the Mg_2Si phases are identified in Figure 5.10a. The existence of these phases corresponds to the previous results shown above. The XRD scan of the *O UAM* samples encompassed a relatively large area, across at least five foils and interfaces. Therefore, any potential phase changes that could occur at the interfaces would be too small to be observable.

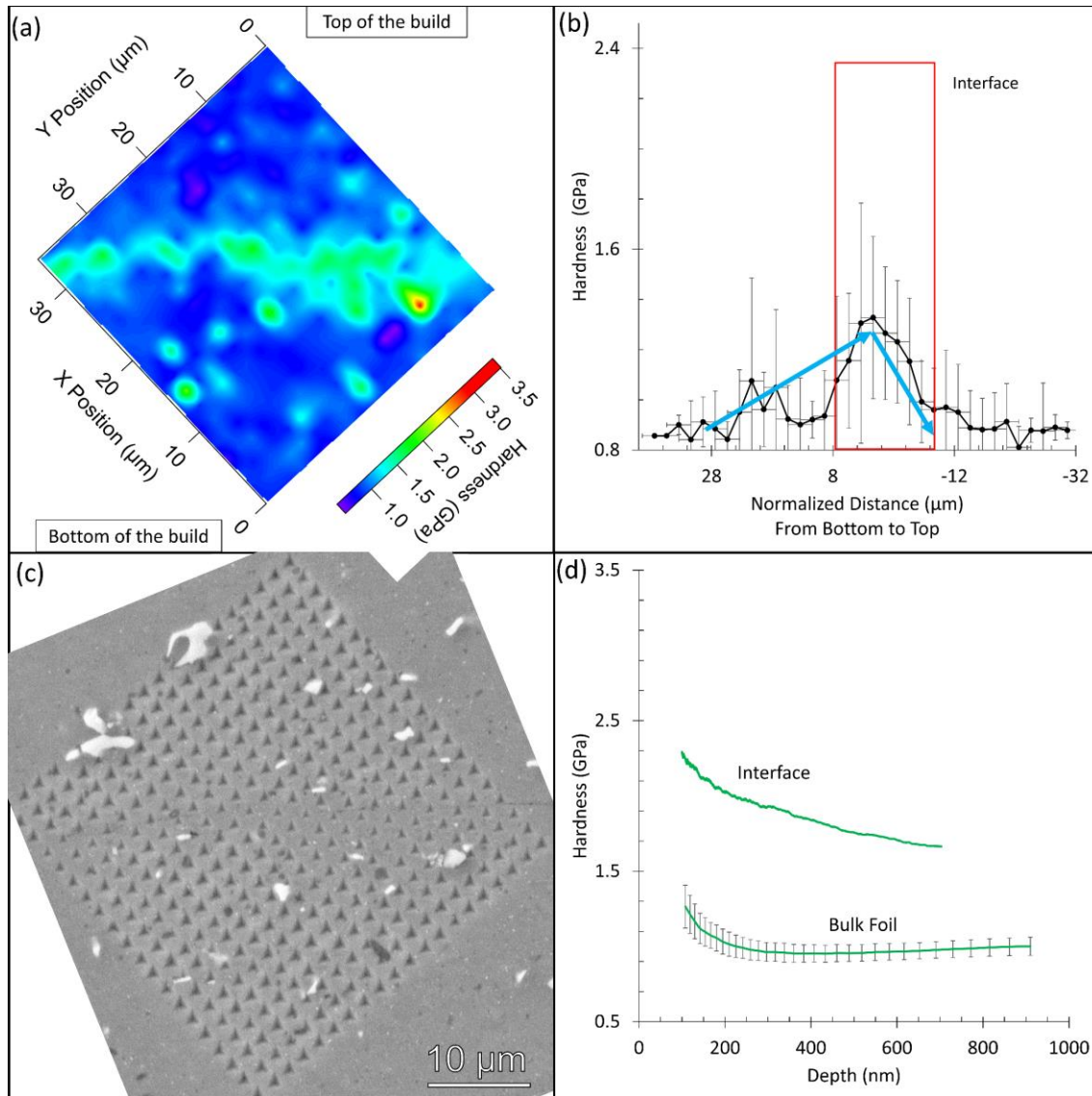


Figure 5.9. Nanoindentation hardness map of the O UAM build. a) Nanoblitz hardness map, b) Average hardness line, c) SEM image of the indent array, d) Hardness vs depth for CSM indents

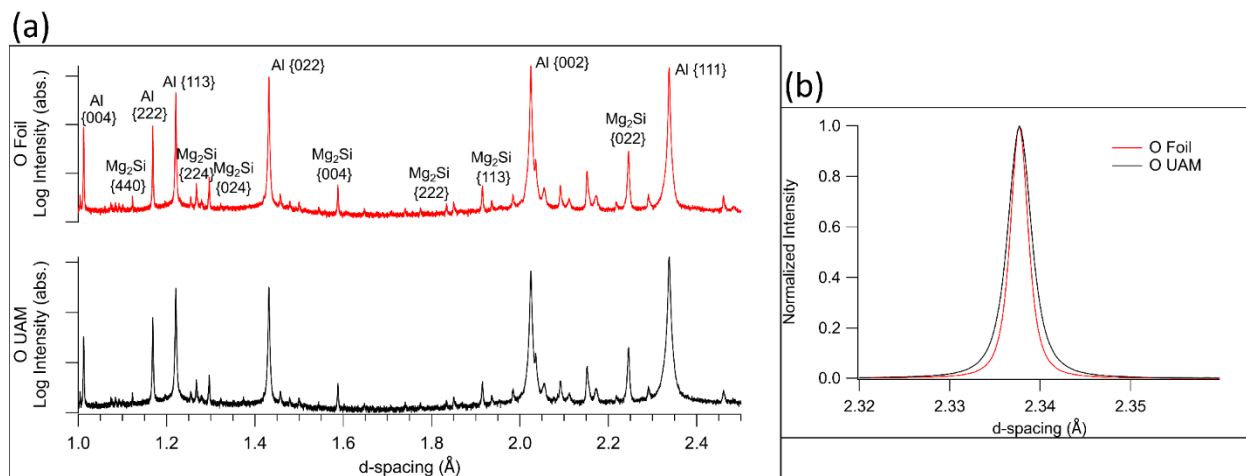


Figure 5.10. XRD of the O Foil and O UAM samples. a) Diffraction patterns, b) Comparison of Al {111} peaks

It should be noted that the diffraction pattern is plotted on a logarithmic scale. Most diffraction peaks are labeled, and the remaining unlabeled peaks are so small that their contribution is negligible.

Although local phase changes at the interfaces would be imperceivable, diffraction broadening from lattice strain in the materials can be observed. An arbitrary peak is chosen to observe the diffraction broadening. The aluminum {111} peak is chosen because it is the strongest peak. The aluminum {111} peak from the *O Foil* and *O UAM* samples are shown normalized and superimposed to demonstrate the diffraction broadening that occurs (Figure 5.10b). The *O UAM* sample has a broader aluminum peak than the *O Foil* sample. This indicates the *O UAM* sample has more crystallographic lattice strain than the *O Foil* sample. Additionally, following Rietveld refinement on the *O Foil* and *O UAM* samples, the generalized mean microstrain values are 1036 and 1607. This indicates that the samples have an increase in lattice strain after the UAM process, likely from additional lattice distortions such as dislocations.

5.3.4 Characterization of Al 6061 T4 Foil (Before UAM)

A STEM image showing the typical microstructure of the *T4 Foil* prior to UAM bonding is shown in Figure 5.11a. The bottom half of the lamella has weak contrast changes from microstructure features. This is because the lamella is slightly too thick for electron transparency there. The top half of the lamella shows dislocation tangles and several precipitates with a plate or rod like morphology. Figure 5.11b, which is a magnified image of the highlighted area shown in Figure 5.11a, shows one large precipitate, several smaller precipitates, and dislocation tangles homogenously distributed throughout the sample. From Figure 5.11a, the dislocation density is $1.68 \times 10^{10} \text{ cm}^{-2}$. The precipitates in the *T4 Foil* are explored with EDS maps (Figure 5.12) to determine their spatial composition. There are several large regions of magnesium and silicon suggesting a Mg_2Si precipitate. There are fewer precipitates in the lower half of the image, although this is likely due to the lamella being too thick, as noted previously. The large Mg_2Si precipitates have a spherical or ellipsoidal morphology.

The *T4 Foil* has fewer precipitates than the *O Foil*, although the precipitates are larger (Feret diameter of 230 nm) with an average spacing of 1.70 μm and a volume fraction of 0.00148. Additionally, since the *T4 Foil* was quenched from a high temperature, it initially has a higher vacancy concentration than the *O* condition. This can lead to slow natural aging of the solute phase^{283,301,315}.

5.3.5 Characterization of Al 6061 T4 UAM

STEM

After the UAM bonding process of the *T4 Foils*, the microstructure was analyzed using TEM (Figure 5.13). The entire TEM lamella is shown in Figure 5.13a.

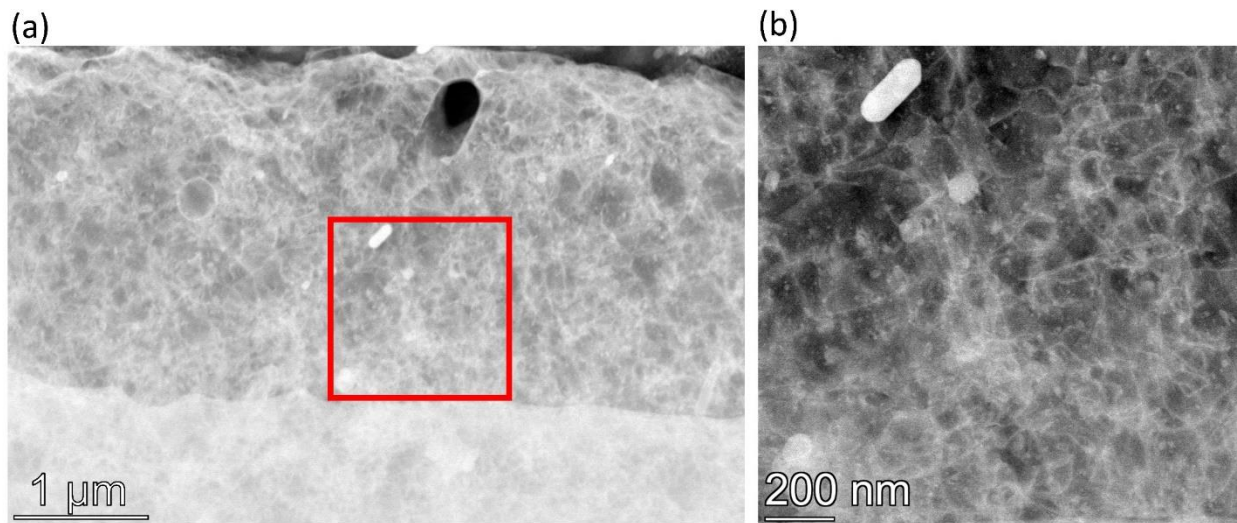


Figure 5.11. STEM image of Al 6061 T4 Foil microstructure. a) HAADF image of entire lamella, b) HAADF of highlighted dislocation network

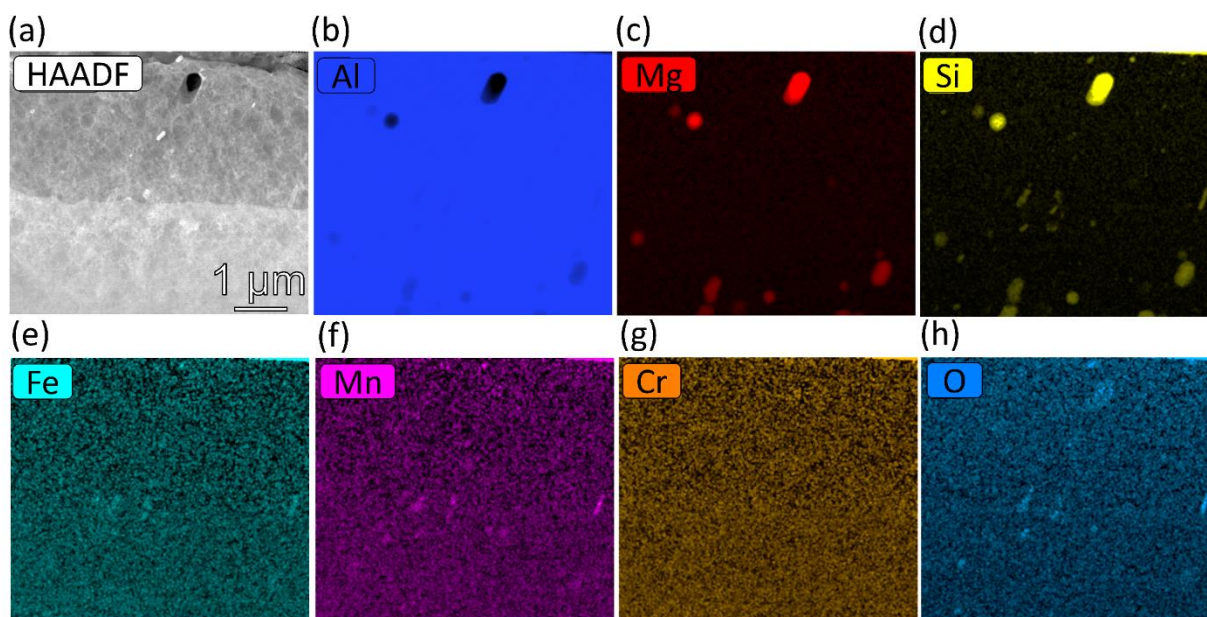


Figure 5.12: STEM / EDS map of Al 6061 T4 Foil. a) STEM HAADF image, b) EDS map of aluminum, c) EDS map of magnesium, d) EDS map of silicon, e) EDS map of iron, f) EDS map of manganese, g) EDS map of chromium, h) EDS map of oxygen

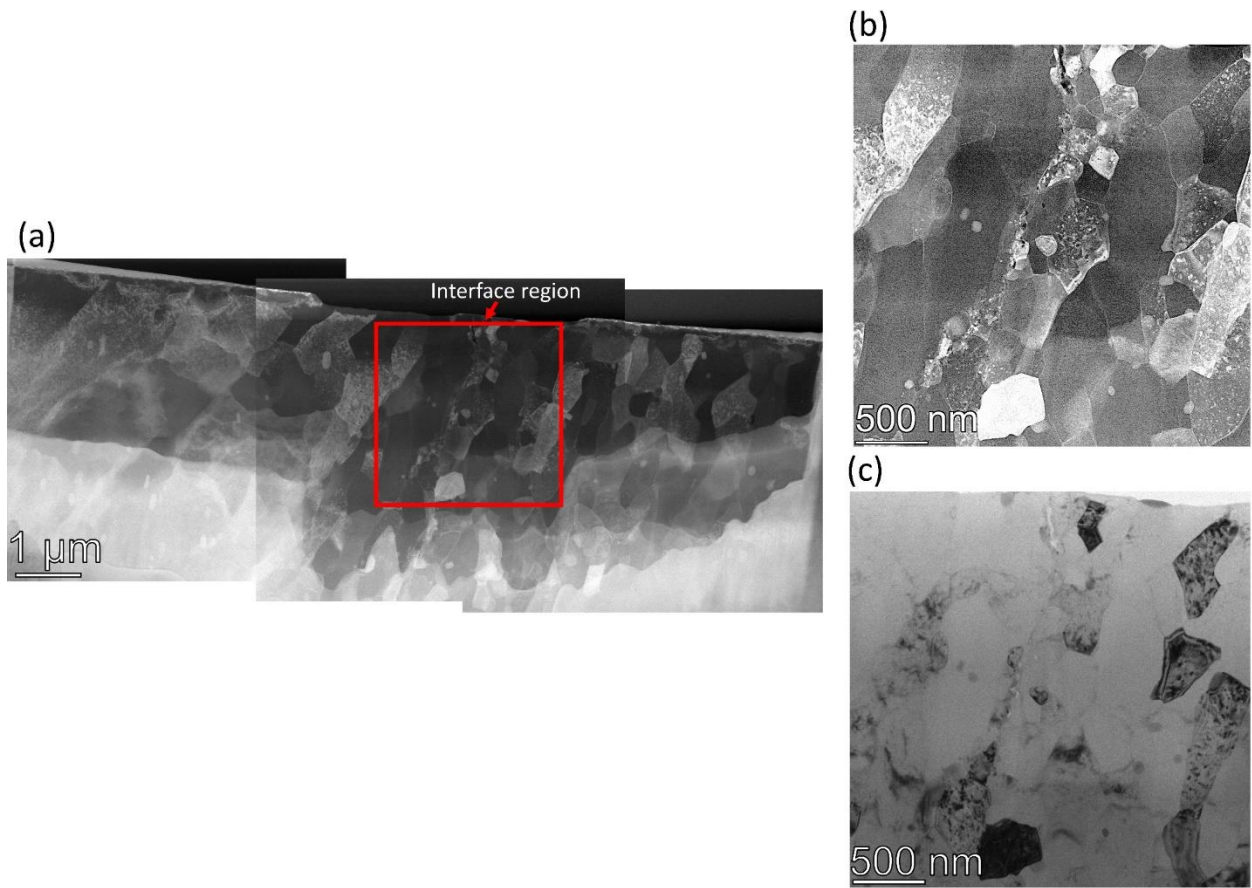


Figure 5.13: STEM/TEM of Al 6061 T4 UAM microstructure. a) STEM HAADF image of the lamella, b) STEM HAADF of the interface, c) TEM BF of the interface

The microstructure several microns away from the interface is an equiaxed grain structure ($610 \text{ nm} \pm 284 \text{ nm}$). The interface between the *T4 Foils* is highlighted and magnified using a HAADF-STEM image (Figure 5.13b) and a TEM BF image (Figure 5.13c). The interface exhibits a refined grain structure ($120 \text{ nm} \pm 79 \text{ nm}$) within a region that is 210 nm to 450 nm in width. The grain size of the *T4 UAM* sample at the interface and in the bulk foil regions is statistically identical to the grain size of the interface and bulk foil regions in the *O UAM* sample. The *T4 UAM* sample has fewer identified precipitates close to the interface, as compared to before the UAM bonding. The remaining precipitates have a plate-like morphology (appear rod-like in the two-dimensional view). At the interface, there are also voids/vacancy clusters along grain boundaries and inside of grains, although there are fewer voids than in the *O UAM* sample.

The composition of the interface region is shown in EDS maps in Figure 5.14. The non-strengthening Fe-Mn-Cr precipitates appear mostly unaffected. The compositional feature most notable is that the interface is strongly enriched in magnesium and oxygen. The few Mg_2Si precipitates in the foil prior to UAM bonding appear completely dispersed into the aluminum after bonding. The interface appears as a sink for magnesium segregation. It is likely that local silicon-rich regions are previous Mg_2Si precipitates. The Mg_2Si precipitates could have dissolved, the magnesium diffused away, and the silicon was left behind. This composition of the *T4 UAM* sample is like the *O UAM* sample. The Mg_2Si precipitate decomposed, and diffusion occurred toward the interface. Unlike the *O UAM* sample, the *T4 UAM* sample also has oxygen detected at the interface, although it should be noted that oxygen is difficult to detect using EDS techniques^{194,209}.

Fractography

The overview fracture surface image (Figure 5.15a) demonstrates there were approximately twelve *T4 Foils* contained in the gage region for the tensile testing. Further magnifications of the fracture surfaces (Figure 5.15b & Figure 5.15c) shows ductile fracture was present during deformation. Like the *O UAM* sample, the *T4 UAM* sample has dimples throughout the fracture surface suggesting precipitates were present. Although there appears to be reduction of area prior to fracture, it is less pronounced than in the *O UAM* sample, which is also indicated by the stress-strain curves (Figure 5.2) and work hardening coefficient.

Unlike the *O UAM* sample, the *T4 UAM* fracture surface shows that the foils separated. The separation of these foils after fracture suggests the interfaces were much harder than the bulk foil regions. As the total composite material deformed, the interface regions likely reached their yield point and plastically deformed before the middle of the foil. As the material continued to deform, the foils broke away from each other to continue plastically deforming.

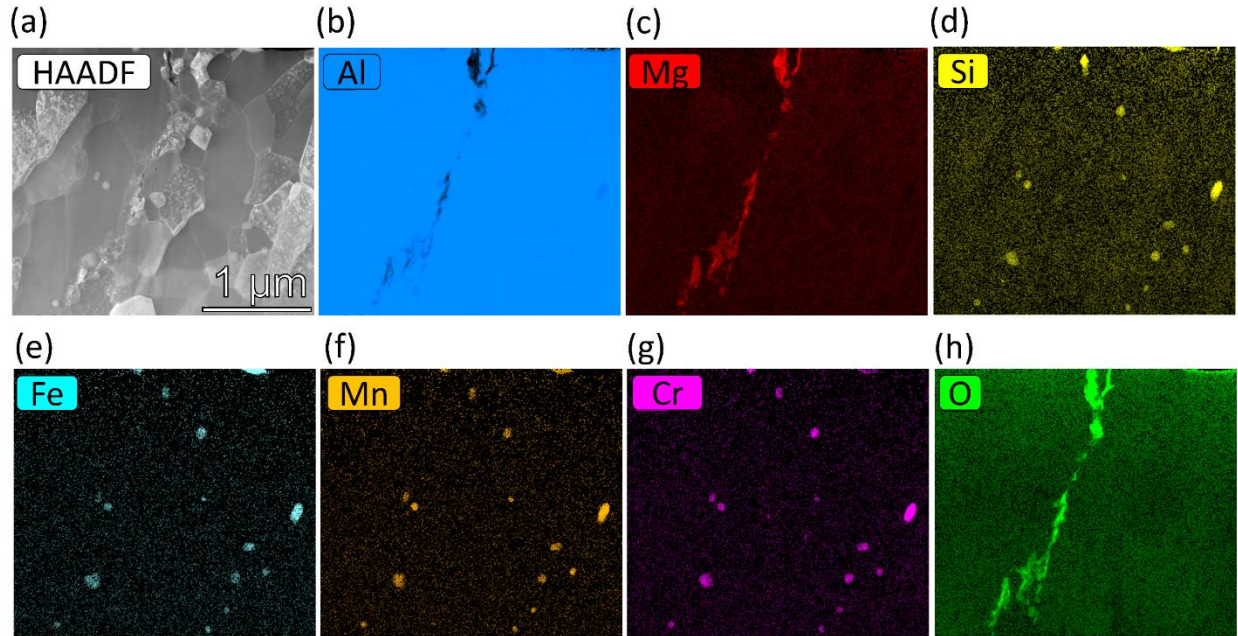


Figure 5.14: SEM/EDS map of Al 6061 T4 UAM microstructure. a) STEM HAADF image, b) EDS map of aluminum, c) EDS map of magnesium, d) EDS map of silicon, e) EDS map of iron, f) EDS map of manganese, g) EDS map of chromium, h) EDS map of oxygen

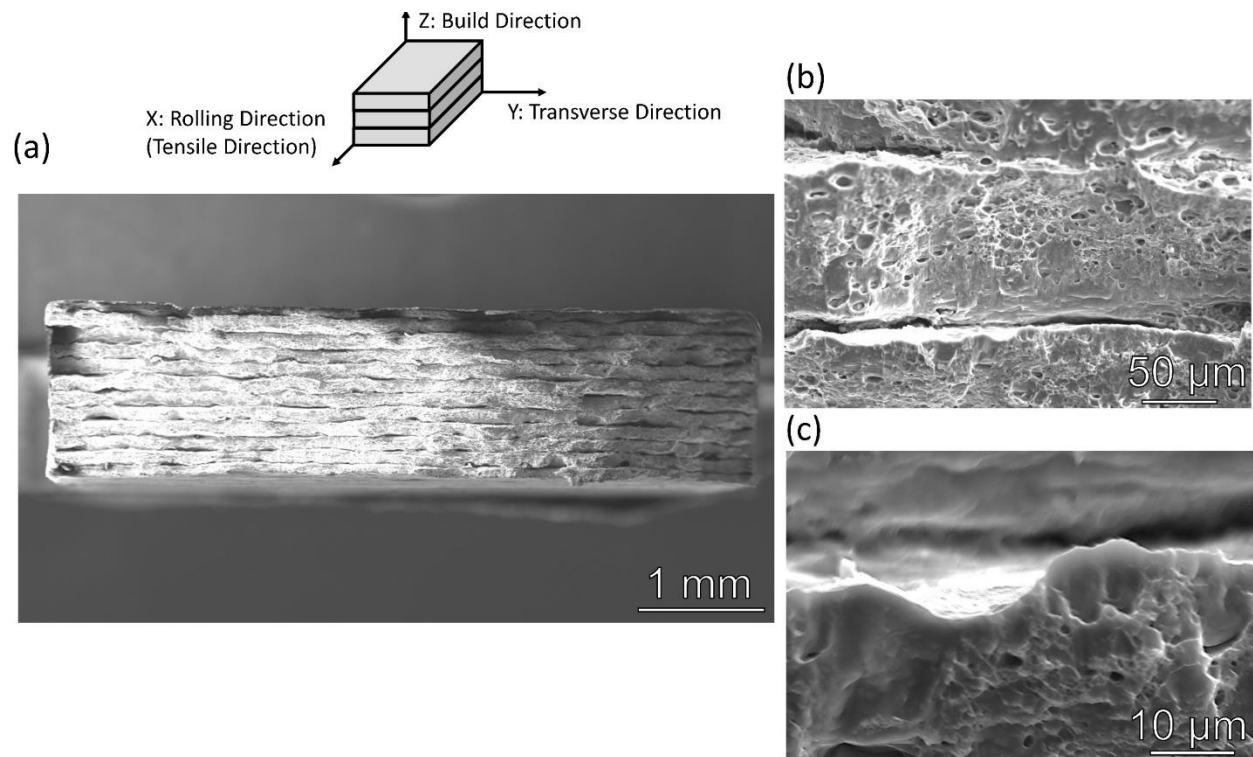


Figure 5.15: Tensile fracture surface of the T4 UAM sample. a) Overview of the entire fracture surface, b) magnification of several foils, c) further magnification of two foils and there interface

Nanoindentation

Nanoindentation was performed on the *T4 UAM* sample (Figure 5.16). The low depth nanoblitz hardness contour (Figure 5.16a) is rotated for visual aid so the top of the build is oriented on the top of the image. Like the *O UAM* interface (Figure 5.9), the *T4 UAM* interface is harder than the bulk foil regions. The normalized hardness line profile (Figure 5.16b) shows the average and standard deviation of the nanoblitz hardness values. Compared with the *O UAM* sample (Figure 5.9b) it can clearly be seen that the *T4 UAM* sample and interfaces are harder than those in the *O UAM* sample. The SEM image of the indent array (Figure 5.16c) is rotated to correspond to the hardness contour plot. From the image, the indents near the interface appear shallower than the indents further away into the bulk foil regions. Therefore, the hardness depth dependence should be addressed. Like the *O UAM* interface, the nanoindentation information from the *T4 UAM* interface demonstrates asymmetry. There is a gradual hardness increase going from the bottom foil to the interface, then a sharper hardness decrease going into the top foil. The interface width, as determined by nanoindentation, is approximately $10\ \mu\text{m} \pm 2\ \mu\text{m}$. The CSM indentations on the interface and the foil bulk region (Figure 5.16d) demonstrate that the hardness also has an indentation depth dependence. Evaluation of the hardness increase at the interface while removing the depth dependence will be discussed in the section below.

X-ray Diffraction

The diffraction from the *T4 Foil* and *T4 UAM* samples can be observed using XRD (Figure 5.17). The diffraction patterns of these samples are shown below in Figure 5.17a with the aluminum and Mg_2Si phases identified. Like the XRD results discussed above, the large sampling volume here makes distinguishing phase differences between the interface and bulk foil regions very difficult or impossible.

The diffraction broadening of the aluminum phase can be observed by focusing on a main aluminum peak. The aluminum {111} peak of the *T4 Foil* and the *T4 UAM* sample is normalized and superimposed to demonstrate the broadening between the samples (Figure 5.17b). The *T4 UAM* sample has a broader aluminum peak than the *T4 Foil* sample. This means there is more crystallographic strain in the bonded sample than in the foil sample. Additionally, the generalized mean microstrain values of the aluminum in the *T4 Foil* and *T4 UAM* sample, as calculated by Rietveld Refinement, are 1813 and 2600, respectively. This demonstrates the material's crystal lattice is in a more strained state following UAM bonding, likely due to its increased dislocation density.

5.4 Discussion

The above results have demonstrated significant changes occurred in materials following the UAM bonding process. To understand this, the microstructure evolution of the materials can be rationalized.

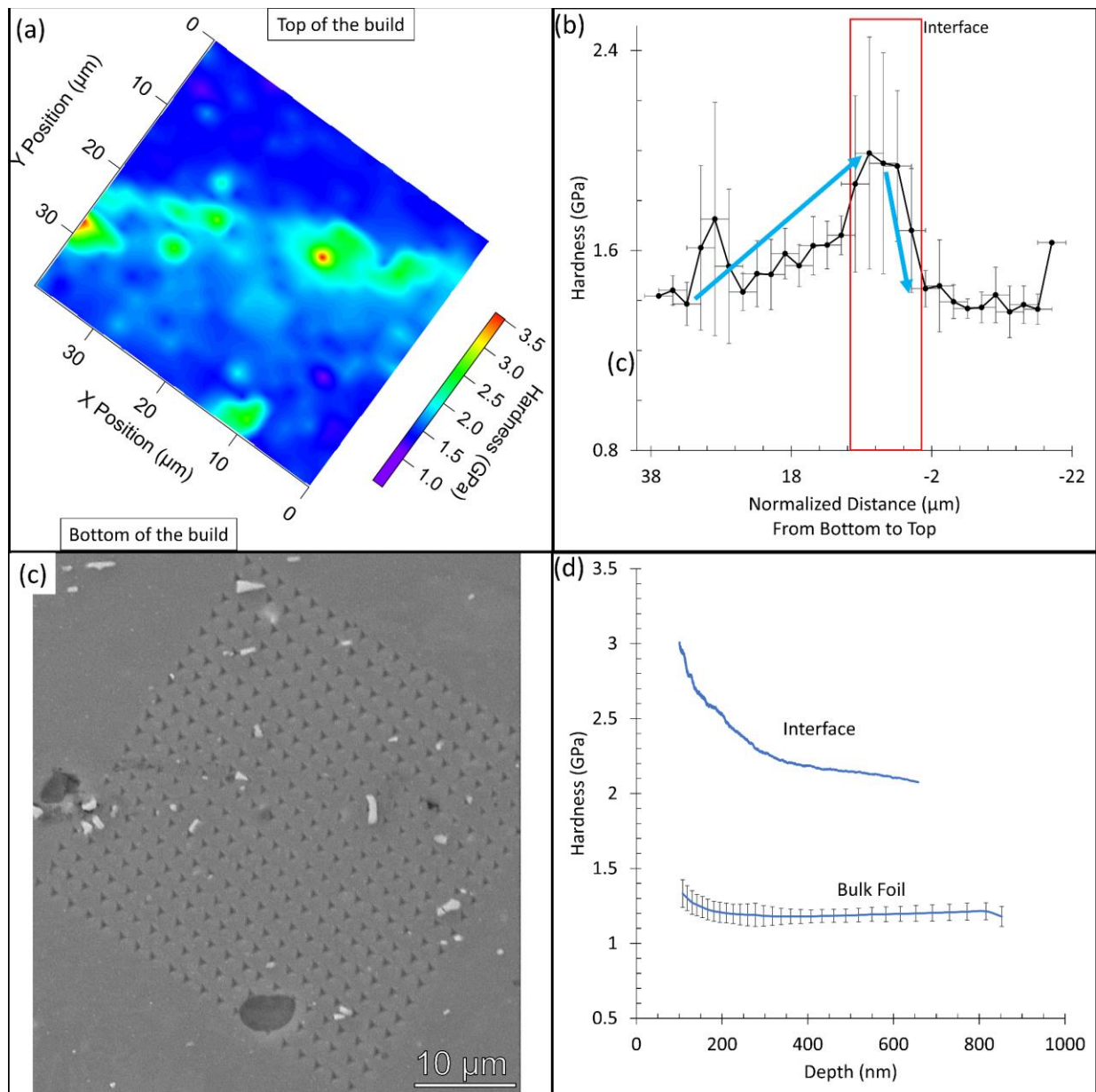
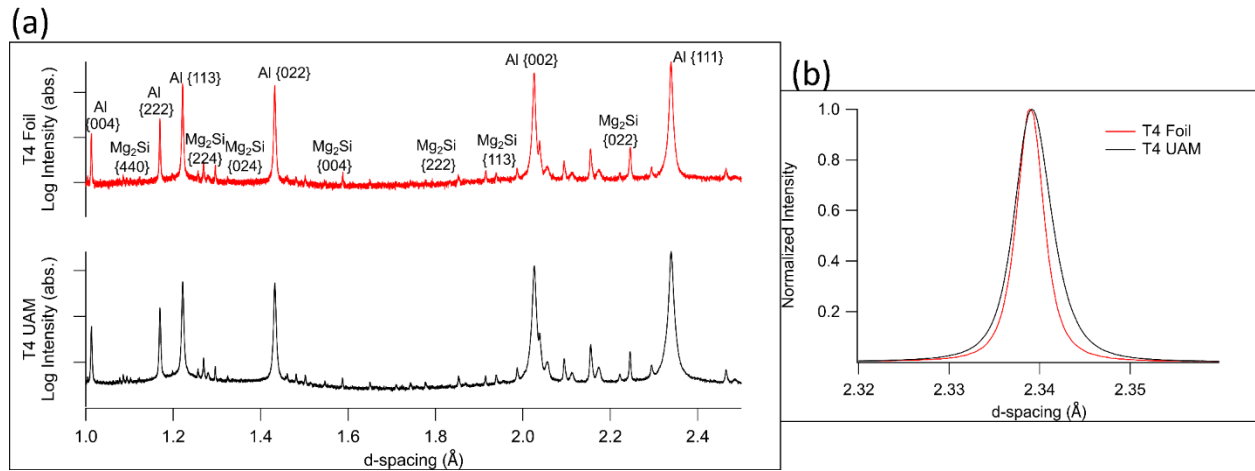


Figure 5.16. Nanoindentation hardness map of the T4 UAM build. a) Hardness map, b) Average hardness line, c) SEM image of the indent array, d) Hardness vs depth for CSM indents



5.4.1 Microstructure Evolution

As observed in the TEM images of the foil samples (Figure 5.3 & Figure 5.11), the materials before bonding have a large grain structure with tangled dislocations, likely from the rolling process to make the foils. The original *O Foil* microstructure has a dislocation cells structure ($\rho = 1.06 \times 10^{10} \text{ cm}^{-2}$) and a 0.00396 volume fraction of Mg_2Si precipitates, and the *T4 Foil* microstructure has dislocation tangles ($\rho = 1.68 \times 10^{10} \text{ cm}^{-2}$) with a 0.00148 volume fraction of Mg_2Si precipitates. After the UAM bonding process (Figure 5.5 & Figure 5.13), the bulk foil regions have relatively large grains ($\sim 600 \text{ nm}$) while the interfaces have extremely small grains ($\sim 100 \text{ nm}$). This suggests the UAM process caused significant plastic deformation to the interfaces during bonding, refining the grain structure. Despite the different starting microstructure between the two materials, the UAM plastic deformation refined the materials in a similar manner.

The STEM-EDS results (Figure 5.6 & Figure 5.14) suggest that the Mg_2Si is no longer present near the UAM interfaces. Instead, clusters of silicon are present, and the interface is enriched with magnesium. This suggests the atoms within the precipitate debonded, and the magnesium atoms diffused towards the interface. For the Al6061 alloy, the covalently bonded Mg_2Si precipitate³¹⁶, has an equilibrium solubility limit of approximately 595°C ³¹⁷. Therefore, below this solubility temperature, the magnesium and silica in the Al6061 alloy should exist in a stable Mg_2Si precipitate phase within the aluminum matrix. If the aluminum alloy is brought above this temperature and rapidly cooled, such as in the heat affected zone of TIG welding, a solid solution of solute elements can be created^{318,319}. If the material is not brought above this solubility limit, it is currently unknown how the precipitates could have dissolved. To the author's knowledge, the only other known studies of Mg_2Si precipitates dissolving at low temperature are the result of an acidic corrosive environment for several hours^{320,321}. It is hypothesized that the plastic deformation from the UAM process resulted in the dissolution of the precipitates and/or could have decreased the solubility limit.

Once the elements debonded, there was elemental diffusion of the magnesium towards the interface. To rationalize the diffusion of magnesium, traditional diffusion expressions using Fick's Laws and Brownian motion can be considered. Previous UAM studies of embedded thermocouples and thermal imaging cameras have been used to estimate thermal profiles during UAM bonding^{49,50,99,100,118,122,123}. Given the current UAM processing conditions, a peak temperature could be around 200°C , although thermodynamic calculations of aluminum UAM bonding suggest temperatures could rise up to 300°C ⁵⁵. The exact thermal profile here is difficult to determine due to the rapid nature of the UAM bonding process. Given these considerations, a peak temperature of 250°C can be assumed here, and the total thermal profile time t , including heating up and cooling down, is 0.5 seconds. Assuming the thermal profile as noted, the lattice diffusivity D of magnesium in aluminum from the Sigli et al.³²² review article is $10^{-14} \text{ cm}^2/\text{s}$.

Assuming the clusters of silicon in Figure 5.6 & Figure 5.14 are previous Mg_2Si precipitates, the distance from a silicon cluster to the magnesium enriched interface could be considered as a diffusion distance x . The diffusion distance here is approximately 1 μm . Given the estimated total bonding time of 0.5 seconds, Fick's 2nd law, $x \sim \sqrt{Dt}$, can be used to find an approximate diffusivity of the magnesium ($2 \times 10^{-8} \text{ cm}^2/\text{s}$). The experimental diffusivity here is 6 orders of magnitude larger than the diffusivity predicted from the thermal profile. Clearly thermal diffusion cannot describe the observed atomic motion and additional diffusion processes are present.

As Pagan et al.⁶⁵ suggested, accelerated diffusion could be possible at UAM interfaces from enhanced point defect vacancy concentrations caused by the severe plastic deformation. To calculate the enhanced vacancy concentration present, Brownian motion diffusion can be considered, as shown in Equation 5.1. Here a_0 is the lattice constant, X_v is the vacancy concentration, ν is the Debye frequency of the atomic vibrations on its lattice site, E_m is the vacancy migration energy (0.61 eV in Al¹⁷⁰), k is the Boltzmann constant ($8.617 \times 10^{-5} \text{ eV/K}$), and T is the absolute temperature^{146,147,149,150,323}.

$$D = a_0^2 X_v \nu \cdot \exp\left(-\frac{E_m}{kT}\right) \quad \text{Equation 5.1}$$

To rationalize the observed elemental diffusion, vacancy concentrations can be calculated at the UAM interface assuming the thermal profile, as noted above. These can be compared with the solubility limit temperature of the Mg_2Si precipitate and the thermal equilibrium concentration of vacancies (

Table 5.2). Clearly a significantly large concentration of vacancies must have been created from the plastic deformation from the UAM process. The plastic deformation and enhanced vacancy concentration could have also decreased the solubility limit of the Mg_2Si precipitate resulting in the precipitate dissolving.

Although the bonding temperature could be higher than indicated, which would decrease the vacancy concentration, other short circuit diffusion pathways may also be occurring. The UAM process is known to cause dynamic recrystallization at the interfaces^{46,87,94,97}. Recrystallization occurs as large plastic strains deform the crystals until they reorient into new lower energy crystals. The recrystallized grains are often separated by high angle grain boundaries (misorientation $> 15^\circ$)¹⁸⁹ which sweep across the material during the recrystallization event, sometimes more than once. Several UAM studies investigating grain boundary refinement have found a significant increase in the concentration of high angle grain boundaries at interfaces, and more high angle grain boundaries are observed during higher energy UAM^{99,187}. In the present study, the high angle grain boundaries could provide additional diffusion pathways for the magnesium to travel. Finally, as noted in the x-ray diffraction results, high dislocation densities could be in the samples. Pipe diffusion through dislocation cores could also occur during UAM bonding. This would accelerate the migration of magnesium atoms.

Table 5.2. Vacancy Concentrations

Temperature (°C)	X_v (Thermal Equilibrium)	X_v (UAM interface)
250	6.0×10^{-7}	2.3×10^{-1}
595	1.6×10^{-4}	1.5×10^{-3}

Following from the enhanced diffusion, likely through elevated vacancy concentrations, other TEM features along the *O UAM* and *T4 UAM* interfaces can be explored. There appear to be holes in the samples along grain boundaries and in the middle of grains directly at the interfaces. These could be holes due to TEM sample preparation using FIB, although they are only present at the interfaces. It is also possible these features could be vacancy clusters or voids related to the enhanced vacancy concentrations. The hypothesized UAM bonding temperature is 250°C. The onset temperature for vacancy migration (stage III recovery) has been thoroughly reviewed in most metals using isochronal annealing following particle irradiations, and the accepted value in aluminum is -73°C¹⁶⁹. Above this temperature, mono-vacancies become mobile and can coalesce into vacancy clusters. Therefore, it is reasonable to assume that the enhanced concentration of mono-vacancies (which accelerated the magnesium diffusion) also resulted in monovacancies coalescing into visible vacancy clusters.

The next fundamental question to ask is: why was there preferential enhanced diffusion for magnesium atoms? This can be addressed by considering the free energy of the components in the UAM materials. An Ellingham diagram of the free energy of Mg₂Si, SiO₂, Al₂O₃, and MgO can illustrate their potential of formation (Figure 5.18). These free energies were calculated assuming a free gas environment, as opposed to precipitates inside an aluminum matrix. Therefore, these values only approximately represent the formation of these species withing a reasonable margin of error.

In Ellingham diagrams, the standard reference state of an element is calculated as it reacts to form a potential compound (e.g., oxide, carbide, nitride, or intermetallic). The Gibbs free energy of formation for an element in its reference state is zero. Therefore, if an element has an affinity to form a compound, this will result in a decrease in the overall free energy of the system. When comparing multiple reactions, the component with the largest decrease in Gibbs free energy will be the most likely to form³²⁴. Considering the Ellingham diagram, the MgO compound has the greatest reactivity. This suggests that once the magnesium separated from silica, the MgO could be preferentially formed. Although Ellingham diagrams do not provide guidance for reaction kinetics, the thermodynamic calculations demonstrate the feasibility of the magnesium and oxygen that are observed at the interface. Since the diffusivity of magnesium and silica in an aluminum matrix are approximately equivalent,³²² the kinetic process for preferable atomic movement of magnesium over silica is currently unknown. The potential dissolution and diffusion of precipitate atoms during UAM should be considered by future researchers.

5.4.1 Evaluation of Strengthening

The strength of the Al 6061 material is due to several factors in the bulk foil regions and at the foil-foil interfaces. As noted from the EDS analysis, the Mg₂Si precipitates are present everywhere except the interfaces.

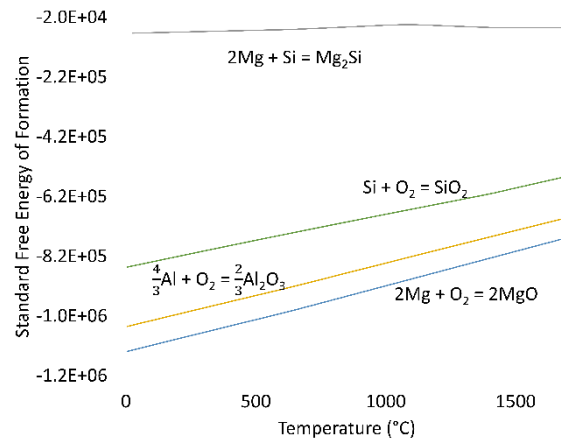


Figure 5.18 Ellingham diagram

Since these precipitates are several hundred nanometers in diameter, strengthening would occur as mobile dislocations bow around the precipitates, as opposed to shearing them. The classical approach for dislocation bowing strength¹⁰² can be used here:

$$\Delta\sigma_{\text{bowing}} = \frac{MGb}{2r\left[\frac{6}{\pi}v_f^{-1/3} - 1\right]}, \text{ where } M \text{ is the Taylor factor } (\sim 3.06 \text{ for equiaxed FCC and BCC}$$

materials), G is the shear modulus, b is the magnitude of the Burgers vector of the gliding dislocation, r is the radius of the precipitate, and v_f is the volume fraction of the precipitates in the matrix. Considering the observed size and spacing of the Mg_2Si precipitates, the dislocation bowing strengths would be approximately 27.8 MPa and 15.6 MPa in the *O UAM* bulk foil region and the *T4 UAM* bulk foil region, respectively.

Additionally, the materials contained a significant dislocation density. Strain hardening can occur in materials as dislocation tangles interact with each other. This Frank-Read dislocation interaction can result in strain hardening and dislocation multiplication. The traditional equation for dislocation strain hardening¹⁰² is $\Delta\sigma_{SH} = M\alpha Gb\sqrt{\rho}$, where M is the Taylor Factor, α is approximately 0.1, G is the shear modulus, b is the magnitude of the mobile dislocation burgers vector, and ρ is the dislocation density. Using the dislocation density determined previously, the strain hardening prior to UAM bonding could be 23.4 MPa and 29.5 MPa for the *O UAM* and the *T4 UAM* bulk foil regions, respectively. These are approximately equivalent within experimental error. As noted from the x-ray diffraction data, the lattice strain increased after the UAM bonding, which could increase the strain hardening at the interfaces further. The utilization of the potential increase in strain hardening will be discussed further in the proceeding section.

At the foil-foil interfaces, the grain sizes became significantly smaller. Hall²³⁴ and Petch²³⁵ described yield strength increase $\Delta\sigma_{HP}$ from smaller grains d as a result from dislocations that pile up against grain boundaries. The specific material strength of a grain boundary to dislocations, k_y , has been thoroughly studied and is shown in the Cordero et al. review article²³⁶. The commonly accepted k_y value for aluminum is 90 MPa $\mu\text{m}^{1/2}$ ^{325–327}. This allows for the Hall-Petch equation, $\Delta\sigma_{HP} = k_y d^{-1/2}$ to be used to rationalize the increased strength near the bonded interfaces from the reduced grain sizes, as determined earlier. For the *O UAM* condition, the grain boundary strength at the interface would be 283 MPa, while the grain boundary strength in the bulk foil region would be 114 MPa. Therefore, the *O UAM* strength increase attributable to reduced grains sizes at the interface is 169 MPa. In a similar manner, the *T4 UAM* grain boundary strength at the interface is 254 MPa, while the grain boundary strength in the bulk foil region is 115 MPa. Therefore, the *T4 UAM* yield strength increase from reduced grain sizes at the interface is 139 MPa. The grain boundary strengthening at the interfaces of the *O UAM* sample and the *T4 UAM* sample are nearly equivalent within experimental error.

The vacancy clusters at the UAM interfaces could also contribute to strengthening. As migrating dislocations interact with vacancy clusters, they interact with the elastic strain field created by the clusters. The strain field from the empty lattice space is due to the volumetric dilation from the surrounding atoms. This strain field is proportional to the

concentration of vacancy defects ^{272,275,328,329}. For large clusters acting as strong dislocation obstacles, the dispersed barrier Seeger model ²⁷² can be used, $\Delta\sigma_{Seeger} = M\alpha\mu b\sqrt{Nd}$, in which M is the Taylor factor, α is the defect cluster barrier strength which depends on the size of the voids (~ 1.0 for the present voids²⁷⁸), μ is the shear modulus, and b is the magnitude of the Burgers vector of the gliding dislocation, N is the cluster density, and d is the clusters size. Another potential model for describing the hardening from vacancy clusters is the weak barrier Friedel-Kroupa-Hirsch (FKH) model ^{273,274}, in which the strength is proportional to $dN^{2/3}$. An estimate of the vacancy clusters size from the TEM images could be 10 nm for both the *O* UAM interface and the *T4* UAM interface. The cluster density, within the radius of the low-depth indentation plastic zone field, could be $9.1 \times 10^{14} \text{ cm}^{-3}$ for the *O* UAM interface and $2.3 \times 10^{14} \text{ cm}^{-3}$ for the *T4* UAM interface. Using the Seeger strengthening model, this results in a strength increase of 69 MPa for the *O* UAM interface and a strength increase of 34 MPa for the *T4* UAM interface. Finally, it should be noted that the voids observed could have originated from vacancy clusters and been further expanded due to FIB damage. Therefore, the cluster sizes and strengths should be considered as upper limits rather than exact values. Additionally, it is possible that with large fractions of voids or cavities, mechanical softening can occur as opposed to hardening ³³⁰. For voids well beyond ten nanometers in size, softening has been attributed to the annihilation of dislocations as the large cavities act as dislocation sinks rather than dislocation obstacles ³³¹.

Studies of UAM bonded Al 3003 H-18 ⁴⁶ and Al 6061 H-18 ²¹¹ observed a decrease in bulk tensile strength, not an increase. How can we understand these differences? Sojiphan ⁹⁷ hypothesized that UAM materials can be considered as a function of the overall stored energy. A cold rolled material (H-18 condition) has a higher initial energy state than an annealed material. This is due to the work hardening, grain deformation, and dislocation network created from cold rolling. If a cold rolled material is annealed, the stored energy will decrease as static recrystallization occurs. Alternatively, if a low energy annealed material is hot worked, the stored energy will increase due to the deformation process.

Sojiphan hypothesized that UAM structures are the result of the combination of dynamic recrystallization and dynamic recovery. A material will decrease in stored energy when static recrystallization dominates during bonding, while a material will increase in stored energy if dynamic recrystallization and dynamic recovery through adiabatic heating dominate during bonding. This causes recrystallization to not occur as fast, and the material ends up in a lower energy state ⁹⁷. A similar mechanism could be occurring in this present study. It is hypothesized that the tempered and annealed materials were in a low energy state prior to UAM bonding. After bonding, dynamic recrystallization occurred along with dynamic recovery and adiabatic heating. This hypothesis could also be connected to the microstructure features observed. The initial foils had intricate dislocation tangles and cell structures. After bonding, the foil bulk regions had relatively large grain structures without the dislocation cell wall structures. Additionally, the region with refined grain sizes is very small ($< 1 \text{ }\mu\text{m}$) compared to the width of other UAM interfaces with grain refinement (10s of μm) ^{45,55,57,63,88,89,94,95,122}. This could indicate that

dynamic recrystallization was limited while dynamic recovery and adiabatic heating occurred. The annealed and tempered materials increased their energy state from the UAM bonding. This resulted in the observed microstructural changes and the increased tensile strength.

The nanoindentation data (Figure 5.9 & Figure 5.16) demonstrates the *O UAM* and *T4 UAM* interfaces were harder than the bulk foil materials, although the indent depths were also different. Since there is a depth dependence to nanoindentation hardness, the indentation size effect must be considered. The indentation size effect refers to when shallow depth nanoindentation values are larger than bulk hardness values as determined using traditional indentation techniques^{218–224}. The Nix-Gao technique²²⁵ is the most popular method to obtain estimates for bulk equivalent hardness from depth-dependent hardness data. Although it has received criticism^{226–229}, it is currently the

best available method that can guide us. The Nix-Gao equation $\frac{H}{H_0} = \sqrt{1 + \frac{h^*}{h}}$ calculates the bulk equivalent hardness H_0 and the characteristic size effect length scale h^* using the hardness values H at their respective depths h ²²⁵. When the hardness squared is plotted against the reciprocal of depth, the intercept of the line created is H_0^2 and the slope is related to h^* . The Nix-Gao hardness plots using the CSM indentation technique of the bulk foil region and the interface for the *O UAM* and *T4 UAM* samples are shown in Figure 5.19a. The bulk equivalent hardness of the *O UAM* sample in the bulk foil is 0.89 GPa with a h^* length parameter of 66.4 nm, while the interface has an equivalent hardness of 1.62 GPa and h^* of 279 nm. The bulk equivalent hardness of the *T4 UAM* sample in the bulk foil is 1.16 GPa with h^* of 32.7 nm, and the interface has an equivalent hardness of 1.85 GPa with h^* of 549 nm. By comparing the bulk equivalent hardness for the bulk foil to the interface (Figure 5.19b), clearly the interfaces are harder for both samples. Although the UAM interfaces have a hardness increase using depth dependent hardness measurements, the Nix-Gao approximation demonstrates that the interfaces have a non-depth dependent hardness increase. This can be used for more accurate determination of the interface strengthening characteristics.

The Tabor relationship $H \sim 3\sigma_y$ ^{217,230,231} is commonly used to compare the traditional Vickers hardness to yield strength. Zhu et al.²³² recently demonstrated the Tabor relationship does not consider indentation surface pileup effects and could overestimate the yield strength determined from nanoindentation. Therefore, a more advanced model for comparing the Nix-Gao bulk equivalent hardness to nanoindentation yield strength is $\sigma_y^{NI} = 0.285H_0$. For the *O UAM* sample, the nanoindentation yield strength is 0.254 GPa in the bulk foil and 0.462 at the interface. The *T4 UAM* sample has a nanoindentation yield strength of 0.331 GPa in the bulk foil and 0.527 GPa at the interface.

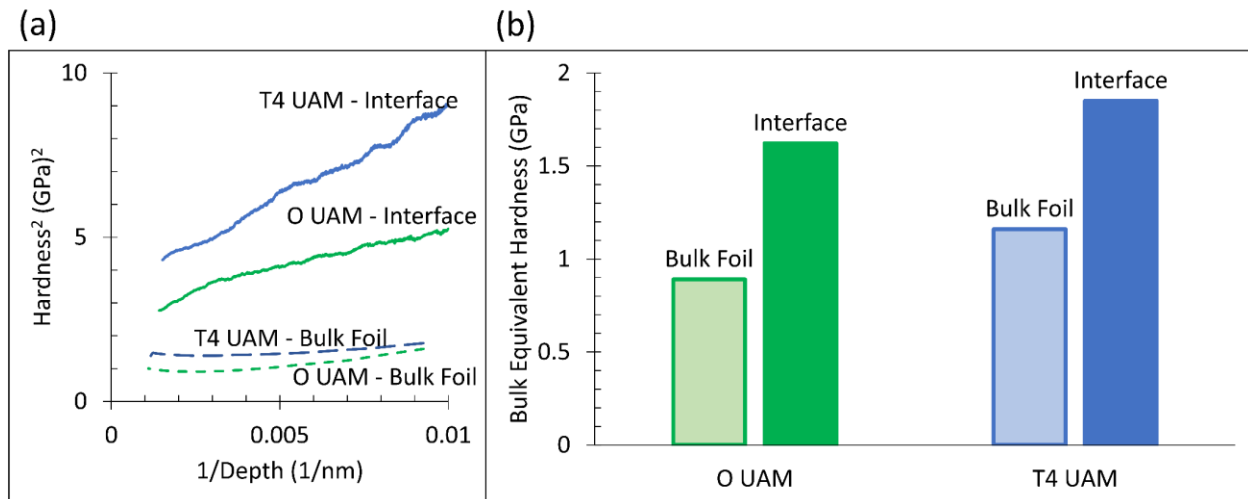


Figure 5.19. Analysis of indentation hardness increase. a) Nix-Gao relationship for the O UAM and T4 UAM conditions, b) Bulk equivalent hardness values in the bulk foil interior and at the interfaces.

5.4.1 Composite Model of Hardening

As described previously, the UAM process resulted in a complex microstructure evolution and an array of various dislocation obstacles. Tensile testing from the UAM build occurred with a load applied parallel to the foil-foil interface. This is a classic iso-strain condition (Voigt condition) as described by Courtney³³² and illustrated below (Figure 5.20). Since the tensile axis is parallel to the interface axis, the total stress exerted on the material σ_c is the sum of the forces experienced by each of the material sections (σ_{foil} and $\sigma_{interface}$) multiplied by their relative volume fraction (V_{foil} and $V_{interface}$)³³² $\sigma_c = \sigma_{foil}V_{foil} + \sigma_{interface}V_{interface}$.

As determined by the STEM-EDS analysis, the bulk foil region is strengthened by dislocation bowing and dislocation forest interactions. The STEM and XRD analysis demonstrate that the interfaces have dislocation obstacles of reduced grain sizes, vacancy clusters, and increased lattice strain, likely from elevated dislocation densities. Since these microstructure obstacles are considered long-range dislocation obstacles with comparable strengths, it is appropriate to combine them at each location using a root mean square superposition approach^{102,279,280}. The overall UAM build can be described as a composite structure using a combination of the microstructure features

$$\text{at the various locations: } \sigma_{UAM} = \sqrt{(\sigma_{SH})^2 + (\sigma_{bowing})^2} V_{foil} + \sqrt{(\sigma_{HP})^2 + (\sigma_{seeger})^2 + (\sigma_{SH})^2} V_{interface}$$

The strengthening contribution at the interface from grain boundaries is much larger than contributions from vacancy clusters or additional dislocation densities. Using the upper limit approximation of vacancy cluster strengthening, the contribution would be less than 8% of the composite strength. Although cluster strengthening values were calculated earlier, it should be repeated that these values represent liberal maximums since FIB damage could have exaggerated their size. Therefore, their potential contribution to the overall strengthening should be considered as near the maximum limit. In a similar manner, considering if the dislocation density at the interface reached as high as 10^{12} cm^{-2} (the maximum achievable limit), the contribution from Frank-Read type interactions could contribute less than 4% to the overall strengthening. Since these two dislocation obstacles provide negligible contributions to the strengthening, they can be safely ignored in this present analysis. Therefore, the composite strengthening

equation can be considered as: $\sigma_{UAM} = \sqrt{(\sigma_{SH})^2 + (\sigma_{bowing})^2} V_{foil} + \sigma_{HP} * V_{interface}$. If an estimate of the volume fraction of the interfaces to the volume fraction of the foil were determined by the ratio of the width of the refined grains at the interfaces to the width of the bonded foils, the volume fraction of the foil would be 99% and the interfaces would be 1%. Using the previous calculations of strain hardening, dislocation bowing, and Hall-Petch strength, the σ_{UAM} is approximately 37.6 MPa for the *O* UAM sample and 34.4 for the *T4* UAM sample. These calculations would signify that the interface has negligible contributions to the overall strength of the material.

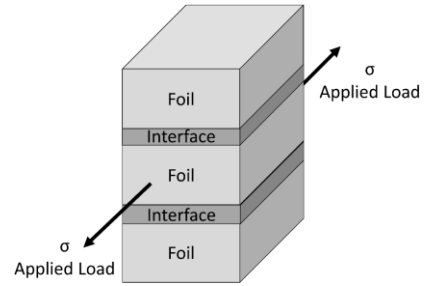


Figure 5.20. Voigt iso-strain condition of the foils and interface

This is not the case, and it contradicts the previous experimental results. The interfaces became harder than the bulk material and they significantly increased the strength of the overall composite material. Instead, the Voigt model estimates the interfaces are only a small component of the composite strength.

The Voigt model also does not capture if the interface and foil regions enter plastic deformation at different applied displacements. As shown from the tensile testing results, the foils have a lower yield strength than the built structure. Therefore, if the built structure is a composite of the foil regions and the interfaces, it is likely that the foil regions reached their yield strength and began plastic deformation prior to the interfaces reaching their yield point. This is also supported by the differences in the bulk equivalent hardness values of the interfaces and bulk foil regions. During tensile testing, there is a simultaneous combination of elastic and plastic deformation in the interfaces and foil regions. This is a non-trivial consideration that the Voigt model cannot predict. This could have contributed to the strength differences found between the tensile testing and the composite model. Finally, it should be noted that some of the microstructure analysis was performed using high magnification characterization techniques. Variations in the microstructure could exist at different spatial locations that were not captured here.

5.5 Summary and Conclusion

Microstructure evolution and strengthening effects from Ultrasonic Additive Manufacturing were evaluated here. Al 6061 was pre-treated into the annealed *O* and tempered *T4* conditions, then after UAM bonding, tensile testing (in the rolling, *x*-direction) revealed the bonded material became significantly stronger. Characterization was performed on multi-length scales including sub-size tensile testing, nanoindentation, x-ray diffraction, scanning electron microscopy, transmission electron microscopy, and energy dispersive spectroscopy.

The characterization revealed that the foil-foil interfaces of the bonded materials became stronger than the bulk foil regions. Significant crystal lattice changes occurred at the interface regions that dominantly contributed to the overall strengthening. This includes an increase in aluminum lattice strain, Mg_2Si precipitates dissolving, creation of point defect vacancies, enhanced diffusion of magnesium atoms, mono-vacancies coalescing into vacancy clusters, and refinement of grain sizes. These microstructure changes occurred because of dynamic recrystallization, dynamic recovery, and adiabatic heating of the material. By UAM bonding of annealed and tempered aluminum materials, the lower stored energy state material was increased, which resulted in increased strength and the microstructure changes.

5.6 Acknowledgements

Preconditioning of the aluminum was performed at Ohio State University (OSU). The UAM bonding, tensile testing, and transmission electron microscopy (TEM) was also performed at OSU. Scanning electron microscopy (SEM) and TEM preparation using Focused Ion Beam (FIB) machining was performed at University of Tennessee, Knoxville (UTK) Institute for Advanced Materials and Manufacturing (IAMM). Nanoindentation was performed in collaboration with Jennifer Hay at KLA-Tencor. Use of the Advanced Photon Source at Argonne National Laboratory was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. The funding for this research was supplied from the Air Force National Laboratory under contract FA864920P0998. Work at the Oak Ridge National Laboratory Manufacturing Demonstration Facility was supported by the DOE Office of Energy Efficiency And Renewable Energy (EERE) Advanced Manufacturing Offices (AMO).

CHAPTER 6

**PHASE TRANSFORMATION IN
HEXAGONAL CLOSED PACKED
MATERIALS DURING ULTRASONIC
ADDITIVE MANUFACTURING**

Abstract

This paper reports evidence for phase transformations of hexagonal closed packed materials during the high strain rate ($\sim 10^5 \text{ s}^{-1}$) plastic deformation ultrasonic additive manufacturing (UAM) process. The phase transformations, captured by X-ray diffraction, electron backscatter diffraction, and convergent beam electron microscopy, are rationalized due to the strain induced phase transformation created by UAM and the introduction of elements, observed by energy dispersive X-ray spectroscopy, that can stabilize a body centered cubic structure. The elements are introduced through non-equilibrium point defect vacancy concentrations, which accelerates interdiffusion of elements. The physics described here is also used to design interlayers and surface modifications, which are experimentally shown to improve the bonding of difficult to weld materials.

6.1 Introduction

This work is motivated by the unique microstructure development that was observed following UAM bonding of titanium. To the author's knowledge, these are the first reported results of bonding titanium during ultrasonic additive manufacturing (UAM). Since a thorough review of UAM has been provided earlier, (Chapter 2.3) only a brief description will be described below as it relates to the current study.

A majority of UAM studies have focused on low strength FCC materials, such as aluminum, copper, and nickel, due to limitations of UAM bonding^{45,55,63,97,98,186}. The recent introduction of higher power UAM machines has allowed the bonding of more difficult to weld metals^{56,133,211,333} using several advances including a Stellite coated sonotrode (Figure 6.1), although there have been only a few successful trials of bonding HCP materials. Sridharan et al.⁶² and Wolcott et al.⁵⁹ demonstrated successful bonding of titanium-aluminum bi-layers. Using electron backscatter diffraction (EBSD), the authors concluded that the aluminum (FCC crystal structure) exhibited significant grain refinement and texture evolution while the titanium (HCP crystal structure) resisted plastic deformation.

Successful UAM bonding of HCP zirconium was shown by Massey et al.⁶⁸. Significant foil tearing was observed and an α/β titanium alloy was used to mitigate this. UAM bonding of zirconium resulted in grain refinement and shear twinning near the UAM interfaces. Using shear texture evaluation, the authors suggested that during bonding, the material reached at least 400°C. Titanium enrichment (from the buffer layer) was also observed at the interface, suggesting that mechanically driven elemental mixing occurred between the zirconium and titanium.

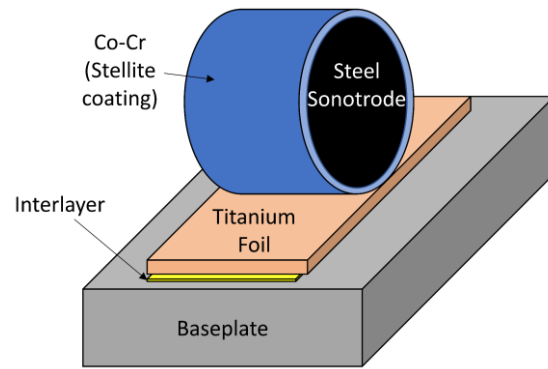


Figure 6.1. Schematic of UAM Bonding Process

An analogous study of ultrasonic spot welding of titanium could also provide context. Mukhametgalina et al.³³⁴ observed significant grain refinement at titanium interfaces, and the authors suspected that a reversible $\alpha \rightarrow \beta \rightarrow \alpha$ phase transformation occurred. During the severe plastic deformation, α grains transformed to β grains, and flowed into the gaps at the interfaces due to their lower flow stress. As the temperature decreased after welding, β grains transformed back into α . The authors suspected a large concentration of lattice defects were created during bonding, which resulted in the observations. To date there have been very few experimental studies of UAM bonding of HCP materials. This current research demonstrates the first known example of UAM bonding HCP titanium. Successful solid-state UAM bonding of titanium has a wide range of industrial applications due to its high strength, low density, and excellent corrosion properties³³⁵. Furthermore, understanding bonding through the severe plastic deformation of HCP materials offers a wide range of potential applications.

6.2 Experimental Procedure

Foils (~ 150 μm thick) of grade 2, commercially pure (CP), titanium foils and grade 5 titanium, Ti-6Al-4V, foils were welded to a Ti-6Al-4V baseplate. These foils were welded directly to the baseplate, and to improve UAM bonding, Ti-6Al-4V foils were also bonded to the baseplate while placing a thin (~25 μm) aluminum (Al 1100) interlayer foil or pure vanadium interlayer foil between the titanium and the material beneath. An alternate method of UAM bonding improvement was performed by sputtering (~200 nm) vanadium onto the surface of a CP Ti foil prior to bonding. Sputtering was performed by placing a CP Ti foil in an AJA ATC 2000 sputtering system. The system was at a base pressure of $\sim 3 \times 10^{-7}$ Torr with a sputtering pressure of 5 mTorr Ar. The sample was rotated while vanadium was sputtered onto the sample for one hour at 200 watts.

UAM bonding was performed on the titanium foils, and when the titanium had an interlayer or surface treatment, the sample was oriented so that surface mated with the material beneath. A schematic of this welding orientation is shown in Figure 6.1. UAM bonding of the titanium, with and without interlayers, used a normal force of 8500 N, amplitude of 34.7 μm , and a speed of 50 inch/min using a Stellite-coated sonotrode horn. UAM bonding of titanium with a sputtered vanadium surface used a normal force of 9000 N, amplitude of 39.9 μm , and a speed of 50 inch/min with a Stellite-coated sonotrode horn.

Samples were cold mounted and mechanically polished down to a 0.05 μm surface finish using standard metallography procedures. Electron microscopy for imaging and energy dispersive spectroscopy (EDS) used a field emission Zeiss Gemini 450 with an acceleration voltage of 15 kV and a current of 20 nA. The EDS analysis used the semi-quantitative ZAF correction technique. Electron backscatter diffraction (EBSD) was performed on a field emission Zeiss Crossbeam 550 using an acceleration voltage of 25 kV and a current of 10 nA. Extreme care was observed to collect EDS and EBSD information on the same viewing region of a given sample. Lab x-ray diffraction was performed using a Panalytical Empyrean diffractometer with a copper x-ray source.

Rietveld Refinement was performed using GSAS-II software. Preparation for transmission electron microscopy (TEM) was performed using a focused ion beam FEI Quanta 3D 200i with a gallium ion source. The sample was thinned progressively down to 5kV with 48pA. Transmission electron microscopy was performed on a 200 kV field emission Zeiss Libra MC, and convergent beam electron diffraction was performed using a 5 μm condenser aperture with a 240 mm camera length.

6.3 Results

6.3.1 Initial Materials Prior to UAM

6.3.1.1 CP Ti Foil Before UAM

The commercially pure (CP) titanium foil was analyzed prior to ultrasonic additive manufacturing (UAM) to provide a baseline of comparison. CP Ti is often sold in different grades ranging from 1 to 4, depending on the levels of impurities including oxygen and iron³³⁵. For example, grade 4 CP Ti can have an oxygen concentration of 0.4 wt.%, iron concentration of 0.5 wt.%, and exhibit yield strength, σ_y (stress at 0.2% plastic strain) of 480 MPa. In contrast, grade 1 CP Ti can have low impurity concentration (<0.18 wt.% O and <0.20 wt.% Fe) leading to soft foils with σ_y of 170 MPa. The CP Ti used here is grade 2 (<0.25 wt.% O, <0.30 wt.% Fe, σ_y of 275 MPa). Using grade 2 CP Ti, the phase transformation temperatures can be calculated using Thermo-calc[®] software²⁹⁰. The calculations (Figure 6.2) show that the CP Ti transforms from hexagonal closed packed (HCP) crystal (also referred as α -phase) structure to body centered cubic (BCC) crystal structure (also referred as β -phase) at $\sim 944^\circ\text{C}$ and to liquid above 1694°C . Therefore, at room temperature, we expect 100% HCP in CP Ti alloys with a small amount of BCC. However, the BCC phase will only be stable if the iron is allowed to partition during normal β to α transformation conditions.

Experimental analysis was performed on the grade 2 CP Ti (Figure 6.3). Figure 6.3a is the scanning electron microscopy (SEM) image of the foil, Figure 6.3b is the band contrast, and Figure 6.3c is the inverse pole figure (IPF) of the α phase. Electron backscatter diffraction (EBSD) analysis demonstrates a uniform and random orientation of grains. Clearly the α phase is the only phase present, which the thermodynamic equilibrium calculations also predict. Additionally, on the top of the foil, a small twin feature in the 0001 orientation is present along the original rolling direction of the foil. The chemical composition of the foil was examined using energy dispersive spectroscopy (EDS) (Figure 6.3d). The titanium X-rays are the only distinguishable peaks. This also confirms that within the limits of detection, the CP Ti used in this study is pure and free from other elements. The common casting impurity elements present in grade 2 CP Ti, such as iron, could still exist in the material, although they would be below the detectable limit in SEM-EDS techniques.

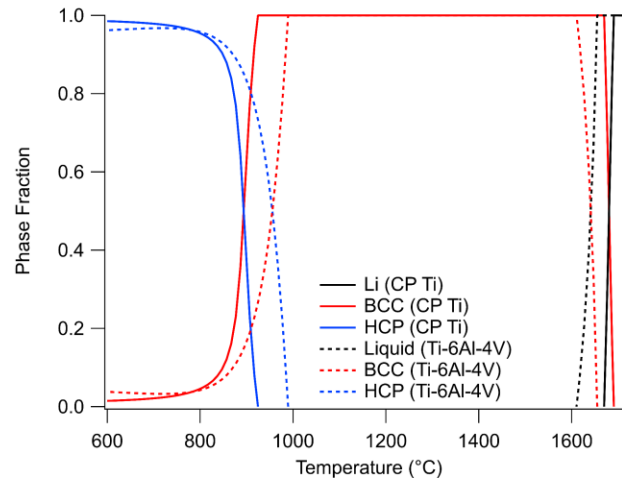


Figure 6.2. Simulated Phase Fractions of CP Ti and Ti-6Al-4V versus temperature

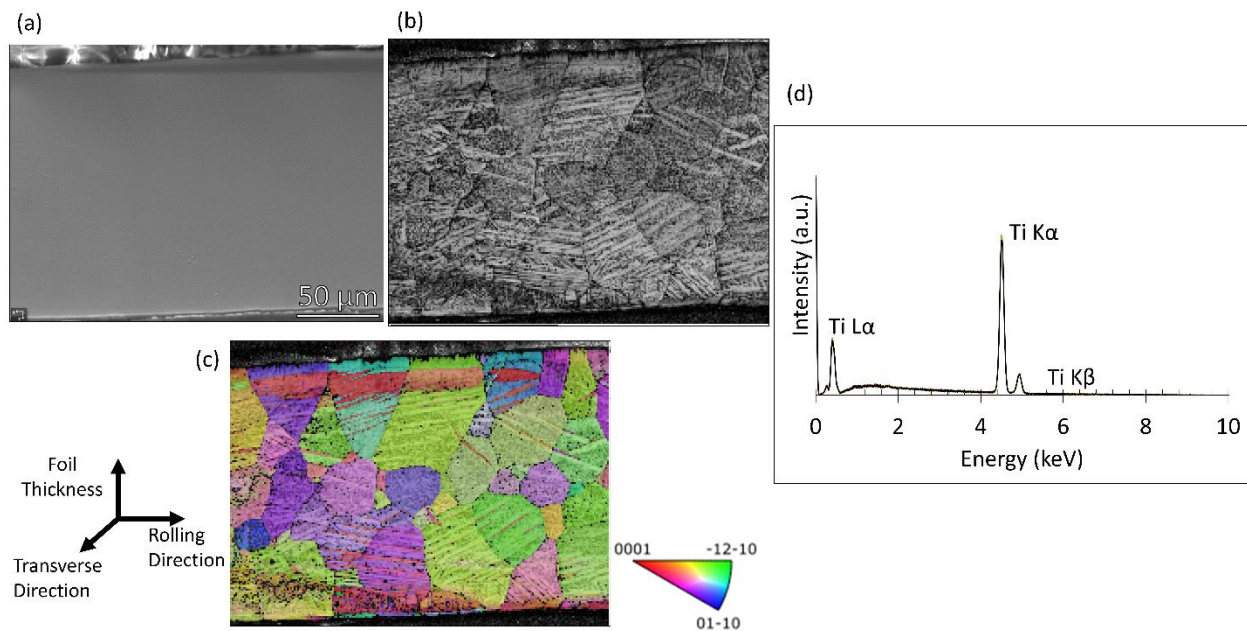


Figure 6.3. As-Received CP Ti Foil. a) SE image, b) Band Contrast, c) Ti HCP-IPF, d) EDS Spectrum

6.3.1.2 Ti-6Al-4V Foil Before UAM

The Ti-6Al-4V foil was also characterized prior to bonding for comparison. Thermocalc® calculations (Figure 6.2) demonstrate that in the Ti-6Al-4V material the α phase is dominant, although a small percent of β phase could also be present. The T_β point is slightly higher than in the CP Ti material. Experimental characterization of the as-received Ti-6Al-4V foil (Figure 6.4) indicates similar results to those above. The SEM image (Figure 6.4a) demonstrates that the foil is uniform. The EBSD analysis shows uniform band contrast throughout the foil (Figure 6.4b). The IPF of the α phase and the β phase are shown in Figure 6.4c & d, respectively. These calculations suggest 99% of the foil has the α phase. EDS characterization of the foil, shown with the EDS spectrum (Figure 6.4e), calculates that the foil is 92 wt. % Ti, 4 wt. % Al, and 3 wt.% V. The EDS and EBSD characterization demonstrate that the Ti-6Al-4V foil has an expected structure and composition within accepted experimental error³³⁵.

6.3.1.3 Vanadium Interlayer Before UAM

As mentioned previously, a thin ~25 μm vanadium foil was used for one of the scenarios of improving bonding of Ti-6Al-4V. Prior to bonding, the vanadium interlayer was examined to confirm its composition and structure (Figure 6.5). An overview BSE image (Figure 6.5a) shows a uniform foil structure. Wavy lines are present in the image, likely a result of the foil rolling process. The EDS map of vanadium and EDS spectrum (Figure 6.5b & c) demonstrate the foil is entirely vanadium with no impurities above the detectable SEM-EDS limit. The EBSD band contrast and BCC-IPF pattern (Figure 6.5d & e) further demonstrate a uniform and homogenous structure in the vanadium foil. Slight image drifting occurred during EBSD characterization resulting in reduced image quality.

6.3.2 UAM Bonding Materials

6.3.2.1 CP Ti Foil After UAM Bonding

Once the CP Ti foil was successfully bonded using UAM, the material was characterized (Figure 6.6) in an orientation normal to the rolling direction of the sonotrode, as indicated. The SEM-BSE (backscatter electron) image of the bonded foil (Figure 6.6a) demonstrates significant features are present on the top surface of the foil, that were in contact with the sonotrode.

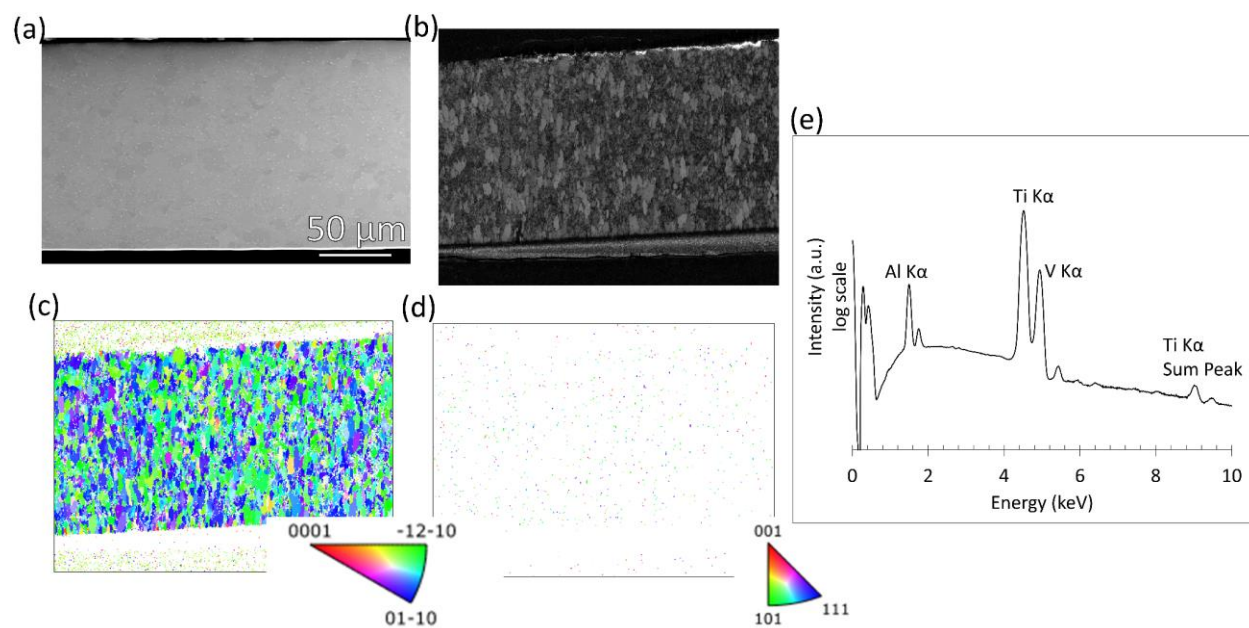


Figure 6.4. As-Received Ti-6Al-4V Foil. a) SE Image, b) Band Contrast, c) Ti HCP-IPF, d) Ti BCC - IPF, e) EDS Spectrum

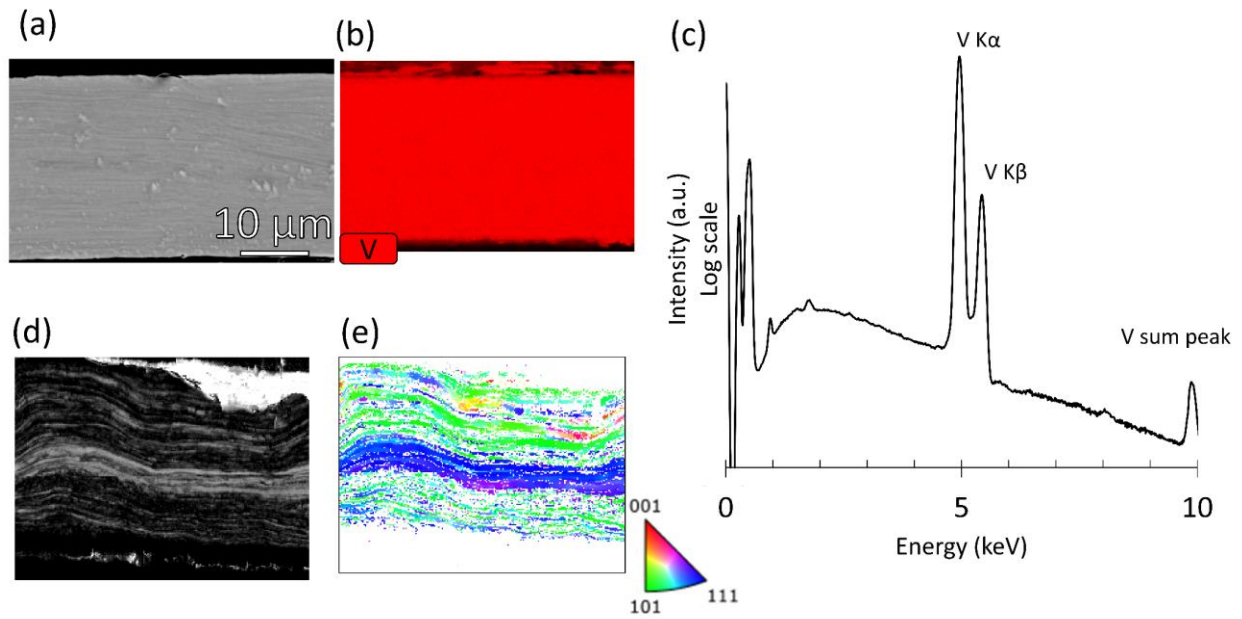


Figure 6.5. As-Received Vanadium Foil Interlayer. a) BSE image, b) V-EDS Map, c) EDS Spectrum, d) Band Contrast, e) BCC-IPF

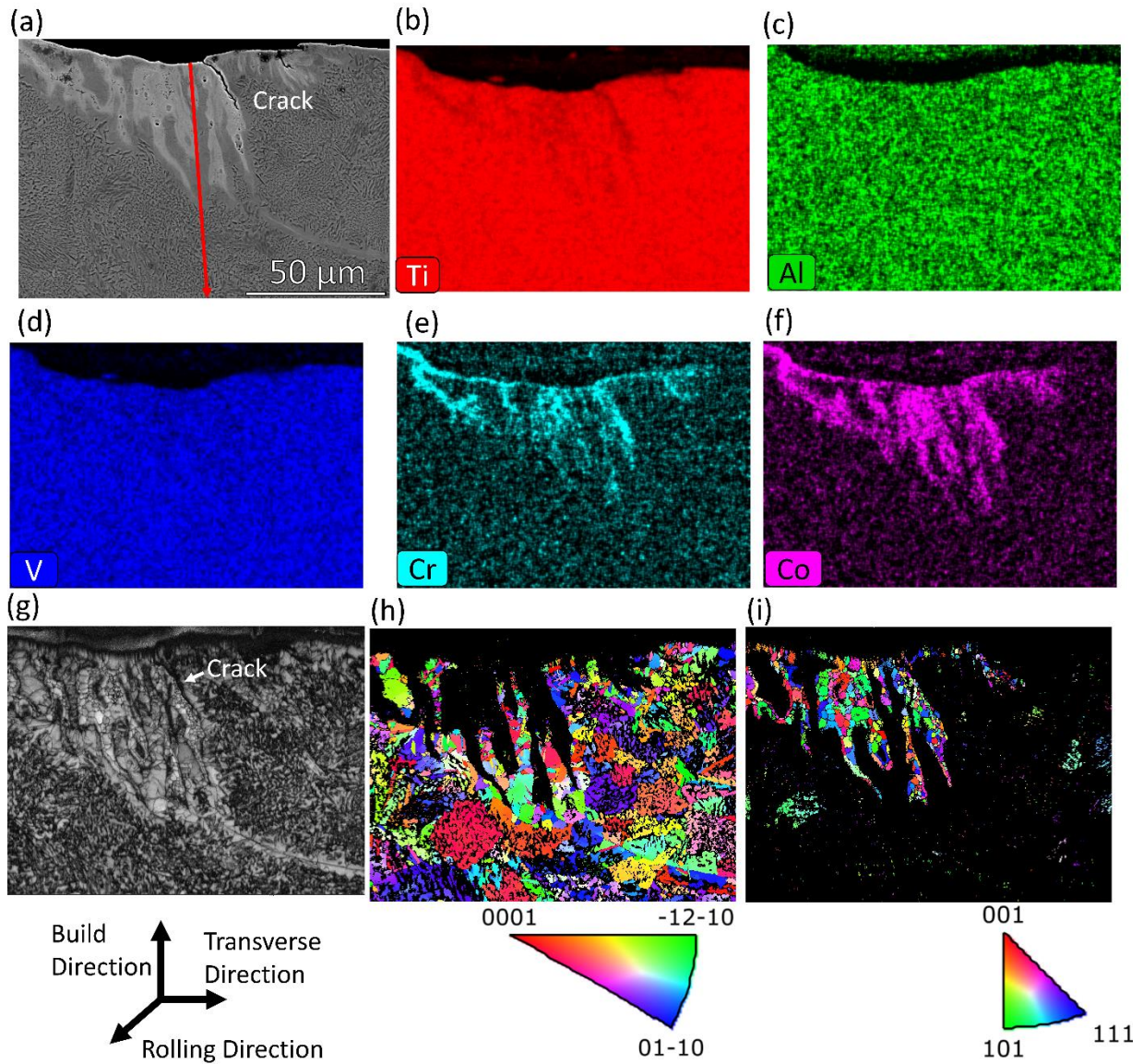


Figure 6.6. Bonded CP Ti Foil: EDS and EBSD Maps. a) BSE Image, b) Ti-EDS Map, c) Al-EDS Map, d) V-EDS Map, e) Cr-EDS Map, f) Co-EDS Map, g) Band Contrast, h) Ti HCP-IPF, i) Ti BCC-IPF

Additionally, a crack is present on the right side of these features. The crack and other features appear to start at the top of the foil and progress downwards into the sample. A line is drawn on the image to indicate the direction of the EDS line scan. The quantified EDS maps of titanium, aluminum, and vanadium (Figure 6.6b-d) demonstrate mostly uniform concentrations of these elements throughout the sample. Quantified EDS maps of impurity elements chromium and cobalt (Figure 6.6e, f) show high concentrations of these elements are present near the top of the foil. Since these elements were not present in the foil prior to bonding, they were likely introduced during the UAM process. The UAM sonotrode horn had Stellite coating (Co-Cr alloy), therefore it is suspected these impurity elements came from the Stellite coating. Care was taken to characterize the sample using EBSD within the same field of view as the EDS analysis.

Throughout the sample, the EBSD band contrast (Figure 6.6g) demonstrate significant decrease in quality as compared to before bonding (Figure 6.3b). Near the crack and outside the crack there is an increase in pattern quality showing small almost equiaxed grains. The IPF of the α phase (Figure 6.6h) and the β phase (Figure 6.6i) show that most of the sample retained the α phase, although the β titanium phase is also present near the top of the foil. The existence of the β phase titanium in the UAM bonded CP Ti foil represents a significant deviation from the equilibrium of titanium. The β phase titanium is present at the same location as the higher concentration of impurity cobalt and chromium elements. The grains in the β phase appear small and roughly circular (or spherical in three dimensions). The α phase directly surrounding the β phase has small grains with several twin features oriented roughly perpendicular to the direction of the protruding β phase. At the bottom of the IPF image, the α phase has large grains and appears mostly undisturbed. The contrast changes from the BSE image, the shape of the cobalt and chromium introduction, and the direction of the β phase into the sample appear as sharp protrusions beginning at the top of the foil and extending downward into the sample in finger-like features.

The EDS data is shown in Figure 6.7. The spectrum from the entire region (Figure 6.7a) has the X-ray peaks of titanium, chromium, and cobalt identified. A silicon $K\alpha$ peak is also present in the spectrum, but this is likely an artifact from the polishing process, therefore it is not labeled or quantified. The EDS line scan (as indicated in Figure 6.6a) is shown in Figure 6.7b with the titanium, chromium, and cobalt concentrations. These impurity elements appear within twenty microns from the top of the foil and up to ~ 20 wt. %. Due to the unusual nature of the observed β phase in CP Ti, X-ray diffraction (XRD) was also performed (Figure 6.8). The sample was oriented such that the X-rays probed the top surface of the sample, as indicated by the diagram. From this orientation, approximately 50% of the data collected is from within 1.2 μm of the top surface, and 90% of the data collected is from within 4 μm of the top surface³³⁶. The calculated phase fractions following Rietveld Refinement (Table 6.1) show significant concentrations of the titanium α phase and the β phase on the top surface of the bonded foil.

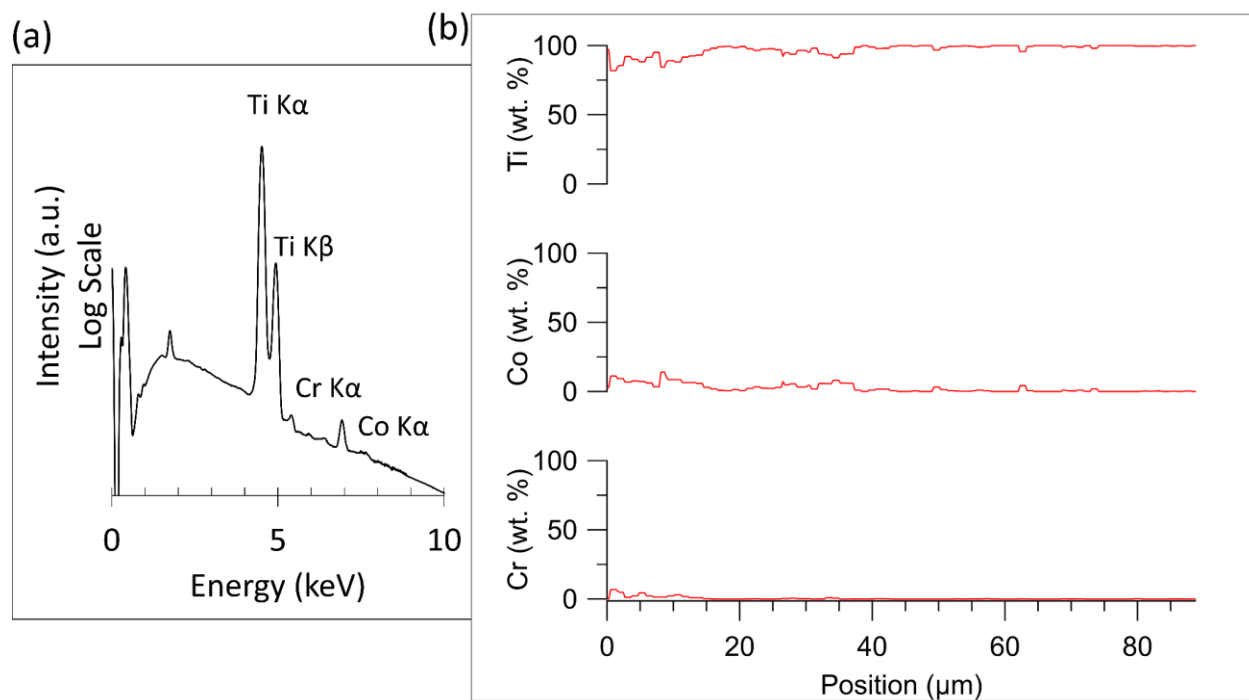


Figure 6.7. EDS Data of Bonded CP Ti Foil. a) EDS Spectrum, b) EDS Line Scan of Titanium, Cobalt, and Chromium

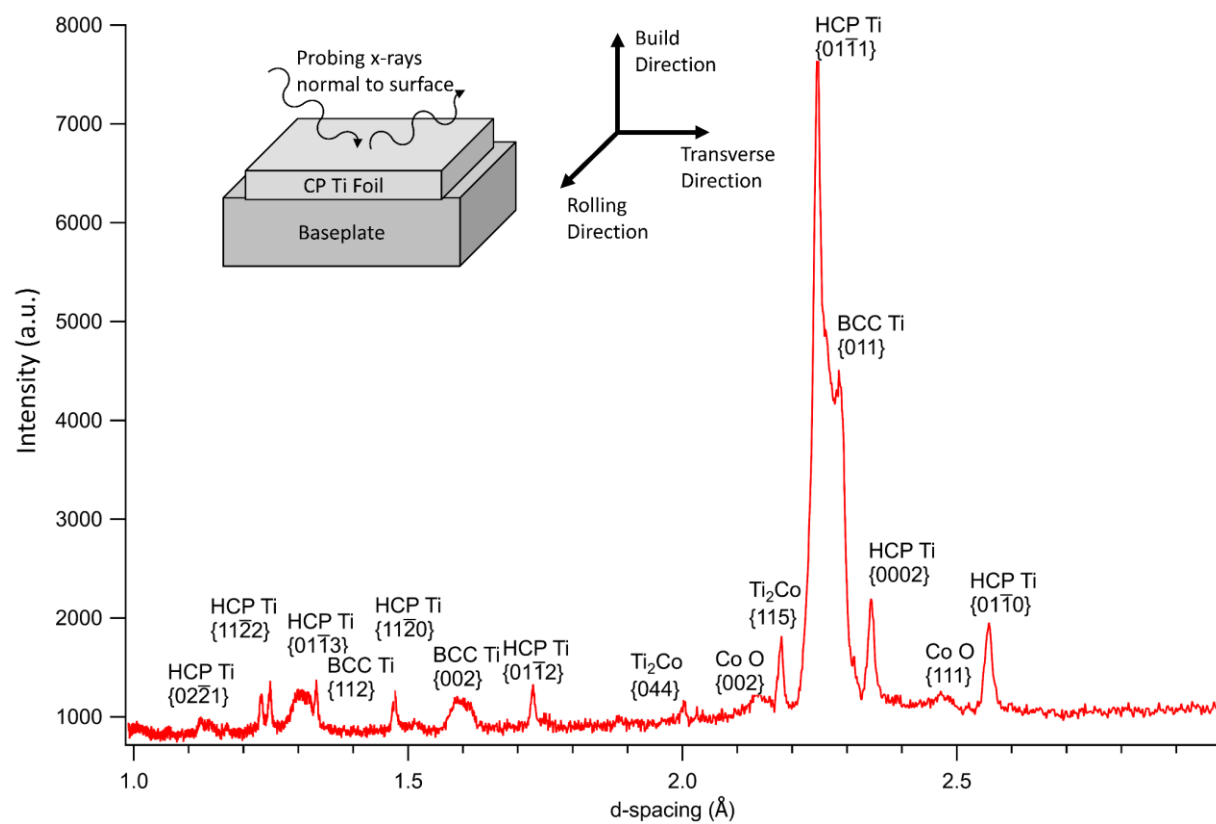


Figure 6.8. X-ray Diffraction Normal to the Top Surface of the Bonded CP Titanium Foil

Table 6.1. Calculated phase fractions from x-ray diffraction on the bonded foil

Phases	Weight Percent
α -Ti	58.3 %
β -Ti	38.2 %
Ti ₂ Co	2.0 %
CoO	1.5 %

Additionally, the intermetallic Ti_2Co and oxide CoO phases are present, although their concentrations are relatively small, which is why they are difficult to detect using EBSD analysis. Confirming the presence of β phase using EBSD and XRD methods significantly increase our confidence that this phase is present. The above results indicate that successful bonding of titanium also corresponds to the $\alpha \rightarrow \beta$ titanium phase transformation.

6.3.2.2 Ti-6Al-4V Foil After UAM Bonding

After the Ti-6Al-4V foil was UAM bonded to the baseplate, it was characterized using EDS and EBSD (Figure 6.9). All the sample images are oriented normal to the rolling direction of the sonotrode (like the bonded CP Ti sample, Figure 6.6), therefore image orientation diagrams are not repeated for these samples. Several distinct features are present on the top of the bonded Ti-6Al-4V foil. From the BSE overview image (Figure 6.9a), swirl features are present on the top of the foil. A red line is drawn on the image to indicate the direction of the EDS line scan shown later. Quantified EDS maps of the titanium, aluminum, vanadium, cobalt, and chromium (Figure 6.9b-f) demonstrate mostly uniform concentrations of titanium, aluminum, and vanadium, while cobalt and chromium have been introduced on the top surface of the foil in swirl-like features. EBSD characterization was also performed in the same viewing region. There is increased band contrast at the top of the image as compared to deeper in the sample (Figure 6.9g). The IPF of the α phase (Figure 6.9h) and the β phase (Figure 6.9i) demonstrates that the α phase is present throughout most of the foil, while the top of the sample has the β phase.

The EDS data from the sample is shown in Figure 6.10. The EDS spectrum from the entire area (Figure 6.10a) shows the identified X-ray peaks, and the EDS line scan (Figure 6.10b) demonstrates the concentrations of titanium, cobalt, and chromium as a function of distance from the sample surface. The cobalt and chromium impurity elements are within 30 microns of the top surface of the material and have large concentrations, with cobalt beyond 50 wt.% within the first several microns.

The bonded CP Ti and the bonded Ti-6Al-4V have several comparable features. In both samples, there is significant introduction of cobalt and chromium onto the top of the foil and β titanium formation. In the CP Ti sample, the UAM bonding results in finger-like features created on the top of the sample, while the Ti-6Al-4V sample has swirl-like features created on the top of the sample. The Ti-6Al-4V sample also has more penetration of the cobalt and chromium elements than the CP Ti sample.

6.3.2.3 Ti-6Al-4V Foil After UAM Bonding Using an Aluminum Interlayer

UAM bonding of titanium is very difficult, and often results in the foil bonding to the sonotrode instead of the baseplate, which tears the material.

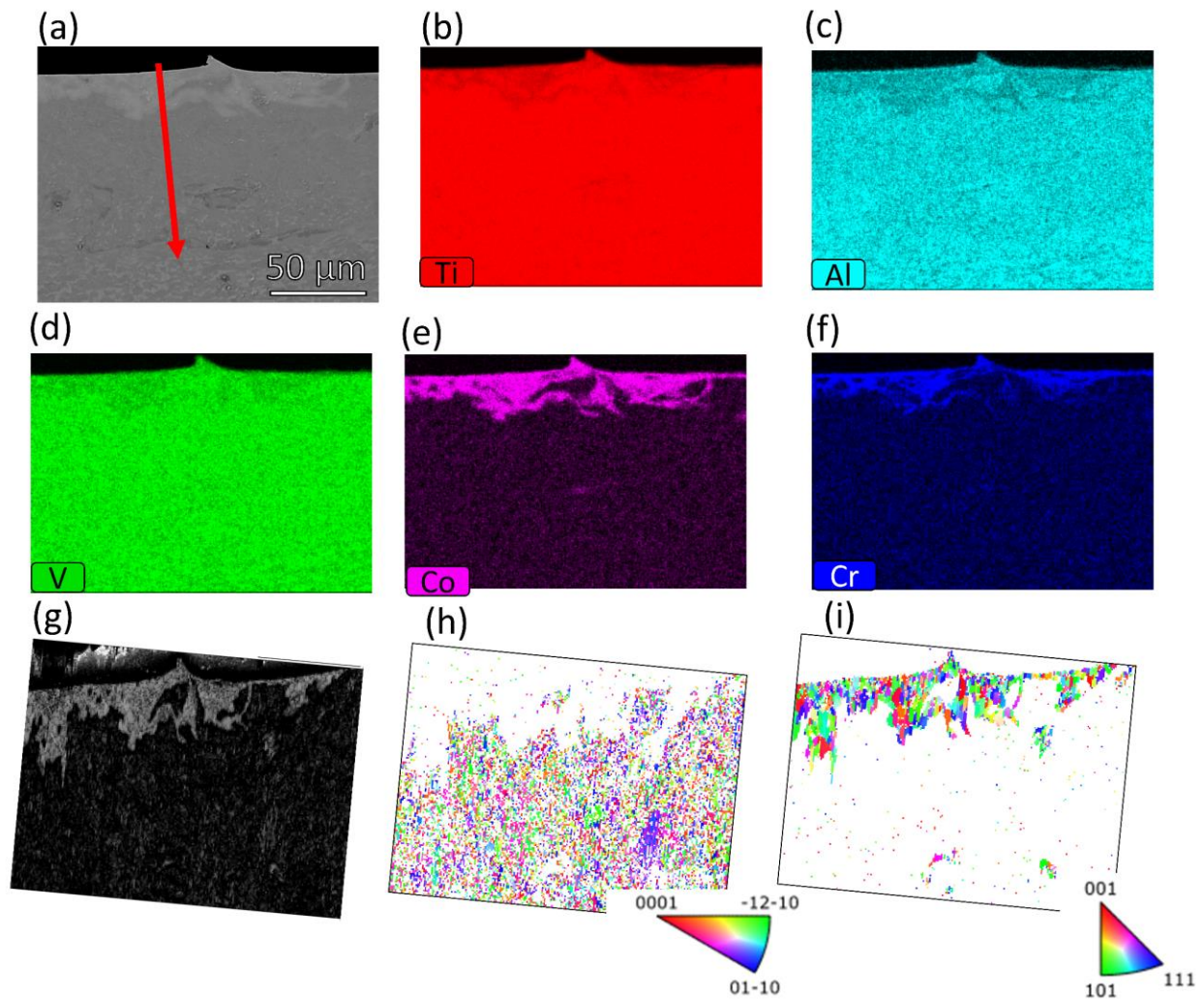


Figure 6.9. Bonded Ti-6Al-4V Foil: EDS and EBSD Maps. a) BSE Image (with line indicated line scan), b) Ti-EDS Map, c) Al-EDS Map, d) V-EDS Map, e) Co-EDP Map, f) Cr-EDS Map, g) Band Contrast, h) Ti HCP-IPF, i) Ti BCC-IPF

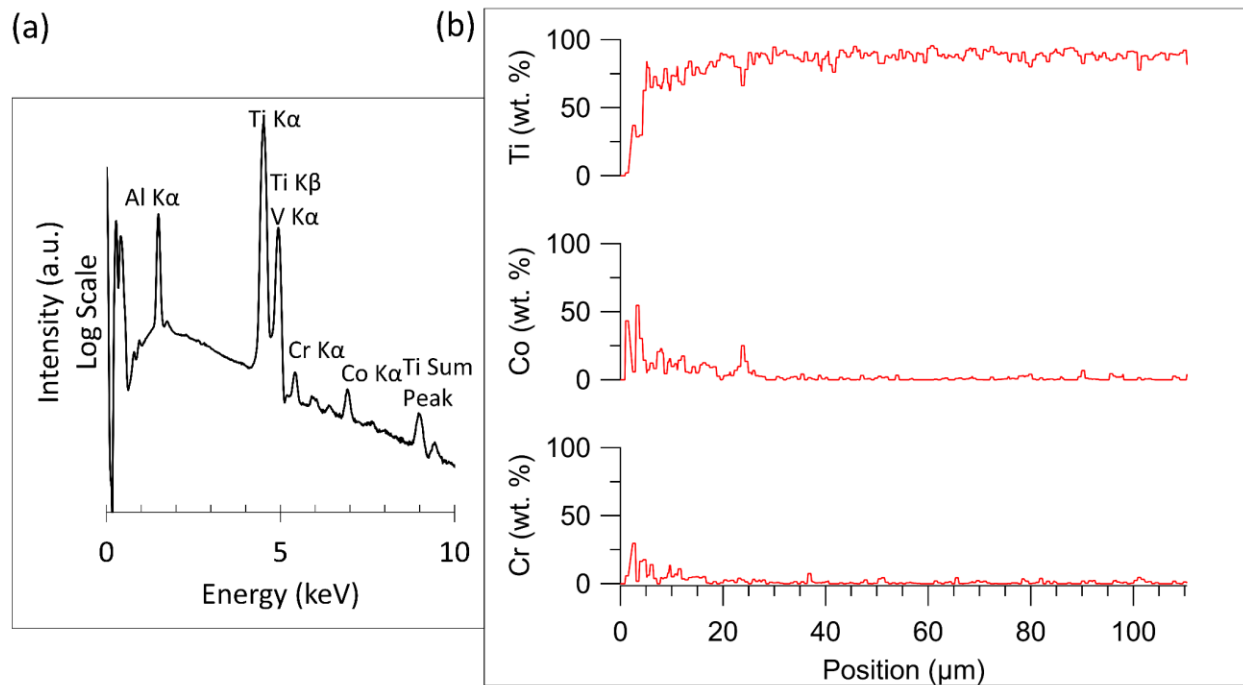


Figure 6.10. EDS Data of Bonded Ti-6Al-4V Foil. a) EDS Spectrum, b) EDS Line Scan of Titanium, Cobalt, and Chromium

To improve the UAM bonding ability of titanium, we hypothesize that the local crystal structure could be altered. The first hypothesis is that if elements could more easily diffuse, then perhaps the bonding could be improved. To improve the interdiffusion of elements (which occurs primarily with atomic exchanges with vacancies through the Kirkendall effect), the material could be altered to allow a higher concentration of vacancies which could allow more atomic exchange pathways. This can be done by increasing the material's ability to form vacancies by decreasing the vacancy formation energy of the material. The introduction of aluminum can provide this effect because it has a low vacancy formation energy (E_v^f of Al: 0.67 eV¹⁷⁰ vs E_v^f of α Ti: 1.97 eV³³⁷). Assuming a linear rule of mixtures for the combination of vacancy formation energies, the total vacancy formation energy should decrease. As discussed in the proceeding section, aluminum also increases the β transus point of titanium. This allows for the analysis of UAM HCP bonding by increasing the interdiffusion of elements without an $\alpha \rightarrow \beta$ phase transformation.

To test this hypothesis, a Ti-6Al-4V foil was bonded to the baseplate using a thin aluminum interlayer between the foil and the baseplate. During UAM, some of the foil bonded, but most of the material cracked and broke off. Characterization was performed on a region of the material that remained mostly connected to the baseplate (Figure 6.11). SEM analysis (Figure 6.11a) shows that the titanium and aluminum interlayer appear intermixed with each other. There are several distinct regions of lower contrast elemental mixed materials surrounding higher contrast titanium. These regions are near the large crack in the sample, on the top surface of the sample, and on pathways connecting them. The quantified EDS maps (Figure 6.11b-f) of titanium, aluminum, vanadium, cobalt, and chromium demonstrate that the aluminum is mixed throughout the sample at the locations of dark SEM image contrast. This indicates that the aluminum interlayer mixes with the titanium. There is likely a weakly bonded joint which results in fracture of the material. The vanadium, cobalt, and chromium EDS maps indicate there are not significant concentrations of these elements in the sample.

EBSD analysis in this same region also demonstrates mixing of the materials during UAM bonding. The band contrast (Figure 6.11g) is poor throughout most the sample, suggesting small and/or heavily deformed grains are present. A small region at the bottom right of the image near the crack has slightly higher band contrast, suggesting larger grains there. The IPF of the α phase (Figure 6.11g), the β phase (Figure 6.11i), and the aluminum FCC phase (Figure 6.11j) suggest that most of the material retains the α phase. Near the regions with a high aluminum concentration and larger grains, the aluminum FCC phase and the β phase are detected. The low band contrast throughout the sample reduces our confidence in phase identification. The similarity in the FCC and BCC structures leads us to suspect that the β phase was not created in this sample.

The EDS data from this region can be further analyzed (Figure 6.12). The EDS spectrum from the entire viewing window is shown in Figure 6.12a, and the various elements and sum peaks are identified. An EDS line scan, along the path indicated in Figure 6.11a, is shown in Figure 6.12b.

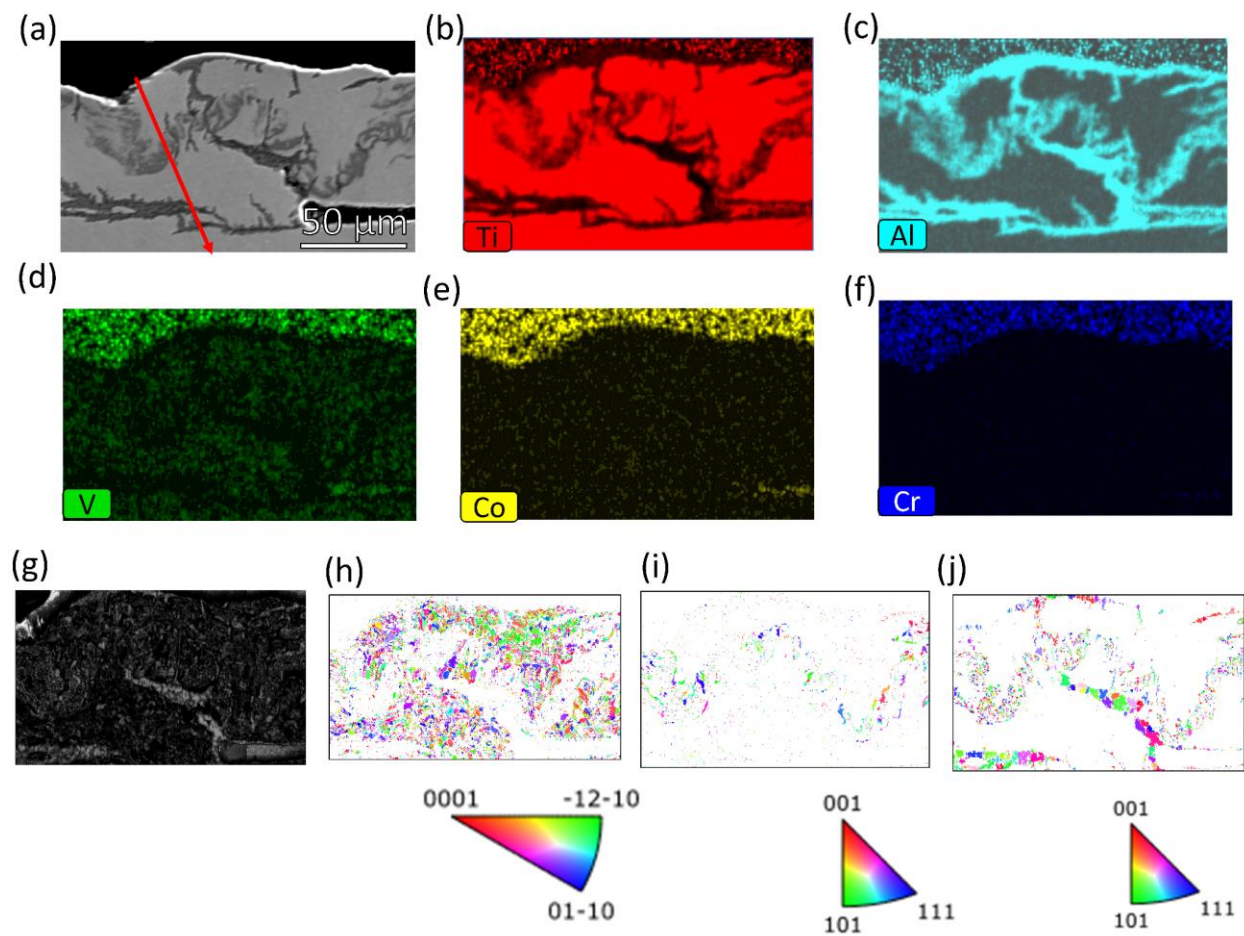


Figure 6.11. Bonded Ti-6Al-4V Foil using an Aluminum Interlayer: EDS and EBSD Maps. a) SEM (with indicated line scan), b) Ti-EDS Map, c) Al-EDS Map, d) V-EDS Map, e) Co-EDS Map, f) Cr-EDS Map, g) Band Contrast h) Ti HCP-IPF, i) Ti BCC-IPF, j) Al - IPF,

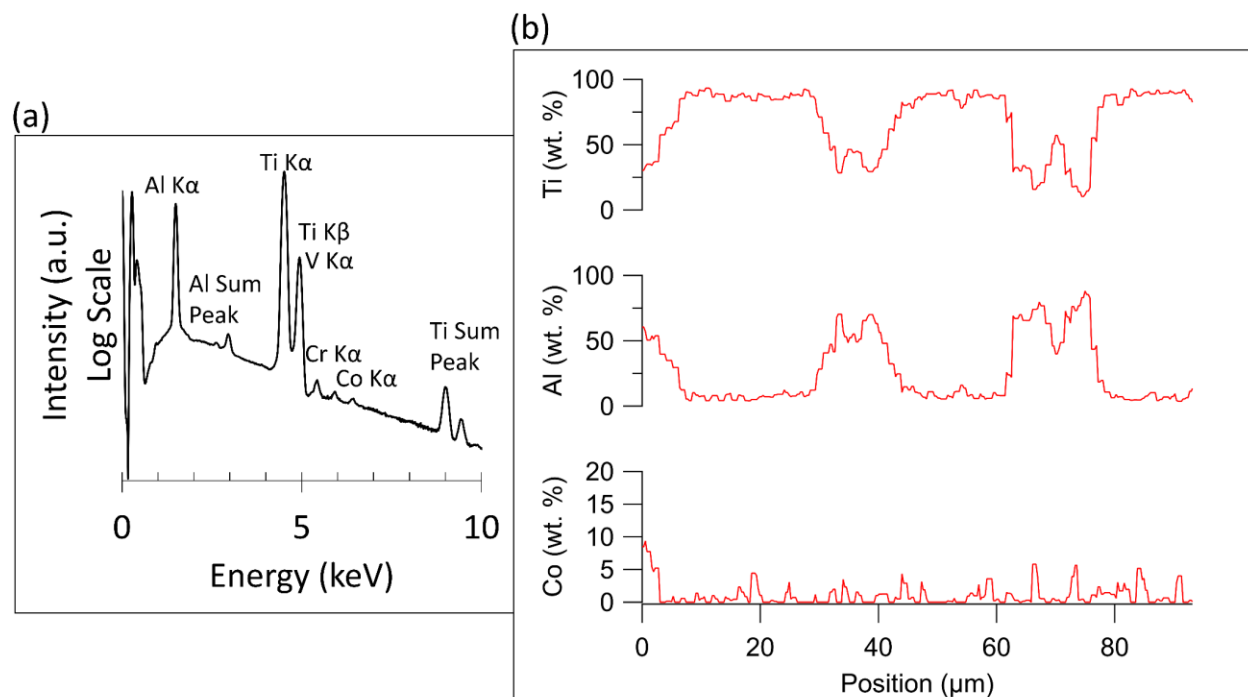


Figure 6.12. EDS Data of Bonded Ti-6Al-4V Foil Using an Aluminum Interlayer. a) EDS Spectrum, b) EDS Line Scan of Titanium, Cobalt, and Chromium

The elements of titanium, aluminum, and cobalt are shown. Intimate intermixing of titanium and aluminum has occurred as the concentrations have exceeded a 50%-50% mixing point. Additionally, a small amount (~5 wt.%) of cobalt is present.

6.3.2.4 Ti-6Al-4V Foil After UAM Bonding Using a Vanadium Interlayer

As mentioned previously, it is hypothesized that the UAM bonding ability of titanium could be improved by altering the local crystal structure of the material. If the β phase could have increased stability, then perhaps the bonding ability could be improved. As demonstrated above, $\alpha \rightarrow \beta$ phase transformation could occur during successful bonding of titanium as impurity elements of cobalt and chromium are introduced. Although cobalt and chromium are β stabilizing elements, they are considered β eutectic stabilizing elements. This means that when a small percentage of cobalt and chromium (up to 8.4 wt.% and 12.5 wt.% and respectively) are introduced, they can reduce the β transus point. Although when larger concentrations of these elements are introduced, the β transus point increases, which makes it more difficult to form the β phase²⁹⁰ (Figure 6.13a&b). In an alternate manner aluminum is an α stabilizing element. This means that the introduction of aluminum to titanium will increase the β transus point, making it more difficult to form the β phase. This can be considered as contributing to the lack of β phase observed in Figure 6.11. Instead, Vanadium was chosen for the current hypothesis because it can reduce the β transus point in titanium with all concentrations (Figure 6.13d). If the formation of the β phase is beneficial for bonding, then the introduction of vanadium should improve the UAM bonding ability. Furthermore, once there is a $\alpha \rightarrow \beta$ phase transformation, the crystal structure has a lower vacancy formation energy (α Ti: 1.97 eV³³⁷ vs β Ti: 1.1 eV³³⁸). Therefore, higher concentrations of vacancies and enhanced interdiffusion can occur. To test this hypothesis, vanadium was applied to titanium prior to UAM bonding. In this first scenario, a thin interlayer foil of vanadium was laid underneath a Ti-6Al-4V foil prior to bonding. In the second scenario discussed later, vanadium was sputtered onto the surface of CP Ti foil prior to bonding.

UAM bonding of titanium using a vanadium interlayer was successful. Due to this success, continued bonding of a titanium foil with a vanadium interlayer was performed. The final built structure that was examined has three layers of the titanium and vanadium combination. Imaging of this material (Figure 6.14) reveals several distinct features. An overview of the entire build (Figure 6.14a) demonstrates the multiple Ti-6Al-4V foils and vanadium interlayers. Like the bonded Ti-6Al-4V foil without an interlayer (Figure 6.9), swirls are present on top of the Ti-6Al-4V foil and on the top of the last foil added (top of the image). This suggests that the swirls are the result of the contact with the sonotrode. A magnification of the boundary of Ti-6Al-4V foils and a vanadium interlayer (Figure 6.14b) shows that the titanium and vanadium experience significant plastic deformation. In the undeformed region of the titanium, a typical basketweave microstructure is present. Closer to the vanadium, the Ti-6Al-4V has a quite different structure. The titanium has a higher contrast and has larger equiaxed grains.

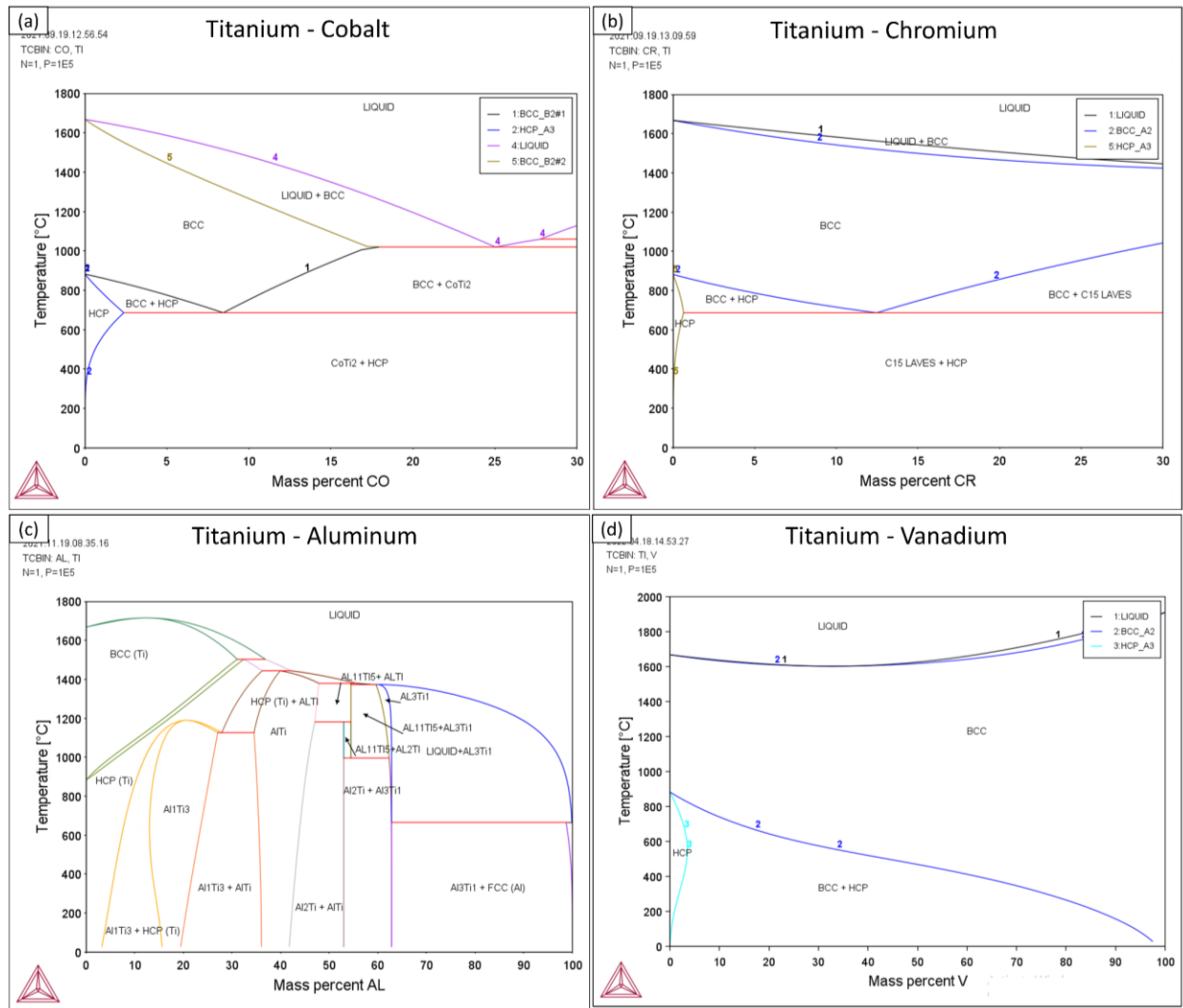


Figure 6.13. Phase diagrams of alloying elements with titanium²⁹⁰. a) Ti-Co, b) Ti-Cr, c) Ti-Al, d) Ti-V

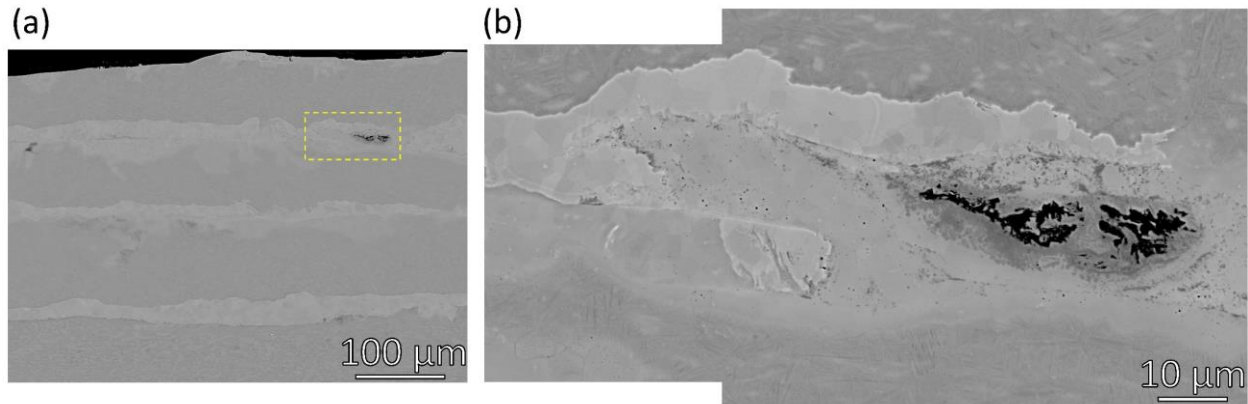


Figure 6.14. Images of Bonded Ti-6Al-4V Foils with Vanadium Interlayers. a) BSE Overview, b) BSE Image of Dashed Box Region

Additionally, the vanadium interlayer is significantly deformed. It appears that the titanium plastically flowed upward through the vanadium interlayer, pushing it up above the original interlayer boundary. Vanadium exists above and below the titanium. Additionally, there are large cracks on the right side of the image, and distinct dark contrast globular features surrounding the cracks. In addition to the large cracks, small (~200 nm) circular voids are present throughout the high contrast region of titanium. The nature of these voids is discussed further in the proceeding section.

The region shown in Figure 6.14b was further characterized using EDS and EBSD all within the same field of view (Figure 6.15). Figure 6.15a is an SEM image of the region of interest, repeated for comparison. A red line is drawn on the image indicating the direction of the EDS line scan. Quantified EDS maps of titanium, aluminum, vanadium, cobalt, and chromium are shown in Figure 6.15b-f. The highest concentration of titanium and aluminum is in the Ti-6Al-4V foils, and the vanadium is predominantly in the interlayer foil. The cobalt and chromium are mostly within the Ti-6Al-4V foil near the interlayer, although they are also inside the vanadium interlayer. The EBSD band contrast (Figure 6.15g) indicates there is reduced image quality in Ti-6Al-4V foils, and higher image quality near the foil interface and in the vanadium interlayer. The IPF of the titanium α phase (Figure 6.15h) shows that the HCP phase is present throughout the undeformed region of the Ti-6Al-4V foil. The IPF of the titanium β phase (Figure 6.15i) shows large equiaxed BCC grains. The BCC phase is detected in the vanadium and in the titanium. This indicates that the EBSD IPF map is convoluted by including the BCC vanadium and the BCC titanium. The higher pattern quality in the titanium near the interlayer is likely a result of the titanium transforming into the β phase. The α titanium likely has more stored dislocations and is more deformed, while the β phase has fewer dislocations and is less distorted. Between the β titanium and the vanadium there is a region approximately 2 μm thick which has reduced image quality. This suggests finer grains could be present between the materials. Quantification of the EDS data is shown in Figure 6.16. The EDS spectrum (Figure 6.16a) shows the various identified X-ray peaks. The EDS line scan (Figure 6.16b) follows the path indicated in Figure 6.15a. The line scan shows the elemental concentrations of titanium, vanadium, and cobalt. This demonstrates the titanium and vanadium are intermixed from the plastic deformation, and there are smooth diffusion profiles between the two materials. The cobalt impurity element is more dominantly present in the titanium rich regions, but cobalt is also distinctly present in the vanadium rich regions. Prior to UAM bonding, the vanadium interlayer did not contain impurity elements (Figure 6.5), and the vanadium was never in contact with the sonotrode.

6.3.2.5 CP Ti Foil After UAM Bonding Using a Vanadium Sputtered Surface

The second scenario of using vanadium to improve bonding of titanium is now demonstrated. In this case, a thin surface treatment of vanadium was applied via sputtering to a CP Ti foil. After successful UAM bonding, the structure and interface were characterized (Figure 6.17).

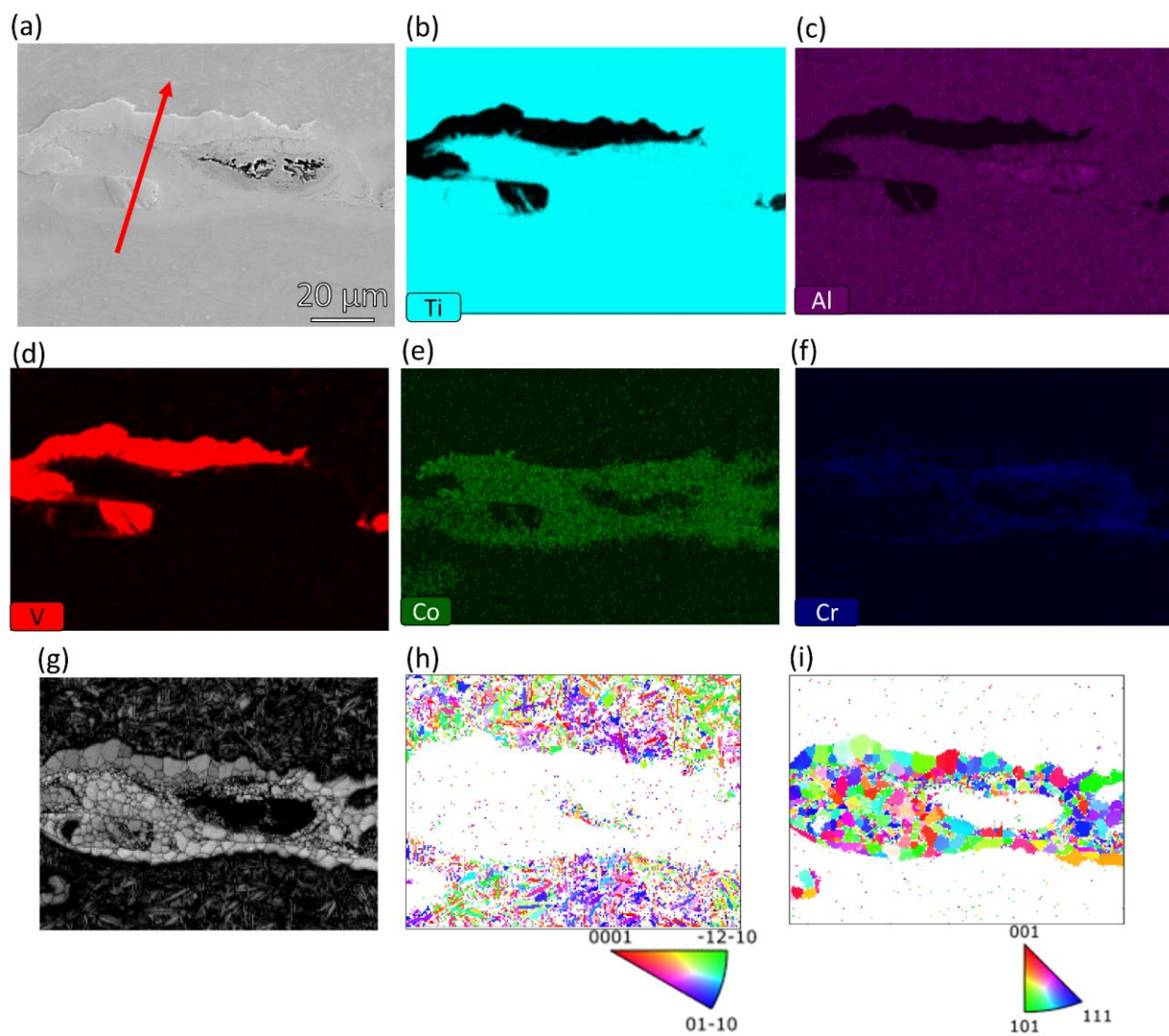


Figure 6.15. Bonded Ti-6Al-4V Foil using a Vanadium Interlayer: EDS and EBSD Maps.
 a) SEM (with indicated line scan), b) Ti-EDS Map, c) Al-EDS Map, d) V-EDS Map, e) Co-EDS Map, f) Cr-EDS Map, g) Band Contrast, h) Ti HCP-IPF, i) Ti BCC-IPF

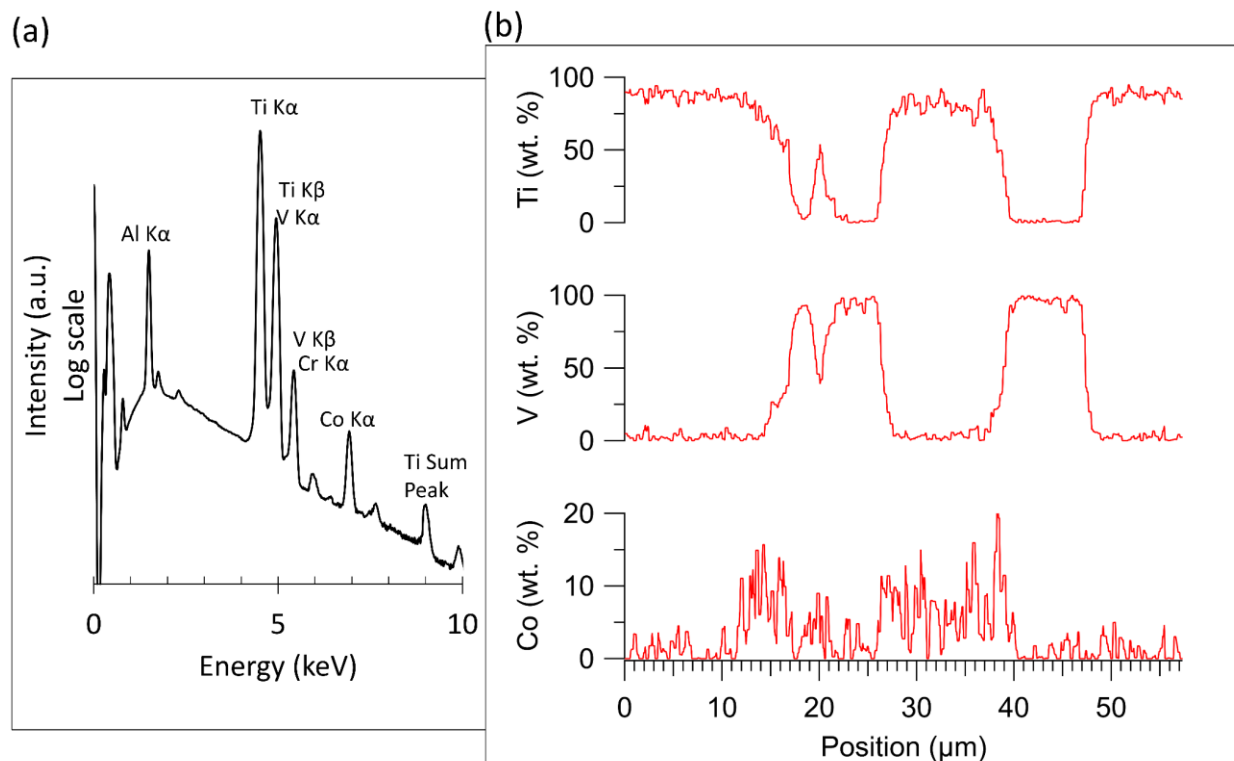


Figure 6.16. EDS Data of Bonded Ti-6Al-4V Foil Using a Vanadium Interlayer. a) EDS Spectrum, b) EDS Line Scan of Titanium, Vanadium, and Cobalt

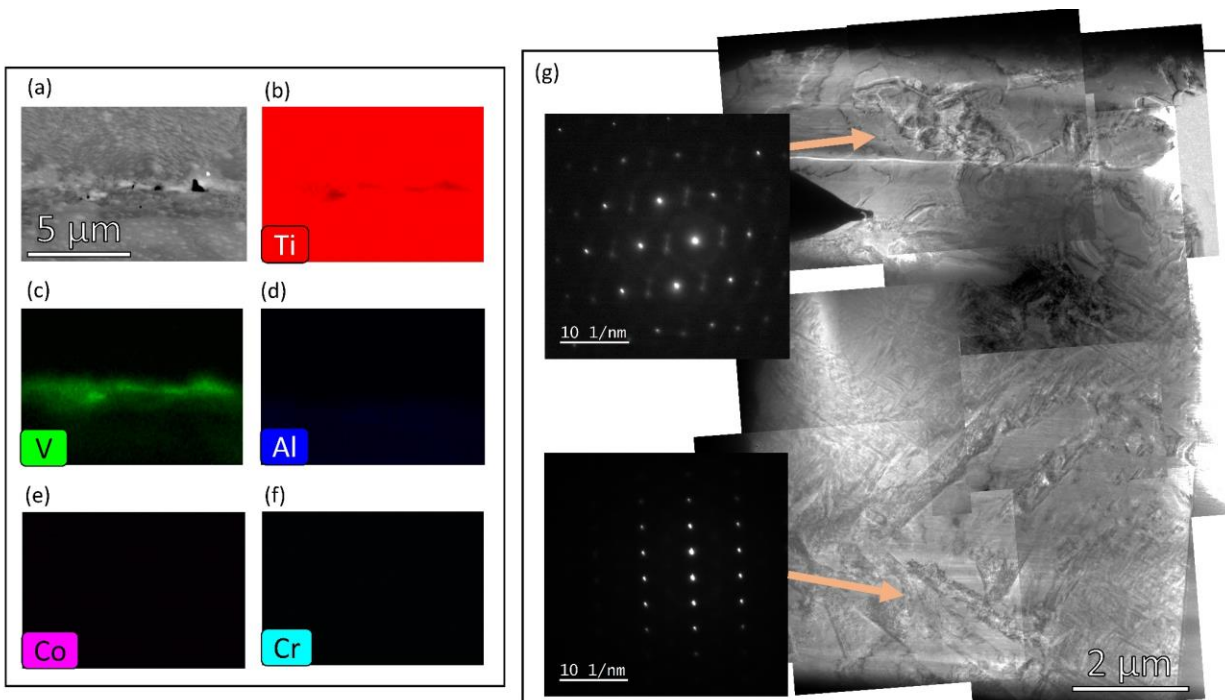


Figure 6.17. Bonded titanium with a sputtered vanadium surface. a) BSE image, b) Ti-EDS map, c) V-EDS map, d) Al-EDS map, e) Al-EDS map, f) Co-EDS map, g) TEM-BF and CBED

Using BSE imaging and SE-EDS techniques (Figure 6.17a-f), the interface can be clearly observed. The BSE contrast of the titanium changes at the interface and several small voids are present. A higher concentration of vanadium is present at the interface although there is not a significant delineation between the vanadium and the titanium, suggesting thorough intermixing between elements. No significant concentrations of aluminum, cobalt, or chromium are observed. The titanium interface was then further characterized using transmission electron microscopy (TEM) bright field (BF) imaging along with convergent beam electron diffraction (CBED). This was performed to understand the crystallographic structure of the material since the features are comparable with the spatial resolution of EBSD, limiting its use here. TEM-BF imaging was performed on the entire thinned sample and CBED was performed at specific locations as indicated (Figure 6.17g). Within the first few microns on the top of the TEM-BF image, a bright line is present. This is the interface that was targeted during focused ion beam (FIB) preparation. Small whisker type grains are present throughout the titanium surrounding the interface. CBED was performed at regions in the titanium that were suspected to contain the α structure and the transformed β structure. The CBED diffraction pattern far away from the interface is the HCP $[2\bar{1}\bar{1}1]$ zone axis, and the CBED diffraction pattern at the interface is the BCC $[\bar{1}\bar{1}1]$ zone axis. Figure 6.17 demonstrates that at the interface, the sputtered vanadium intermixes with the titanium resulting in an $\alpha \rightarrow \beta$ phase transformation.

6.4 Discussion

6.4.1 Evaluation of the Thermal Condition Reached During UAM

UAM is considered a solid-state low time and temperature bonding process. The time t of the thermal profile experienced during bonding is approximately 0.5 seconds^{55,99}. To rationalize the atomic motion observed here, a diffusion profile between materials can be considered (Figure 6.16 of the vanadium interlayer between Ti-6Al-4V foils). The diffusion distance x of 3.5 μm can be used to calculate an approximate diffusivity D value using Fick's 2nd law $x \sim \sqrt{Dt}$ between the titanium and the vanadium. This is shown in Table 6.2. UAM studies of other HCP materials have estimated a thermal profile reaching as high as 400°C⁶⁸. The diffusivity of α Ti and β Ti^{337–339} can be compared for this temperature and even higher temperatures such as the β eutectic transus point with cobalt (650 °C) or the beta transus point for vanadium (944 °C). Table 6.2 demonstrates that the estimated experimental diffusivity of this study is far above that expected for α or β titanium at mild or even extreme temperatures. As shown in Table 6.2, even for these very high temperatures, the thermal equilibrium diffusivity is insufficient to explain the atomic motion; therefore, other processes are most likely present.

Table 6.2. Diffusivity of Titanium

Temperature (°C)	Diffusivity, α Ti (m^2/s)	Diffusivity, β Ti (m^2/s)	Experimental Diffusivity (m^2/s)
400	3.3×10^{-23}	2.2×10^{-16}	
650	6.9×10^{-18}	2.6×10^{-15}	
944	2.0×10^{-14}	4.9×10^{-14}	
			4.9×10^{-11}

As shown in previous UAM studies^{65,282,340}, very large point defect vacancy concentrations can be created during the plastic deformation UAM bonding. These vacancies can enhance atomic diffusion by increasing the number of lattice sites available for atomic migration. The expression for Brownian atomic motion, $D = a_0^2 X_v \nu \cdot \exp\left(-\frac{E_m}{kT}\right)$, can be used to rationalize the concentration of vacancies present. Here a_0 is the lattice constant, X_v is the vacancy concentration, ν is the Debye frequency of the atomic vibrations on its lattice site, E_m is the vacancy migration energy, k is the Boltzmann constant (8.617×10^{-5} eV/K), and T is the absolute temperature^{146,147,149,150,323}. The vacancy concentration in titanium would be approximately 3×10^{-5} - 2×10^{-4} depending for the temperature reached during bonding.

The cobalt and chromium elements in the titanium are likely introduced when a diffusion couple is created between the Stellite sonotrode and the titanium. Accelerated interdiffusion then occurs due to a high concentration of point defect vacancies. Enhanced concentrations of vacancies are also created at the interfaces resulting in the interlayers and elemental surface modifications diffusing during bonding.

There is also evidence of the cobalt element entering into the vanadium interlayer (Figure 6.15 & Figure 6.16). As noted previously, the cobalt is not present in the vanadium interlayer prior to UAM (Figure 6.5) and the sonotrode never touches the vanadium interlayer (Figure 6.1). Therefore, the cobalt must have diffused from the sonotrode into the titanium, and then when the subsequent layer is added on top, the cobalt back diffuses into the vanadium.

6.4.2 Strain Induced Phase Transformation During UAM

The introduction of β phase can be rationalized on the role of the introduction of elements such as Co, Cr, V, and Al to the titanium, as well as the plastic strain induced on the material. In pure titanium alloys, as per thermodynamic calculations, the onset of the allotropic α to β transus temperature (T_β) is calculated to be 881.4°C. As suggested from the results above, the β transus temperature can also decrease with the addition of certain elements. The rate of the β transus temperature reduction as a function of solute fraction (~2%) can be calculated using the Thermo-calc® program²⁹⁰ using the TCTI2 module: $d(T_\beta)/d(\text{wt. fraction Co}) = -2098$; $d(T_\beta)/d(\text{wt. fraction Cr}) = -1959$; $d(T_\beta)/d(\text{wt. fraction V}) = -1595$; $d(T_\beta)/d(\text{wt. fraction Al}) = 2299$. Clearly cobalt, chromium, and vanadium decrease T_β as they are added to titanium (hence the negative $d(T_\beta)/d(\text{wt. fraction solute})$ values). Therefore, as these elements diffuse into titanium, they make it easier for the β phase to form, which we experimentally observe. Conversely aluminum increases T_β as it is added to titanium. This makes it more difficult for the β phase to form, therefore it is not surprising that we do not observe the β phase to form with the aluminum interlayer.

In addition to the introduction of elements, the stability of the α phase can be considered from a thermodynamic perspective. At temperatures below T_β , the α phase is more

thermodynamically stable than the β phase. Therefore, the α phase has a lower Gibbs free energy and the material cannot overcome the energetic barrier to form the β phase³⁴¹. If the α phase has significant plastic deformation, the phase will become more deformed and work hardened, and the Gibbs free energy of that phase will increase with respect to the β phase. As temperature or the amount of deformation increases, the energy barrier to form the β phase decreases. This can happen until the β phase is more thermodynamically stable than the α phase, allowing the nucleation of the β phase at lower temperatures (reduction of the T_β point)³⁴². This strain induced phase transformation has been observed in several studies of plastic deformation on titanium alloys^{342–352}. In fact, Kumar et al. demonstrated that cyclic thermo-mechanical plastic deformation can result in strain accumulation increasing the amount of β phase³⁴⁴. Since the UAM process creates plastic deformation through a biaxial stress state, i.e. the normal force and transverse force (from the sonotrode oscillating at 20 kHz), it is reasonable to conclude that the fraction of the transformed titanium β phase could be higher than that seen through uniaxial tension or compression tests.

During thermal reversals, the β titanium phase nucleates inside of grains at lattice defects and along grain boundaries^{353,354}. As the β grains grow, they sweep across the transformed and untransformed material consuming smaller grains³⁵⁵. Phase transformations during hot deformation occur at stress concentration locations³⁴², grain boundary triple points³⁴⁷, and at lattice defects such as dislocations^{349,351}. As deformation occurs at higher strain rates, more lattice defects or sub-grain boundaries could be formed. The higher concentration of defects can then facilitate further nucleation and growth of the β phase.

Prada et al.³⁴⁵ and Guo et al.³⁵⁰ found that a higher fraction of titanium would have a strain induced β phase transformation with higher applied strains and strain rates. A longer holding time at an elevated temperature results in more β phase reverting back into the α phase. Xu and Zhu³⁴⁸ demonstrated that the amount of retained β phase depends on the cooling rate of the titanium. When the material is rapidly cooled (above 15 °C/s) β phase can remain, while slower cooling allows the β phase to revert back to the α phase³⁴⁸. For the present study, the high strain rate UAM deformation could reduce the T_β point, inducing more β phase to form while the short bonding time, along with the heavily deformed structure, would mitigate the reverse transformation back to α phase. Since the UAM process has a total bonding time of 0.5 seconds, the α phase does not have time to transform back, and β phase remains.

6.4.3 Voids Created During UAM

In addition to the diffusion of elements and phase transformations, there are other features present in the materials such as voids and material cracking at the titanium-vanadium joint (Figure 6.14b). The voids in this image are roughly 200 nm in diameter. The voids that are commonly observed at UAM interfaces are lack of contact voids between mating foil surfaces. These voids are created because of imperfect contact

between the asperities of the rough surfaces. These voids are typically tens of microns in diameter and are described as jagged parabola-like defects^{98,356}. Since the voids observed here are smaller, circular, several microns away from the interface, and fully encapsulated by titanium, they are likely not non-contact voids. Nanometer sized voids (~7 nm in diameter) have been previously observed along UAM interfaces due to vacancy clusters from the agglomeration of individual point defect vacancies^{65,282,340}. Vacancy clusters observed due to irradiation damage are typically 1-10 nm in diameter²⁷⁸, and vacancy clusters observed from other types of high strain rate plastic deformation are 1-2 nm in diameter^{105,106}. The voids observed here are distinct from vacancy clusters because they are much larger. Larger voids or porosity are typically not observed in materials subject to severe plastic deformation^{32,33,134,189,357–360}. The phase transformation of $\alpha \rightarrow \beta$ titanium is also not expected to create voids since the transformation is diffusionless and the two phases have similar molar volumes^{335,341}.

Clearly the above methods are insufficient to understand the voids present in the bonded joints. Although the individual microstructure changes are insufficient to explain the microvoids, the material in the present study had a complex combination of phase transformations and plastic deformation. Therefore, plastic deformation of dual phase titanium alloys could provide some insight regarding these voids. As titanium plastically deforms during hot working, a complex microstructure evolution occurs. This includes phase transformations, dislocation multiplication and pile-up, dynamic recovery, and dynamic recrystallization³⁶¹. Since the HCP α phase is a harder material than the BCC β phase, these microstructure changes can manifest as mechanical strengthening, softening, and strain mismatch. When dual phase titanium alloys have significant plastic deformation, the mechanical heterogeneity between the α phase and the β phase can result in stress concentrations.

High resolution TEM analysis by Wu et al.³⁶² in an α/β titanium alloy demonstrated that initial plastic deformation can begin uniformly in the α phase, then as uniform deformation is difficult to proceed, microvoids appear at α/β interfaces and further deformation results in void growth. After plastic deformation, significant dislocation entanglements and shear bands were found at an α/β interface that was incoherent. This demonstrates that the α/β interface experiences much higher stress than at grain interiors. Microvoids were found throughout their material with 83% of the voids at α/β interfaces. These voids were the result of deformed grains making sharp interfaces and stress concentrations during deformation. The authors also found voids inside of β grains, although these voids were the result of non-uniform grains creating uneven strains. In the present study, the β grains are mostly uniform in shape, suggesting an uneven strain would not be created there. This indicates that the microvoids are created at α/β interfaces, then α titanium continues to transform into β titanium which results in the voids being surrounded in β titanium. Continued plastic deformation can result in microvoid growth and coalescence, although small, recrystallized grain boundaries can hinder their growth. When the microvoids are not hindered by recrystallized grain boundaries, they can grow to a critical size and further UAM plastic deformation can

shear the material. This results in the material developing large tears, as seen on the right side of Figure 6.14b.

6.4.4 Benefits of Altering the Crystal Structure During UAM

UAM bonding is achieved primarily due to the plastic deformation of the crystal structure. During bonding of titanium, the aluminum interlayer accelerates interdiffusion through enhanced concentrations of point defect vacancies, although the titanium remains in the α phase resulting the material cracking. For bonding with vanadium, the β titanium phase is promoted. This increases the ability of UAM to plastically slip and deform because of the higher number of β phase slip systems. Once the titanium transforms to the β phase, there is a lower vacancy formation energy which can enhance the vacancy concentration and promote more interdiffusion of elements. Once the β phase is formed, the material can more easily deform which increases UAM bonding. Once the β phase is formed, plastic deformation on the α/β interphase can result in large voids, which might be detrimental to mechanical properties. The UAM plastic deformation continues in this cycle of phase transformation, vacancy formation, and interdiffusion of elements during the bonding process.

Future improvements to UAM bonding can be obtained by performing surface treatments or adding small interlayers at the faying interfaces. Vanadium and aluminum interlayers are specifically relevant for understanding the fundamental mechanisms associated with UAM bonding of titanium based on the thermodynamic calculations of their solute interactions with titanium (in particular, their influence on lowering the beta transus temperature in titanium). Materials of high interest for future surface treatments include those that increase the stability of the material to plastically deform. Additionally, it is demonstrated that UAM can alter the crystal structure of materials during bonding. The high strain rate plastic deformation causes enhanced interdiffusion and phase transformation of materials. This is a significant discovery that could be used for future material design and modification.

6.5 Conclusion

This study demonstrates the successful UAM bonding of titanium in the hexagonal close packed, α phase, using commercially pure titanium and the Ti-6Al-4V alloy. As the titanium bonds, interdiffusion of elements occurs. Elements that are introduced which reduce T_β result in the titanium forming the β phase, while elements that do not lower the T_β do not result in the titanium phase transformation and result in poor bonding (build fracture). In addition to the introduction of elements promoting an $\alpha \rightarrow \beta$ phase transformation, the phase transformation is rationalized due to a strain induced phase transformation in the material from the plastic deformation UAM process. This paper demonstrates techniques well suited for improving the UAM bonding ability of HCP materials. This is through a designed approach to increase the ability of plastic deformation to occur in the materials.

6.6 Acknowledgements

Sputtering was performed at the University of Tennessee, Knoxville (UTK) Institute of Advanced Materials and Manufacturing (IAMM). UAM bonding was performed at Ohio State University (OSU) and Oak Ridge National Laboratory (ORNL). Scanning electron microscopy and associated spectroscopy was performed at the ORNL - Manufacturing Demonstration Facility (MDF). Focused ion beam machining was performed at the ORNL – Low Activation Materials Design and Analysis Laboratory (LAMDA) by Mr. Gavin Mattingly. X-ray diffraction and transmission electron microscopy was performed at UTK-IAMM by the corresponding author with the mentorship of Dr. Michael Koehler and Dr. Gerd Duscher, respectively. The funding for this research was supplied from the Air Force National Laboratory under contract FA864920P0998.

CHAPTER 7

EFFECTS OF SURFACE ROUGHNESS ON

PLASTIC DEFORMATION FROM

ULTRASONIC ADDITIVE

MANUFACTURING

7.1 Introduction to Asperity Collapse

The above sections have described significant effects can occur due to plastic deformation on Ultrasonic Additive Manufacturing (UAM) interfaces. This has been rationalized using high resolution characterization techniques. A critical issue to address is whether these same effects would be observed at all UAM bonded locations or just the locations that were characterized.

As discussed in Section 2.2.2, during solid-state joining metals come in contact and surface asperities collapse as the materials join. An understanding of asperity deformation has been a classic research topic as it relates to material friction²³¹ and solid-state joining³⁶³. It has been studied empirically for contact resistance welding³⁶⁴, diffusion bonding³⁶, and cold roll bonding^{33,201,365}. The collapse of asperities is considered as a fundamental requirement for UAM bonding^{87,89} and surface roughness effects have been noted as causing joint variation across UAM interfaces^{45,63,98,366,367}.

During solid-state bonding, Tang et al.³⁶⁵ empirically observed that increasing the surface roughness increases the total bond strength (Figure 7.1a-b). In a classic textbook, Bhushan³⁶³ has described asperity collapse during solid state joining. During the initial stages of material contact, there are three points of contact (definition of a plane). These first microasperities will elastically deform, then yield, plastically deform, and collapse. Once the microasperities collapse, the surrounding asperities will take on the load and continue the cycle of elastic deformation, yielding, plastic deformation, and collapsing. The rate at which asperities collapse depends on the asperity's size, shape, distance between other asperities Figure 7.1c.

As asperities plastically deform, the material work hardens. Consider the work hardening during asperity deformation in the hypothetical, two-dimensional situation described below (Figure 7.2). Consider that surface **a** has an asperity height of 5 μm and surface **b** has an asperity height of 1 μm . As the surfaces collapse, the material with larger asperities (surface **a**) has more material to plastically deform and work harden, than the material with smaller asperities (surface **b**). Therefore, it could be suspected that a larger asperity height (rougher surface) should have a higher bond strength. Furthermore, on a given faying surface, there should be variation in work hardening at various locations. By considering points (1) and (2) on surface **a** it is clear to see that there is a different amount of material between the top of the rough surface and the final midpoint of the plane after final asperity collapse. Therefore, there should be notable work hardening variation across the bonded surface due to the variation in the surface profile prior to bonding.

Real materials do not have uniform, two-dimensional asperities. Instead, they consist of a random three-dimensional array of asperities with different heights and spacings. Unfortunately, prior to solid-state bonding contact, it is not trivial to determine exactly where the initial points of contact will be, or what the surface profile distribution surrounding the contact points are.

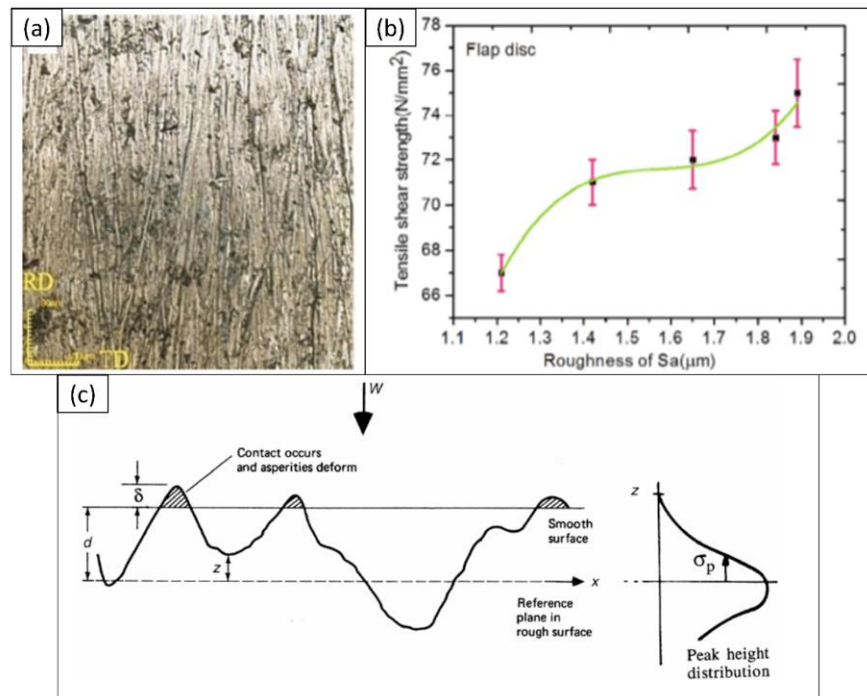


Figure 7.1. Surface roughness during solid-state bonding. a) Example of rough surface for increased bonding³⁶⁵, b) Experimental increase in surface roughness and corresponding bond strength³⁶⁵, c) Local surface asperities in contact prior to collapse³⁶³

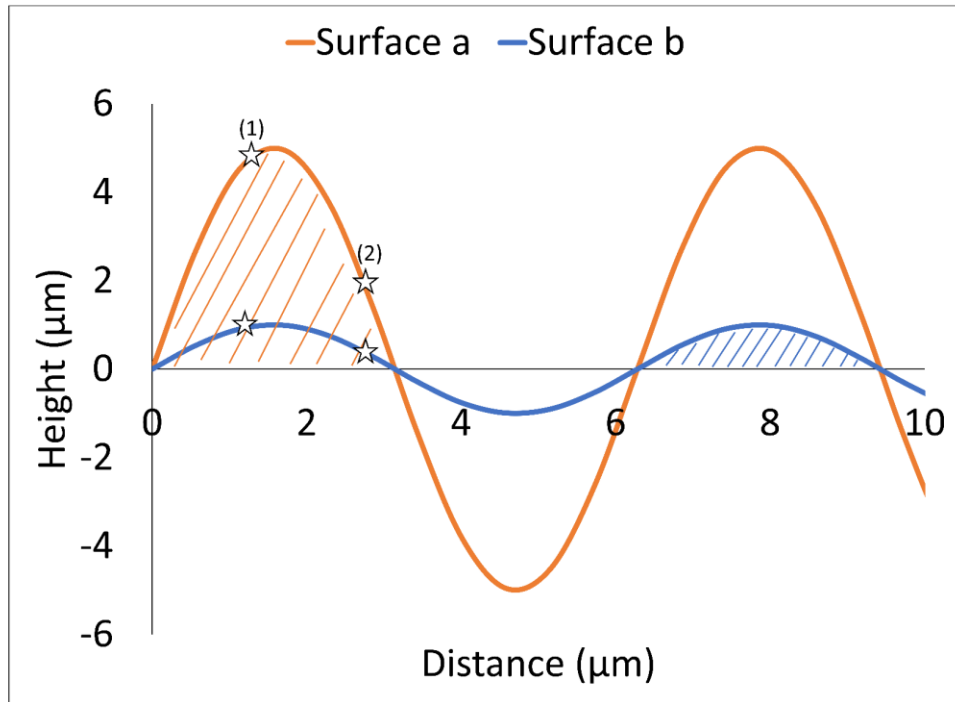


Figure 7.2. Hypothetical surface profile with a 5 μm asperity height and 1 μm asperity height

Additionally, when surfaces come into contact, the location of the initially yielding microasperities depend on planes between the surfaces, their relative angles, and the curvature of the surfaces.

Despite these inherent challenges, initial surface contact has been previously considered during UAM bonding. Johnson ³⁶⁷ demonstrated that UAM surface contact has additional challenges. This is because instead of a uniaxial tensile load being applied, a bi-axial stress state is introduced (normal stress and shear stress from the sonotrode). Surface profilometry of the metal due to contact from the sonotrode (Figure 7.3) demonstrates that there can be various contact states that can develop. This includes direct contact between the sonotrode and the metal foil, horizontal contact, or no contact. In addition to the 10s of microns of surface height difference observed, variation in grain refinement is observed across the surfaces with the different types of sonotrode contact. Grain refinement at UAM interfaces is considered as a result of a dynamic recrystallization process from the intense plastic deformation ^{62,94,96–98}. Therefore, the variation in grain refinement across the different surface locations indicates that variation in plastic deformation occurred at these different locations. A valid conclusion would be that notable work hardening variation exists across UAM interfaces.

7.2 Evaluation of Surface Contact Variation

Work hardening variation exists across UAM bonded interfaces, although a working model of the total magnitude or spatial distribution of the variation is not currently clear. Therefore, the next question is: can this be tested or quantified? A push-pin test is the most common and straightforward method of determining the total bonding strength of joined materials, and it has been commonly used to evaluate UAM builds ^{45,59,60,63,368}. During this test, a flat punch is pushed through the UAM sample normal to the foil-foil interface. In general, a higher calculated stress from the pin is expected to indicate a material that with higher bonding.

Given that a random distribution of work hardening is present at the foil-foil interfaces, it is important to consider the spatial location of where the pin should be applied to test the interface. There are rough surfaces between the materials in contact during UAM bonding, but there is also a rough surface on the pin used for the testing. Given these several compounding rough surfaces, any uncharacterized surface variation could lead to characterization results distinct from the desired testing results. Therefore, the surface of a push-pin should be carefully analyzed.

Although the flat end of a push-pin should have a nominally flat surface, the real surface is far from ideal. The contact distribution from a flat punch was analyzed by Pau et al. ³⁶⁹ using ultrasonic waves and correlated with finite element modeling (Figure 7.4a).

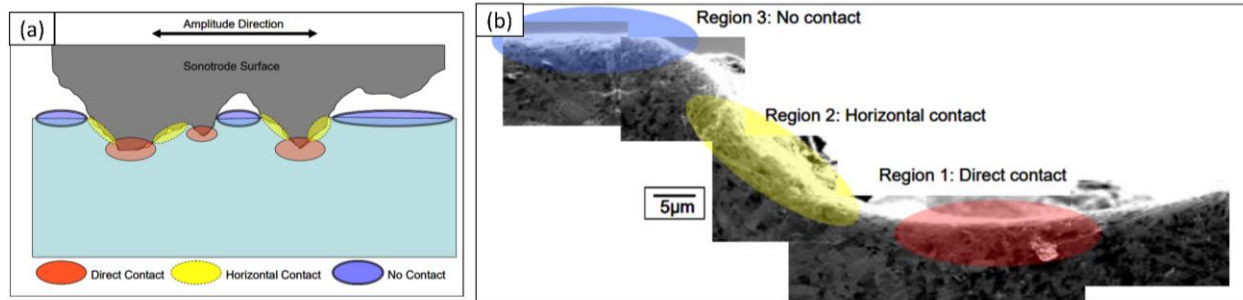


Figure 7.3. Surface roughness and contact during UAM ³⁶⁷

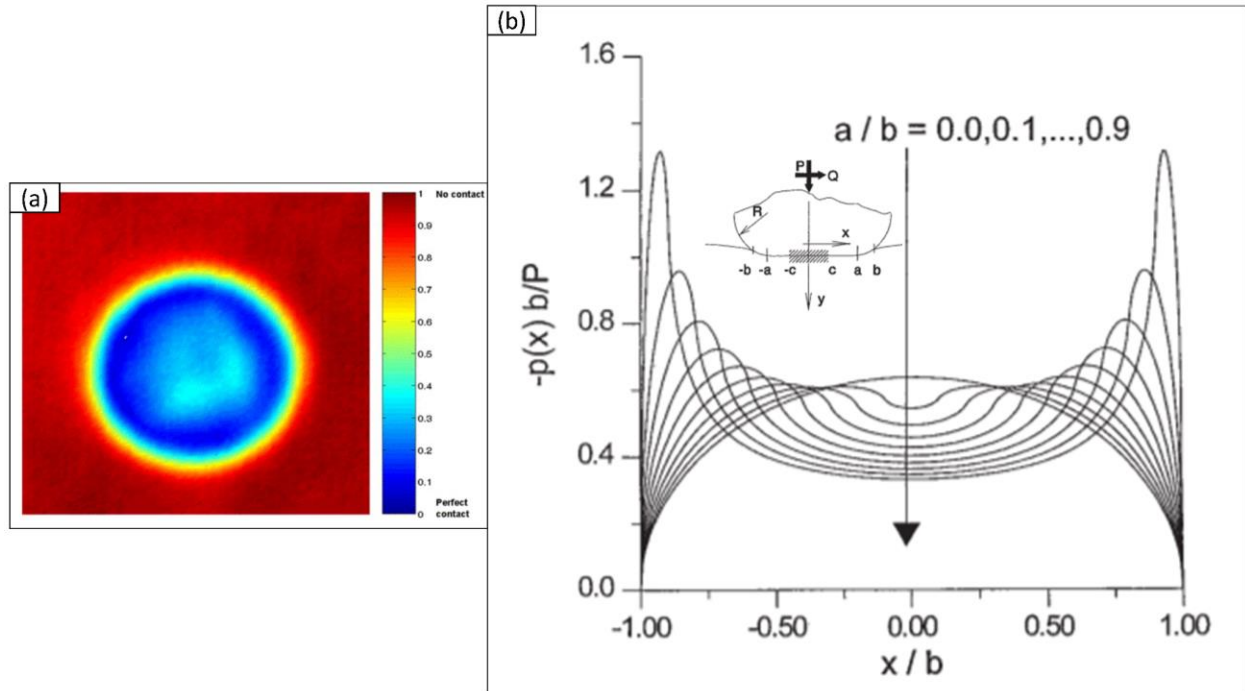


Figure 7.4. Surface contact of flat punch. a) Through ultrasonic waves and finite element modeling ³⁶⁹, b) Through computational calculations ³⁷⁰

Their analysis demonstrated that the center of the pin had the most perfect contact pressure, although it was non-uniform, and outward from the center of the pin had less contact pressure. The one flat punch in their analysis demonstrated a non-uniform and heterogeneous contact pressure across the surface. Care should be taken in extrapolating these results as the repeatability and reproducibility of this surface profile was not examined across commonly manufactured push-pins. Therefore, the exact surface contact profile for a random push-pin used in a future experiment cannot be estimated.

Additionally, the contact pressure distribution on a flat punch has been modeled by Ciavarella et al.³⁷⁰ (Figure 7.4b). In this scenario, position x is the center of the flat punch, position a is the location of the flat part of the punch boundary, and position b is the total contact half-width. The pressure distribution across the surface of the flat punch can be calculated, and it is a function of the ratio of a/b . As this ratio changes from 0.0 to 0.9, the pressure distribution across the surface slowly changes from a maximum at the center and minimum on the outside, to a minimum at the center and a maximum at the outside. The contact distribution estimated above assumes a smooth flat punch surface. Any surface irregularities or rough points add more sharp irregularities to the surface contact distribution. Since the exact surface distribution of a flat punch is not known prior to testing, the surface pressure from the push-pin cannot be determined.

In addition to considering the contact pressure on a push-pin surface, these contact pressure arguments can be applied to the contact between the sonotrode-foil interface or the foil-foil interface. The exact surface geometry of the foil and sonotrode (positions x , a , and b) are not known, and the location and distribution of surface roughness is not known. Therefore, the pressure distribution from the sonotrode to the bonded foils and between bonded foils is not known and cannot be accurately estimated.

As discussed, the contact pressure distribution from the push-pin, from the sonotrode-foil interface, and from the foil-foil interface is unknown. Additionally, the work hardening distribution across the foil-foil interfaces cannot be accurately estimated in a simple manner. For a push-pin test, the pin will contact the material at a distinct location. A representative location for pin-material contact is not known. Therefore, the observed force-displacement curves from the push-pin test could be the result of several different factors as listed above rather than just the work hardening from the foil-foil surface roughness (Figure 7.5).

Given the myriad uncertainties present in surface roughness analysis of UAM, obtaining accurate and representative measurements is questionable. The next logical question to ask is: could analysis be performed using a large statistically significant number of samples? Could the various uncertainties be simplified and only the effects of foil-foil surface roughness remain?

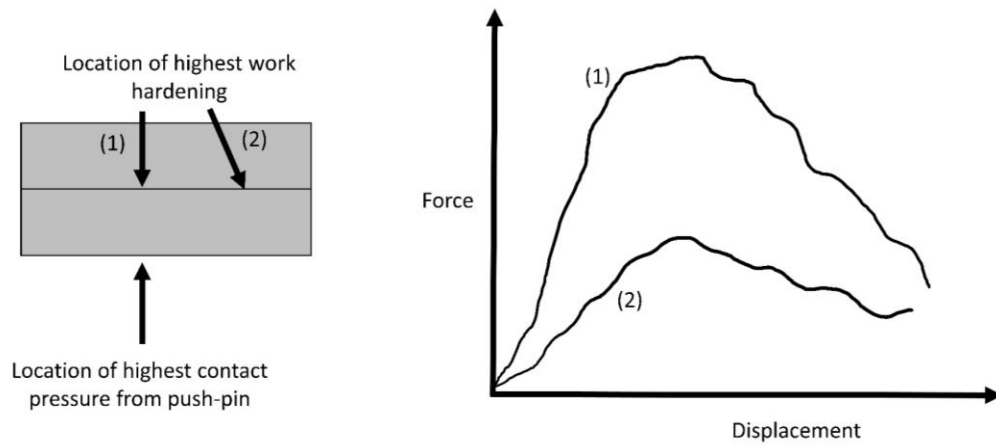


Figure 7.5. Variation in measured strength vs position

Towards this end, Wolcott et al.³⁶⁸ performed UAM bonding using Al 6061. The authors bonded many samples with a textured foil surface ($R_a \sim 5.7 \mu\text{m}$) and with a non-textured foil surface ($R_a \sim 0.12 \mu\text{m}$). The non-textured bonding was created by performing a milling flat pass across a foil surface followed by continued UAM bonding. After bonding, push-pin testing was performed on the samples. Similar peak forces were measured between the samples and a slightly lower average energy was observed for the non-textured sample. Statistical analysis was then performed using a t-test ($\alpha = 0.05$). The t-test found a p value of 0.21. Since the p value was greater than the α value ($p > \alpha$), the tests could not prove that the samples were statistically different. Surface roughness could not be effectively evaluated as contributing to UAM bonding strength. This is likely due to the various other factors that were described above.

7.3 Conclusion

It is extremely likely that a random and unknown distribution of work hardening exists across UAM foil-foil interfaces. There is an unknown distribution of contact pressure between the foil-foil interface, the sonotrode-foil interface, and between a push pin-material interface used for testing. At this point, the evaluation of work hardening variation across the surface of bonded materials is not trivial to effectively evaluate, control, or minimize. Future analysis of the effect of work hardening variation across solid-state bonded materials is important to consider, although the various uncertainties and variations should be carefully considered prior to any testing or analysis. This chapter has demonstrated that it is safer to consider direct observations of the UAM interface microstructure as points in space rather than representing the interface everywhere across the material.

CHAPTER 8

CONCLUSIONS AND FUTURE WORK

8.1 Significant of the work done

Several material systems have been studied after bonding through ultrasonic additive manufacturing (UAM). Material changes have been observed related to enhanced diffusion, nano-void formation, precipitate dissolution, and phase transformation. Many of the observed material changes at the interfaces were accompanied by or the result of significant point defect vacancy concentrations.

An embedded optical fiber – foil interface was analyzed using electron microscopy and spectroscopy. Results demonstrated enhanced elemental migration across the interfaces. Multiple material combinations and locations were used to study the effect. The observed interdiffusion was compared with the expected diffusion, and several orders of magnitude difference was seen. To explain the enhanced interdiffusion, high vacancy concentrations must be present at the interfaces.

The same embedded optical fiber – foil interface was analyzed using nanoindentation and electron microscopy. Local interface strengthening was observed. The corresponding microstructure refinement showed not only reduced grain sizes and elevated dislocation densities, but also the creation of vacancy clusters. The point defect vacancy concentration necessary to cause the vacancy clusters were calculated and the values agree with the vacancy concentration rationalized in the previous study.

A tempered aluminum structure was bonded and analyzed through multi-scale characterization techniques such as tensile testing, x-ray diffraction, nanoindentation, and electron microscopy. Material strengthening was observed at multiple length scales. Several microstructure evolution effects occurred including the dissolution of magnesium-silicon precipitates and diffusion of magnesium out of the precipitate. Given the bonding conditions, thermal equilibrium diffusion could not account for the atomic migration, therefore enhanced vacancy concentrations were likely created. Additionally, vacancy clusters were observed near the interfaces. This offers secondary evidence for the existence of point defect vacancies created by UAM.

Bonding of hexagonal closed packed (HCP) titanium was performed using UAM. The UAM process resulted in a phase transformation to the body centered cubic (BCC) phase. The strain induced phase transformation was stabilized through the atomic movement of certain elements. Interlayers and surface modifications were performed on the HCP material demonstrating methods to improve the bonding ability of these materials.

Although advanced characterization was performed on the microstructure evolution of materials created using UAM, care should be taken in extrapolating these results to all UAM interfaces. Variations in the work hardening on UAM interfaces can occur due to surface profile differences across the joined materials. A critical evaluation of these uncertainties is a non-trivial pursuit.

The chapters in the dissertation have demonstrated that plastic deformation during solid-state UAM bonding can create enhanced vacancy concentrations which significantly alter the microstructure. This microstructure evolution includes accelerated interdiffusion of elements, strengthening effects, precipitate dissolution, and phase transformation. Through understanding the kinetics of plastic deformation during UAM, material improvements can be made to UAM which can enhance the bonding ability for very difficult to weld materials.

The work is significant because it demonstrates that the UAM process not only requires oxide removal and asperity collapse, but plastic deformation is also a fundamental requirement of UAM bonding. Therefore ASM handbooks describing the fundamental processes of UAM ^{47,87} should be updated to reflect this new finding. This dissertation has also demonstrated that elemental introduction can result from the solid-state welding shear actuator (sonotrode in the UAM process). Additionally, UAM can be used to create entirely new materials from the high-strain rate plastic deformation. For example, room temperature stabilize BCC titanium was produced through this work.

The dissertation also quantified plastic deformation induced vacancies. The vacancy concentrations found were many orders of magnitude higher than equilibrium values predicted (X_v : $10^{-4} \gg 10^{-15}$). Vacancy concentrations were calculated using two different methods (interdiffusion calculations and observed vacancy clusters). These independent calculations produced self-similar values adding to the confidence of these results. Plastic deformation induced vacancies was a theory only postulated in metallurgy textbooks ^{102,113}. This dissertation has provided one of the few experimental pieces of evidence of this effect which can enable a more thorough understanding.

Future work expanding on this dissertation could include direct measurements of vacancies. This dissertation indirectly calculated vacancy concentrations that must be present to explain microstructure features. Vacancies could be directly measured using techniques such as positron annihilation spectroscopy. This could provide further insight into the vacancies that are formed.

Additionally, a constitutive expression of deformation induced vacancies could be developed. If a different strain, strain rate, stress state, temperature, geometry, etc. is applied, the concentration of vacancies developed might change. Following this, a more thorough understanding of the process of deformation induced vacancy formation could be created.

This dissertation also demonstrates improvements in the UAM bonding of materials. By advancing the understanding of the fundamentals of UAM bonding, future work can enhance the plastic deformation ability of materials bonding by UAM. This can enable UAM bonding of very difficult to weld materials such as high strength titanium or zirconium alloys, other HCP crystal structure materials, exotic alloy types, or superalloy

designs. This can enable the continued application of UAM bonding for many applications (discussed in Section 2.3.1) including advanced nuclear energy.

The UAM process demonstrated a potential method of creating materials with altered phases and compositions. For example, room temperature stable BCC titanium was shown here. A few select materials were demonstrated in this dissertation, although UAM bonding might be viable for opening new avenues of creating new novel materials.

The solid-state UAM process was used in this dissertation, although other high-strain rate deformation processes could also be considered. These processes could provide viable routes for creating deformation induced vacancies or the creation of new materials as previously discussed.

The high strain rate deformation of titanium during UAM demonstrated that a strain induced phase transformation occurred. Future work could consider evaluating how much deformation is required to reach the critical point to cause a phase transformation. The UAM induced phase transformation also illustrates another valuable future point of research. The BCC titanium phase is not as mechanically strong as the HCP titanium phase. Therefore, if the strain induced phase transformation could be created, and then reversed, the bonding could be performed and the mechanical strength at the interface could be maximized. Future research could investigate the stability of strain induced phase transformations. This is important for not only UAM bonded interfaces, but any material that undergoes a strain induced phase transformation. For comparison, stress induced phase transformations occur during the deformation of shape memory alloys. The diffusion-less phase transformation is reversible upon applying heat or other stimuli or bias applied to the material ³⁷¹. Potential research could include understanding the oriented defects or precipitates associated with the shape memory effect to generally understand what make martensitic phase transformations reversible.

Ultimately, this dissertation developed an understanding of the microstructure evolution during UAM through crystallographic lattice defects. A continued understanding of the kinetics of lattice defects and material deformation can enable future advanced materials and systems to be developed. This has a wide array of potential applications including nuclear, aerospace, biomedical, mechanical, and defense industries.

REFERENCES

1. Administration, U. S. E. I. U.S. Energy Facts Explained. <https://www.eia.gov/energyexplained/us-energy-facts/> (2021).
2. Liou, J. What are Small Modular Reactors (SMRs)? *IAEA International Atomic Energy Agency* <https://www.iaea.org/newscenter/news/what-are-small-modular-reactors-smrs> (2021).
3. Betzler, B. R. *et al.* Transformational Challenge Reactor preconceptual core design studies. *Nucl. Eng. Des.* **367**, 110781 (2020).
4. Energy, O. of N. 4 Major Opportunities for Additive Manufacturing in Nuclear Energy. <https://www.energy.gov/ne/articles/4-major-opportunities-additive-manufacturing-nuclear-energy> (2019).
5. Laboratory, O. R. N. Lowering Costs, Accelerating Innovation. <https://tcr.ornl.gov/why-tcr/> (2020).
6. Dalton, D. US / TVA To Invest \$200M in Plans for SMR At Clinch River Nuclear Site. *Nucnet* <https://www.nucnet.org/news/tva-to-invest-usd200m-in-plans-for-smr-at-clinch-river-nuclear-site-2-1-2022> (2022).
7. Energy, D. GE Hitachi Announces Dominion Energy as Investor in BWRX-300 Small Modular Reactor. *General Electric Press Release* <https://www.ge.com/news/press-releases/ge-hitachi-announces-dominion-energy-investor-bwrx-300-small-modular-reactor> (2018).
8. Energy, G. H. N. The BWRX-300 Small Modular Reactor. <https://nuclear.gepower.com/build-a-plant/products/nuclear-power-plants-overview/bwrx-300> (2022).
9. Energy, O. of N. Ultra Safe Nuclear Licenses New Method for 3D Printing Advanced Reactor Components. <https://www.energy.gov/ne/articles/ultra-safe-nuclear-licenses-new-method-3d-printing-advanced-reactor-components> (2022).
10. TerraPower. A Nuclear Innovation Company. <https://www.terrapower.com/>.
11. Yurman, D. Hyperion to Build Small Modular Reactor at Savannah River. *EnergyCentral* <https://energycentral.com/c/ec/hyperion-build-small-modular-reactor-savannah-river> (2010).
12. Holtec. Holtec International. *Holtec Users Group* <https://holtecinternational.com/products-and-services/smr/> (2022).
13. Corporation, F. NuScale - Small Modular Reactor (SMR) Nuclear Technology. *Fluor Corporation* <https://www.fluor.com/projects/nuscale-power-small-modular-reactor-nuclear> (2022).
14. ASTM-International. Standard terminology for additive manufacturing technologies. *ASTM International* F2792-12a (2012).
15. Frazier, W. E. Metal Additive Manufacturing: A Review. *J. Mater. Eng. Perform.* **23**, 1917–1928 (2014).
16. Mukherjee, T. & DebRoy, T. Mitigation of lack of fusion defects in powder bed fusion additive manufacturing. *J. Manuf. Process.* **36**, 442–449 (2018).
17. Sundar, V. *et al.* Flaw identification in additively manufactured parts using x-rya computed tomography and destructive serial sectioning. *J. Mater. Eng. Perform.* **30**, 4958–4964 (2021).
18. Griffith, M. L. *et al.* Laser engineered net shaping (LENS) for the fabrication of

- metallic components. in *Annual Meeting of the Joint Working Group* (1996).
19. Mudge, R. P. & Wald, N. R. Laser Engineered Net Shaping Advances Additive Manufacturing and Repair. *Weld. J.* **86**, 44–48 (2007).
20. Matz, J. E. & Eagar, T. W. Carbide Formation in Alloy 718 During Electron-Beam Solid Freeform Fabrication. *Metall. Mater. Trans. A* **33**, 2559–2567 (2002).
21. Baufeld, B., Brandl, E. & Biest, O. van der. Wire based additive layer manufacturing: Comparison of microstructure and mechanical properties of Ti-6Al-4V components fabricated by laser-beam deposition and shaped metal deposition. *J. Mater. Process. Technol.* **211**, 1146–1158 (2011).
22. Sames, W. J., List, F. A., Pannala, S., Dehoff, R. R. & Babu, S. S. The Metallurgy and Processing Science of Metal Additive Manufacturing. *Int. Mater. Rev.* **61**, 315–360 (2016).
23. Saboori, A. *et al.* Application of directed energy deposition-based additive manufacturing in repair. *Appl. Sci.* **9**, 3316 (2019).
24. Elliott, A., AlSalhi, S., Merriman, A. L. & Basti, M. M. Infiltration of nanoparticles into porous binder jet printed parts. *Am. J. Eng. Appl. Sci.* **9**, (2016).
25. Cramer, C. L., Weiber, N. R., Aguirre, T. G., Lowden, R. A. & Elliott, A. M. Shape retention and infiltration height in complex wc-co parts made via binder jet of wx with subsequent co metl infiltration. *Addit. Manuf.* **29**, 100828 (2019).
26. Cordero, Z. C., Siddel, D. H., Peter, W. H. & Elliott, A. M. Strengthening of ferrous binder jet 3d printed components through bronze infiltration. *Addit. Manuf.* **15**, 87–92 (2017).
27. Arcam-AB. EBM Hardware. www.arcam.com/technology/electron-beam-melting/hardware/ (2015).
28. Sciaky. Additive Manufacturing. www.sciaky.com/additive_manufacturing.html (2014).
29. Custompartnet.com. 3D printing. www.custompartnet.com/wu/3d-printing (2015).
30. Graff, K. F., Short, M. & Norfolk, M. Very high power ultrasonic additive manufacturing (VHP UAM) for advanced materials. in *Solid Freeform Fabrication Symposium* (2010).
31. Quadir, M. Z., Wolz, A., Hoffman, M. & Ferry, M. Influence of processing parameters on the bond toughness of roll-bonded aluminum strips. *Scr. Mater.* **58**, 959–962 (2008).
32. Tsuji, N. *et al.* Microstructural Change of Ultrafine-Grained Aluminum During High-Speed Plastic Deformation. *Mater. Sci. Eng. A* **350**, 108–116 (2003).
33. Li, L. *et al.* Progress in Cold Roll Bonding of Metals. *Sci. Technol. Adv. Mater.* **023001**, 1–11 (2008).
34. Huang, Y., Ridley, N., Humphreys, F. J. & Cui, J. Diffusion bonding of superplastic 7075 aluminium alloy. *Mater. Sci. Eng. A* **266**, 295–302 (1999).
35. Wang, C., Zhao, T., Wang, G., Gao, J. & Fang, H. Superplastic Forming and Diffusion Bonding of Ti – 22Al – 24Nb Alloy. *J. Mater. Process. Tech.* **222**, 122–127 (2015).
36. Zuruza, A. S., Li, H. & Dong, G. Effects of Surface Roughness on the Diffusion Bonding of Al Alloy 6061 in Air Effects of surface roughness on the diffusion bonding of Al alloy 6061 in air. *Mater. Sci. Eng. A* **270**, 244–248 (1999).

37. Calvo, F. A., URENA, A., GOMEZ DE SALAZAR, J. M. & MOLLEDA, F. Special features of the formation of the diffusion bonded joints between copper and aluminium. *J. Mater. Sci.* **23**, 2273–2280 (1988).
38. Somekawa, M., Watanabe, H., Mukai, T. & Higashi, K. Low temperature diffusion bonding in a superplastic AZ31 magnesium alloy. *Scr. Mater.* **48**, 1249–1254 (2003).
39. Kautz, R. D. D. Fundamentals of Friction Welding. *ASM Handb.* **6A**, (2011).
40. Midling, O. T. & Grong, O. A process model for friction welding of Al-Mg-Si alloys and Al-SiC metal matrix composites - I. HAZ temperature and strain rate distribution. *Acta Metall. Mater.* **42**, 1595–1609 (1994).
41. Bahrani, A. S., Black, T. J. & Crossland, B. The Mechanics of Wave Formation in Explosive Welding. *Proc. R. Soc. Lond. A. Math. Phys. Sci.* **296**, 123–136 (1967).
42. Zhang, Y. *et al.* Application of High Velocity Impact Welding at Varied Different Length Scales. *J. Mater. Process. Technol.* **211**, 944–952 (2011).
43. White, D. R. Ultrasonic Consolidation of Aluminum Tooling. *Adv. Mater. Process.* 64–65 (2003).
44. White, D. Ultrasonic Object Consolidation. *United States Patent* (2003).
45. Schick, D. E. Characterization of Aluminum 3003 Ultrasonic Additive Manufacturing. (Ohio State University, MS Thesis, 2009).
46. Schick, D. E. *et al.* Microstructural Characterization of Bonding Interfaces in Aluminum 3003 Blocks Fabricated by Ultrasonic Additive Manufacturing. *Weld. J.* **89**, 105–115 (2010).
47. Graff, K. Ultrasonic Additive Manufacturing. *ASM Handb.* **6A**, 731–741 (2011).
48. Schick, D. *et al.* Transient Thermal Response in Ultrasonic Additive Manufacturing of Aluminum 3003. *Rapid Prototyp. J.* **17**, 369–379 (2011).
49. Patel, V. K., Bhole, S. D. & Chen, D. L. Influence of Ultrasonic Spot Welding on Microstructure in a Magnesium Alloy. *Scr. Mater.* **65**, 911–914 (2011).
50. Fujii, H. T., Goto, Y., Sato, Y. S. & Kokawa, H. Microstructure and Lap Shear Strength of the Weld Interface in Ultrasonic Welding of Al Alloy to Stainless Steel. *Scr. Mater.* **116**, 135–138 (2016).
51. Mostafavi, S., Hesser, D. F. & Markert, B. Effect of Process Parameters on the Interface Temperature in Ultrasonic Aluminum Wire Bonding. *J. Manuf. Process.* **36**, 104–114 (2018).
52. Fabrasonic. Ultrasonic additive manufacturing. <https://www.youtube.com/watch?v=5s0J-7W4i6s> (2011).
53. Wolcott, P. J. & Dapino, M. J. Ultrasonic Additive Manufacturing. *Addit. Manuf. Handb. Prod. Dev. Def. Ind.* 275–313 (2017) doi:10.1201/9781315119106.
54. Hehr, A. & Norfolk, M. A Comprehensive Review of Ultrasonic Additive Manufacturing. *Rapid Prototyp. J.* (2019) doi:10.1108/RPJ-03-2019-0056.
55. Sriraman, M. R., Babu, S. S. & Short, M. Bonding Characteristics During Very High Power Ultrasonic Additive Manufacturing of Copper. *Scr. Mater.* **62**, 560–563 (2010).
56. Kuo, C.-H., Sridharan, N., Han, T., Dapino, M. J. & Babu, S. S. Ultrasonic Additive Manufacturing of 4130 Steel Using Ni Interlayers. *Sci. Technol. Weld. Join.* **24**, 382–390 (2019).

57. Sridharan, N., Norfolk, M. & Babu, S. S. Characterization of Steel-Ta Dissimilar Metal Builds Made Using Very High Power Ultrasonic Additive Manufacturing (VHP-UAM). *Metall. Mater. Trans. A* **47**, 2517–2528 (2016).
58. Obielodan, J. O. *et al.* Optimization of the Shear Strengths of Ultrasonically Consolidated Ti/Al 3003 Dual-Material Structures. *J. Mater. Process. Technol.* **211**, 988–995 (2011).
59. Wolcott, P. J. *et al.* Characterisation of Al–Ti Dissimilar Material Joints Fabricated using Ultrasonic Additive Manufacturing. *Sci. Technol. Weld. Join.* **21**, 114–123 (2016).
60. Sridharan, N., Wolcott, P., Dapino, M. & Babu, S. S. Microstructure and Mechanical Property Characterisation of Aluminium–Steel Joints Fabricated using Ultrasonic Additive Manufacturing. *Sci. Technol. Weld. Join.* **22**, 373–380 (2016).
61. Hopkins, C. D., Dapino, M. J. & Fernandez, S. A. Statistical Characterization of Ultrasonic Additive Manufacturing Ti/Al Composites. *J. Eng. Mater. Technol. Trans. ASME* **132**, 1–9 (2010).
62. Sridharan, N., Wolcott, P., Dapino, M. & Babu, S. S. Microstructure and Texture Evolution in Aluminum and Commercially Pure Titanium Dissimilar Welds Fabricated Using Ultrasonic Additive Manufacturing. *Scr. Mater.* **117**, 1–5 (2016).
63. Truog, A. G. Bond Improvement of Al/Cu Joints Created by Very High Power Ultrasonic Additive Manufacturing. (Ohio State University, MS Thesis, 2012).
64. Sietins, J. M., Gillespie, J. W. & Advani, S. G. Transmission electron microscopy of an ultrasonically consolidated copper-aluminum interface. *J. Mater. Res.* **29**, 1970–1977 (2014).
65. Pagan, M. *et al.* Interdiffusion of Elements During Ultrasonic Additive Manufacturing. *Metall. Mater. Trans. A* **52**, 1142–1157 (2021).
66. Petrie, C. M. *et al.* Embedded Metallized Optical Fibers for High Temperature Applications. *Smart Mater. Struct.* **28**, 055012 (2019).
67. Guo, H., Gingerich, M. B., Headings, L. M., Hahnlen, R. & Dapino, M. J. Joining of carbon fiber and aluminum using ultrasonic additive manufacturing (UAM). *Compos. Struct.* **208**, 180–188 (2019).
68. Massey, C. P., Havrilak, C. J., Gussev, M. N., Terrani, K. A. & Nelson, A. T. Ultrasonic Additive Manufacturing of Zirconium: Pilot Results. *Mater. Lett.* **302**, 130330 (2021).
69. Hahnlen, R. & Dapino, M. J. NiTi-Al interface strength in ultrasonic additive manufacturing composites. *Compos. Part B Eng.* **59**, 101–108 (2014).
70. Petrie, C. *et al.* Embedded Fiber-Optic Sensors for In-Pile Applications. *11th Nucl. Plant Instrumentation, Control. Human-Machine Interface Technol. NPIC HMIT 2019* 459–468 (2019).
71. Monaghan, T., Capel, A. J., Christie, S. D., Harris, R. A. & Friel, R. J. Solid-state additive manufacturing for metallized optical fiber integration. *Compos. Part A Appl. Sci. Manuf.* **76**, 181–193 (2015).
72. Hahnlen, R. & Dapino, M. J. Active metal-matrix composites with embedded smart materials by ultrasonic additive manufacturing. in *Industrial and Commercial Applications of Smart Structures Technologies* 764500 (2010).
doi:<https://doi.org/10.1117/12.848853>.

73. Norfolk, M. & Johnson, H. Solid-State Additive Manufacturing for Heat Exchangers. *JOM* **67**, 655–659 (2015).
74. Friel, R. J. Power ultrasonics for additive manufacturing and consolidating of materials. in *Power Ultrasonics* 313–335 (Loughborough University, 2013).
75. Monaghan, T., Harding, M. J., Christie, S. D. R., Harris, R. A. & Friel, R. J. Complementary catalysis and analysis within solid state additively manufactured metal micro flow reactors. *Sci. Rep.* **12**, 1–13 (2022).
76. Dapino, M. J. Smart Structure Integration Through Ultrasonic Additive Manufacturing. *ASME 2014 Conf. Smart Mater. Adapt. Struct. Intell. Syst. SMASIS 2014* **2**, 1–8 (2014).
77. Scheidler, J. J. & Dapino, M. J. Stiffness tuning of FeGa structures manufactured by ultrasonic additive manufacturing. *Ind. Commer. Appl. Smart Struct. Technol. 2014* **9059**, 905907 (2014).
78. Burns, J. R., Petrovic, B., Chandler, D. & Terrani, K. A. Reactor physics phenomena in additively manufactured control elements for the High Flux Isotope Reactor. *Ann. Nucl. Energy* **115**, 403–414 (2018).
79. Hehr, A., Wenning, J., Terrani, K., Babu, S. S. & Norfolk, M. Five-Axis Ultrasonic Additive Manufacturing for Nuclear Component Manufacture. *JOM* **69**, 485–490 (2017).
80. Terrani, K. *et al.* Demonstration of Advanced Manufacturing Techniques for Production of Nuclear Core Structures: Ultrasonic Additive Manufacturing of Hybrid Structures Resembling HFIR Control Plates. *OSTI* 2–3 (2008).
81. Friel, R. J. & Harris, R. A. Ultrasonic Additive Manufacturing - A Hybrid Production Process for Novel Functional Products. *Procedia CIRP* **6**, 35–40 (2013).
82. Masurtschak, S., Friel, R. J., Gillner, A., Ryll, J. & Harris, R. A. Fiber laser induced surface modification/manipulation of an ultrasonically consolidated metal matrix. *J. Mater. Process. Technol.* **213**, 1792–1800 (2013).
83. Ram, G. D. J., Robinson, C., Yang, Y. & Stucker, B. E. Use of ultrasonic consolidation for fabrication of multi-material structures. *Rapid Prototyp. J.* **13**, 226–235 (2007).
84. Hyer, H. C., Sweeney, D. C. & Petrie, C. M. Functional Fiber-Optic Sensors Embedded in Stainless Steel Components Using Ultrasonic Additive Manufacturing for Distributed Temperature and Strain Measurements. *Addit. Manuf.* **52**, 102681 (2022).
85. Petrie, C. M., Sridharan, N., Hehr, A., Norfolk, M. & Sheridan, J. High-Temperature Strain Monitoring of Stainless Steel using Fiber Optics Embedded in Ultrasonically Consolidated Nickel Layers. *Smart Mater. Struct.* **28**, 085041 (2019).
86. Tylecote, R. F. *The Solid Phase Welding of Metals*. (Edwards Arnold, 1968).
87. Sridharan, N. & Petrie, C. M. Ultrasonic Additive Manufacturing. *ASM Handb.* **24**, 247–260 (2020).
88. Johnson, K., Edmonds, H. C., Higginson, R. L. & Harris, R. A. New Discoveries in Ultrasonic Consolidation Nano-Structures Using Emerging Analysis Techniques. *Proc. Inst. Mech. Eng. Part L J. Mater. Des. Appl.* **225**, 277–287 (2011).
89. Fujii, H. T., Shimizu, S., Sato, Y. S. & Kokawa, H. High-Strain-Rate Deformation

- in Ultrasonic Additive Manufacturing. *Scr. Mater.* **135**, 125–129 (2017).
90. Rabinowicz, E. *Friction and Wear of Materials*. (Wiley, 1965).
 91. Bowden, F. P. & Rowe, G. W. The adhesion of clean metals. *Proc. R. Soc. Lond. A* **233**, 429–442 (1955).
 92. Courtney-Pratt, J. S. & Eisner, E. The Contact of Metallic Bodies. *Proc. R. Soc. Lond. A. Math. Phys. Sci.* **238**, 529–550 (1957).
 93. Lu, Y., Huang, J. Y., Wang, C., Sun, S. & Lou, J. Cold welding of ultrathin gold nanowires. *Nat. Nanotechnol.* **5**, 218–224 (2010).
 94. Dehoff, R. R. & Babu, S. S. Characterization of Interfacial Microstructures in 3003 Aluminum Alloy Blocks Fabricated by Ultrasonic Additive Manufacturing. *Acta Mater.* **58**, 4305–4315 (2010).
 95. Ward, A. A. & Cordero, Z. C. Junction Growth and Interdiffusion during Ultrasonic Additive Manufacturing of Multi-Material Laminates. *Scr. Mater.* **177**, 101–105 (2020).
 96. Adams, B. L. *et al.* Accessing the elastic-plastic properties closure by rotation and lamination. *Acta Mater.* **56**, 128–139 (2008).
 97. Sojiphan, K. Effects of Very High Power Ultrasonic Additive Manufacturing Process Parameters on Hardness, Microstructure, and Texture of Aluminum 3003-H18 Alloy. (Ohio State University, PhD Dissertation, 2015).
 98. Shimizu, S. *et al.* Mechanism of Weld Formation During Very-High-Power Ultrasonic Additive Manufacturing of Al Alloy 6061. *Acta Mater.* **74**, 234–243 (2014).
 99. Sriraman, M. R., Gonser, M., Fujii, H. T., Babu, S. S. & Bloss, M. Thermal Transients During Processing of Materials by Very High Power Ultrasonic Additive Manufacturing. *J. Mater. Process. Technol.* **211**, 1650–1657 (2011).
 100. Sriraman, M. R. *et al.* Thermal Transients During Processing of 3003 Al-H18 Multilayer Build by Very High-Power Ultrasonic Additive Manufacturing. *Metall. Mater. Trans. B* **43B**, 133–144 (2012).
 101. Mohamed, H. A. & Washburn, J. Mechanism of Solid State Pressure Welding. *Weld. J. (Miami, Fla)* **54**, 302–310 (1975).
 102. Dieter, G. E. *Mechanical Metallurgy*. (McGraw-Hill, 2016).
 103. Mecking, H. & Estrin, Y. The Effect of Vacancy Generation on Plastic Deformation. *Scr. Mater.* **14**, 815–819 (1980).
 104. Kiritani, M. Similarity and difference between fcc, bcc and hcp metals from the view point of point defect cluster formation. *J. Nucl. Mater.* **276**, 41–49 (2000).
 105. Kiritani, M. *et al.* Defect Structures Introduced in FCC Metals by High-Speed Deformation. *Radiat. Eff. Defects Solids* **157**, 53–74 (2002).
 106. Ohkubo, H. *et al.* Positron Annihilation Study of Vacancy-Type Defects in High-Speed Deformed Ni, Cu and Fe. *Mater. Sci. Eng. A* **350**, 95–101 (2003).
 107. Zehetbauer, M., Steiner, G., Schafler, E., Korznikov, A. V. & Korznikova, E. Deformation Induced Vacancies with Severe Plastic Deformation: Measurements and Modelling. *Mater. Sci. Forum* **503–504**, 57–64 (2009).
 108. Huang, Y., Robson, J. D. & Prangnell, P. B. The formation of nanograin structures and accelerated room-temperature theta precipitation in a severely deformed Al-4 wt.% Cu alloy. *Acta Mater.* **58**, 1643–1657 (2010).

109. Straumal, B. B. *et al.* Formation of nanograined structure and decomposition of supersaturated solid solution during high pressure torsion of Al-Zn and Al-Mg alloys. *Acta Mater.* **52**, 4469–4478 (2004).
110. Straumal, B. *et al.* Thermal evolution and grain boundary phase transformations in severely deformed nanograined Al-Zn alloys. *Acta Mater.* **56**, 6123–6131 (2008).
111. Militzer, M., Sun, W. P. & Jonas, J. J. Modelling the effect of deformation-induced vacancies on segregation and precipitation. *Acta Metall.* **42**, 133–141 (1994).
112. Seitz, F. On the generation of vacancies by moving dislocations. *Adv. Phys.* **8732**, 43–90 (1952).
113. Hull, D. & Bacon, D. J. *Introduction to Dislocations*. (Elsevier Ltd, 2011).
114. Cizek, J. *et al.* Structural characterization of ultra fine-grained interstitial-free steel prepared by severe plastic deformation. *Acta Mater.* **105**, 258–272 (2016).
115. Čížek, J. *et al.* The Development of Vacancies during Severe Plastic Deformation. *Mater. Trans.* **60**, 1533–1542 (2019).
116. Sridharan, N. *et al.* Evaluation of microstructure stability at the interfaces of Al-6061 welds fabricated using ultrasonic additive manufacturing. *Mater. Charact.* **139**, 249–258 (2018).
117. Sridharan, N., Isheim, D., Seidman, D. N. & Babu, S. S. Colossal Super Saturation of Oxygen at the Iron-Aluminum Interfaces Fabricated using Solid State Welding. *Scr. Mater.* **130**, 196–199 (2017).
118. Chen, Y. C., Bakavos, D., Gholinia, A. & Prangnell, P. B. HAZ Development and Accelerated Post-Weld Natural Ageing in Ultrasonic Spot Welding Aluminium 6111-T4 Automotive Sheet. *Acta Mater.* **60**, 2816–2828 (2012).
119. Girifalco, L. A. & Herman, H. A model for the growth of guinier-preston zones - the vacancy pump. *Acta Metall.* **13**, 583–590 (1965).
120. Petrie, C. M., Sridharan, N., Hehr, A., Norfolk, M. & Sheridan, J. Embedding Fiber-Optic Strain Sensors Using Ultrasonic Additive Manufacturing. in *Advanced Manufacturing and Material Science: General* vol. 120 438–441 (2019).
121. Hehr, A. *et al.* Integrating Fiber Optic Strain Sensors into Metal Using Ultrasonic Additive Manufacturing. *JOM* **70**, 315–320 (2018).
122. Haddadi, F. & Tsivoulas, D. Grain Structure, Texture and Mechanical Property Evolution of Automotive Aluminium Sheet During High Power Ultrasonic Welding. *Mater. Charact.* **118**, 340–351 (2016).
123. Ward, A. A., French, M. R., Leonard, D. N. & Cordero, Z. C. Grain Growth During Ultrasonic Welding of Nanocrystalline Alloys. *J. Mater. Process. Technol.* **254**, 373–382 (2018).
124. Gunduz, I. E., Ando, T., Shattuck, E., Wong, P. Y. & Doumanidis, C. C. Enhanced diffusion and phase transformations during ultrasonic welding of zinc and aluminum. *Scr. Mater.* **52**, 939–943 (2005).
125. López-Higuera, J. M., Cobo, L. R., Incera, A. Q. & Cobo, A. Fiber optic sensors in structural health monitoring. *J. Light. Technol.* **29**, 587–608 (2011).
126. Li, H. N., Li, D. S. & Song, G. B. Recent applications of fiber optic sensors to health monitoring in civil engineering. *Eng. Struct.* **26**, 1647–1657 (2004).
127. Kersey, A. D. Optical fiber sensors for permanent downwell monitoring applications in the oil and gas industry. *IEICE Trans. Electron* **83**, 400–404

- (2000).
128. Kragas, T. K., Williams, B. A. & Myers, G. A. The optic oil field: deployment and application of permanent in-well fiber optic sensing systems for production and reservoir monitoring. in *SPE Annu. Tech. Conf. Exhibition* (2001).
 129. Zaghloul, M. A. S. *et al.* High Spatial Resolution Radiation Detection Using Distributed Fiber Sensing Technique. *IEEE Trans. Nucl. Sci.* **64**, 2569–2577 (2017).
 130. Kong, C. Y. & Soar, R. Method for embedding optical fibers in an aluminum matrix by ultrasonic consolidation. *Appl. Opt.* **44**, 6325 (2005).
 131. Li, Y., Hua, Z., Yan, F. & Gang, P. Metal coating of fiber Bragg grating and the temperature sensing character after metallization. *Opt. Fiber Technol.* **15**, 391–397 (2009).
 132. Baudrand, D. & Bengston, J. Electroless Plating Processes: Developing Technologies for Electroless Nickel, Palladium and Gold. *Met. Finish.* 55–57 (1995) doi:10.1016/0026-0576(95)99502-2.
 133. Sridharan, N. *et al.* Cascading Microstructures in Aluminum-Steel Interfaces Created by Impact Welding. *Mater. Charact.* **151**, 119–128 (2019).
 134. Beyerlein, I. J. *et al.* Emergence of Stable Interfaces Under Extreme Plastic Deformation. *Proc. Natl. Acad. Sci. U. S. A.* **111**, 4386–4390 (2014).
 135. Misra, A. & Thilly, L. Structural metals at extremes. *MRS Bull.* **37**, 965–972 (2012).
 136. Rohatgi, A. WebPlotDigitizer. <https://automeris.io/WebPlotDigitizer> (2020).
 137. Dixon, J. Industrial Radiation Thermometry. *Meas. Control* **20**, 11–16 (1987).
 138. Button, V. Temperature Transducers. in *Principles of Measurement and Transduction of Biomedical Variables* 101–154 (2015). doi:10.1016/b978-0-12-800774-7.00004-0.
 139. Measurement, T. *Measurement and Instrumentation: Theory and Application - Chapter.* (2012). doi:10.1016/B978-0-12-381960-4.00014-0.
 140. Omega. Temperature Measurement Vol 2. *Thermocouple sensors, Connect. wire, Surf. probes accessories* (2000).
 141. Omega. *Unsheathed Fine Gage Thermocouples.*
 142. Newportus. *Unsheathed Fine Gage Thermocouples - J, K, T, E, R & S.* Omega Engineering Inc. (2020).
 143. Lake Shore Cryotronics, I. *Cernox Technical Specifications.* (2019).
 144. Gale, W. F. & Totemeier, T. C. *Smithells Metals Reference Book.* (Elsevier, 2004).
 145. Matsuno, N. & Oikawa, H. Interdiffusion in copper-Base Cu-Al Solid Solutions. *Metall. Trans. A* **6A**, 2191–2194 (1975).
 146. Shewmon, P. *Diffusion in Solids.* Springer (Springer, The Minerals, Metals & Materials Series, 1979). doi:10.1007/987-3-319-48206.
 147. Balluffi, R. W., Allen, S. M. & Carter, W. C. *Kinetics of Materials.* (John Wiley & Sons, 2005).
 148. Philibert, J. One and a Half Century of Diffusion: Fick, Einstein, before and beyond. *J. Basic Princ. Diffus. Theory, Exp. Appl.* **2**, 1–10 (2005).
 149. Einstein, A. *Investigations on the Theory of Brownian Movement.* (New York:

- Dover Publications, Inc., 1956).
150. Smigelskas, A. & Kirkendall, E. Zinc Diffusion in Alpha Brass. *AIME* **XIII**, 130 (1946).
 151. Nakajima, H. The Discovery and Acceptance of the Kirkendall Effect: The Result of a Short Research Career. *JOM* **49**, 15–19 (1997).
 152. Murty, K. L. & Charit, I. *An Introduction to Nuclear Materials*. (Wiley, 2013).
 153. Mehrer, H. *Diffusion in Solids*. (Springer, 2007).
 154. Manning, J. R. & Bruner, L. J. Diffusion Kinetics for Atoms in Crystals. *Am. J. Phys.* **36**, 922–923 (1968).
 155. Manning, J. R. Diffusion and the Kirkendall shift in binary alloys. *Acta Mater.* **15**, 817–826 (1967).
 156. Holdsworth, P. C. W. & Elliot, R. J. Correlated random walk in a multicomponent alloy self-consistent decoupling approximation. *Philos. Mag. A* **54**, 601–618 (1985).
 157. Holdsworth, P. C. & Elliot, R. J. Correlated random walk in a multicomponent alloy Self-consistent decoupling approximation. *Philos. Mag. A* **54**, 601–618 (1986).
 158. Belova, I. V & Murch, G. E. Tracer correlation factors in the random alloy. *Philos. Mag. A* **80**, 1469–1479 (1999).
 159. Compaan, K. & Haven, Y. Correlation Factors for Diffusion in Solids. *Trans. Faraday Soc.* **52**, 786–801 (1956).
 160. Montet, G. L. Integral Methods in the Calculation of Correlation Factors in Diffusion. *Phys. Rev. B* **7**, 650–662 (1973).
 161. Reed-Hill, R. *Physical Metallurgy Principles*. (Cengage, 1964).
 162. Smallman, R. E. & Ngan, A. H. W. *Modern Physical Metallurgy*. (Butterworth & Co, 2013).
 163. Johnson, W. L. Thermodynamic and kinetic aspects of the crystal to glass transformation in metallic materials. *Prog. Mater. Sci.* **30**, 81–134 (1986).
 164. Chan, R. W. Crystal defects and melting. *Nature* **273**, 491 (1978).
 165. Gorecki, F. Comments on vacancies and melting. *Scr. Mater.* **11**, 1051 (1977).
 166. Stoller, R. E. Primary radiation damage formation. *Compr. Nucl. Mater.* **1**, 293–332 (2012).
 167. Averback, R. S. Atomic displacement processes in irradiated metals. *J. Nucl. Mater.* **216**, 49–62 (1994).
 168. Nordlund, K. *et al.* Primary radiation damage: A review of current understanding and models. *J. Nucl. Mater.* **512**, 450–479 (2018).
 169. Zinkle, S. J. 1.03 - Radiation-Induced Effects on Microstructure. *Compr. Nucl. Mater.* **1**, 65–98 (2012).
 170. Wolfer, W. G. *Fundamental Properties of Defects in Metals*. *Comprehensive Nuclear Materials* vol. 1 (Elsevier Inc., 2012).
 171. Fujimoto, M. *Thermodynamics of Crystalline States*. *Journal of Chemical Information and Modeling* vol. 53 (Springer, 2010).
 172. Davey, W. P. Precision measurements of the lattice constants of twelve common metals. *Phys. Rev.* **25**, 753–761 (1925).
 173. Okamoto, H. & Massalski, T. B. *Phase Diagrams for Binary Alloys*. *ASM Intl* (1991).

174. Wang, J., Lu, X., Sundman, B. & Su, X. Thermodynamic assessment of the Au – Ni system. **29**, 263–268 (2005).
175. Elangovan, S., Semeer, S. & Prakasan, K. Temperature and stress distribution in ultrasonic metal welding-An FEA-based study. *J. Mater. Process. Technol.* **209**, 1143–1150 (2009).
176. Zhang, C. & Li, L. A Coupled Thermal-Mechanical Analysis of Ultrasonic Bonding Mechanism. *Metall. Mater. Trans. B* **40**, 196–207 (2009).
177. Feng, Z. *et al.* Modeling of Resistance Spot Welds: Process and Performance. *Weld. Resarch Abroad* **49**, 29–35 (2003).
178. Borg, R. J. & Dienes, G. J. *An Introduction to Solid State Diffusion*. (Academic Press, Inc., 1988).
179. Simensen, C. J. Comments of the Solubility of Carbon in Molten Aluminum. *Metall. Mater. Trans. A* **20A**, 191 (1989).
180. Qiu, C. & Metselaar, R. Solubility of carbon in liquid Al and stability of Al₄C₃. *J. Alloy. Compd.* **216**, 55–60 (1994).
181. Foster, L. M., Long, G. & Hunter, M. S. Reactions Between Aluminum Oxide and Carbon. *J. Am. Ceram. Soc.* **39**, 1–11 (1956).
182. Hari Kumar, K. S. & Raghavan, V. A Thermodynamic Analysis of the Al-C-Fe System. *J. Phase Equilibria* **12**, 275–286 (1991).
183. Mao, Q. *Understanding The Bonding Process of Ultrasonic Additive Manufacturing*. Mechanical Engineering, University of Clemson (2016).
184. Pal, D. & Stucker, B. A study of subgrain formation in Al 3003 H-18 foils undergoing ultrasonic additive manufacturing using a dislocation density based crystal plasticity finite element framework. *J. Appl. Phys.* **113**, (2013).
185. Sriraman, M. R., Fujii, H. T., Gonser, M., Babu, S. S. & Short, M. Bond Characterization in Very High Power Ultrasonic Additive Manufacturing. *21st Annu. Int. Solid Free. Fabr. Symp. - An Addit. Manuf. Conf. SFF 2010* 372–382 (2010).
186. Ji, H., Wang, J. & Li, M. Microstructure Evolution of 1100 Al Alloy Multi-Foils During Ultrasonic Additive Manufacturing. *2012 Int. Conf. Electron. Packag. Technol. High Density Packag.* 1586–1589 (2012).
187. Fujii, H. T., Sriraman, M. R. & Babu, S. S. Quantitative Evaluation of Bulk and Interface Microstructures in Al-3003 Alloy Builds Made by Very High Power Ultrasonic Additive Manufacturing. *Metall. Mater. Trans. A* **42**, 4045–4055 (2011).
188. Cahn, R. W. *Recovery and Recrystallization*. *Physical Metallurgy* (Elsevier B.V., 1996). doi:10.1016/B978-0-444-89875-3.50033-8.
189. Huang, K. & Logé, R. E. A Review of Dynamic Recrystallization Phenomena in Metallic Materials. *Mater. Des.* **111**, 548–574 (2016).
190. Aust, K. & Rutter, J. Grain boundary migration in high-purity lead and dilute lead-tin alloys. *Trans AIME* **215**, (1959).
191. Ma, Q., Liu, C. L., Adams, J. B. & Balluffi, R. W. Diffusion Along [001] Tilt Boundaries in the Au / Ag System - II. Atomistic Modeling and Interpretation. *Acta Metall.* **41**, 143–151 (1993).
192. Mishin, Y. & Herzig, C. Grain boundary diffusion: recent progress and future research. *Mater. Sci. Eng. A* **A260**, 55–71 (1999).

193. Mishin, Y., Herzig, C., Bernardini, J. & Gust, W. Grain boundary diffusion: Fundamentals to recent developments. *Int. Mater. Rev.* **42**, 155–178 (1997).
194. Goldstein, J. I. *et al.* *Scanning Electron Microscopy and Microanalysis. Physicochemical Methods of Mineral Analysis* (1975). doi:10.1007/978-1-4684-2046-3_11.
195. Mueller, J. E., Gillespie, J. W. & Advani, S. G. Effects of interaction volume on X-ray line-scans across an ultrasonically consolidated aluminum/copper interface. *Scanning* **35**, 327–335 (2013).
196. Valiev, R. Z., Islamgaliev, R. K. & Alexandrov, I. V. *Bulk nanostructured materials from severe plastic deformation. Progress in Materials Science* vol. 45 (2000).
197. Chen, M. C., Hsieh, C. C. & Wu, W. Microstructural characterization of Al/Mg alloy interdiffusion mechanism during accumulative roll bonding. *Met. Mater. Int.* **13**, 201–205 (2007).
198. Chen, M. C., Hsieh, H. C. & Wu, W. The evolution of microstructures and mechanical properties during accumulative roll bonding of Al/Mg composite. *J. Alloys Compd.* **416**, 169–172 (2006).
199. Ohsaki, S., Kato, S., Tsuji, N., Ohkubo, T. & Hono, K. Bulk mechanical alloying of Cu-Ag and Cu/Zr two-phase microstructures by accumulative roll-bonding process. *Acta Mater.* **55**, 2885–2895 (2007).
200. Raabe, D., Ohsaki, S. & Hono, K. Mechanical alloying and amorphization in Cu-Nb-Ag in situ composite wires studied by transmission electron microscopy and atom probe tomography. *Acta Mater.* **57**, 5254–5263 (2009).
201. Jamaati, R. & Toroghinejad, M. R. Cold roll bonding bond strengths: Review. *Mater. Sci. Technol.* **27**, 1101–1108 (2011).
202. Saito, Y., Utsunomiya, H., Tsuji, N. & Sakai, T. Novel Ultra-High Straining Process for Bulk Materials Development of the Accumulative Roll-Bonding (ARB) Process. *Acta Metall. Inc.* **47**, (1999).
203. Tsuji, N., Saito, Y., Lee, S. H. & Minamino, Y. ARB (accumulative roll-bonding) and other new techniques to produce bulk ultrafine grained materials. *Adv. Eng. Mater.* **5**, 338–344 (2003).
204. Tsuji, N., Saito, Y., Utsunomiya, H. & Tanigawa, S. Ultra-fine grained bulk steel produced by accumulative roll-bonding (ARB) process. *Scr. Mater.* **40**, 795–800 (1999).
205. Jamaati, R. & Toroghinejad, M. R. Investigation of the parameters of the cold roll bonding (CRB) process. *Mater. Sci. Eng. A* **527**, 2320–2326 (2010).
206. Langenecker, B. Effects of Ultrasound on Deformation Characteristics of Metals. *IEEE Trans. Sonics Ultrason.* **12**, (1966).
207. Colanto, D. S. Electrical Resistivity Measurements to Assess Vacancy Concentration in Aluminum During Ultrasonic Deformation and Vibratory Consolidation of Aluminum-Carbon Nanotube Composites. (Northeastern University, 2010).
208. Cosslett, V. E. & Thomas, R. N. Multiple scattering of 5-30 keV electrons in evaporated metal films II: Range-energy relations. *Br. J. Appl. Phys.* **15**, 1283–1300 (1964).
209. Williams, D. B. & Carter, C. B. *Transmission Electron Microscopy.* Springer

- Science* (Springer, 2011).
210. Han, T. *et al.* Effect of Preheat Temperature and Post-Process Treatment on the Microstructure and Mechanical Properties of Stainless Steel 410 Made via Ultrasonic Additive Manufacturing. *Mater. Sci. Eng. A* **769**, 138457 (2020).
 211. Sridharan, N. *et al.* Rationalization of Anisotropic Mechanical Properties of Al-6061 Fabricated Using Ultrasonic Additive Manufacturing. *Acta Mater.* **117**, 228–237 (2016).
 212. Pharr, G. M., Strader, J. H. & Oliver, W. C. Critical issues in making small-depth mechanical property measurements by nanoindentation with continuous stiffness measurement. *J. Mater. Res.* **24**, 653–666 (2009).
 213. Li, D. & Soar, R. C. Plastic Flow and Work Hardening of Al Alloy Matrices During Ultrasonic Consolidation Fibre Embedding Process. *Mater. Sci. Eng. A* **498**, 421–429 (2008).
 214. Phani, P. S. & Oliver, W. C. A Critical Assessment of the Effect of Indentation Spacing on the Measurement of Hardness and Modulus using Instrumented Indentation Testing. *Mater. Des.* **164**, 107563 (2019).
 215. Vander Voort, G. F. Practical Applications of Quantitative Metallography. in *Practical Applications of Quantitative Metallography* (eds. McCall, J. L. & Steele, J. H.) 85–131 (American Society for Testing and Materials, 1984). doi:10.1520/stp36848s.
 216. Ham, R. K. The determination of dislocation densities in thin films. *Philos. Mag. A* **6**, 1183–1184 (1961).
 217. Tabor, D. Indentation Hardness and Its Measurement : Some Cautionary Comments. *Microindentation Tech. Mater. Sci. Eng. ASTM STP 889* 129–159 (1986).
 218. Stelmashenko, N. A., Walls, M. G., Brown, L. M. & Milman, Y. V. Microindentations on W and Mo oriented single crystals: An STM Study. *Acta Metall. Mater.* **41**, 2855–2865 (1993).
 219. Guzman, M. S. De, Neubauer, G., Flinn, P. & Nix, W. D. The Role of Indentation Depth on the Measured Hardness of Materials. *Mater. Res. Soc. Proc.* **308**, 613 (1993).
 220. Atkinson, M. Further Analysis of the Size Effect in Indentation Hardness Test of Some Metals. *J. Mater. Res.* **10**, 2908 (1995).
 221. Ma, Q. & Clarke, D. R. Size Dependent Hardness of Silver Single Crystals. *J. Mater. Res.* **10**, 853 (1995).
 222. Poole, W. J., Ashby, M. F. & Fleck, N. A. Micro-hardness of Annealed and Work-hardened Copper Polycrystals. *Scr. Mater.* **34**, 559–564 (1996).
 223. McElhaney, K. W., Vlassak, J. J. & Nix, W. D. Determination of Indenter Tip Geometry and Indentation Contact Area for Depth-Sensing Indentation Experiments. *J. Mater. Res.* **13**, 1300–1306 (1998).
 224. Suresh, S., Nieh, T. G. & Choi, B. W. Nano-indentation of Copper Thin Films of Silicon Substrates. *Scr. Mater.* **41**, 951–957 (1999).
 225. Nix, W. D. & Gao, H. Indentation Size Effects in Crystalline Materials: A Law for Strain Gradient Plasticity. *J. Mech. Phys. Solids* **46**, 411–425 (1998).
 226. Huang, Y. *et al.* A Model of Size Effects in Nano-Indentation. *J. Mech. Phys.*

- Solids* **54**, 1668–1686 (2006).
227. Wang, Z. *et al.* On the Crystallographic Anisotropy of Plastic Zone Size in Single Crystalline Copper Under Berkovich Nanoindentation. *Mater. Today Commun.* **25**, 101314 (2020).
 228. Pharr, G. M., Herbert, E. G. & Gao, Y. The Indentation Size Effect: A Critical Examination of Experimental Observations and Mechanistic Interpretations. *Annu. Rev. Mater. Res.* **40**, 271–292 (2010).
 229. Swadener, J. G., George, E. P. & Pharr, G. M. The Correlation of the Indentation Size Effect Measured with Indenters of Various Shapes. *J. Mech. Phys. Solids* **50**, 681–694 (2002).
 230. Tabor, D. The Hardness of Solids. *Rev. Phys. Technol.* **1**, 145–179 (1970).
 231. Tabor, D. Friction - The Present State of Our Understanding. *J. Lubr. Technol.* **103**, 169–179 (1981).
 232. Zhu, P., Zhao, Y., Agarwal, S., Henry, J. & Zinkle, S. J. Toward accurate evaluation of bulk hardness from nanoindentation testing at low indent depths. *Mater. Des.* **213**, 110317 (2022).
 233. Taylor, G. I. Plastic Strain in Metals. *J. Inst. Met.* **62**, 307–324 (1938).
 234. Hall, E. O. The Deformation and Ageing of Mild Steel: III Discussion of Results. *Proc. Phys Soc., Sec. B* **64**, 747–755 (1951).
 235. Petch, N. J. The Cleavage Strength of Polycrystals. *J. Iron. Steel Inst* **174**, 25–28 (1953).
 236. Cordero, Z. C., Knight, B. E. & Schuh, C. A. Six Decades of the Hall–Petch Effect – A Survey of Grain-Size Strengthening Studies on Pure Metals. *Int. Mater. Rev.* **61**, 495–512 (2016).
 237. Lo, C. C., Augis, J. A. & Pinnel, M. R. Hardening mechanisms of hard gold. *J. Appl. Phys.* **50**, 6887–6891 (1979).
 238. Chew, Y. H., Wong, C. C., Wulff, F., Lim, F. C. & Goh, H. M. Strain rate sensitivity and Hall-Petch behavior of ultrafine-grained gold wires. *Thin Solid Films* **516**, 5376–5380 (2008).
 239. Floreen, S. & Westbrook, J. H. Grain boundary segregation and the grain size dependence of strength of nickel-sulfur alloys. *Acta Metall.* **17**, 1175–1181 (1969).
 240. Sonon, D. E. & Smith, G. V. Effect of grain size and temperature on the strengthening of nickel and nickel-cobalt by carbon. *Trans. Am. Inst. Met. Eng* **242**, 1527–1533 (1968).
 241. Nakada, Y. & Keh, A. S. Solid-solution strengthening in Ni-C Alloys. *Metall. Trans. A* **2**, 441–447 (1971).
 242. Wilcox, B. A. & Clauer, A. H. The role of grain size and shape in strengthening of dispersion hardened nickel alloys. *Acta Metall.* **20**, 743–757 (1972).
 243. Thompson, A. W. Yielding in nickel as a function of grain or cell size. *Acta Metall.* **23**, 1337–1342 (1975).
 244. Hughes, G. D., Smith, S. D., Pande, C. S., Johnson, H. R. & Armstrong, R. W. Hall-Petch strengthening for the microhardness of twelve nanometer grain diameter electrodeposited nickel. *Scr. Mater.* **20**, 93–97 (1986).
 245. El-Sherik, A. M., Erb, U., Palumbo, G. & Aust, K. T. Deviations from Hall-Petch behavior in as-prepared nanocrystalline nickel. *Scr. Mater.* **27**, 1185–1188 (1992).

246. Ebrahimi, F., Bourne, G. R., Kelly, M. S. & Matthews, T. E. Mechanical properties of nanocrystalline nickel produced by electrodeposition. *Nanostructured Mater.* **11**, 343–350 (1999).
247. Schuh, C. A., Nieh, T. G. & Yamasaki, T. Hall-Petch breakdown manifested in abrasive wear resistance of nanocrystalline nickel. *Scr. Mater.* **46**, 735–740 (2002).
248. Samuels, L. E. & Mulhearn, T. O. An Experimental Investigation of the Deformed Zone Associated with Indentation Hardness Impressions. *J. Mech. Phys. Solids* **5**, 125–134 (1957).
249. Johnson, K. L. *Contact Mechanics*. (Cambridge University Press, 1985).
250. Fleischer, R. L. Substitutional Solution Hardening. *Acta Metall.* **11**, 203–209 (1963).
251. Ralls, K., Courtney, T. H. & Wulff, F. *Introduction to Materials Science and Engineering*. (John Wiley & Sons, 1976).
252. Akhtar, A. & Teghtsoonian, T. Solid solution strengthening of magnesium single crystals - I alloying behavior in basal slip. *Acta Metall.* **17**, 1339–1349 (1969).
253. Yasi, J. A., Hector, L. G. & Trinkle, D. R. First-principles data for solid-solution strengthening of magnesium: From geometry and chemistry to properties. *Acta Mater.* **58**, 5704–5713 (2010).
254. Nakada, Y. & Keh, A. S. Solid solution strengthening in Fe-N single crystals. *Acta Metall.* **16**, 903–914 (1968).
255. Caceres, C. H. & Rovera, D. W. Solid solution strengthening in concentrated Mg-Al alloys. *J. Light Met.* **1**, 151–156 (2001).
256. Gao, L., Chen, R. S. & Han, E. H. Effects of rare-earth elements Gd and Y on the solid solution strengthening of Mg Alloys. *J. Alloys Compd.* **481**, 379–384 (2009).
257. Gao, L., Chen, R. S. & Han, E. H. Solid solution strengthening behaviors in binary Mg-Y single phase alloys. *J. Alloys Compd.* **472**, 234–240 (2009).
258. Walbruhl, M., Linder, D., Agren, J. & Borgenstam, A. Modelling of solid solution strengthening in multicomponent alloys. *Mater. Sci. Eng. A* **700**, 301–311 (2017).
259. Fleischer, R. L. Solution hardening. *Acta Metall.* **9**, 996–1000 (1961).
260. Fleischer, R. L. Solution hardening by tetragonal distortions: Application to irradiation hardening in F.C.C. crystals. *Acta Metall.* **10**, 835–842 (1962).
261. Kaye, G. W. C. & Laby, T. H. *Tables of physics and chemical constants*. (Longman, 1993).
262. Maddin, R. & Cottrell, A. H. Quench Hardening in Aluminum Single Crystals. *Philos. Mag. A* **46**, 735–743 (1955).
263. Zehetbauer, M. Effects of non-equilibrium vacancies on strengthening. *Mech. Corros. Prop. Ser. A, Key Eng. Mater.* **97–98**, 287–306 (1994).
264. Townsend, J. R., DiCarlo, J. A., Nielsen, R. L. & Stabell, D. The elastic bulk effect of point defects in metals. *Acta Metall.* **17**, 425–436 (1969).
265. Dieckamp, H. & Sosin, A. Effect of electron irradiation on metal. *J. Appl. Phys.* **27**, 1416–1418 (1956).
266. Robrock, K.-H. & Schilling, W. Diaelastic modulus change of aluminium after low temperature electron irradiation. *J. Phys. F Met. Phys.* **6**, 303–314 (1976).
267. Corbett, J. W. *Electron Radiation Damage in Semiconductors and Metals*.

- (Academic Press, Inc., 1966).
268. Zinkle, S. J. & Singh, B. N. Analysis of Displacement Damage and Defect Production Under Cascade Damage Conditions. *J. Nucl. Mater.* **199**, 173–191 (1993).
 269. Poerschke, R. & Wollenberger, H. The Decomposition of Low Temperature Irradiated Cu-Ni Alloys Upon Isochronal Annealing. *Radiat. Eff. Defects Solids* **49**, 225–232 (1980).
 270. Nakata, K., Takamura, S. & Kobiyama, M. Recovery of yield stress in dilute Ni alloys after electron and neutron irradiations at low temperatures. *J. Nucl. Mater.* **178**, 40–47 (1991).
 271. Bartels, A., Dworschak, F. & Weigert, M. Isochronal recovery and damage rate measurements in electron-irradiated dilute NiGe. *J. Nucl. Mater.* **149**, 160–167 (1987).
 272. Seeger, A. Dispersed Barrier Modeling. in *Proc. 2nd UN Conf on Peaceful Uses of Atomic Energy, Geneva, vol. 6* 250 (1958).
 273. Friedel, J. Weak Obstacle Model. in *Dislocations, Pergamon*.
 274. Kroupa, F. & Hirsch, P. B. Elastic interaction between prismatic dislocation loops and straight dislocations. *Discuss. Faraday Soc.* **38**, 49–55 (1964).
 275. Vook, R. W. & Wert, C. A. Expansion of Copper Upon Low-Temperature Deuteron Irradiation. *Phys. Rev.* **109**, 1529–1537 (1958).
 276. Simmons, R. O. & Balluffi, R. W. X-ray Study of Deuteron-Irradiated Copper Near 10K. *Phys. Rev.* **109**, 1142–1152 (1958).
 277. Tewordt, L. Distortion of the Lattice Around an Interstitial, a Crowdion, and a Vacancy in Copper. *Phys. Rev.* **109**, 61–68 (1958).
 278. Tan, L. & Busby, J. T. Formulating the Strength Factor α for Improved Predictability of Radiation Hardening. *J. Nucl. Mater.* **465**, 724–730 (2015).
 279. Foreman, A. J. E. & Makin, M. J. Dislocation Movement Through Random Arrays of Obstacles. *Philos. Mag. A* **14**, 911–924 (1966).
 280. Odette, G. R. & Lucas, G. E. Recent Progress in Understanding Reactor Pressure Vessel Steel Embrittlement. *Rad. Eff. Def. Solids* **144**, 189–231 (1998).
 281. Frank, F. C. & Read, W. T. Multiplication Processes for Slow Moving Dislocations. *Phys. Rev.* **79**, 722–723 (1950).
 282. Pagan, M., Ohmura, T., Ling, W., Zinkle, S. J. & Babu, S. S. Strengthening Effects at Dissimilar Metal Interfaces Created by Ultrasonic Additive Manufacturing. *Metall. Mater. Trans. A (Under Rev.* (2022).
 283. ASM. Heat Treating of Aluminum Alloys. *ASM Handb.* **4**, 841–879 (1991).
 284. Merle, B., Maier-Kiener, V., Rupert, T. J. & Pharr, G. M. Current Trends in Nanomechanical Testing Research. *J. Mater. Res.* **36**, 2133–2136 (2021).
 285. Liu, Z., Zhang, J., He, B. & Zou, Y. High-Speed Nanoindentation Mapping of a Near-Alpha Titanium Alloy Made by Additive Manufacturing. *J. Mater. Res.* **36**, 2223–2234 (2021).
 286. Magazzeni, C. M. *et al.* Nanoindentation in Multi-Modal Map Combinations: A Correlative Approach to Local Mechanical Property Assessment. *J. Mater. Res.* **36**, 2235–2250 (2021).
 287. Oliver, W. C. & Pharr, G. M. An Improved Technique for Determining Hardness

- and Elastic Modulus Using Load and Displacement Sensing Indentation Experiments. *J. Mater. Res.* **7**, 1564–1583 (1992).
288. Li, X. & Bhushan, B. A Review of Nanoindentation Continuous Stiffness Measurement Technique and its Applications. *Mater. Charact.* **48**, 11–36 (2001).
 289. Oliver, W. C. & Pharr, G. M. Measurement of Hardness and Elastic Modulus by Instrumented Indentation: Advances in Understanding and Refinements to Methodology. *J. Mater. Res.* **19**, 3–20 (2004).
 290. Thermo-Calc Software. Thermo-Calc Software. (2021).
 291. Laboratory, A. N. Advanced Photon Source: Beamline 11-BM: High Resolution Powder Diffraction. *U.S. Department of Energy*
<https://11bm.xray.aps.anl.gov/description.html> (2018).
 292. Wang, J. et al. A Dedicated Powder Diffraction Beamline at the Advanced Photon Source: Commissioning and Early Operational Results. *Rev. Sci. Instrum.* **085105-1–7** (2008).
 293. Will, G. *Powder Diffraction: The Rietveld Method And The Two Stage Method To Determine and Refine Crystal Structures From Powder Diffraction Data.* (Springer, 2006).
 294. Young, R. A. *The Rietveld Method.* (Oxford University Press, 1995).
 295. Considère, A. Memoire Sur L'emploi Du Fer Et De L'acier Dans Les Constructions. *Ann. Ponts Chaussees* **9**, 574 (1985).
 296. Kaufman, J. G. Understanding the Aluminum Temper Designation System. *Introd. to Alum. Alloy. Tempers* 39–76 (2000) doi:10.1361/iaat2000p039.
 297. Ding, S., Shi, Q. & Chen, G. Flow Stress of 6061 Aluminum Alloy at Typical Temperatures During Friction Stir Welding Based on Hot Compression Tests. *Metals (Basel)*. **11**, 1–15 (2021).
 298. ASM International. Wrought Aluminum (WA). *Atlas Stress. Curves* 299–309 (2014).
 299. Smith, W. F. *Structure and Properties of Engineering Alloys.* (1981).
 300. Wang, J., Zhou, Q., Shao, S. & Misra, A. Strength and Plasticity of Nanolaminated Materials. *Mater. Res. Lett.* **5**, 1–19 (2017).
 301. Abood, A. N., Saleh, A. H. & Abdullah, Z. W. Effect of Heat Treatment on Strain Life of Aluminum Alloy AA 6061. *J. Mater. Sci. Res.* **2**, 51–59 (2013).
 302. Kaufman, J. G. Understanding Wrought and Cast Aluminum Alloys Designations. *ASM Int. Chapter 3*, 23–37 (2000).
 303. Li, D. A Review of Microstructure Evolution During Ultrasonic Additive Manufacturing. *Int. J. Adv. Manuf. Technol.* **113**, 1–19 (2021).
 304. Čížek, J., Melikhova, O., Barnovská, Z., Procházka, I. & Islamgaliev, R. K. Vacancy Clusters in Ultra Fine Grained Metals Prepared by Severe Plastic Deformation. *J. Phys. Conf. Ser.* **443**, (2013).
 305. Vo, N. Q., Odunuga, S., Bellon, P. & Averbach, R. S. Forced Chemical Mixing in Immiscible Alloys During Severe Plastic Deformation at Elevated Temperatures. *Acta Mater.* **57**, 3012–3019 (2009).
 306. Kiritani, M., Urban, K. & Yoshida, N. Formation of Submicroscopic Vacancy Clusters and Radiation-Induced Refining in Metals By Electron-Irradiation At High Temperatures. *Radiat. Eff.* **61**, 117–126 (1982).

307. Guzmán, I. *et al.* Comparative in Mechanical Behavior of 6061 Aluminum Alloy Welded by Pulsed GMAW with Different Filler Metals and Heat Treatments. *Materials (Basel)*. **12**, 1–14 (2019).
308. Zhang, Z., Xu, H., Wu, S. & Liu, Y. Effects of Combined Pre-straining and Pre-aging on Natural Aging and Bakehardening Response of an Al-Mg-Si alloy. *Acta Metall. Sin. (English Lett.)*. **26**, 340–344 (2013).
309. Maisonnnette, D., Suery, M., Nelias, D., Chaudet, P. & Epicier, T. Effects of Heat Treatments on the Microstructure and Mechanical Properties of a 6061 Aluminium Alloy. *Mater. Sci. Eng. A* **528**, 2718–2724 (2011).
310. Puttick, K. E. Ductile Fracture in Metals. *Philos. Mag.* **4**, 964–969 (1959).
311. Rogers, H. C. The Tensile Fracture of Ductile Metals. *AIME Trans* **218**, 498–506 (1960).
312. Crussard, C. *Fracture*. (John Wiley & Sons, 1959).
313. Das, A., Das, S. K. & Tarafder, S. Correlation of Fractographic Features with Mechanical Properties in Systematically Varied Microstructures of Cu-Strengthened High-Strength Low-Alloy Steel. *Metall. Mater. Trans. A* **40A**, 3138–3416 (2009).
314. Broek, D. The Role of Inclusions and Fracture. *Eng. Fract. Mech.* **5**, 55–66 (1972).
315. Milkereit, B., Giersberg, L., Kessler, O. & Schick, C. Isothermal Time-Temperature-Precipitation Diagram for an Aluminum Alloy 6005A by In Situ DSC Experiments. *Materials (Basel)*. **7**, 2631–2649 (2014).
316. Van Bueren, M. R. J., Voermans, F. & Van Kempen, H. Bonding in Mg₂Si Studied with X-ray Photoelectron Spectroscopy. *J. Phys. Chem* **99**, 9519–9522 (1995).
317. Tang, Y., Du, Y., Zhang, L., Yuan, X. & Kaptay, G. Thermodynamic description of the Al-Mg-Si system using a new formulation for the temperature dependence of the excess Gibbs energy. *Thermochim. Acta* **527**, 131–142 (2012).
318. Qin, J. *et al.* Coarsening behavior of Mg₂Si precipitates during post homogenization cooling process in Al-Mg-Si alloy. *J. Alloys Compd.* **902**, 162851 (2022).
319. Hakem, M. *et al.* Effect of Microstructure and Precipitation Phenomena on the Mechanical Behavior of AA6061-T6 Aluminum Alloy Weld. *Int. J. Adv. Manuf. Technol.* **102**, 2907–2918 (2019).
320. Linardi, E., Haddad, R. & Lanzani, L. Stability Analysis of the Mg₂Si Phase in AA 6061 Aluminum Alloy. *Procedia Mater. Sci.* **1**, 550–557 (2012).
321. Li, L. L. *et al.* SVET Study of Galvanic Corrosion of Al/Mg 2 Si Couple in Aqueous Solutions at Different pH. *J. Electrochem. Soc.* **164**, C240–C249 (2017).
322. Sigli, C., Maenner, L., Sztur, C. & Shani, R. Phase Diagram, Solidification and Heat Treatment of Aluminum Alloys. in *Aluminum Alloys, Vol. 1* 87–98 (1998).
323. Philibert, J. *Atom Movements: Diffusion and Mass Transport in Solids*. (Les Editions de Physiques, Les Ulis, 1991).
324. Ellingham, H. J. T. Reducibility of Oxides and Sulphides in Metallurgical Processes. *J. Soc. Chem. Ind.* **53**, 125–159 (1944).
325. Hultgren, F. Grain Boundary and Substructure Hardening in Aluminum. *Trans. Am. Inst. Met. Eng* **230**, 898–903 (1964).

326. Hansen, N. The Effect of Grain Size and Strain on the Tensile Flow Stress of Aluminum at Room Temperature. *Acta Metall.* **25**, 863–869 (1977).
327. Fujita, H. & Tabata, T. The Effect of Grain Size and Deformation Sub-Structure on Mechanical Properties of Polycrystalline Aluminum. *Acta Metall.* **21**, 355–365 (1973).
328. Osetsky, Y. N. & Bacon, D. J. Atomic-scale mechanisms of void hardening in bcc and fcc metals. *Philos. Mag.* **90**, 945–961 (2010).
329. Osetsky, Y. N. & Stoller, R. E. Atomic-scale mechanisms of helium bubble hardening in iron. *J. Nucl. Mater.* **465**, 448–454 (2015).
330. Worswick, M. J. & Pick, R. J. Void growth and constitutive softening in a periodically voided solid. *J. Mech. Phys. Solids* **38**, 601–625 (1990).
331. Yang, L. X. *et al.* Effects of He radiation on cavity distribution and hardness of bulk nanolayered Cu-Nb composites. *J. Nucl. Mater.* **487**, 311–316 (2017).
332. Courtney, T. H. *Mechanical Behavior of Materials*. (McGraw-Hill, 1990).
333. Han, T. *et al.* Effect of Weld Power and Interfacial Temperature on Mechanical Strength and Microstructure of Carbon Steel 4130 Fabricated by Ultrasonic Additive Manufacturing. *Manuf. Lett.* **25**, 64–69 (2020).
334. Mukhametgalina, A. A., Murzinova, M. A. & Nazarov, A. A. Weld Quality and Microstructure Development in Ultrasonically Welded Titanium Joints. *Metall. Mater. Trans. A* (2022) doi:10.1007/s11661-021-06583-0.
335. Lütjering, G. & Williams, J. C. *Titanium*. Springer (2007). doi:10.5005/jp/books/11706_12.
336. Cullity, B. D. *Elements of X-ray Diffraction*. (Addison-Wesley Pub. Co., 1978).
337. Tunde Raji, A. *et al.* Ab Initio Pseudopotential Study of Vacancies and Self-Interstitials in HCP Titanium. *Philos. Mag.* **89**, 1629–1645 (2009).
338. Smirnov, G. Non-Arrhenius Diffusion in BCC Titanium: Vacancy-Interstitialcy Model. *Phys. Rev. B* **102**, 184110 (2020).
339. Lindwall, G. *et al.* Diffusion in the Ti-Al-V System. *J. Phase Equilibria Diffus.* **39**, 731–746 (2018).
340. Pagan, M. *et al.* Strengthening of Tempered Aluminum During Ultrasonic Additive Manufacturing. *Unpubl. Work* (2022).
341. Porter, D. A. & Easterling, K. E. *Phase Transformations in Metals and Alloys*. (Springer Science and Business Media LLC, 1992).
342. Koike, J. *et al.* Stress-Induced Phase Transformation During Superplastic Deformation in Two-Phase Ti-Al-Fe Alloy. *Acta Mater.* **48**, 2059–2069 (2000).
343. Jonas, J. J., Aranas, C., Fall, A. & Jahazi, M. Transformation Softening in Three Titanium Alloys. *Mater. Des.* **113**, 305–310 (2017).
344. Kumar, S., Kamath, R., Nandwana, P., Chen, Y. & Babu, S. Dynamic Phase Transformations in Additively Manufactured Ti-6Al-4V During Thermo-Mechanical Gyrations. *Materialia* **14**, (2020).
345. Prada, B. H., Mukhopadhyay, J. & Mukherjee, A. K. Effect of Strain and Temperature in a Superplastic Ni-Modified Ti-6Al-4V Alloy. *Mater. Trans. JIM* **31**, 200–206 (1990).
346. Foul, A., Jr, C. A., Guo, B. & Jonas, J. J. Dynamic Transformation of $\alpha \rightarrow \beta$ Titanium at Temperatures Below the β - Transus in Commercially Pure Titanium.

- Mater. Sci. Eng. A* **722**, 156–159 (2018).
347. Matsumoto, H., Yoshida, K., Lee, S. H., Ono, Y. & Chiba, A. Ti-6Al-4V Alloy with an Ultrafine-Grained Microstructure Exhibiting Low-Temperature-High-Strain-Rate Superplasticity. *Mater. Lett.* **98**, 209–212 (2013).
 348. Xu, C. & Zhu, W. Transformation Mechanism and Mechanical Properties of Commercially Pure Titanium. *Trans. Nonferrous Met. Soc. China* **20**, 2162–2167 (2010).
 349. Guo, B., Semiatin, S. L., Liang, J., Sun, B. & Jonas, J. J. Opposing and Driving Forces Associated with the Dynamic Transformation of Ti-6Al-4V. *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.* **49**, 1450–1454 (2018).
 350. Guo, B., Semiatin, S. L., Jonas, J. J. & Yue, S. Dynamic Transformation of Ti-6Al-4V During Torsion in the Two-Phase Region. *J. Mater. Sci.* **53**, 9305–9315 (2018).
 351. Guo, B., Liu, Y. & Jonas, J. J. Dynamic Transformation of Two-Phase Titanium Alloys in Stable and Unstable States. *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.* **50**, 4502–4505 (2019).
 352. Aranas, C. *et al.* Determination of the Critical Stress for the Initiation of Dynamic Transformation in Commercially Pure Titanium. *Scr. Mater.* **133**, 83–85 (2017).
 353. Jourdan, C., Gastaldi, J. & Grange, G. Heterogeneous Nucleation During the Titanium $\alpha \leftrightarrow \beta$ Transformation Studied by Synchrotron X-ray Topography. *Acta Metall.* **36**, 2979–2987 (1988).
 354. Jourdan, C., Gastaldi, J. & Grange, G. Nucleation of the Titanium α and β Phases. In Situ Study of the Dislocation Role by Synchrotron X-ray Topography. *Phase Transitions* **14**, 201–208 (1989).
 355. Seward, G. G. E., Celotto, S., Prior, D. J., Wheeler, J. & Pond, R. C. In Situ SEM-EBSD Observations of the HCP to BCC Phase Transformation in Commercially Pure Titanium. *Acta Mater.* **52**, 821–832 (2004).
 356. Ram, G. D. J., Yang, Y., George, J., Robinson, C. & Stucker, B. E. Improving Linear Weld Density in Ultrasonically Consolidated Parts. 692–708 (2006).
 357. Perry, M. E. J. *et al.* Tracing Plastic Deformation Path and Concurrent Grain Refinement During Additive Friction Stir Deposition. *Materialia* **18**, 101159 (2021).
 358. Alaneme, K. K. & Okotete, E. A. Recrystallization Mechanisms and Microstructure Development in Emerging Metallic Materials: A Review. *J. Sci. Adv. Mater. Devices* **4**, 19–33 (2019).
 359. Razumov, I. K., Yermakov, A. Y., Gornostyrev, Y. N. & Straumal, B. B. Nonequilibrium Phase Transformations in Alloys Under Severe Plastic Deformation. *Phys.-Usp* **733** (2020).
 360. Kar, A., Yadav, D., Suwas, S. & Kailas, S. V. Role of Plastic Deformation Mechanisms During the Microstructural Evolution and Intermetallics Formation in Dissimilar Friction Stir Weld. *Mater. Charact.* **164**, 110371 (2020).
 361. Gao, P. F., Guo, J., Zhan, M., Lei, Z. N. & Fu, M. W. Microstructure and Damage Based Constitutive Modelling of Hot Deformation of Titanium Alloys. *J. Alloys Compd.* **831**, (2020).
 362. Wu, D., Liu, L., Zhang, L., Wang, W. & Zhou, K. Tensile Deformation Mechanism and Micro-Void Nucleation of Ti-55531 Alloy with Bimodal Microstructure. *J.*

- Mater. Res. Technol.* **9**, 15442–15453 (2020).
363. Bhushan, B. & Petralia, P. *Principles and Applications of Tribology*. (John Wiley & Sons, 2013).
 364. Babu, S. S., Santella, M. L., Feng, Z., Riemer, B. W. & Cohron, J. W. Empirical model of effects of pressure and temperature on electrical contact resistance of metals. *Sci. Technol. Weld. Join.* **6**, 126–132 (2001).
 365. Tang, C., Liu, Z., Zhou, D. & Wu, S. Surface Treatment with the Cold Roll Bonding Process for an Aluminum Alloy and Mild Steel. *Strength Mater.* **47**, 150–155 (2015).
 366. Li, D. & Soar, R. Influence of Sonotrode Texture on the Performance of an Ultrasonic Consolidation Machine and the Interfacial Bond Strength. *J. Mater. Process. Technol.* **209**, 1627–1634 (2009).
 367. Johnson, K. Interlaminar subgrain refinement in ultrasonic consolidation. (Loughborough University, 2008).
 368. Wolcott, P. J., Hehr, A., Pawlowski, C. & Dapino, M. J. Process improvements and characterization of ultrasonic additive manufactured structures. *J. Mater. Process. Technol.* **233**, 44–52 (2016).
 369. Pau, M., Leban, B. & Baldi, A. Experimental analysis of contact for the indentation of a flat rounded punch. *Int. J. Solids Struct.* **43**, 7959–7965 (2006).
 370. Ciavarella, M., Hills, D. A. & Monno, G. The influence of rounded edges on indentation by a flat punch. *Proc. Inst. Mech. Eng. Part C J. Mech. Eng. Sci.* **212**, 319–327 (1998).
 371. Bellouard, Y. Shape memory alloys for microsystems : A review from a material research perspective. *Mater. Sci. Eng. A* **482**, 582–589 (2008).

VITA

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