Micro & nano scale mechanical testing and assembly with applications to metal based microsystems

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A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
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Doctor of Philosophy

in

The Department of Mechanical Engineering

by

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This dissertation is dedicated to
my beloved parents, for their endless love,
support and encouragement.
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Metal-based high-aspect-ratio microscale structures (HARMS) are fundamental building blocks for functional metallic micro devices. This dissertation focuses on addressing several problems in fabrication and assembly of metal based microchannel devices. First, the materials’ responses to mechanical deformation at micro & nano scales, namely the mechanical “size effect”, have been explored by molding single crystal Al with long rectangular diamond punches and long wedge shaped indenters. It is noticed that the contact pressure of rectangular punches pressed into single crystal Al strongly depends on the punch width, while that of long wedge shaped indenters depends on the included wedge angle. We observed large discrepancies between characteristic lengths obtained from predictions based on the Nix-Gao model and those derived from experimental results. Our results suggest that the characteristic length maybe dependent on the deformation geometry.

The mold inserts are coated with hard ceramic thin films, which could reduce friction and act as barriers for surface chemical reactions during molding at elevated temperatures. The adhesion between thin film and substrate, a persisting topic in thin film technologies and surface engineering, remains critical in the present case. Therefore, nominal shear strength of the interface between TiN thin film and Si substrate was evaluated through customized compression test of micro cylinders containing inclined film/substrate interfaces. Non-tapered micro cylinders with diameters ranging from 5µm to 1µm were prepared by focused ion beam “lathe milling”, which was realized by a script based ion milling program. As compared to previous procedures for testing film/substrate interfacial mechanical integrity, results obtained by following this new
microscale testing protocol have less scatter and are more conducive to correlating interfacial structure/chemistry to interfacial failure.

Appropriate bonding technology is critical to forming functional micro devices. Cu based HARMS were bonded by sandwiching an Al thin foil in between a Cu sheet metal containing HARMS features and a flat Cu sheet metal counterpart, utilizing formation of a eutectic interfacial liquid. Phase and structure evolution of the Cu/Al/Cu interface, as well as the interfacial mechanical properties, were characterized.
CHAPTER 1
INTRODUCTION TO MICRO-MANUFACTURING: FABRICATION AND ASSEMBLY

1.1 Introduction

Since their conceptualization in laboratories as an outgrowth of curiosity-based research in the 1970’s, Micro-electro-mechanical systems (MEMS) devices have been studied intensely over the last two decades. At present, MEMS find applications in high-end systems as well as popular consumer devices. A broad spectrum of materials, inclusive of the four major classes of materials, silicon, metal and alloys, ceramics, and polymers, have been incorporated into MEMS [1]. As compared to silicon, metal and alloys have higher thermal and electrical conductivities, and are more mechanically robust. While thin metal films have been used in integrated circuit (IC) chips for a long time, various metal/alloys and their related processing have also been developed for MEMS [2]. Examples include micromotors, microactuators, microsensors, and integrated power converters [3, 4, 5], as well as heat-exchangers with high-aspect-ratio microscale structures (HARMS) [6, 7].

Major processes for functional MEMS devices could be grouped into three categories: micro components fabrication through different techniques, integration & assembly, and characterization & testing. Fabrication techniques for metal-based HARMS include LiGA (Lithographie, Galvaniformung, Abformung), micro-milling and other forms of micro-machining, reactive-ion etching (RIE) and deep reactive-ion etching (DRIE). These fabrication techniques have disadvantageous aspects, such as relatively low production speed, relatively high cost, significant hardware requirements, which impede their adoption to a wider range of applications. In specific reference to metal-
based microdevices, in order to make them more competitive in the market place, simpler, faster, and more reliable fabrication techniques are definitely in need.

Direct molding replication of metal-based HARMS has been successfully demonstrated in our laboratory at Louisiana State University Department of Mechanical Engineering over the past decade. HARMS based on a wide range of metals, such as Pb, Zn [8], Al [9], Cu [10], have been fabricated by molding replication with surface- and bulk- engineered microscale mold inserts. The mechanical response during microscale compression molding has been measured experimentally and analyzed through contact mechanics modeling [11] as well as through preliminary finite element simulation [12]. To form functional metallic microdevices from HARMS basic building blocks, proper assemble technique is necessary. A transient-liquid-phase (TLP) bonding approached has been employed and demonstrated in Al/Al-Ge/Al [13] and Cu/Sn/Cu [14] systems.

In this chapter, conventional micro-fabrication techniques are reviewed, together with progress made in preparing metal-based HARMS and bonding technologies to form functional microdevices. Three classes of experiments were conducted to probe the mechanical response of materials at micro/nano scales, namely, micro pillar compression, micro compression molding, and instrumented nanoindentation.

1.2 Approaches to Micro Manufacturing

At the present time, most micro and nano fabrication techniques are outgrowth of processing techniques for silicon semiconductors and silicon microchips. The key to micro- and nano- manufacturing lies in the ability to apply those techniques to the realm of mass production, where MEMS devices need to be fabricated in a fast and economical manner. [15]
1.2.1 Conventional Microfabrication Techniques

LIGA is a German acronym for Lithographie, Galvanoformung, Abformung (Lithography, Electroplating, and Molding), and is a historically important technique used for creation of metallic HARMS [16, 17]. The conventional LiGA process begins with exposing a thick layer of resist through a patterned mask to high energy X-ray radiation, usually from a synchrotron source, followed by dissolution of the damaged materials in exposure, leaving a negative relief replica of the mask pattern as shown in Fig. 1.1. Then metals can be electrodeposited into the developed resist recesses, with the remaining resist removed thereafter. The remaining metal structure can serve as either the final products or as mold inserts for precision plastic molding [18]. There are two main categories of LiGA process, X-ray LIGA, which produces high-aspect ratio structures using X-rays generated by an electron synchrotron, and UV LiGA, which uses ultraviolet light to create comparatively lower aspect ratio structures, but with higher experimental accessibility and affordability than the former.

The advantages of X-ray LiGA lie in the primary characteristics of X-rays, which have shorter wave length, higher intensity, and a very large depth of focus (DOF). These characteristics enable the creation of high aspect ratio (more than 100) structures with parallel and smooth side walls. A key factor of X-ray LiGA is the resist material, which requires high sensitivity to X-rays, high resolution, resistance to chemical, ion, or plasma etching, thermal stability of >140°C, and a matrix or resin absorption of less than 0.35µm⁻¹ at wavelengths of interest. One important resist material is poly methyl methacrylate or PMMA [19]. Another challenge is the making of the mask, which consists of a pattern of X-ray-absorbing material (a material with a high atomic number,
Figure 1.1  Typical LIGA process: (a) X-ray/UV Radiation, (b) Development, (c) Electrodeposition, (d) Mold insert, (e) Compression molding, (f) Demolding.

Z, such as gold) on a substrate transparent to X-rays (a low Z material, e.g., Ti, Si, SiC, Si$_3$N$_4$, BN, Be). The high cost of synchrotron radiation and the complication of mask making impede the application of X-ray lithography. Alternative techniques have attracted attention, such as electron-beam and ion-beam lithography, laser based processes, and UV lithography. Compared to its X-ray counterpart, UV lithography employs an inexpensive ultraviolet light source to expose an epoxy-based photoresist, typically SU-8 [20, 21, 22], which is a transparent, negative, and more sensitive resist material [23, 24, 25]. The unmasked areas in the polymer exposed to X-ray or UV light have been changed, and chemicals etch them away. With electrochemical and electroless techniques [26], a series of metals and alloys can be deposited into the resist recesses,
such as Au, Cu, Cr, Ni and Ni-alloys [27]. After removing the residual resist, the deposited metal/alloy serves as a mold insert for mass replication through compression molding or hot embossing [28], as well as injection molding [29].

Micro milling [30] and grinding [31], usually referring to micro end milling and grinding, could be considered as an extension of conventional milling and grinding to the micro scales. It has been employed to fabricate microscale molds and masks for the development of micro components [32], micro-mirrors, fiber-optics connectors, and micro-displays [33]. Compared to LIGA process with the help of expensive masks and synchrotron X-ray, these techniques are cost effective, convenient for individual components rather than large batch sizes, and able to monitor the in-process quality of the components[34]. Micro tools play a pivotal role in micro milling and grinding processes, controlling feature sizes and surface finish of the micro components finally produced. Tool wear is a severe problem for micro-milling, which influences the geometry and the surface quality of the products. Size effects during cutting, as the specific energy increases with decrease in deformation size, are factors which enhance tool wear [35]. Single crystal diamond, because of its outstanding hardness, high thermal conductivity, high elastic moduli, is the preferred tool material for micro-milling of non-ferrous materials. Nowadays, commercialized chemical vapor deposited (CVD) diamond-cutting tools are available. These advanced tiny tools combined with computer numeric control (CNC) [36], are the foundations for realization of micron and even submicron levels of resolution for ultra-precision micro-manufacturing purposes.

Focused ion beam (FIB) is now becoming increasingly available as a powerful technique for maskless implantation, metal patterning, IC repair, etc. [37, 38, 39]. FIB
can also be incorporated into a system with both electron and ion beam columns, allowing ion beam micromachining and simultaneous electron beam monitoring. More impressively, three-dimensional (3D), geometrically-complex devices could be realized by a special technique of “lathe milling”, where the specimen was set on a multi-axis stage controlled by computer programming [40, 41]. It resembles machining in a lathe but with the cutting tool replaced by a focused ion beam, with consequently much smaller part sizes. High quality surface finish could be obtained after milling, but with ion implantation into machined surfaces.

Typical electro-mechanical machining includes electrical-discharge-machining (EDM), laser beam machining, and dry etching. EDM, sometimes colloquially referred to as spark cutting, is a machining process by a series of rapidly recurring electrical discharges between two electrodes, separated by a dielectric liquid [42]. One electrode is the tool-electrode, while the other is the work piece. When the two electrodes approach a critical distance, the intensity of the electrical field between them exceeds the strength of the dielectric liquid, initiating an electrical discharge through which materials are removed from both electrodes. The material removal mechanism during EDM process has been studied [43, 44]. Micro EDM (μEDM) has attracted a lot of recent attention since this technique, which have been in existence for over fifty years [45], was introduced into the realm of micro fabrication [46]. Based on a thermal material removal mechanism, the primary characteristics of μEDM include the absence of process force and independence from mechanical properties of the work piece. These characteristics allow machining of a wide range of electrically conductive materials. Three main categories of major industrial relevance are micro-die sinking (μ-die sinking) [47], micro-
wire electrical discharge machining (μ-WEDM) [48], and micro-electrical discharge drilling (μ-ED drilling) [49]. During μEDM processes, materials are removed from both the tool and the work piece. Tool wear is therefore a serious problem, as well as machining induced surface cracking and materials modification within the near-surface layer [50, 51, 52].

While conventional lithographic techniques for making three dimensional shapes are limited to unidirectional extensions of two dimensional patterns, laser beam machining is capable of constructing truly three-dimensional structures without the need of a mask. Usually, carbon dioxide (CO₂) lasers and neodymium yttrium aluminum garnet (Nd:YAG) lasers are favored over other laser types because of their higher power output [53, 54, 55]. Recent progress made in laser machining includes the use of nanosecond pulsed lasers for nanoscale ablation of thin metal films and nanoscale patterning of Au nanoparticle films [56, 57]. The advantages of laser based machining are its versatility, site-specific operation, and rapid prototyping capability with the combination of CNC positioning systems [58]. The drawbacks of this direct writing technique are also obvious: it is a serial machining process which results in low material removal rates [59]; it also elevates the surface roughness [60, 61]. Therefore, additional surface treatments might be required depending on the application requirements.

1.2.2 Progress in Techniques for Fabricating Metal Based HARMS

The above mentioned micro fabrication techniques have been widely used in the semiconductor industry. Other than silicon chips, metal-, ceramic-, and polymer-based microsystems and microcomponents are also of great interest to bioscience and engineering, chemistry, aerospace, and medicine. Fabrication of metal-based HARMS
could be achieved through LiGA, RIE or DRIE, µEDM. The drawbacks of these techniques, such as high cost, low production speed, and significant tool wear, present significant barriers to economical mass production. Abformung, the mold replication step in LiGA, provides a concept of high-throughput mass production. Before 2003, direct molding replication of HARMS from LiGA fabricated metal mold inserts was only achieved in polymeric materials [28]. The extension of direct molding replication to metals and alloys is desirable. Commercialization of metallic HARMS and microdevices based on metallic HARMS may be achieved through low-cost, high-throughput, repeated molding replication with appropriately designed, durable mold inserts. We have successfully demonstrated direct molding replication within a wide range of metals from soft to hard, such as Pb and Zn [8], Al [9], Cu [10], Ni and NiTi [62]. However, there are also several challenges needing to be addressed. The first one is the fabrication technique of mold inserts, which will greatly affect the strength of the insert at elevated temperatures during molding. The second one is that materials behave differently at micro/nano scales as compared to situations involving macroscale deformation. Usually, the materials tend to be much “stronger” as the size decreases. In turn, lifetime of the mold inserts or other tools may be shortened significantly. Another problem is the diffusion and friction between the inserts and molded materials at elevated temperatures, which are detrimental to the mold inserts both chemically and mechanically.

1.3 Mechanical Responses of Materials during Deformation at Micro Scale

In conventional mechanics, it is known that the strength of a material, which is considered an intensive property, depends on the characteristic length scale of a particular microstructure or “intrinsic size”, such as grain and precipitate size, dislocation density,
twin boundary spacing, etc. [63]. However, extensive studies on the mechanical properties of materials at micrometer scale or sub-micrometer scale, such as micro/nano pillar compression [64, 65], instrumented nanoindentation [66], microtorsion [67], microbending [68], etc., unambiguously demonstrated that the strength of material exhibited a strong dependence on the external sample size or “extrinsic size,” such as pillar diameter, film thickness, etc. [69]. The explanation for these various size effects included the phenomenological strain gradient plasticity theory [70], “geometrically necessary dislocation” based strain gradient plasticity [71, 72] for nanoindentation size effect, and “dislocation starvation” mechanisms for microcompression [73]. In what follows, a short review on experiments showing size effects and basic theories explaining the phenomena is provided.

1.3.1 Size Effect in Micropillar Compression

Uchic and Nix [74] have reported small scale mechanical behavior with uniaxial compression methodology on cylindrical nanopillars fabricated by FIB machining. As it is shown in fig. 1.2(a), the yield strengths of cylindrical Ni specimens increased significantly as the diameters of the tested specimens decreased, indicating a strong dependence of yield strength on specimen extrinsic size, in this case the cylinder diameter. Figure 1.2(b) shows an SEM image of the specimen after compression, where dislocations burst and swept through the entire inclined cross section. Greer and Nix [75] extended this methodology into the nano scale, where the results showed that compression strength of Au nanopillars reached ~50 times higher than that of the bulk. Since then, plasticity in small volumes during compression and tension have received intense studies, which were carried out on Ni and Ni based superalloys [76, 77, 78], Au
[79, 80, 81], Cu [82, 83, 84, 85], and Al [86, 87, 88]. Dou and Derby [89] have summarized the results of micropillar compression for single crystalline Au, Al, Ni, and Cu and reported a universal law of the form $\frac{\tau_{\text{res}}}{\mu} = A \left( \frac{d}{b} \right)^m$, where $\mu$ is the shear modulus, $\tau_{\text{res}}$ is the resolved shear stress onto $<110>/\{111\}$ slip system, $d$ is the pillar diameter and $b$ is the Burgers vector. It is shown that the recent published results for both compression
and tension of fcc metallic micropillars follows the above-mentioned power-law dependence between the flow stress and sample size. Figure 1.3 shows a combination of recent published data after scaling, where the shear stress normalized by the appropriate shear modulus appears near linearly with diameters of micropillars normalized by the Burgers’ vectors. It shows clear evidence that the strength of material highly depends on the extrinsic size of the specimen under microcompression and microtension.

1.3.2 Nanoindentation Size Effect

As research of the mechanical properties of materials extends into smaller and smaller length scales, it was realized in the early 1980s that load and depth sensing indentation methods would be very important for mechanical property characterization. Load and depth sensing indentation instruments have been developed [91, 92, 93, 94]. Pethica and Oliver [95] performed instrumented indentation tests on Ni, Au, and Si using indenter penetration depths as low as 20nm, with indentation depth monitored continuously during loading and unloading and areas of the indent impressions determined by SEM. Since the indentation hardness is defined as the impression load over the projected contact area, the experimental uncertainties mainly comes from the load and projected area measurement. When it goes to nanoscale, measurement of the projected area is challenging due to tip rounding, “sink-in” effects, etc. Instrumented nanoindentation has been improved by the work of Doerner and Nix [96] as well as Oliver and Pharr [97]. It is shown to be possible that determination of mechanical properties such as modulus and hardness could be directly derived from experimentally measured load/unload force-depth curves, with the unloading stiffness directly related to the projected contact area under load. The load and depth sensing indentation
instruments were widely used to investigate mechanical properties of materials at micro/nano scales.

Intensive studies of nanoindentation show that hardness is highly dependent on the indenter penetration depth within the range of 0.1 to 10µm [98, 99, 100, 95, 96]. Ma and Clarke [101] reported the size-dependent hardness of single crystal silver when the indentation size is below ~5µm. As it is shown in Fig. 1.4, the hardness value rises from 400MPa to 800MPa when the equivalent indenter diameter decreases from ~16µm to ~0.88µm. To explain the indentation size effect, Fleck and Hutchinson [70] introduced the so-called strain gradient plasticity theory, which is based on the concept of geometrically necessary dislocations (GNDs). Incorporating an internal constitutive material length parameter, various size effects in plastically deforming metals could be successfully described. Fleck further points out the strong dependence of nanoindentation hardness on indenter size resulted from the large strain gradients under

![Figure 1.4](image.png)

Figure 1.4  Hardness plotted as a function of the equivalent indenter diameter [101].
Figure 1.5  Schematic of dislocation configuration along the surface of indentation [102]

the impression. Nix and Gao [71, 72, 102] suggested a mechanism based SGP theory which is the most cited theory to explain the ISE so far. A brief review of the Nix-Gao model is given below. Nix-Gao pointed out that when a rigid conical indenter is pressed into an elastic half space, the plastic deformation underneath the indenter is accommodated by circular loops of GNDs. As it is shown in the following schematic, Fig. 1.5, the angle between the surface of the conical indenter and the plane of the surface is taken to be $\theta$. Assuming the individual dislocation loops being spaced equally as shown in Fig.1.5, it is easy to show that:

$$\tan \theta = \frac{h}{a} = \frac{b}{s}, \quad s = \frac{ba}{h}, \quad (1.1)$$

and the GND-density could be expressed as

$$\rho_G = \frac{3}{2bh} \tan^2 \theta, \quad (1.2)$$

where $b$ is the Burgers vector, $a$ is the contact radius, $h$ is the indentation depth, and $s$ is the spacing of dislocation. Following the Taylor relation [103, 104], the deformation resistance can be estimated as follows:

$$\tau = \alpha Ub \sqrt{\rho_G + \rho_s}, \quad (1.3)$$
where $\alpha$ is a constant, $\mu$ is the shear modulus and $\rho_s$ is the density of statistically stored dislocations (SSDs) [105]. Following the Mises flow rule [106] and Tabor’s rule, expressions could be found:

$$\frac{H}{H_0} = \sqrt{1 + \frac{h^*}{h}},$$

(1.4)

where $H_0 = 3\sqrt{3\alpha\mu b \rho S}$ is the size-independent hardness, arising from the statistically stored dislocations alone, and the characteristic length $h^*$ could be expressed as

$$h^* = \frac{81}{2} b \alpha^2 \tan^2 \theta \left(\frac{\mu}{H_0}\right)^2.$$  

(1.5)

The Eq. (1.4) reveals that the hardness is equal to $H_0$ at large penetration depths, while a size effect is included when the indentation depth $h$ decreases to the same order of magnitude as $h^*$. A linear relationship between $H^2$ and $1/h$ is easy to be noticed. The so-called characteristic length is related to the indentation angle $\theta$.

### 1.3.3 Micro Molding

The mechanical response of the materials during molding is also of great interest. Instrumented micromolding of elemental Al [107] and elemental Cu [108] were conducted at different temperatures with surface coated microscale mold inserts, which consists of an array of long, rectangular punches showed in Fig. 1.8(a) and Fig. 1.9(a). Companion uniaxial tensile testing of macroscale Al and Cu specimens were performed. For the mechanical response of Al, pressure-depth curves at different temperatures approximate that of an elasto-perfectly plastic solid as shown in Fig 1.6(a). When deformation occurs at a constant strain rate $\varepsilon$, material flow stress $\sigma_f$ remains equal to its yield stress $\sigma_y$, independent of plastic strain. A simple, one parameter scaling law were applied to the measured pressure and depth ($P-d$) curves, where the average molding
pressure normalized by $\sigma_y$ at corresponding molding temperatures is independent of temperature. It could be seen from Fig. 1.6(b) that the molding $P$-$d$ curves collapsed to a universal curve after this simple, one-parameter scaling. For the mechanical response of Cu, significant strain hardening and dynamic recrystallization were observed during deformation within the temperature range from $\sim$400°C to $\sim$600°C at moderate strain rates. With a similar scaling method, where the contact pressure normalized by an appropriate flow stress representative of plastic flow of Cu at large plastic strains, a set of P-$d$ curves at different temperatures were scaled to one universal curve. Further extension of this experiment into the nano scale and studying the mechanical responses of material in nano scale molding are of great interest.

![Figure 1.6](image)

**Figure 1.6** A simple, one parameter scaling of pressure-depth curves from Al molding experiments at different temperatures: (a) $P$-$d$ curves (b) an universal curve after scaling

### 1.4 Strength and Surface Endurance for Mold Inserts

The ability of the micro mold inserts to maintain an as-high-as-possible strength at the relevant molding temperatures is critical for obtaining high quality replica. Following the conventional LiGA process, Ni mold inserts with nanocrystalline structures formed by electrodeposition will lose 50% of its yield strength at room
temperature when heated to ~400°C due to significant grain growth [109]. This undesirable reduction of the yield strength of the insert hinders the realization of replication. Attempts to electrodeposit alloys with higher strength at elevated temperatures, such as Ni-Fe [110], Ni-Mo [111], and Ni-Co-Fe [112], have also been made. But the results showed little improvement due to the complex electrochemical reactions for electrodeposition of alloys. To improve the mechanical properties of the insert bulk at high temperatures, mold inserts with microscale structures were fabricated out of refractory metals and alloys with techniques such as µEDM. HARMS inserts with simple geometries were fabricated out of refractory metals and alloys, such as Ta and the Ni-based superalloy Inconel.

Chemical interaction between mold inserts and molded metal surfaces occurred during compression molding at high temperatures. Chemical interactions can lead to bonding, insert breakage, and damage to the molded features as the insert is withdrawn. Figure 1.7 shows an example of broken LiGA fabricated Ni micro mold insert and molded Al features [9]. Figure 1.7 (a) shows a molded Al plate with a microhole matrix. It is noticed that some Ni microposts were broken in the microholes and most of hole edges are torn away from one side during demolding, which is further confirmed by carefully examining the mold inserts where some Al remnant still sticks on, as shown in figure 1.7(b). This chemical/mechanical interaction should be controlled, otherwise it will speed up tool wear as well as affect the quality of the molded features. To solve this problem, a thin layer of ceramic coating was chosen and deposited onto the insert surface conformally with an inductively coupled plasma (ICP) assisted hybrid chemical/physical vapor deposition (CVP/PVD) technique [113, 114]. Nanoscale structure, mechanical
properties, and tribological characteristics were studied in detail in two-phase nanocomposite coating systems based on amorphous hydrogenated carbon (a-C:H) [115, 116, 117, 118, 119, 120, 121] and amorphous silicon nitride (a-Si:N) [122, 123, 124]. As it is shown in Fig. 1.8(a) and Fig. 1.9(a), two inserts with long rectangular punch arrays fabricated by µEDM were coated with amorphous hydrogenated carbon and amorphous silicon nitride respectively. Figures 1.8(b) and 1.9(b) show molded Al microchannels and molded Cu microchannels, which have smooth side-walls and no torn structures, in contrast to what is shown in Fig. 1.7(a). With the above described techniques, HARMS replications have been achieved successfully in a series of metals.

Figure 1.7 Al and mold inserts after demolding: (a) overview of the molded Al surface; (b) Al remnant on Ni pillar side surface [9].

Figure 1.8 Coated rectangular mold inserts and molded Al: (a) Ti-C:H coated Ta insert; (b) molded Al micro-channel array[62].
1.5 MEMS Packaging Techniques

Without appropriate packaging techniques, hardly any microdevice could be fabricated. It serves to integrate all the required components for system application together to form a functional device. The three main functions of MEMS packaging are mechanical support, protection from the environment, and electrical connection to other system components [125, 126]. Different MEMS application usually requires different package design to optimize and meet the needs of the system. Methods for bonding Si based microsystems, including anodic bonding [127], direct bonding [128, 129] and intermediate layer bonding [130], have been reported. Anodic bonding is a field assisted or electrostatic wafer bonding procedure without any intermediate layer, usually used for connecting silicon/glass and metal/glass through electric fields [131]. Direct bonding, also called silicon fusion bonding, is a wafer bonding process based on chemical bond interactions between two contacting surfaces [132].

Anodic bonding, known as field assisted thermal and electrostatic bonding, is commonly used to bond silicon to glass wafers. Fig 1.10 represents a typical schematic of an anodic bonding set-up. A piece of sodium-rich glass was placed on top of a silicon
wafer and a constant negative bias with respect to the electrically grounded silicon is held. Bonding will occur at temperatures between 180ºC and 500ºC on a hot plate in atmosphere or under vacuum; typical voltages ranging from 200V and 1000V depend on

![Schematic of Anodic bonding silicon wafer to sodium-rich glass.][133]

the thickness of the glass and temperature. Electromechanical, electrostatic, thermal mechanisms and combinations thereof accounts for the bond formation. Under elevated temperatures and electric field, it is suggested that the glass becomes a conductive solid electrolyte and the sodium ions contained within the glass migrate toward the cathode. Disadvantages of anodic bonding are the high electrical field, migration of sodium, the mismatch in thermal expansion coefficient, and the viscous behavior of the glass [15].

Metal alloy bonding is suitable for MEMS devices consisting of metals and oxides with different thermal expansion coefficients. It could be made at low temperatures, for example SnBi alloys below 200ºC, but can withstand temperatures above 500ºC. The bond line width could be significantly reduced compared to other bond methods. (<100 µm) and it is also electrically conductive which could be served as electrical connections facilitating vertical integration.[134]
Silicon fusion bonding is direct bonding of silicon to silicon based on a chemical reaction between surface OH-groups or grown oxides covering the wafer. The bonding temperature is usually higher than 1000°C which might prevent its use in certain applications. It also requires high flatness and microroughness less than ~4 nm, as compared to ~1µm for anodic bonding. But it offers strong and hermetic bonds, up to 20MPa [135].

Intermediate layer bonding uses an additional material layer to join the components being bonded. Among various intermediate layer bonding strategies, eutectic bonding is of interest. The merits of eutectic bonding at the bonding interface includes lowering of the bonding temperature by melting depressant intermediate layers, reducing thermal stress induced damage, and increasing bonding quality. Eutectic systems like Au-Si [136] and Al-Ge [137] have been investigated. The phase diagram of Al-Ge system is composed of only a single eutectic reaction with the eutectic temperature \( T_e = 424°C \), which is much lower than the melting temperature of bulk Al, \( T_m = 660°C \) [138]. Therefore it is possible to use a Ge intermediate layer to bond Al components. Likewise, Al and Sn can be used for bonding Cu-based structures. For bonding Al HARMS, a thin Al-Ge composite layer was sputter co-deposited onto Al faying surfaces [139]. Microstructures and compositions of the co-deposited Al-Ge layer have been examined by SEM, TEM, XPS, EDS, which shows an Al-Ge phase separation and also the formation of an metastable Al-Ge amorphous phase during sputter deposition instead of a mixture of terminal Al and Ge phases [140]. The coated Al surfaces were then bonded face-to-face under vacuum with a base pressure \(~10^{-7} \) Torr. The strength of the bonded interface was examined through uniaxial tensile testing, which showed that the
interfacial tensile strength was all above ~70MPa [13]. A direct application of this method resulted in bonding of Al-based HARMS heat exchangers. Bonding quality and heat transfer performance have been tested thoroughly [141]. For bonding Cu-based HARMS devices, free-standing thin foils of Sn were sandwiched in between two Cu surfaces rather than employing vapor deposited interface bonding layers. As a result, the bonding process was simplified and its cost lowered. The eutectic liquid bonding of Cu with Sn thin foil showed good quality and reliability [14].

1.6 Motivation and Outline of the Dissertation

Conventional techniques for micromanufacturing and different materials responses under deformation at micro-/nano- scales have been introduced in Chapter 1 in terms of experiments and theories of various “size effects”. However several problems still remain to be answered. First, is there an intrinsic length scale for a material? Second, if so, how does it relate to the other physical parameters of the material, or does it depend on deformation geometry? To answer those questions, mechanical responses of single crystal Al indented by a series of rectangular blades with different width ranging from 5 µm to 550 nm were studied in Chapter 2. Long triangular wedge shaped diamond indenters were prepared and indentations were made on single crystal Al, the results of which are presented in Chapter 3.

It was shown previously that thin hard coatings such as Ti-C:H, TiN, AlN, could reduce the friction and chemical reaction between the contacting surfaces of the mold inserts and the molded materials. Coating delamination could have an detrimental effect on lifetime of coated mold inserts. Thus the “old” topic of adhesion between thin
ceramic films and substrates will be explored in Chapter 4 through the employment of new instrumentation and techniques.

Although we have already showed successful bonding of Cu based HARMS with a Sn thin foil melting point depressant, the requirements for higher bonding quality and endurance at elevated temperatures provides the motivation for seeking other bonding agents, such as Al, which may have increased high temperature durability. Chapter 5 covers the mechanical characterization of the Cu/Al/Cu bonding interface as well as phase evolution during the bonding process.

Chapter 6 provides a brief summary of the results and conclusions as well as recommendations for future work.

1.7 References


CHAPTER 2
FROM MICRO TO NANO SCALE MOLDING OF METALS: SIZE EFFECT DURING MOLDING OF SINGLE CRYSTAL AL WITH RECTANGULAR STRIP PUNCHES

2.1 Introduction

Pattern replication by compression molding is a manufacturing technique that is particularly suited to mass production. One well-known application of replication technology in twentieth-century life is the fabrication of vinyl records of sound, in which patterns are replicated in parallel with high fidelity and high throughput from a master [1]. In the micro realm, the LiGA microfabrication protocol (Lithography, Galvanoformung, Abformung) [2], combining deep lithography on polymeric resists with metal electrodeposition and pattern replication by compression molding, is a prominent technique for producing high-aspect-ratio microscale structures (HARMSs) [3]. The compression molding (Abformung) step in LiGA is the key to low-cost high-throughput production. For two decades since the inception of LiGA, only polymeric HARMSs have been replicated from high-aspect-ratio mold inserts by molding [4]. Since 2003, replication of metallic HARMSs by direct compression molding has been successfully demonstrated in soft metals such as Pb [5] and Al [6], as well as harder metals such as Cu [7] and Ni [8].

The mechanics of metal micromolding is of interest. During the molding process, the total compression force applied on the insert, $P$, can be measured as a function of the insert penetration into the molded material or the molding depth, $d_m$. The molding response is defined as the average molding pressure, $p = P/A_c$ with $A_c$ being the nominal contact area between the insert and the molded material, vs. molding depth, i.e., the $p$-$d_m$
curve. Understanding how material properties of the molded metal influence the molding response is important for molding process design.

Molding response was studied in the simple case of micromolding of polycrystalline Al [9], using mold inserts consisting of a parallel array of long, rectangular punches of nominally identical geometry. The width of each individual punch, w, was ~150μm. In-situ measurements of P-d curves were correlated to companion uniaxial tensile testing of macroscale Al specimens at corresponding molding temperatures and relevant strain rates (T and $\dot{\varepsilon}$). Because stress-strain ($\sigma - \varepsilon$) curves for macroscale Al specimens approximate that of an elastic-perfectly-plastic solid at values of T and $\dot{\varepsilon}$ relevant to micromolding, Al’s flow stress $\sigma_f$ at large plastic strain remains equal to its initial yield stress $\sigma_y$. In this case, it was shown that, although measured $p-d_m$ curves vary significantly as T changes, the scaled molding response curves, e.g., $p/\sigma_y - d_m/w$ curves, collapse onto an approximately universal curve. Thus this simple one-parameter scaling was shown to describe successfully measured response of Al micromolding, using the only relevant mechanical property of the molded Al, $\sigma_y$, as the scaling parameter. The fact that measured response of Al micromolding is scalable by $\sigma_y$ obtained from macroscale uniaxial tensile tests indicates the process of Al micromolding at w~150μm is adequately described by continuum mechanics, a fact further verified by detailed comparison of experimental molding response curves to results of finite element analysis (FEA) incorporating $\sigma - \varepsilon$ curves obtained from macroscale tensile tests [10]. At w~150μm, it was further shown for cases where the molded metal exhibits significant strain hardening and dynamic recrystallization, e.g., elemental Cu, that molding response curves exhibiting significant variations over T can still be collapsed onto an
approximately universal curve by a similar one-parameter scaling, provided that the scaling parameter is an appropriately defined macroscopic flow stress $\sigma_f$ corresponding to a large plastic strain [11].

Replication of metal-based patterns with characteristic lengths of $\sim 1 \mu m$ or below is of interest in a number of applications, from optical gratings [12] to meta-materials exhibiting unusual optical properties [13]. Although replication of Al-based patterns with a characteristic length of $\sim 5 \mu m$ was demonstrated through room-temperature molding, no quantitative measurement of the molding response was made [14]. Quantitative knowledge of the response of metal micromolding as the characteristic length scale decreases from above $10 \mu m$ to $\sim 1 \mu m$ or below is both of fundamental interest and of interest to molding process design at the corresponding length scales.

Within the past two decades, size effects in plasticity have received intense scrutiny [15, 16]. The most extensively studied experimental configuration is the indentation size effect (ISE) [17, 18], which has been shown to be present in metals [19] as well as in ceramics [20]. Some studies investigated the influence of indenter shape on observed ISE, e.g., when spherical indentation and conical indentation are compared [21, 22]. Relative to these more studied indentation configurations, the geometry of micro/nano scale molding differs because the geometry of the mold insert is much closer to that of a two-dimensional projection and the extent of plastic deformation within the molded material is much larger [10]. In this chapter, we report our findings on the molding response of a single crystal Al specimen with a long, rectangular, strip punch as the punch width decreases from microns to submicron. We further compare the molding response in the strip punch geometry to that in the more conventional pyramidal
indentation geometry. In Section 3.2, the experimental procedures are reported. Section 3.3 presents the experimental data on the dependence of molding response on punch width, and compares it to conventional ISE when the same single crystal Al specimen is indented by a pyramidal Berkovich indenter. The results of structural characterization of the Al specimen underneath the molded features are further reported. Section 3.4 provides a brief summary of the present results.

2.2 Experimental Procedures

2.2.1 Specimen

A <110> oriented Al single crystal specimen mounted in an epoxy cylinder (MTS Systems Corp., Knoxville, TN) was employed for the micro and nano scale indentation and molding experiments.

2.2.2 Instrumented Indentation with a Berkovich Diamond Tip

Depth-sensing indentation experiments were carried out on a Nanoindenter XP System (MTS Systems Corp., Knoxville, TN) with nominal load and displacement resolutions of 50nN and 0.01nm, respectively. All experiments were conducted at room temperature. A three-sided pyramidal Berkovich diamond tip was used. The machine compliance and the projected tip area as a function of the indenter contact depth, \( h_c \), was calibrated following the Oliver and Pharr method, assuming that the Young’s modulus and Poisson’s ratio for the specimen, \( E \) and \( \nu \), are independent of the depth of indentation [23, 24]. A reduced modulus \( E_r \) was defined,

\[
\frac{1}{E_r} = \frac{1-v_i^2}{E} + \frac{1-v_i^2}{E_i},
\]

in which the quantities \( E_i, \nu_i \) are respectively the Young’s modulus and Poisson’s ratio for the indenter. For the Berkovich diamond indenter, \( E_i \) and \( \nu_i \) are respectively 1170GPa.
and 0.07. A fused silica standard supplied with the Nanoindenter XP system was used as the calibration specimen, for which E and v are respectively 72GPa and 0.18. For the Berkovich diamond indenter/fused silica specimen combination, the value of $E_r$ is ~70GPa.

Raw indentation loading and unloading curves were obtained in the force-controlled mode using constant loading and unloading rates, without holding when the maximum load, $P_{max}$, was reached. Multiple load vs. indenter displacement, $P-h$, curves were obtained at one $P_{max}$ value, and $P_{max}$ was varied to obtain a complete set of calibration data. Figure 2.1(a) displays a series of $P-h$ curves obtained from the fused silica calibration specimen, corrected for instrument drift. The unloading curves were fitted to a power-law expression. These power-law fits were used to determine the specimen initial unloading stiffness,

$$S_{max} = \left( \frac{dP}{dh} \right)_{P_{max}},$$

(2.2)

Such experimentally determined $S_{max}$ values were in turn used to determine the indenter contact depth at $P_{max}$,

$$h_c(P_{max}) = h(P_{max}) - \varepsilon \frac{P_{max}}{S_{max}},$$

(2.3)

where $\varepsilon$ is a geometric constant, $\varepsilon = 0.72$ for conical indenters and $\varepsilon = 0.75$ for indenter shapes that are paraboloids of revolution. Further, the $S_{max}$ values are used to determine the projected contact area at $P_{max}$, $A_c(P_{max})$, through its connection to the initial unloading stiffness and the depth-independent reduced modulus,

$$S_{max} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A_c(P_{max})},$$

(2.4)
after subtraction of the machine compliance contribution. The inset of Fig 2.1(a) shows values of $E$ plotted vs. $h_c$, after the proper indenter area function $A_e = A_e(h_c)$ was used. $E$ remains close to 72GPa independent of $h_c$, attesting to the correctness of the calibration procedure and showing that the presently determined area function for the Berkovich indenter is valid in the range of $\sim 20\text{nm} < h_c < 3000\text{nm}$.

A comparison was made of the experimentally determined area function for the Berkovich indenter to that generated from a simple geometric model of a conical indenter.

![Image](image_url)

Figure 2.1 Calibration of the Berkovich indenter: (a) load vs. displacement curves obtained from the fused silica standard. The inset shows the Young’s modulus of the fused silica standard as a function of the indenter contact depth, when the proper indenter area function is applied; (b) the indenter area function vs. the indenter contact depth. The lines denote values of a model area function of a conical indenter tangent to a spherical tip with different tip radii.

...tangential to sphere with radius $r$ at the indenter tip. At large contact depths, values from the model area functions are largely independent of the tip radii, and fit well with the experimental area function. At small contact depths, Fig 2.1(b) shows that model area functions with assumed tip radii between 150nm and 200nm describe the experimental data more closely. Thus for the present Berkovich indenter, the calibration results suggest an indenter tip radius between 150nm to 200nm. A set of instrumented
Berkovich indentations were performed on the <110> oriented single crystal Al specimen after calibration.

**2.2.3 Instrumented Micro-/nano- Scale Molding with Rectangular Strip Punches**

A series of rectangular strip punches, with widths ranging from 5µm to 0.55µm, were fabricated from one commercial, truncated, conical diamond tip (MicroSTAR Technologies, Huntsville, TX) by non-contact cutting with a focused Ga\(^+\) ion beam. A FEI Quanta3D FEG Dual-Beam focused ion beam (FIB) instrument equipped with two co-focal columns, a Schottky emission scanning electron column with a nominal resolution of 1.2nm and a high-current focused Ga\(^+\) ion column with a nominal resolution of 7nm, was used for punch fabrication. Figure 2.2(a) shows a secondary electron (SE) image of the rectangular diamond strip punch after the first Ga\(^+\) cut, at width×height×length dimensions of 10×12×30µm. This same diamond strip punch was then sequentially cut to widths of 5 µm, 3 µm, 1.5 µm, 1.2 µm, 0.9 µm, and 0.55 µm, keeping the punch length unchanged. The length of the punch was designed to be sufficiently long such that molding can be considered to occur under approximately plane

![Secondary electron images of the FIB-cut rectangular strip diamond punch: (a) after the initial FIB cut with dimensions of 10×12×30µm; (b) after the last FIB cut with dimensions of 0.55×5×30µm.](image-url)
strain conditions. As shown in Fig. 2.2(b), the smallest punch dimensions achieved in this series of experiments, while maintaining sharp corners, flat top surface, and smooth sidewall surfaces, was 0.55×5×30µm.

This sequence of ion beam cutting generated a series of long rectangular diamond strip punches with decreasing widths. After one cut was completed and the desired punch width/height reached, the top and sidewall surfaces of the punch were ion polished to maintain the sharpness of the punch features. This punch was then used to carry out at least five repeated molding runs on the same <110> oriented single crystal Al specimen used for Berkovich indentation, using the same Nanoindenter XP System. All experiments were conducted at room temperature. The height of the punch was maintained such that contact to the specimen occurred only at the top and sidewall surfaces of the punch. Recorded raw molding data consisted of total punch force vs. total punch displacement, \( P-d \). Figure 2.1(a) shows a typical \( P-d \) curve recorded when the single crystal Al specimen was molded with the diamond strip punch of 1.5µm width.

![Graph](image1.png)

**Figure 2.3** Raw response of single crystal Al molded by a rectangular strip punch of 1.5µm width: (a) a typical total force vs. total punch displacement curve; (b) the initial portion of the total force vs. total punch displacement curve together with the average load frame stiffness curve.
Qualitatively similar data were recorded at other punch widths. In all cases, raw $P$-$d$ curves exhibit an approximately linear initial portion followed by a second portion, in between which there is an abrupt change in slope.

The raw $P$-$d$ curves, one of which is shown in Fig. 2.3(a), include a load frame stiffness contribution. Similar to Berkovich indentation, the measured $P$-$d$ curve includes both the punch penetration into the specimen and an apparent punch displacement due to the load frame stiffness. To determine the load frame stiffness contribution in the case of rectangular strip punch with a flat bottom, advantage was taken of the fact that the punch penetrates very little into the specimen at small $P$. Separate $P$-$d$ curves, with the maximum $P$ value about one tenth of that for the actual molding run, were collected on a different area of the same specimen. SEM examination of the Al specimen surface was made in the region where these small-load indentations were made, which confirmed that little specimen penetration occurred as a result. These small-load $P$-$d$ curves were then averaged and fitted with a straight line passing through the origin. The slope of this line was taken as the average load frame stiffness for this series of repeat molding runs, $S_f$. It was further assumed that $S_f$ is a constant independent of the punch penetration depth or load. The actual punch penetration or molding depth, $d_m$, is then obtained from

$$d_m = d - \frac{P}{S_f} \quad (2.5)$$

Figure 2.1(b) shows the initial portion of the raw $P$-$d$ curve shown in Fig. 2.3(a), together with the calculated apparent punch displacement due to the average load frame stiffness. Figure 2.1(b) shows that this calculated punch displacement adequately describes the initial portion of the raw $P$-$d$ data, and indicates that the load frame stiffness contributes dominantly to this initial data portion. Figure 2.1(b) also shows that the initial portion of
the measured $P-d$ curve contains small bumps and deviations from the average stiffness curve. Such bumps and deviations may be reflections of several factors, including imperfections in punch geometry due to the ion cutting process, deviations of the actual load frame stiffness from a constant, inadequacies in the small-load indentation experiments, etc. These considerations notwithstanding, $d_m$ calculated from Eq. (2.5) was taken as a reasonable estimate of the actual molding depth, and $P$ vs. $d_m$ was taken to be the actual molding response and analyzed subsequently in Section 3.3.

### 2.2.4 Structural Examinations

In order to understand measured response of the Al single crystal specimen during Berkovich indentation and micro-/nano- scale molding, companion structural examinations were conducted with FIB microscopy and transmission electron microscopy (TEM). Within the FIB instrument, scanning electron microscopy (SEM) imaging could be achieved in the electron-induced secondary electron (SE) mode or the ion-induced secondary electron (ISE) mode. To characterize the micro/nano scale structure of the Al specimen under the indent, site-selective cross-sectional TEM specimens were prepared by FIB cutting of the deformed specimen region followed by lift-out of a thin specimen slice. To protect the specimen surface, a thin Pt layer was deposited by Ga$^+$ ion catalyzed vapor phase deposition from a Pt-containing gaseous metalorganic source prior to FIB cutting. The specimen lift-out was accomplished with an OmniProbe W microprobe. The lift-out specimen was transferred to a special TEM specimen grid placed within the FIB instrument and thinned to electron transparency by glancing angle Ga$^+$ ion beams of decreasing voltages and currents. To alleviate possible specimen damage by the Ga$^+$ ion beam, end polish of the electron transparent specimens
was accomplished with 750V Ar\textsuperscript{+} ions at 7 degree tilts on both sides using a Technoorg Gentle Mill (Technoorg Linda Ltd. Co. Budapest, Hungary). Structural characterization was performed on a JEOL JEM2010 instrument operated at 200kV.

2.3 Results and Discussion

Figure 2.4 summarizes the results of instrumented Berkovich indentation on the single crystal Al specimen. Figure 2.4(a) shows values of Young’s modulus vs. the indenter contact depth, assuming that the Poisson’s ratio of Al is 0.33. As $P_{\text{max}}$ decreases from 60mN to 1mN, $h_c$ decreases from $\sim 3.1\mu$m to $\sim 260$nm. Data taken within this widely varying range of $h_c$ values show that $E$ remains approximately a constant independent of $h_c$ and that $E = 68.6\pm 3.7$GPa, consistent with the known Young’s modulus of bulk Al, $E(\text{Al}) \sim 69$GPa. Data shown in Fig. 2.4(a) confirms the validity of the instrument/indenter calibration and the correctness of the Berkovich indentation measurements. The corresponding specimen hardness $H$, defined as

$$
H(P_{\text{max}}) = \frac{P_{\text{max}}}{A_c(P_{\text{max}})}
$$

(2.6)
increases smoothly as $h_c$ decreases. Following Ma and Clarke [18], a characteristic length scale for indentation is obtained by converting the indenter projected contact area to an indent diameter $D$,

$$D(P_{\text{max}}) = \frac{\sqrt{4A_c(P_{\text{max}})}}{\pi}.$$  \hspace{1cm} (2.7)

Figure 2.4(b) plots measured $H$ values vs. $D$. $H$ increases by about a factor of 2 from below 250MPa to about 500MPa as $D$ decreases from ~25μm to ~2μm, confirming the existence of an indentation size effect when the single crystal Al specimen is indented by a Berkovich indenter. Figure 2.4(b) further shows that the measured $H$-$D$ curve is well described by the Nix-Gao expression [25],

$$H = H_0 \sqrt{1 + \frac{D^*}{D}},$$  \hspace{1cm} (2.8)

where $D^*$ is a characteristic length parameter. The line in Fig. 2.4(b) was obtained through a non-linear least-squares fit of the Nix-Gao expression to the present data, which yielded respectively $H_0 = 220\pm1$GPa and $D^* = 6.6\pm0.2$μm. Taken together, data presented in Fig. 2.4 are consistent with numerous previous observations of the ISE with pyramidal indenters. In the case of Berkovich indentation, $H$ defines a characteristic pressure, which depends on the characteristic length of indentation, $D$.

Figure 2.5 summarizes the results of micro-/nano-scale molding performed on the same single crystal Al specimen. Figure 2.5(a) shows a series of measured molding response curves, $p - d_m/w$, obtained from long, rectangular strip punches with widths $w$ decreasing from 5μm to 0.55μm. Normalizing the total force on the punch by the nominal contact area, i.e., punch width×length, and normalizing the punch penetration depth by $w$ enables quantitative comparison of data obtained from different punches.
Figure 2.5  Results of micro-/nano- scale molding of the single crystal Al specimen with long rectangular punches of different widths: (a) molding response curves in terms of nominal contact pressure vs. normalized molding depth; (b) characteristic molding pressure vs. punch width.

Results of several independent molding runs at each $w$ value are superimposed on Fig. 2.5(a), and serve as an indication of the experimental variability. The uncertainty in determining the actual load frame stiffness translates into an uncertainty in determining the actual molding depth, which manifests itself in the initial wobbles exhibited by the $p - \frac{d_{m}}{w}$ curves shown in Fig. 2.5(a), including some apparently negative displacement values. It should be pointed out that the actual values of these apparently negative displacements are small, e.g., within 50nm from zero in the case of $w = 0.9 \mu m$. Nevertheless, they are non-physical, and reflect an artifact when the average system stiffness contribution is subtracted from experimental measured total punch displacement values. These apparently negative displacement values therefore indicate an experimental deficiency in terms of the imprecise knowledge of the actual system stiffness. This deficiency notwithstanding, it is clear from Fig. 2.5(a) that all measured molding response curves exhibit similar qualitative behavior, possessing an initial section where $p$ increases rapidly with very little punch penetration into the molded material, followed by an abrupt turn-over and a second section where $d_{m}$ increases significantly.
with only slight increase in $p$. This behavior is substantially similar to previous Al micromolding experiments and the accompanying FEA, at a characteristic length of $\sim 150\mu$m [10]. In the Al micromolding case, the FEA shows that the characteristic molding pressure, well represented by that at the turn-over point on the molding response curve, is approximately three times the Al yield stress.

Figure 2.5(a) shows that nearly identical molding response curves are observed at $w$ values of $5\mu$m and $3\mu$m. This suggests that the present punch length/width ratios, 6-to-1 or greater, approximate plane strain molding conditions sufficiently well, and further, that the single crystal Al specimen appears to behave mechanically in an identical manner at $w$ values of $5\mu$m and $3\mu$m. As $w$ further decreases, measured molding response curves remain qualitatively similar but deviate from one another in that the turn-over points show a clear increase in pressure as $w$ decreases. Thus the data show, in the present case of plane strain molding, that the characteristic molding pressure appears to be $w$ dependent, and increases significantly as $w$ decreases to $1.5\mu$m and below. To obtain a quantitative measure of this increase, the second and more compliant section of each measured molding response curve, within the range $0.05 < d_m/w < 0.3$, was fitted with a straight line and back extrapolated to obtain an intercept on the pressure axis. This intercept was taken as the characteristic molding pressure. Figure 2.5(b) plots the so-determined characteristic molding pressure against the punch width. In this case, the punch width defines the characteristic length scale by virtue of the geometry of molding by long, rectangular, strip punches under conditions approximating plane strain. In Fig. 2.5(b), the error bar on the punch width stems from a collection of dimension measurements performed at different punch locations on one micrograph and from
different micrographs. The error bar on the characteristic pressure stems from extrapolating molding response data from a number of repeat molding runs. Data shown in Fig. 2.5(b) indicate with certainty the presence of a size effect as the single crystal Al specimen is molded with a long, rectangular, strip punch as the punch width transitions from the micron to the submicron regime. The data shown in Fig. 2.5(b) was fitted to a Nix-Gao type expression,

$$ p = p_0 \sqrt{1 + \frac{w^*}{w}}. \quad (2.9) $$

Figure 2.5(b) shows that the parameter set $p_0 = 220$GPa and $w^* = 2.5\mu$m provides an adequate description of the data.

Using the indent diameter as the characteristic length scale in Berkovich indentation has been well accepted, following the work of Ma and Clarke [18] and others. As stated above, the punch width serves as the characteristic length scale in molding by long, rectangular, strip punches. Figure 2.6 plots the characteristic pressures measured during Berkovich indentation as well as during molding by strip punch against the corresponding characteristic lengths. The most distinctive feature displayed in Fig. 2.6 is

![Figure 2.6 Characteristic molding pressure vs. characteristic length scale in Berkovich indentation and strip punch molding.](image)
the fact that, although an ISE appears to be present in both cases, the characteristic pressures exhibit very different dependence on the characteristic length. In the Berkovich indentation case, the characteristic pressure starts to increase when $D$ decreases to below $20\mu m$, but in a smooth and gradual manner. In the case of molding by strip punch, the characteristic pressure remains relatively flat until $w$ reaches $\sim3\mu m$, and increases much more sharply with further decrease in $w$. Data shown in Fig. 2.6 provides a clear example for the influence of indenter geometry on the manifestation of ISE. Alternatively stated, the characteristic length appears to be dependent on the indenter geometry or the distribution of stress/strain underneath the indenter, and not a unique function of the indented material. Measured on the same single crystal Al specimen, the present data sets shown in Fig. 2.6 thus offer an experimental test case for size-dependent plasticity theories.

Figure 2.7 shows the morphology of molded features in the single crystal Al specimen. Figures 2.7(a) and 2.7(b) show SE images of typical features molded by strip

![Figure 2.7](image-url)  
**Figure 2.7** Morphology of molded features in the single crystal Al specimen: (a) an SE image of a typical feature molded with the strip punch of 5$\mu m$ width; (b) an SE image of a typical feature molded with the strip punch of 1.2$\mu m$ width; (c) an SE image of a site-selective lift-out specimen containing a trench molded by the strip punch of 1.2$\mu m$ width. The Pt filling of the molded trench and the Pt covering of the specimen surface are visible.
punches with widths of 5μm and 1.2μm, respectively. Molded features have straight
sidewalls, flat bottoms, sharp corners, and relatively sharp sidewall to bottom transitions.
Figure 2.7(c) shows an SE image of a typical site-selective Al lift-out specimen. This
specimen was molded by the strip punch of 1.2μm width, and shown in Fig. 2.7(c) in the
state prior to final thinning to electron transparency. To protect the specimen from ion
beam damage during FIB cutting, Ga⁺ ion catalyzed Pt deposition was first used to
completely fill the molded trench and then used to cover the entire specimen surface.
The lift-out specimen encompasses a large region underneath the molded feature,
~7.5μm×17.5μm in size. The Pt deposition over the specimen top surface reveals a slight
sinking-in of the specimen surface around the molded trench.

The specimen shown in Fig. 2.7(c) was thinned to electron transparency and
examined with TEM. Figure 2.8(a) shows a TEM bright-field (BF) micrograph of the
specimen region immediately underneath the molded trench. The single crystal nature of
the original Al specimen was confirmed by independent lift-outs from pristine regions on
the same specimen, where subsequent TEM examinations showed that the lift-out
specimen remained single crystal in structure. In contrast, Fig. 2.8(a) shows clear
evidence of the formation of new nanoscale Al grains around the molded trench. The
specimen orientation was such that one such Al nanograin immediately next to the right
hand side trench corner is in the <112> zone-axis orientation, with the associated selected
area electron diffraction pattern (SADP) shown in the inset of Fig. 2.8(a). As the
specimen orientation was changed, different Al nanograins around the trench came into
strong contrast. Tilting experiments within the microscope showed that the tilt angles
between these Al nanograins were small, typically less than 15 degrees. Apart from the
formation of these Al nanograins, the dislocation density within the specimen does not appear to be high. Figure 2.8(b) shows another TEM BF micrograph around the left hand side of the molded trench. It reveals the presence of a number of Al nanograins with well-defined grain boundaries along the side of the trench, with grain sizes of 100-200nm.

Figure 2.8 Structure of the Al specimen underneath the trench molded with the strip punch of 1.2µm width: (a) a BF micrograph in the <112> zone axis orientation of a nanograin around the right corner of the molded trench. The corresponding SADP from the nanograin is shown in the inset; (b) a BF micrograph of the left side of the molded trench. Nanoscale grains and dislocation walls are visible.

In addition to these Al nanograins, Fig. 2.8(b) shows clear evidence for dislocation wall formation adjacent to the molded trench. Previous TEM examination of single crystal Cu specimens underneath pyramidal indentation showed evidence of dislocation loop formation and dislocation propagation far away from the indent [26]. The structural evidence shown in Fig. 2.8(b) suggests the additional possibility that dislocations generated from the punch indentation may organize into walls, leading subsequently to formation of new nanoscale grains. Such nanograin formation in turn leads to dislocation absorption at the grain boundaries and decreases the residual dislocation density underneath the molded feature.
2.4 Summary

The present study shows that micro to nano scale compression molding to large plastic strains can be achieved in single crystal Al specimens at room temperature. Micro-/nano- scale compression molding creates deep plastic imprints in Al that are faithful in shape to the mold insert, and therefore offers a potential avenue for rapid fabrication of micro-/nano- scale metal-based structures. A detailed comparison between indentation size effects in one single crystal Al specimen in the pyramidal indentation geometry and the strip punch indentation geometry is made. Our results show the presence of significant indentation size effects in both pyramidal and strip punch indentation geometries, but a distinctly different dependence of the characteristic pressure on the corresponding characteristic length. The present observation of the existence of a significant dependence of the characteristic length on indenter geometry suggests that this characteristic length is not a unique function of the indented material, but is dependent on the stress/strain distribution underneath the indenter. Our results add knowledge to the general area of metal molding, and offer an experimental test case for size-dependent plasticity theories.

2.5 References


CHAPTER 3
SIZE DEPENDENCE OF THE PLANE-STRAIN RESPONSE OF SINGLE CRYSTAL AL TO INDENTATION BY DIAMOND WEDGES

3.1 Introduction

While conventional plasticity theories contain no explicit dependence on a material length scale, intense interest in the last two decades on the mechanical response of materials at increasingly smaller characteristic lengths motivated the development of plasticity theories containing an explicit dependence on strain gradients [1,2]. The multitude of experiments conducted within the same time frame demonstrating the dependence of materials’ mechanical response on a length scale, or the existence of various “size effects”, may be grouped into three main categories of micro-torsion [3], micro-bending [4], and micro/nano indentation [5, 6]. Among these three categories, most experiments have been conducted with depth-sensing indentation instruments to demonstrate the existence of the indentation size effect (ISE), manifested in an increase in the projected contact pressure with a decrease in a characteristic indent dimension [7,8].

Nix and Gao [9], based on the concept of geometrically necessary dislocations, provided a framework in which rationalization of experiments demonstrating the existence of the ISE can be made. Indentation experiments showing a size effect have mostly been conducted with three-dimensional (3D) indenters of either a pyramidal or a spherical shape [10]. Some studies investigated the influence of indenter shape on observed ISE, for example, pyramidal indentation and spherical indentation have been compared. In cases of pyramidal or spherical indentation, the experimental results have been shown to be largely consistent with the Nix-Gao model [11, 12]. In comparison to
3D indentation, micro/nano scale indentation in two-dimensional (2D) plane-strain configurations has been much less studied.

A number of practical applications motivate further quantitative studies of elasto-plastic indentation in 2D geometries. For example, 2D microscale indentation is a useful fabrication technique for direct replication of microscale patterns in metals [13,14]. Experimentally measured mechanical response of metals in plane-strain indentation at a characteristic length scale of greater than 100μm has been shown to be consistent with continuum mechanics predictions [15, 16]. Replication of metal-based patterns with characteristic lengths of ~1μm or below is also of interest for efficient fabrication of optical gratings [17] and meta-materials exhibiting unusual optical properties [18]. One recent experiment compared manifestations of ISE when a single crystal Al specimen was indented by a 3D pyramidal Berkovich indenter and a 2D long, rectangular, strip punch. Results of this experiment suggested that the relationship between the characteristic contact pressure and the characteristic contact dimension depends on indenter geometry [19]. Such results provide motivation for further 2D micro/nano indentation experiments.

In this chapter, we report results of micro/nano indentation of a half space comprised of single crystal Al with diamond wedges that are long in the y-direction (Fig. 3.1). Instrumented indentations were carried out with 2D wedge diamond indenters with different included angles, 2φ. The total force applied on the indenter, \( F \), was measured as a function of the indenter total displacement, \( h \). For a given wedge indenter of total length \( L \), measurements were made at a wide range of loads. The rest of this chapter is organized as follows. In Section 3.2, the experimental procedures are described,
including indenter fabrication and the measurement of force-deflection response. Section 3.3 presents a method for obtaining the projected contact width for 2D wedge indentation from measured force-deflection curves, while Section 3.4 describes an experimental validation of the method. Section 3.5 then presents the wedge indentation results and compares them to predictions made from an extension of the Nix-Gao model. The chapter closes with some concluding remarks in Section 3.6.

3.2 Experimental Procedures for Characterizing Wedge Indentation Response

A <110> oriented Al single crystal specimen mounted in an epoxy cylinder (Agilent Technologies, Knoxville, TN) was employed for the micro/nano scale wedge indentation experiments. Depth-sensing indentation experiments were carried out on a Nanoindenter XP System (MTS Systems Corp., Knoxville, TN) with nominal load and displacement resolutions of 50nN and 0.01nm, respectively.

All indentation experiments were conducted at room temperature. A series of long wedge diamond indenters were fabricated from one commercial, truncated, conical diamond tip (MicroSTAR Technologies, Huntsville, TX) by non-contact cutting with a focused Ga⁺ ion beam. A FEI Quanta3D FEG Dual-Beam focused ion beam (FIB)
instrument equipped with two co-focal columns, a Schottky emission scanning electron column with a nominal resolution of 1.2nm and a high-current focused Ga$^+$ ion column with a nominal resolution of 7nm, was used for indenter fabrication.

Figure 3.2(a) shows a secondary electron (SE) image of one triangular diamond wedge indenter, with a total length of 48µm in its finished state. Figure 3.2(b) shows an SE image of the indenter taken in the orientation along the long axis of the wedge. Prior to finishing the indenter fabrication, ion polishing with decreased Ga$^+$ currents was conducted on the two wedge surfaces and the two end surfaces of the indenter to minimize surface roughness and maximize the sharpness of the wedge features. Fig 3.2(a)

![Figure 3.2](image)

Figure 3.2 (a) An overview SE image of the finished diamond wedge indenter with an included angle of 33°, with the tip of the wedge pointing upward; (b) an SE image taken along the long axis of the same wedge.

that finished wedge surfaces and end surfaces are smooth after ion polishing. From Fig. 3.2(b) and similar images at higher magnifications, the included wedge angle and the tip radius of the wedge were determined to be $2\phi = 33\pm1^\circ$ and ~200nm, respectively. The size of the ion polished portion of the wedge indenter was sufficiently large such that contact to the Al specimen occurred only on smooth surfaces. This indenter was then used to indent the single crystal Al specimen at varying loads.

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After a series of indentation runs were performed on the single crystal Al specimen, the 33° diamond wedge was then cut by Ga⁺ ion beam to form a second wedge indenter with an included angle of \(2\phi = 53\pm1°\). The total length of the indenter remained unchanged at 48µm. After a series of indentation runs were performed with the 53° wedge indenter, a third wedge indenter was again formed from it by Ga⁺ ion beam cutting, resulting in a wedge with an included angle of \(2\phi = 93\pm1°\). Due to additional ion polishing of the end surfaces, the total length of the 93° wedge decreased to 46µm. Geometries and surface roughness of the 53° and 93° wedges were similar to those of the 33° wedge, shown in Fig. 3.2. As will be shown in more detail later on, the indentation loads were such that the ratio of the contact width to the total wedge length stayed below 1:6 for all indentations, and below 1:10 for indentations exhibiting size dependence. Thus the lengths of the three wedge indenters were judged to be sufficiently long such that all indentations runs can be considered to occur under plane-strain conditions.

Raw wedge indentation loading and unloading curves were obtained in the force-controlled mode using constant loading and unloading rates, without holding when the maximum load, \(F_{\text{max}}\), was reached. At least ten indenter total force versus indenter total displacement curves, or \(F-h\) curves, were obtained at each \(F_{\text{max}}\) value. The value of \(F_{\text{max}}\) was varied to obtain an entire set of indentation data.

For 2D indentations, the load per unit wedge length, \(P\), is defined by

\[
P = \frac{F}{L}.
\]  

Figure 3.3 shows a typical set of \(P-h\) curves, recorded when the single crystal Al specimen was indented with the 53° wedge to different \(P_{\text{max}} = \frac{F_{\text{max}}}{L}\) values. For the entire set of indentation data, \(L\) remained a constant. Therefore raw \(F-h\) curves and \(P-h\)
curves have the same shape and differ by only a scaling constant. Qualitatively similar data were recorded other two wedges. In all cases, raw wedge indentation $P-h$ curves

![Figure 3.3](image)

Figure 3.3  A typical set of raw 2D wedge indentation data, plotted as load per unit wedge length vs. indenter total displacement, obtained when the $53^\circ$ wedge was used to indent the single crystal Al specimen.

exhibited approximately linear loading and unloading segments.

Measured indenter total displacement included both the indenter penetration into the specimen and a displacement due to finite load frame stiffness. To determine the latter contribution to the wedge indentation data, a separate load frame stiffness calibration was conducted using a 3D pyramidal Berkovich diamond indenter to indent the same Al specimen. Separate Berkovich indentation $F-h$ curves were obtained with the maximum total indenter displacement $h_{\text{max}}$ ranging from 2$\mu$m to 6$\mu$m, comparable to corresponding $h_{\text{max}}$ values for wedge indentation at the largest loads. The frame stiffness value, determined following the Oliver-Pharr calibration procedures for Berkovich indentation [20], was $\sim 2.2 \times 10^4$ mN/$\mu$m. In comparison, the slope of the unloading curve determined from raw $F-h$ curves obtained from wedge indentation through linear fits to the unloading segment data was $\sim 1.2 \times 10^3$ mN/$\mu$m. Hence the load frame stiffness is a
factor of 18 times larger than the stiffness of the indentation process, and consequently we chose to ignore any contributions to the total displacement from the frame. The raw $F-h$ curves obtained from wedge indentation runs were thus taken as the relationship between the indenter force and the actual indenter penetration into the Al specimen.

Examinations of the wedge-indentated single crystal Al specimen were conducted through SE imaging with the FIB instrument. To characterize the morphology of the micro/nano scale indents made on Al, surface SE images were supplemented by images of site-selective cross sections prepared by Ga$^+$ ion cutting of the indented specimen region. Prior to FIB cutting, a Pt layer was deposited by Ga$^+$ ion catalyzed deposition from a Pt-containing gaseous metalorganic source. In addition to protecting the specimen surface from ion beam damage during cutting, the Pt deposition also serves to delineate the impressions made by wedge indentation.

3.3 Theoretical approach for obtaining contact widths from indentation unloading curves

As oriented in Fig. 3.1, the long axis of the wedge is aligned with the $y$ axis, while the indentation direction is aligned with the $z$ direction. Hence for sufficiently long wedges, a plane-strain configuration exists in the $x$-$z$ plane, as shown in Fig. 3.4. Herein $P$ is the force per unit length as in Eq. (3.1), and $w = 2a$ the width of the contact produced by $P$ when the included vertex angle of the wedge is $2\phi$.

We seek a means of interpreting experimentally measured $P-h$ curves in terms of the projected contact pressure or hardness, $H$. For the 2D configuration of Fig. 3.4, $H$ at the maximum load may be defined by

$$H = \frac{P_{\text{max}}}{w}. \quad (3.2)$$
Figure 3.4 A cross-sectional schematic of contact between the wedge indenter and the indented specimen.

In Eq. (3.2), \( w \) is, in effect, the contact area per unit length at \( P_{\text{max}} \). While \( w \) can be measured by directly imaging the residual indent imprint when it is sufficiently large in size, such measurements for \( w \) become increasingly uncertain as the imprint width reduces to the micron and submicron range of interest here.

To meet this challenge, we look to adapt the approach of Oliver and Pharr [20] for axisymmetric 3D indentation to the current 2D indentation configuration. The key aspect of the Oliver-Pharr procedure to be adapted stems from the appreciation that the unloading behavior of elasto-plastic indented materials can be captured by the elastic indentation response of these materials [21]. This insight enables a relationship between the slope of the initial unloading curve and the contact area at maximum load to be developed. As a result, there is no need to directly measure the contact area to obtain hardness values.

More precisely, for the parabolic indenters used in [20] to approximate the Berkovich indenters employed experimentally, the indenter displacement, \( h \), is given by
In the first of Eqs. (3.3), \( a \) is now the radius of the contact circle, and \( R \) is the radius of curvature at the vertex of the parabolic indenter. In the second of Eqs. (3.3), \( F \) continues as the total load force, and \( E_c \) is the contact modulus defined by

\[
E_c = \left( \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \right)^{-1},
\]

wherein \( E \) and \( E_i \) are the Young’s moduli of the indented material and the indenter, respectively, while \( \nu \) and \( \nu_i \) are the corresponding Poisson’s ratios. Because Hertz chose to approximate spherical indenters with paraboloids, the results in Eq. (3.3) are essentially Hertzian and from [22] (alternatively, see, e.g. [23], p. 427).

Eliminating \( a \) from Eqs. (3.3) and rearranging gives,

\[
F = \frac{4}{3} E_c \sqrt{R} h^3.
\]

Differentiating Eq. (3.5) to obtain the unloading slope \( S = dF/dh \), then using the first of Eqs. (3.3) to remove \( R \), we obtain

\[
S = \frac{2}{\sqrt{\pi}} E_c \sqrt{A},
\]

where \( A = \pi a^2 \) is the projected contact area. Equation (3.6) thus offers a means of obtaining \( A \) from experimentally measured \( S \). The Oliver-Pharr analysis has been shown to be valid for axisymmetric rigid punches with shapes of paraboloids of revolution [24].

Here, therefore, we want to develop the analogue of Eq. (3.6) for 2D indentation. Compared to the preceding derivation for the 3D case, an added difficulty exists for the 2D case. This is because there is no real 2D counterpart to the first of the 3D relations in Eqs. (3.3) for the displacement \( h \). In 3D, \( h \) is effectively relative to null displacements at
infinity for an elastic half-space, and in this sense could be viewed as absolute. No such absolute displacements exist for elastic half-planes with net forces on their surfaces. This is a consequence of the Green’s function for displacements in elastic half-planes under normal surface loading being logarithmically unbounded at infinity, the Green’s function coming from Flamant’s solution for a normal line-load on an elastic half-plane (see, e.g., [23], p. 16).

To overcome this difficulty, we introduce a datum at a remote depth $D \gg a$ (Fig. 3.4; not to scale). Then we define $h$ to be the central displacement of the indenter relative to the displacement at $D$. That is,

$$h = u_z|_{z=0} - u_z|_{z=D}, \quad (3.7)$$

where $u_z$ is the displacement of the elastic half-plane on the $z$-axis.

Following Oliver and Pharr [20], we approximate our wedge-shaped indenters with parabolas, as indicated by the dotted line in Fig. 3.4. Then we can evaluate $h$ of Eq. (3.7) as follows. For plane strain in the $y$ direction (Fig. 3.1), the normal strain in the $z$ direction is related to the normal stresses, $\sigma_x, \sigma_z$, in an isotropic elastic half-plane by

$$\frac{\partial u_z}{\partial z} = \left[\sigma_z - \nu(\sigma_x + \sigma_z)\right]/2G \quad (3.8)$$

where $G = E/(2(1+\nu))$ is the shear modulus of the half-plane. Hence Eq. (3.7) has

$$h = \int_0^D \left[\nu(\sigma_x + \sigma_z) - \sigma_z\right] \frac{dz}{2G}. \quad (3.9)$$

To determine the stresses in Eq. (3.9), we draw on Hertz’s solution for the contact stress under a smooth, rigid, parabolic indenter on an elastic half-plane (see, e.g., [23], p. 102), and evaluate the integrals resulting from using the contact stress in concert with a stress
Green’s function from the Flamant line load on a half plane ([23], p. 16). Thus on the z-axis

\[ \sigma_x + \sigma_z = \frac{4P}{\pi a} \left( \zeta - \sqrt{1 + \zeta^2} \right), \quad \sigma_z = \frac{-2P}{\pi a \sqrt{1 + \zeta^2}}, \]

(3.10)

wherein \( a \) has reverted to its 2D designation, and \( \zeta = z/a \). The expressions in Eqs. (3.10) are consistent with the general solution for the interior stresses in a half-plane under a parabolic indenter [25]. Substituting Eqs. (3.10) into Eq. (3.9) and integrating gives

\[ h = \frac{P}{\pi G} \left[ (1 - \nu) \sinh^{-1} \Delta + \nu \Delta \left( \Delta - \sqrt{1 + \Delta^2} \right) \right], \]

(3.11)

where \( \Delta = D/a \). Hence asymptotically for \( D \gg a \)

\[ h = \frac{P}{\pi G} \left[ (1 - \nu) \ln 2 \Delta - \frac{\nu}{2} \right] + O(\Delta^{-2}) \text{ as } \Delta \to \infty. \]

(3.12)

For Hertzian contact of a 2D parabolic indenter,

\[ a = \left( \frac{4PR}{\pi E_c} \right)^{1/2}, \]

(3.13)

the 2D counterpart to the second of Eqs. (3.3) (see, e.g., [23], p. 427). Introducing Eq. (3.13) into \( \Delta \) of Eq. (3.11) then exposes the full dependence of \( h \) on \( P \) and leads to

\[ h = \frac{-P}{2\pi G} \left[ (1 - \nu) \ln \left( \frac{PR}{\pi E_c D^2} \right) + \nu \right], \]

(3.14)

for the dominant contributions when \( D \gg a \). For the present 2D configuration, we define the unloading stiffness as

\[ S = \frac{dP}{dh}. \]

(3.15)

Hence on differentiating Eq. (3.14), using Eq. (3.13) to remove \( R \), and reintroducing \( E \), we obtain
\[ S = \pi E \frac{(1+n) \ln \left( \frac{4D}{w} \right) - 1}{(1-\nu) \ln \left( \frac{4D}{w} \right) - 1}. \]  
(3.16)

Equation (3.16) is the sought-after 2D counterpart to Eq. (3.6) because it relates \( S \) to the contact width \( w \).

### 3.4 Experimental validation of the theoretical approach for obtaining contact widths

In contrast to the 3D indentation case, where knowledge of elastic moduli and the indentation unloading slope \( S \) uniquely determines the actual contact area, Eq. (3.16) shows that, in the case of 2D wedge indentation, only a ratio involving the actual contact width \( w \) to a datum depth \( D \) is so determined. Therefore we utilize the fact that we are able to experimentally measure \( w \) at sufficiently large loads and attendant size scales, and make a determination of \( D \) and so calibrate the approach outlined in Section 3. That is, we measure \( w \) directly by imaging the residual indent impression made at a sufficiently large load and calculate the corresponding unloading slope \( S \) from experimentally measured \( P-h \) curves, then invert Eq. (3.16) to obtain the corresponding value of \( w/D \). One thus arrives at a determination of \( D \) by combining \( P-h \) curve measurements with imaging. Moreover, by making a range of wedge indentations at sufficiently large loads, we can check for the consistency of the value of \( D \), and so validate the approach to a degree.

Figure 3.5(a) shows an SE image of a FIB cross section across a typical indent in the Al specimen made by the 53° wedge. The Ga\textsuperscript{+} catalyzed Pt layer covering the Al specimen shows a lighter contrast and is easily distinguishable from Al. The cross sectional image of the indent impression illustrates the flatness of the wedge surfaces and the sharpness of the wedge tip region. Indication of sink-in is perceivable by examining
the Al surface, delineated by the Al/Pt boundary. The transition between the top surface and the indentation impression appears to be rather abrupt, at least for the large indents similar to the one shown in Fig. 3.5(a). Figure 3.5(b) shows a plan-view SE image of one entire indent impression made in Al with the $53^\circ$ wedge. At least four width measurements were made from this indent, from which an average value for $w$ obtained was $5.9\mu m$. For this particular indent, the maximum difference from the average $w$ value was less than $0.3\mu m$, or less than 5%. A $\pm5\%$ scatter band is representative of contact width measurements by imaging on large indent impressions with $w$ greater than $3\mu m$. Contact width measurements made from plan-view images, such as that shown in Fig. 3.5(b), are also consistent with the corresponding cross-sectional images, such as that shown in Fig. 3.5(a).

Five indent impressions were made in the Al specimen with the $53^\circ$ wedge at large loads, with $P-h$ curves measured in the process. Actual contact widths were
measured through imaging following procedures described above. From the accompanying $P-h$ curves, linear least squares fits were made to the data contained within the 100%-70% portion of the unloading segment. From fitted values of $S$, values of the ratio $w/D$ were calculated by inverting Eq. (3.16). Fitting the unloading $P-h$ data with a power-law expression did not yield any significant differences in results.

Consistent with the expectation that the datum point is far below the indent and remains essentially fixed, the ratio $w/D$ is expected to be linearly proportional to $w$. One way to demonstrate this linear proportionality is illustrated in Fig. 3.6, which plots calculated $w/D$ values versus values of imaged contact width $w$ for these five data points. For these five indents, $w$ values were between 5.0µm and 6.5µm and fell in a range where direct imaging is expected to yield accurate measures of the actual contact width. Error in $w$ represents the 5% scatter band described above. Error in $w/D$ represents calculated

---

Figure 3.6  Correlation between the $w/D$ ratio calculated from analysis of wedge indentation unloading curves and the contact width obtained from direct imaging. The straight line going through the origin is obtained through a linear fit to the data from five indents made at large loads.
standard deviation from repeated indentation runs. A linear least squares fit, constrained to go through zero, was made through these five data points. The fit yielded an adjusted R-square value of 0.997 (adj. $R^2$, [26]), indicating reasonable agreement between fitted linearly varying values and corresponding experimental values.

An alternative way to express the same linear proportionality between $w/D$ values calculated from wedge indentation unloading curves and average values of contact width obtained from direct imaging of indent impressions is to calculate a value of the datum depth $D$ by taking the ratio between the two. For these five indents, this calculation yielded $D = 166\pm8\mu$m. This demonstrates that this datum depth stays constant to ±5% for indents made by the same wedge at large loads. Furthermore, the value of this datum depth is indeed much larger than the extent of the contact, consistent with the assumption made in deriving Eq. (3.16).

Therefore, values of the actual contact width $w$ for other indents made at smaller loads were calculated from the corresponding unloading $w/D$ values referenced to the linear fit shown in Fig. 3.6. Analogous data correlating $w/D$ obtained from wedge indentation unloading curves and direct imaging of contact width at large loads were obtained for the 33° and 93° wedges. Values of $w$ for indents made at smaller loads were similarly calculated for these two included wedge angles. Once $w$ was obtained, the projected contact pressure or hardness was calculated from Eq. (3.2). The actual contact depth $h_c$ at the maximum load was then calculated from

$$h_c = \frac{w}{2} \tan \theta$$  \hspace{1cm} (3.17)

In Eq. (3.17), the indentation angle $\theta$, the angle the wedge surface makes with the original solid surface, is complementary to $\phi$ (Fig. 3.4).
3.5 Wedge indentation results and discussion

Figure 3.7(a) collates data obtained from indentation of the single crystal Al specimen by the 33°, 53°, and 93° wedges, in all cases shown as \( H \) vs. \( w \). Standard deviations in \( H \) and \( w \) were calculated from repeated indentation runs at the same nominal load. For all three included angles, the wedge indentation data show clearly the presence of an ISE, manifested in an increase in \( H \) of 40% or more as \( w \) decreases from \( \sim 6 \mu m \) down to below 1\( \mu \)m. At first glance, data from 33°, 53°, and 93° wedges crowd together, prompting the question that whether \( w \) would act as a universal length scale independent of the wedge angle. Reexamination of the data reveals that this is not the case. Figure 3.7(b) re-plots the same single crystal Al wedge indentation data as \( H \) vs. \( h_c \), with the conversion between \( h_c \) and \( w \) given by Eq. (3.17). This re-plotting not only spreads the data out over a wide range of \( h_c \), it also shows more clearly that the dependence of \( H \) on \( h_c \) or \( w \) cannot be described by a single function.

The three sets of \( H \) vs. \( h_c \) data, obtained from the 33°, 53°, and 93° wedges, were fitted to a Nix-Gao expression,
in which $h^*$ is the characteristic length parameter and $H_o$ is the limit to the projected contact pressure as $h_c$ goes to infinity. The non-linear least squares fit to the 93° wedge data is shown in Fig. 3.8, taking both $H_o$ and $h^*$ as free parameters. It is apparent that the Nix-Gao expression describes the 93° wedge data well, resulting in an adj. $R^2$ value of 0.975 for the fit. Separate fitting to the three set of wedge indentation data was performed, with fitting results given in Table 3.1. Fits of comparable quality were obtained. Fitting to the 53° and 93° wedge indentation data yielded consistent $H_o$ values of ~270MPa, while the fitted value of $H_o$ for the 33° wedge indentation data is 232MPa.

Table 3.1 shows that $h^*$ varies significantly with the included wedge angle.

The three sets of $H$ vs. $w$ data were similarly fitted to a Nix-Gao type expression, 

$$H = H_o \left(1 + \frac{h^*}{h_c}\right)$$

(3.18)

Figure 3.8 A non-linear, least-squares fit of the 93° wedge data to the Nix-Gao expression shown in Eq. (3.18).
fitted. The fitted values of \( w^* \) are listed in Table 3.1 as well. Consistent with the wedge geometry expressed through Eq. (3.17), the ratio of fitted \( h^* \) and \( w^* \) values varies linearly with \( \tan \theta \). The dependence of the characteristic length \( h^* \) on the indentation angle \( \theta \) is shown in Fig. 3.9. Values of \( h^* \) exhibit an approximately linear variation with \( \tan^2 \theta \).

![Figure 3.9](image)

**Figure 3.9** The dependence of the values of fitted characteristic length \( h^* \) on the indentation angle \( \theta \).

**Table 3.1** Nix-Gao fit to wedge indentation data as a function of the contact depth or width.

<table>
<thead>
<tr>
<th>( 2\phi ) (deg)</th>
<th>( \theta ) (deg)</th>
<th>( H_o ) (MPa)</th>
<th>( h^* ) (( \mu )m)</th>
<th>( w^* ) (( \mu )m)</th>
<th>adj. ( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>73.5</td>
<td>232±11</td>
<td>7.9±1.2</td>
<td>4.7±0.7</td>
<td>0.965</td>
</tr>
<tr>
<td>53</td>
<td>63.5</td>
<td>265±24</td>
<td>4.8±1.3</td>
<td>4.8±1.3</td>
<td>0.909</td>
</tr>
<tr>
<td>93</td>
<td>43.5</td>
<td>272±4</td>
<td>0.96±0.08</td>
<td>2.0±0.2</td>
<td>0.975</td>
</tr>
</tbody>
</table>

A simple 2D extension of the Nix-Gao model to wedge indentation can be made. Following Ref [9], Fig. 3.10(a) shows a schematic of wedge indentation in which \( s \) is the spacing between individual slip steps on the wedge surface. Figure 3.10(b) shows that, differing from the 3D conical indentation case, here geometrically necessary dislocations (GNDs) are generated underneath the wedge indenter parallel to its long axis. Each GND...
Figure 3.10  (a) A 2D schematic for GND injection into the material by wedge indentation, after Nix and Gao [9]; (b) A 3D rendering of injection of straight GNDs parallel to the long axis of the wedge indenter.

has length $L$. The wedge geometry dictates

$$\tan \theta = \frac{h}{w/2} = \frac{b}{s}, \quad s = \frac{b}{h} \left( \frac{w}{2} \right),$$

(3.19)

where $b$ is the Burgers vector. The total length of GNDs injected, $\lambda$, is given by

$$\lambda = 2L \frac{w/2}{s} = 2L \frac{h}{b}.$$  

(3.20)

Making an assumption analogous to the original Nix-Gao model development that the volume into which the GNDs are injected is a semi-circular cylinder with radius $w/2$, length $L$, and volume $V = L \frac{\pi \left( \frac{w}{2} \right)^2}{2}$, then the density of GNDs is given by

$$\rho_o = \frac{\lambda}{V} = 4 \frac{h}{\pi bh} \left( \frac{w}{2} \right)^2 = \frac{4}{\pi bh} \tan^2 \theta.$$  

(3.21)

Following the development of Ref [9] exactly with value of the GND density given by Eq. (3.21) leads to Eq. (3.18), with the characteristic length $h^*$ given by

$$h^* = \frac{108b^2 \alpha^2}{\pi} \left( \frac{G}{H_0} \right)^2 \tan^2 \theta.$$  

(3.22)
In Eq. (3.22), $G$ continues as the shear modulus and $\alpha$ is a constant, taken to be 0.5 in Ref.[9]. The expression for $h^*$, given by Eq. (3.22), differs from the original Nix-Gao expression only by the constant coefficient that here is $108/\pi$ instead of $81/2$ in Ref. [9].

Equation (3.22) shows an identical dependence of $h^*$ on the indentation angle as the original Nix-Gao model for conical indentation with $h \propto \tan^2 \theta$. Such an angular dependence is consistent with data shown in Fig. 3.9. The magnitude of the $h^*$ given by the Nix-Gao model, in the present case of Al wedge indentation, is also of interest. Taking parameter values corresponding to the present case of Al, $G = 26$ GPa, $b = 0.286$ nm [27], and $H_o = 270$ MPa, the proportionality constant in front of $\tan^2 \theta$ in Eq. (3.22) takes the value of $\sim 22.8 \mu$m if $\alpha$ is taken to be 0.5, in accordance with the original Nix-Gao model. The values of $h^*$ yielded by Eq. (3.22) are therefore $\sim 260 \mu$m, $\sim 92 \mu$m, and $\sim 21 \mu$m in the cases of the 33°, 53°, and 93° wedges, respectively. The ratios of the values of $h^*$ so estimated to those obtained from fitting of wedge indentation data, shown in Table 3.1, ranges from 19 to 33 and averages to $\sim 25$. It should be noted that the exact value of the proportionality constant in Eq. (3.22) depends on the assumption made in extending the Nix-Gao model. For example, assuming the GNDs injected into the indented material are contained within a circular cylinder with radius $w/2$ would decrease the constant by a factor of 2. It is, however, difficult to account for the factor of $\sim 25$ discrepancy between the $h^*$ values obtained from model estimates and data fits through such slight modifications to the model assumptions. Thus it appears that, although the extension of the Nix-Gao model to the wedge indentation situation reflects the observed dependence of $h^*$ on the indentation angle, it overestimates the magnitude of this characteristic length. It is of interest to point out that a previous evaluation of strain
gradient plasticity theories with application to bending of thin metal foils also noted that the magnitude of the characteristic length appears to be overestimated according to the Nix-Gao model [28]. Further studies are required to develop a more detailed understanding.

3.6 Concluding remarks

Micro/nano scale 2D wedge indentation experiments were conducted on a single crystal Al specimen at room temperature at three different included wedge angles. A method for obtaining the actual contact widths from analysis of experimental unloading curves in combination with imaging of wedge indent impressions made at high loads is proposed. This method, based on 2D elastic contact mechanics solutions, was used to obtain the hardness as a function of the contact width or depth. The present results show clear evidence of an indentation size effect over the range of wedge angles studied. The observed dependence of the projected contact pressure on the contact depth is consistent with the Nix-Gao relationship, Eq. (3.18). A significant dependence of the characteristic length on the indentation angle is observed (Table 3.1). The observed dependence of the characteristic length on the indentation angle is shown to be consistent with a 2D extension of the Nix-Gao model to the wedge indentation situation. Such an extension, however, over estimates the magnitudes of the characteristic length as compared to values deduced from experimentation. Quantitatively analyzed 2D wedge indentation offers another experimental test configuration for size-dependent plasticity theories.

3.7 References


CHAPTER 4
A NEW EXPERIMENTAL APPROACH TO EVALUATE THE MECHANICAL INTEGRITY OF INTERFACES BETWEEN HARD COATING AND SUBSTRATES

4.1 Introduction

Evaluation of the mechanical integrity of interfaces between thin coatings and substrates is a long-standing subject of interest in surface engineering and thin film mechanics, and a repeated topic of focused discussion within the last twenty years [1]. Because coating/substrate systems vary widely, from polymeric coatings on metallic substrates to hard ceramic coatings on ceramic substrates, a wide range of experimental methods have been conceived to test coating/substrate interfacial integrity. These methods include the pull and peel [2], scratch [3], indentation [4, 5], tension [6], and laser spallation [7] tests.

Deposition of thin, hard, ceramic coatings has become an important method for engineering surfaces of mechanical components and manufacturing tools [8]. This class of applications are characterized by high contact stresses and high cycle loading, such as those experienced by ceramic coatings on cutting tools [9] and gears [10]. In order for the ceramic coating to survive such high-stress and high-cycle contact, the interface region between coating and substrate is so strong that pull and peel tests, in which auxiliary loading pads are attached by glues onto the coating surface [2], usually do not lead to failure of the coating/substrate interface. Although scratch testing may yield relative rankings between different coatings on the same substrate at fixed test geometry, its configuration is often too complex to allow a quantitative measure of interfacial mechanical properties [11].
Indentation tests with axisymmetric [4] or long wedge [5] indenters have been performed on brittle ceramic coatings deposited on ductile substrates. In these tests, plastic deformation of the substrate caused by deep indents into the substrate exerts additional in-plane compressive loading on the coating, leading to coating spallation away from the indent impression. The extent of coating spallation can be used to determine a value of the coating/substrate interfacial toughness. Such indentation tests have yielded quantitative toughness measures in coating/substrate systems with relatively low interfacial toughness [4, 5], and proved insufficient to cause coating/substrate interfacial failure beyond the indent impression at higher interfacial toughness values [12]. A full understanding of such indentation tests also requires a detailed elasto-plastic analysis which is dependent upon the mechanical properties of the particular substrate being tested [13].

In the tension test configuration, ductile substrates onto which brittle ceramic coatings are deposited are loaded in tension and deformed plastically. For thin coatings, the same strain is experienced by the coating and the substrate, with the substrate strain being plastic and the coating strain being elastic. This strain leads to transverse cracking in the coating perpendicular to the direction of tensile loading. Once transverse cracking occurs, tensile loading of the thin coating occurs through shear stresses at the coating/substrate interface region. The density of transverse cracks increases with increasing substrate plastic strain to a plateau value, beyond which further increase in substrate plastic strain does not cause additional decrease in crack spacing [6]. From the initial strain at which cracking develops, an apparent failure stress in tension is derived for the coating. Combining this apparent failure stress with the minimum spacing of
transverse cracks in the coating at large substrate strain, a limiting shear strength of the coating/substrate interface region is derived [6, 14].

In laser spallation tests, a high-fluence laser pulse is directed toward the backside of the substrate, and sets up a compression pulse traveling toward the coating/substrate interface. Upon reflection at the interface, the pulse turns tensile. The magnitude of the tensile pulse may reach the interfacial tensile strength, in which case coating spallation is induced. From the critical laser fluence, a measure of the tensile strength of the coating/substrate interface is obtained [7].

Surface engineering of mechanical components and manufacturing tools by coatings often involves deposition of complex interfacial materials with the goal of promoting adhesion of thin hard coatings to the substrate [10]. Quantitative assessment of interfacial strength is desirable. While the tension test may yield a value for the limiting interfacial shear strength, it is indirect, subject to large scatter, and is not conducive to yielding information on the critical material location/structure controlling interfacial failures [15]. While the laser spallation test has yielded quantitative measures of the interfacial tensile strength in simple cases, it places high demands on the back surface quality and attenuation properties of the substrate, and may not be easily applied to cases of practical surface engineering interest. In the surface engineering and coatings field, a premium is therefore placed on effective testing protocols which can yield quantitative information on interfacial failure and be conducive to correlating interfacial chemistry and structure to interfacial failures. In this chapter, we report a new testing protocol, in which inclined coating/substrate interfaces contained within microscale
cylindrical pillars are failed by direct compression loading in the pillar axial direction. TiN coatings on Si substrates were used as an example to illustrate this protocol.

### 4.2 Experiments and Results

Deposition of TiN coatings was carried out at room temperature in an ultra-high-vacuum physical/chemical vapor deposition tool, which housed a 13.56MHz inductively coupled plasma (ICP) and multiple balanced magnetron sputter sources [15, 16]. The sputter sources faced the center of the deposition chamber, with a base pressure of \(< 3\times10^{-9}\text{Torr}\). Cleaned Si(100) substrates, 2in in diameter, were first placed into a load lock, evacuated to \(\leq 3\times10^{-7}\text{Torr}\), and then transferred to a holder placed at the center of the deposition chamber. The substrates were rotated at \(~12\text{rpm}\) during deposition. Four pure Ti (99.99%) targets were operated in the dc current-controlled mode. The entire deposition sequence occurred in \(~10\text{mTorr}\) of Ar (99.999%+). The Si substrate was first subjected to an Ar ICP etch for ~5min at a bias voltage of -50V. Immediately after etching, an elemental Ti interlayer, \(~200\text{nm}\) in thickness, was deposited onto the substrate by sputtering the Ti targets in Ar with ICP assist. Deposition of TiN coating layers, \(~5\mu\text{m}\) in thickness, occurred immediately after Ti interlayer deposition in an Ar/N\(_2\) (99.999%+) ICP. To ensure a reasonable deposition rate at close to stoichiometry, the input N\(_2\) flow was kept close to but below the pressure hysteresis point. During TiN deposition, a total input ICP power of 1000W was applied and an electrical bias voltage of -30V was applied to the substrate.

As-deposited TiN/Ti/Si(100) specimens were cut to pieces of smaller size. A stainless steel (SS) sheet metal, \(~700\mu\text{m}\) in thickness and cut to the same size, were bonded face to face to a TiN/Ti/Si(100) piece with M-Bond 610 adhesive. The bonded
assembly was then embedded in commercial epoxy, with the TiN/Ti/Si interface pre-aligned with a 45° inclination to the epoxy top surface. After epoxy curing, its top surface was then polished by SiC abrasive from 600 to 1200 grit, and finished with ~1µm diamond suspension. Figure 4.1(a) shows an ion-induced secondary electron (ISE) image of both the polished top surface and a cross section of the assembly, taken on an FEI Quanta3D FEG focused ion beam (FIB) instrument combining a field-emission electron source and a high-current Ga⁺ ion source. A thin Pt protection layer was deposited onto the specimen top surface. The cross section was then cut with Ga⁺ ions by reducing the ion current from 50nA to 0.1nA, resulting in a smooth finish. The cross section reveals, in sequence, the mating SS sheet metal, the M-Bond 610 layer, the ~5µm TiN coating layer, the ~200nm Ti interlayer, and the Si substrate. The TiN/Ti/Si interface was indeed oriented 45° to the top surface. The interface between the TiN coating and the Si substrate at the top surface is flat and smooth, without any polishing induced cracks.

Figure 4.1 Fabrication of micro-pillars containing inclined coating/substrate interfaces: (a) an ISE image of a polished TiN/Ti/Si(100) specimen. Both the polished top surface and a FIB cross section are visible; (b) a TiN/Ti/Si micro-pillar with a 45°-inclined interface.
As shown schematically in Fig. 4.1(a), microscale cylindrical pillars were milled from the polished assembly. In order to obtain micro-pillars without significant taper, a FIB script milling program was employed [17], enabling a lathe-like machining process with Ga⁺ ions. Figure 4.1(b) shows an example micro-pillar, with a diameter of ~3.85µm, within which the TiN/Ti/Si interface is inclined 45° to the top surface. With the same method, other micro-pillars were fabricated from the same assembly, with diameters of ~5µm, ~4µm, ~3µm, ~2µm, and ~1µm and at least 5 for each diameter. The minimum distance between the TiN/Ti/Si interface and the pillar top surface, in all cases, was ≥ 2µm.

Compression loading of the TiN/Ti/Si micro-pillars was carried out at room temperature on a MTS NanoIndenter XP with a custom-made, ~10µm×~10µm, flat-ended diamond punch. An increasing load was applied to the pillar top surface using

![Load-displacement curves](image)

**Figure 4.2** Load-displacement curves obtained from compression loading of TiN/Ti/Si micro-pillars with a 45°-inclined interfaces.
displacement-controlled loading, with raw indenter load and displacement monitored continuously. Figure 4.2 shows the collection of measured raw load - displacement curves. For each pillar, the load increased approximately linearly with increasing indenter displacement at the beginning. Then the pillar failed abruptly when the load reached a breaking point, manifested in a large and abrupt displacement excursion: typically 4-5µm. Although the loading program specified a displacement stop, set to 800nm, data shown in Fig. 4.2 indicate that the indenter failed to stop at the set point. The abrupt failure and the inertia of the indenter system led to total displacement excursions of 4-5µm after failure. The unloading curves are thus largely irrelevant, and the main information contained within Fig. 4.2 is the load to failure. As evident from Fig. 4.2, failure loads measured from separate pillars of similar diameters appear to exhibit good repeatability.

The large indenter displacement excursion associated with pillar failure led to impact on what was beneath the indenter, typically destroying the remaining pillar.

![Figure 4.3](image) Figure 4.3 Failure of compression loaded TiN/Ti/Si micro-pillars: (a) failure morphology of one supported micro-pillar; (b) an ISE image of the FIB section of the failed top pillar portion.
specimen. This made detailed examination of the failure location difficult. In order to ascertain the physical location associated with pillar failure, on some pillar specimens, two support structures placed on two sides of the pillar were milled by the Ga\(^+\) ion beam. The height of the support structures were made to be lower than that of the pillar top surface. Such support structures did not influence the compression loading of the pillar by the indenter, but acted as a mechanical stop to the indenter when pillar failure occurred. Figure 4.3(a) shows the typical failure morphology of such supported TiN/Ti/Si micro-pillars. In Fig. 4.3(a), signs of indenter impact on the top of the support structures besides the pillar are evident. It is clear that the pillar failed in a 45°-inclined plane, parallel to the TiN/Ti/Si interface in the as-milled pillar. X-ray energy dispersive spectroscopy (EDS) data collected from the failure plane by electron excitation with incident beam direction parallel to the pillar axis showed signals of Si, Ti, and minor O component. While O signals in the EDS data may result from brief exposures of the specimen to air, the presence of Ti signal in EDS data collected from the failure plane suggests that the failure did not occur within the Si substrate. As marked by the arrow in Fig. 4.3(a), the failed top portion of the original pillar is also evident, with a mating 45°-inclined failure plane. This failed top pillar portion was picked up by an OmniProbe in-situ the FIB instrument, and re-attached by Pt deposition. The entire top pillar portion was then cut in half from the pillar top surface by Ga\(^+\) ions with incidence parallel to the pillar axis. Figure 4.3(b) shows an ISE image of the section, the majority of which exhibits a columnar structure with the column axes aligned parallel to the original growth direction. Such structural features are typical of polycrystalline TiN coatings deposited at low temperatures with ion-assist. Additional material beyond the TiN layer resulted from
sputter re-deposition during FIB sectioning. Observation of the intact, 45°-inclined plane separating the TiN layer from the re-deposited material suggests that it is unlikely that the compression induced failure occurred within the TiN layer.

4.3 Discussion

While TiN and Si are both expected to be brittle at room temperature, the Ti interlayer may exhibit some ductility. The raw axial failure load was therefore converted to a nominal interfacial shear stress at failure for 45°-inclined planes, \( \tau = \frac{\sigma}{2} \), where \( \sigma \) represents the raw failure load divided by the right cross-sectional area of the micro-pillar, i.e., \( \sigma \) is the axial failure stress in compression. Figure 4.4 shows values of \( \tau \) as a function of the pillar diameter \( D \). Since each data point in Fig. 4.4 represents an independent test on a separate pillar, the collection of data shown in Fig. 4.4 again illustrates good repeatability with the present test protocol. Averaged over all data points, \( \tau \) is \( \sim 1.4 \pm 0.1 \) GPa. Measured values of \( \tau \) exhibited essentially no dependence on \( D \) over

![Figure 4.4](image-url)
the range of pillars tested. In an independent series of experiments, the limiting interfacial shear strength of TiN/Ti/steel interfaces, related to the present case but not identical, was determined through the tension test method to be 1.5±0.8GPa [15]. The value of $\tau$, 1.4±0.1GPa, presently determined for interfaces in the TiN/Ti/Si system, is very close to that of the previous tension test results. The observed lack of dependence of $\tau$ on $D$, together with imaging and EDS evidence suggesting that pillar failure was located in the Ti interlayer, suggests that the presently observed compression induced failures of the TiN/Ti/Si micro-pillars containing 45°-inclined interfaces are related to plasticity within the Ti interlayer.

However, there remains a possibility that compression induced failure of the interfacial regions of TiN/Ti/Si micro-pillars is fracture related. Taking a simple example of a cylindrical pillar of diameter $D$ with a circumferential crack of length $a$ loaded in tension, the stress intensity factor is given by $K = Y(a/D) \sigma \frac{a}{\sqrt{2}}$, in which $\sigma$ is the remote loading stress and $Y$ is a weak function of $a/D$ [18]. If failure occurs when $K$ reaches the critical stress intensity factor $K_c$, then the critical remote loading stress, $\sigma_c = K_c / \left(Y(a/D)a^{1/2}\right)$, may not exhibit a strong dependence on $D$ if the crack length remains relatively constant as $D$ varies. The observed lack of dependence of $\tau$ on $D$, shown in Fig. 4.4, does not therefore definitively exclude fracture as a possible failure mechanism. A final determination of the predominant failure mechanism in compression induce failures of micro-pillars containing inclined interfaces requires additional study.

To our knowledge, the presently described protocol for testing coating/substrate interfacial failure through direct compression loading of micro-pillars containing an inclined interface region is new. Large relative errors, ~50%, occur when the tension test
[6] is used to determine the limiting interfacial shear strength in hard coatings with significant residual stresses [15]. In comparison, the present micro-pillar compression tests yield more reproducible failure stresses: typical data scatter at each pillar diameter is ~15%. While large and flat coating/substrate specimens are required for laser spallation tests, the present methodology can be used to fabricate a large number of micro-pillar test specimens from one relatively small sample. With scripted FIB milling, pillar fabrication can become automated and quite rapid. The failure surfaces can be made accessible to high-resolution structural and chemical analysis, and thus conducive to correlating interfacial structure and chemistry with mechanical failures within the interfacial region. Additional studies of coating/substrate interfacial failure using the presently described protocol is expected to contribute to further understanding and effective engineering of interfaces for enhanced coating performance, and are presently underway.

4.4 References


CHAPTER 5
INTERFACE DEVELOPMENT IN CU-BASED STRUCTURES
TRANSIENT LIQUID PHASE (TLP) BONDED WITH THIN AL FOIL INTERMEDIATE LAYERS

5.1 Introduction

Microchannel heat exchangers (MHEs) offer a device configuration through which the rate of solid-liquid convective heat transfer can be greatly increased [1]. Due to higher thermal conductivities and increased ductility of metals, metal-based MHEs possess better heat transfer performance and mechanical robustness as compared to Si-based counterparts. Microscale molding replication is an efficient method for fabrication of metallic high-aspect-ratio microscale structures, and can be used for high-throughput fabrication of open microchannel structures in a range of metals and alloys [2-7]. Open microchannel structures need to be bonded with mating structures to form enclosed microchannel devices. Proper bonding techniques are critical to fabrication of functional metal-based MHEs. Transient liquid phase (TLP) bonding, also known as diffusion brazing [8], has applications from the aerospace industry to the microelectronic industry [9, 10, 11, 12]. A previous study showed that Al-based microchannel devices can be formed by TLP bonding with near-eutectic Al-Ge nanocomposite thin film intermediate bonding layers [13, 14, 15].

General characteristics of the TLP bonding process have been described by MacDonald and Eager [16]. A thin layer acting as a melting point depressant (MPD) is sandwiched between faying metal surfaces, and the entire assembly is heated up. Interaction between the MPD and the base metal leads to the formation of an interfacial liquid layer upon heating, before bulk melting of the base metal occurs. With continued
heating, the interfacial liquid layer widens to a maximum thickness through dissolution of the base metal. Isothermal solidification follows, thereby forming the requisite bond. Such a TLP approach can lower the bonding temperature, lessen thermal stress damage, and dissolve residual contamination on faying surfaces. Tuah-Poku et al. \cite{17} divided the TLP process into four stages, which was further divided by MacDonald and Eager \cite{16} into five stages of solid-state interdiffusion during heat-up, dissolution of the bonding interlayer, widening of the interfacial liquid layer, isothermal solidification, and homogenization of the bonding interface region. As shown in the Cu-Al phase diagram of Fig. 5.1 \cite{18}, an eutectic invariant point exists at 548.2°C and $\text{Al}_{83}\text{Cu}_{17}$, much below
the Cu bulk melting temperature of 1084.6°C. Al is therefore a candidate for MPD in TLP bonding of Cu-based structures.

We have previously shown that Cu-based microchannel devices can be formed by TLP bonding with thin Al foil intermediate bonding layers [19, 20]. Figure 5.2 shows a scanning electron microscopy (SEM) image of a portion of one low-profile, Cu-based, microchannel device containing an array of parallel microchannels. This microchannel device, with a total thickness of ~850μm, was TLP bonded with a thin Al foil with a thickness of ~25μm. Although extensive studies have been performed on Cu-Al intermetallic compound (IMC) formation during solid state interdiffusion reactions [21, 22, 23] as well as reactive diffusion between solid and liquid phases [24], a detailed exposition of the interfacial structural evolution during Cu/Al/Cu TLP bonding has not been reported in the literature. The objective of this chapter is to understand the structural evolution of the Cu/Al/Cu interface region during TLP bonding. How the bonding interface structure influences the average tensile bond strength is studied as well.

Figure 5.2 A cross-sectional image of a portion of one Cu MHE TLP bonded with an Al thin foil intermediate layer, showing an array of parallel microchannels.
In this chapter, a series of Cu/Al/Cu sandwich-like coupon assemblies were TLP bonded at different temperatures. The structure and composition of the bonding interface region were characterized by conventional and focused ion beam (FIB) sectioning, SEM, transmission electron microscopy (TEM), and X-ray energy dispersive spectrometry (EDS). A sequence for structural evolution of the Cu/Al/Cu bonding interface region was proposed and ascertained through monitoring of the entire interfacial interdiffusion, reaction, melting, and re-solidification process by in-situ synchrotron X-ray diffraction (XRD), accompanied by additional structural examination of as-bonded interfaces subjected to further annealing in the solid state. The average tensile strength of TLP bonded Cu/Al/Cu structures was characterized by tensile testing until fracture occurred across the bonding interface region. A companion series of instrumented nanoindentation tests were performed across the bonding interface region, providing supplemental data. Structural examination of tensile fracture surfaces by FIB and SEM provided rationalization of the testing results. Cu microchannel devices TLP bonded with thin Al foil intermediate layers were shown to have bonding interface structures consistent with what were observed in Cu/Al/Cu coupon assemblies. Taken together, the present results provide an understanding of the structural evolution within the Cu/Al/Cu bonding interface region during TLP bonding, and illustrate the potential of applying TLP bonding to fabrication of metal-based microdevices.

5.2 Experimental Procedures

5.2.1 Cu/Al/Cu Coupon Assemblies

Two groups of Cu/Al/Cu sandwich-like coupon assemblies were formed by inserting thin elemental Al foils (Alfa Aesar, 99.999+%) between C11000 Cu
(McMaster-Carr, 99.9+%) coupons. Table 5.1 summarizes the specimen configurations.

One group of coupon assemblies, designated M1, M2, and M3, is used for structural

Table 5.1 Specimen configurations and bonding conditions for Cu/Al/Cu sandwich-like coupon assemblies.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Cu coupon size (mm)</th>
<th>Max. bonding temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>~15×15×3</td>
<td>~560±10</td>
</tr>
<tr>
<td>M2</td>
<td>~15×15×3</td>
<td>~580±10</td>
</tr>
<tr>
<td>M3</td>
<td>~15×15×3</td>
<td>~610±10</td>
</tr>
<tr>
<td>T1</td>
<td>~15×15×13</td>
<td>~560±10</td>
</tr>
<tr>
<td>T2</td>
<td>~15×15×13</td>
<td>~580±10</td>
</tr>
<tr>
<td>T3</td>
<td>~15×15×13</td>
<td>~610±10</td>
</tr>
</tbody>
</table>

examination. One Al foil, with a thickness of 38±7µm, was sandwiched between two
~15mm×~15mm×~3mm Cu coupons to form a ~15mm×~15mm×~6mm assembly. Specimen M1 was bonded at a maximum bonding temperature of ~560°C. Specimens M2 and M3 were bonded at maximum bonding temperatures of ~580°C and ~610°C, respectively. A second group of coupon assemblies, designated T1, T2 and T3, was formed by sandwiching Al foils of the same thickness between Cu coupons of dimensions ~15mm×~15mm×~13mm. The overall dimensions of the so-formed Cu/Al/Cu coupon assemblies were ~30mm×~15mm×~13mm. To accommodate gripping of the T1, T2, and T3 specimens for subsequent tensile testing purposes, one hole, ~4.3mm in diameter, was drilled at one end of each Cu coupon before bonding. The distance from the hole center to the opposing end of the specimen, where the bonding interface will be located, is ~10mm. A bonded specimen and a pair of specially designed adapters are shown in Fig. 5.3. Specimens T1, T2, and T3 are fabricated such that they have the same bonding interface structure as specimens M1, M2, and M3, respectively.
Figure 5.3 Bonded Cu/Al/Cu specimens and specially designed adapters for tensile testing.

As will be shown in this chapter, in addition to the eutectic point at 548.2°C and \( \sim \text{Al}_{83}\text{Cu}_{17} \), the other invariant point relevant to Cu/Al/Cu TLP bonding is the eutectoid point at 567°C and \( \sim \text{Al}_{24}\text{Cu}_{76} \). The choice of maximum bonding temperatures was made such that 560°C is between the eutectic temperature of 548.2°C and the eutectoid temperature of 567°C while the other two maximum temperatures are above the eutectoid temperature, as shown in Fig 5.1.

5.2.2 The TLP Bonding Apparatus and Specimen Preparation

Bonding experiments were carried out on a MTS858 single-axis testing system interfaced to a vacuum chamber. Typical background pressures during bonding were \( \sim 1 \times 10^{-5} \) Torr. Two heating stations were installed within the vacuum chamber. One was mechanically attached to the bottom of the vacuum chamber, and the other was fixed to the top linear actuator of the MTS858 system through a bellow-sealed motion feedthrough. The two heating stations were heated separately by resistive cartridge
heaters and their temperatures were measured by two separate K-type thermocouples. Surfaces of Cu coupons were mechanically polished with silicon carbide papers of decreasing grit sizes and finished with diamond suspensions of 3µm in size. Polished Cu coupons were immersed into ~5% hydrochloric acid for surface oxide removal. Surfaces of Al foils, cleaned with methanol, were similarly treated in ~5% hydrochloric acid solutions. After surface cleaning, Cu/Al/Cu coupon assemblies were placed on the top surface of the bottom heating station with the axial direction perpendicular to the bonding interface. The chamber was evacuated and power was then applied to the heating stations.

5.2.3 TLP Bonding Protocol for Cu/Al/Cu Specimen Assemblies

Coupon assemblies M1, M2, and M3 were bonded by heating to maximum temperatures of ~560°C, ~580°C, and ~610°C, respectively. For specimens M1, M2 and M3, the bottom surface of the top heating station was set close to the top surface of the assembly without actual contact until the upper and lower heating stations both reached ~530°C within ~20min. Then the top heating station was made to contact the assembly by applying a constant compression force, ~100N in magnitude, corresponding to a nominal bonding pressure of ~0.44MPa. After the bonding pressure was applied, the assemblies reached the maximum bonding temperature of ~560°C, ~580°C, and ~610°C within ~2min, ~3min and ~5min respectively. When the system reached the targeted temperatures, a ~5min hold was executed with temperatures and stresses unchanged. The heater power and compression load were removed thereafter. The system temperature decreased to <450°C within ~15min. The specimens were removed from the chamber after the heating stations reached room temperature through natural cooling. In order to obtain the same bonding interface structures as M1, M2, and M3, coupon assemblies T1,
T2 and T3 were bonded in a similar manner, but with different holding durations at the maximum temperatures because of the differences in specimen thermal mass.

5.2.4 In-situ Synchrotron XRD

To probe the various phase transformations occurring in the Cu/Al/Cu interface region during TLP bonding, in-situ synchrotron XRD experiments were carried out at the Advanced Photon Source (APS) at Argonne National Laboratory, on the beamline 12-ID-C,D. A ~10μm thick Al thin film was sputter deposited onto C11000 Cu coupons in an inductive coupled plasma (ICP) assisted physical vapor deposition (PVD) tool. The Cu coupons were mechanically polished and finished with 3μm diamond suspension, cleaned in 5% HCl, and loaded into the deposition tool. Prior to Al deposition, the Cu coupon surface was etched in an Ar ICP, with a -50V bias applied to the coupon. Balanced magnetron sputtering of an elemental Al target (99.9%+) then followed, at a deposition rate of ~20nm/min. The coupon dimensions were ~10mm×~10mm ×~2mm. This Al/Cu bilayer structure is analogous to one half of the Cu/Al/Cu sandwich structure, and allowed X-ray access for obtaining scattering signals from the Al/Cu interface region. Photon energy selection was accomplished with a Si(111) monochromator, and a photon energy of 37.52keV was used for all XRD experiments. This energy corresponding to a X-ray wavelength of 0.33067Å. The XRD setup included a four-circle goniometer, a two-dimensional X-ray detector, and a vacuum specimen chamber with a controlled heating stage [25]. Specimen temperatures were read continuously from a thermocouple. Actual specimen temperature was calibrated against the thermocouple reading by measuring (0006) and (00012) reflections from a single crystal α-Al2O3 specimen and comparing measured d-spacing values to known lattice constant vs. temperature data [26].
The Al₂O₃ specimen had roughly the same dimensions as the Al/Cu bilayer specimens.

In one experiment, an Al/Cu bilayer specimen was heated up from room temperature while diffraction scans were made continuously, with one diffraction scan made every ~1.5 sec in 20 values from 4° to 13° in the Bragg-Brentano configuration.

5.2.5 Cu-based Microchannel Specimens

Cu-based microchannel devices were fabricated by TLP bonding of Cu coupons containing microchannel arrays to flat Cu sheet metals with thin Al foil intermediate layers. Bonding followed protocols similar to that described in Section 5.2.3, with further details given elsewhere [20].

5.2.6 Tensile Testing of TLP Bonded Cu/Al/Cu Coupon Assemblies

Tensile testing was carried out in the direction perpendicular to the bonding interface on a MTS858 single-axis testing system. Rectangular tensile specimens, with overall dimensions of ~7mmx~11mmx~30mm and bonding interface areas of ~7mmx~11mm, were cut from coupon assemblies T1, T2, and T3 with an Struers Accutom-5 precision cutting machine. All specimens were mechanically polished on all four side surfaces to remove cutting induced damage prior to tensile testing.

A special tool was built to minimize damage to TLP bonded Cu/Al/Cu tensile specimens due to gripping. This tool provided holding areas for hydraulic grips and mechanical connections to specimens via a “C-link” arrangement shown in Fig. 5.3. Bolts, ~3.9mm in diameter, were inserted through holes on the C-links and the two holes at each end of the specimen. The bolt diameter was smaller than the hole diameter on the specimen, insuring that no load/twist was applied to the specimen during the gripping process. Further details on the C-link tool were described elsewhere [27]. Total head
displacements were recorded via a linear variable displacement transducer. Calibrated load cells were used to measure the total tensile force. Raw tensile data consisted of total load force versus total head extension.

### 5.2.7 Structural and Compositional Characterization

An FEI Quanta3D FEG Dual-Beam FIB instrument was employed to characterize the interface regions of TLP bonded Cu/Al/Cu specimens, as well as the fracture surfaces after tensile testing. Imaging within the FIB instrument was accomplished with electron-induced secondary electrons (SEs) or ion-induced secondary electrons (ISEs). Ion channeling contrast reveals differently oriented crystal grains in ISE images [28]. Observation of bonding interface regions of coupon assemblies M1, M2, and M3 began by cutting them with a Struers Accutom-5 precision machine into specimens of ~15mm×~7.5mm×~6mm in dimensions. The cut surfaces were mechanically polished to less than 3µm in roughness, followed by chemical etching with a ~5% iron nitrate solution. Specimen examination within the FIB began with a light surface etch with a 30kV Ga\(^+\) beam, after which ion channeling contrast from polycrystalline grains was obtained through ISE imaging. Tensile fracture surfaces were examined with the FIB instrument immediately after tensile testing. Cross-sectional TEM specimens were prepared in-situ the FIB instrument from the Cu/Al/Cu bonding interface region through Ga\(^+\) ion beam cutting, lift-out using an OmniProbe manipulator, and ion beam thinning to electron transparency.

Specimen characterization by TEM and EDS was carried out on a JEOL JEM2010 instrument operated at 200kV, equipped with an EDAX EDS system. Images and selected area diffraction patterns (SADPs) at various locations along bonding
interface regions were obtained. To index accurately the diffraction patterns and obtain relevant lattice parameters, a series of SADPs from a single crystal Si specimen were obtained at the same operating voltage and the same nominal camera length, and compared to the SADPs to be analyzed. Spot mode compositional analysis at various locations within the bonding interface region was accomplished with the EDAX system. Analysis of EDS spectra was carried out with factory-supplied EDAX Genesis2000 software package.

5.2.8 Nanoindentation

Instrumented nanoindentation was conducted at room temperature on a Nanoindenter XP System with a three-sided pyramidal Berkovich diamond indenter. The machine compliance and the projected indenter tip area as a function of the indenter contact depth were calibrated following the Oliver and Pharr procedure [29, 30], using a factory supplied fused silica standard. Indentations were performed across TLP bonded Cu/Al/Cu interface regions, using a maximum load of 30mN and a corresponding maximum indenter displacement of ~1000nm.

5.3 Results and Discussion

5.3.1 Dependence of the Structure of the Interface Region on Bonding Protocol

Three different types of interfacial structures were observed in the TLP bonded Cu/Al/Cu sandwich-like coupon assemblies: the “γ1 structure”; the “eutectoid structure or the “E structure”; and the “E/γ1/E structure”.

5.3.1.1 The “γ1 structure”

A “γ1 structure” was observed in the specimen M1, bonded at ~560°C with a ~5min hold. Figure 5.4(a) shows a typical plan-view ISE image across the interface
region of the as-bonded specimen. The larger grains on both the far left side and far right side belong to the Cu base material. The center region of Fig 5.4(a) shows the bonding interface region, measured to be ~34μm in width and consisted of equi-axed grains with an average size of ~10μm.

Figure 5.4(b) shows a cross-sectional FIB cut with 30kV Ga⁺ beam, perpendicular to the polished external surface. This cut was ~55μm in length and ~20μm in depth and straddled the bonding interface region. A thin Pt strip was deposited onto the top specimen surface prior to Ga⁺ sectioning, and protected the specimen top surface and the cross-sectional surface during cutting. Fine polishing of the rough-cut cross section was accomplished with 30kV Ga⁺ beams of progressively reduced currents. On the cross-sectional surface, ISE imaging exhibits ion channeling contrast. In agreement with Fig 5.4(a), the ISE image of Fig 5.4(b) shows a bonding interface region consisting of equi-axed grains. A few voids are visible within the bonding interface region, one of which is delineated by an arrow in Fig. 5.4(b).

In order to investigate the composition and structure of the material within the bonding interface region, a specimen with a size of ~40μm×~20μm was lifted out, thinned to electron transparency, and examined in the TEM. By exploring all grains within the bonding interface region, the only phase identified was γ₁-Al₄Cu₉. The IMC γ₁-Al₄Cu₉ crystallizes in a cubic structure with a lattice parameter of 8.707Å, the space group $P4_3m$, and 16 Al atoms and 36 Cu atoms per unit cell [31]. Figure 5.5 shows four SADPs obtained from one typical grain, tilted to four different zone axis orientations. To further ascertain the indexing of these SADPS, diffraction simulations were carried out at different zone axis orientations with the JEMS-SE software [32].
Figure 5.4 The Cu/Al/Cu bonding interface structures: (a), (c), and (e) are respectively plan-view ISE images of three typical bonding interfaces collected from the M1, M3, and M2 specimens with the “γ1-Al₄Cu₉ structure”, the “E structure”, and the “E/γ₁/E structure”; (b), (d), and (f) are respectively ISE images of the corresponding cross sections. White arrows point to locations of void formation within the bonding interface region.

Experimentally obtained SADPs, shown in Fig. 5.5, exhibit a complete correspondence with simulated patterns, and were indexed respectively to be the [001], [101], [111], and [113] zone axis patterns of γ₁-Al₄Cu₉. The experimentally determined lattice parameters ranged from 8.2Å to 8.8Å, consistent with the bulk lattice parameter of γ₁-Al₄Cu₉.

Further confirmation was obtained through EDS compositional analysis. Five different grains within the bonding interface region were chosen randomly, and EDS spectra were collected in the spot mode from within these five grains. One typical EDS spectrum is shown in Fig. 5.6. The raw spectra were background removed. The Cu and Al compositions were then obtained through the thin-film standardless quantification
Figure 5.5  Structural analysis by transmission electron diffraction from the bonding interface region of the Cu/Al/Cu specimen M1: (a), (b), (c), and (d) are respectively indexed zone-axis SADPs along the [001], [101], [111], and [113] zones of the $\gamma_1$-$\mathrm{Al}_4\mathrm{Cu}_9$ structure.

Figure 5.6  A typical EDS spectrum obtained from the bonding interface region in the specimen M1.
routine. The analysis results showed that the Al compositions in these five grains were respectively 31.8at.%, 35.6at.%, 35.4at.%, 37.0at.%, and 33.0at.%. These compositions fall within the $\gamma_1$-Al$_4$Cu$_9$ single-phase field with a composition range of 63-69at.%Cu and 37-31at.%Al, as shown in Fig. 5.1. Combining FIB sectioning, ISE imaging, electron diffraction, and EDS, materials located within the bonding interface region of specimen M1 were determined to be single-phase $\gamma_1$-Al$_4$Cu$_9$.

MacDonald and Eager [16] subdivided the entire TLP bonding process into five different stages. During the heat up process, solid state interdiffusion occurs between the bonding interlayer and the base material. In the present case, when the lower heating station reached ~530ºC, the temperature of the bonding interface was determined to be ~350ºC by inserting a thermocouple in the interlayer position. The loss of Al solute during this stage was therefore ignored. After the upper heating station was made to contact the upper surface of the specimen assembly, the temperature of the bonding interface region was quickly raised to ~530ºC and then approached the final bonding temperature. Dissolution of the Al intermediate bonding layer occurred when the eutectic temperature of 548.2ºC was reached. In the case of TLP bonding of Ag/Cu/Ag sandwich-like structures, Tuah-Poku [17] estimated that the dissolution time for a 79µm Cu foil was ~3s. Nakao et al. [33] and Liu et al. [34] have also proposed analytical models in which the interlayer dissolution process could be considered to be instantaneous as compared to other stages. As additional Cu dissolves into the interfacial liquid, the liquid layer finally reaches its maximum width, $W_{\text{max}}$. This maximum width of the interfacial liquid layer could be estimated via mass balance, following Tuah-Poku [17]. In the present case, the bonding interface region of the as-bonded specimen M1
consisted entirely of $\gamma_1$-$\text{Al}_4\text{Cu}_9$. Assuming there is no solute loss during the heat up and the interlayer dissolution stages, mass balance can be expressed as

$$W_0 \rho_{\text{Al}} C_{\text{Al}}^{\text{Al}} = W_{\text{max}} \rho_{\text{Al}_4\text{Cu}_9} C_{\text{Al}_4\text{Cu}_9}^{\text{Al}_4\text{Cu}_9},$$

where $C_{\text{Al}}^{\text{Al}}$ and $C_{\text{Al}_4\text{Cu}_9}^{\text{Al}_4\text{Cu}_9}$ are respectively the Al compositions, in weight fraction, of elemental Al and $\gamma_1$-$\text{Al}_4\text{Cu}_9$. The densities were taken respectively as the bulk densities, $\rho_{\text{Al}} = 2.70 \text{g/cm}^3$ and $\rho_{\text{Al}_4\text{Cu}_9} = 6.84 \text{g/cm}^3$. The compositions were taken respectively as $C_{\text{Al}}^{\text{Al}} = 100\text{wt.}\%$ and $C_{\text{Al}_4\text{Cu}_9}^{\text{Al}_4\text{Cu}_9} = 15.9\text{wt.}\%$. With these parameter values, $W_{\text{max}} \equiv 2.5W_0$. This estimate yields a maximum $\gamma_1$-$\text{Al}_4\text{Cu}_9$ layer width, using a 38$\mu$m thick Al foil, of $\sim 94\mu$m. The observed width of the bonding interface region, $\sim 34\mu$m, is much smaller than that predicted by mass balance. Excess material was observed around the specimen rims at the interface location after TLP bonding, suggesting that a fraction of liquid metal was squeezed out of the interface region during bonding, and that the assumption of solute conservation does not hold for the M1 specimen.

5.3.1.2 The “E structure”

Figure 5.4(c) shows a typical ISE image of the bonding interface from specimen M3, which was bonded at $\sim 610^\circ\text{C}$ with a $\sim 5\text{min}$ hold. The bonding interface region was measured to be $\sim 90\mu$m in width. Large Cu grains with internal twinning are located on both sides of the bonding interface region. Structure of the bonding interface region is further illustrated by the ISE image of the FIB cross section shown in Fig. 5.4(d). The dominant structural feature shown in Fig. 5.4(d) is the fine modulations in image contrast.

Further structural investigation was carried out with TEM on specimens lifted out from the bonding interface region. Two types of SADPs were observed, one was indexed
to the (Cu) terminal solid solution and the other was indexed to $\gamma_1$-$\text{Al}_4\text{Cu}_9$. Bright-field (BF) images of Figs. 5.7(a) and 5.7(b) exhibit a lamellar structure with alternating contrast, characteristic of eutectoid decomposition. With the specimen tilted to (Cu) [110] zone axis in Fig. 5.7(a), (Cu) lamellar structures diffract strongly, leading to a dark contrast in BF. The adjacent $\gamma_1$-$\text{Al}_4\text{Cu}_9$ phases are off zone axis orientation, and exhibit a brighter contrast in BF. Diffraction pattern of (Cu) was obtained from the dark strip location indicated by a white circle. Likewise, Figure 5.7(b) was obtained with the $\gamma_1$-$\text{Al}_4\text{Cu}_9$ phase tilted to [113] zone axis as shown in the diffraction pattern, resulting in a reversed contrast. The selected area aperture location is indicated by the white circle in Fig. 5.7(b). The white arrows in both images indicate the location of one particular thin lamella at the two different specimen tilts. It reveals that, in specimen M3, (Cu) and $\gamma_1$-$\text{Al}_4\text{Cu}_9$ form alternating thin lamellae within the bonding interface region, with an average lamellar period of $\sim$500nm.

Figure 5.7 Eutectoid decomposition within the bonding interface region of the Cu/Al/Cu specimen M3: (a) a TEM BF image with the (Cu) phase tilted to the [110] zone axis orientation; (b) a TEM BF image of the same specimen region as (a), with the $\gamma_1$-$\text{Al}_4\text{Cu}_9$ phase tilted to the [113] zone axis orientation. The white arrows indicate the same lamella at the two different tilts. The circles designate locations of the selected area aperture. The insets show the corresponding diffraction patterns.
Further confirmation was made through compositional analysis. Two EDS spectra were taken in the spot mode respectively from the specimen M3 at the two selected area aperture locations. Analysis of these two spectra showed that the compositions of the two adjacent lamellae were 20.0at.%Al – 80.0at.%Cu and 31.5at.%Al – 68.5at.%Cu. These compositions are located respectively within the (Cu) and $\gamma_1$-$\text{Al}_4\text{Cu}_9$ single-phase fields, and close to their respective phase boundaries. Thus, the compositional information supported the conclusion that the two phases within the alternating lamellae in the bonding interface region were (Cu) and $\gamma_1$-$\text{Al}_4\text{Cu}_9$.

5.3.1.3 The “E/$\gamma_1$/E structure”

A more complex structure of the bonding interface region was found in specimen M2, bonded at ~580°C with a ~5min hold. Figure 5.4(e) shows an ISE image across the bonding interface region. Image contrasts combine those observed from the E structure and the $\gamma_1$ structure. The total interface width was measured to be ~56µm. More structural details were revealed by the ISE image of the FIB cross section, shown in Fig. 5.4(f). It shows that the bonding interface region consisted of three layers. The center layer, designated as A in Fig. 5.4(f), had a width of ~30µm and consisted of polycrystalline grains of ~10µm in size. Electron SADPs obtained from this layer were the same as those shown in Fig. 5.5. EDS spectra obtained from this layer showed that its composition was ~36at.%Al - 64at.%Cu. Thus both structural and compositional data confirm that the A layer is $\gamma_1$-$\text{Al}_4\text{Cu}_9$. Two additional layers were observed on either side of the A layer, designated as B in Fig. 5.4(f) and structurally similar to the E structure. Structural and compositional confirmations were again obtained through electron diffraction and EDS analysis. The average Al compositions in the B layers were
determined from EDS spot mode analysis in the TEM to be ~25at.%Al, consistent with the B layers being the (Cu)/γ₁ eutectoid structure. Thus it is confirmed that the three layers across the bonding interface region are indeed E/γ₁/E.

5.3.2 In-situ Observation of the Interfacial Structural Evolution through Synchrotron XRD

Three different types of Cu/Al/Cu interfacial structures, the “γ₁ structure”, the “E structure”, and the “E/γ₁/E structure”, were formed through different TLP bonding protocols. These structures contain only two simple phases, γ₁ and (Cu), despite the presence of many other IMCs in the Cu-Al phase diagram. In-situ XRD was therefore performed to further elucidate the structural evolution within the Cu/Al/Cu TLP bonding interface region. Figure 5.8 shows a set of 2D XRD profiles, obtained from one sputter

![Figure 5.8](image)

Figure 5.8 In-situ synchrotron XRD monitoring of the structural evolution within an Al/Cu bilayer specimen: (a), (b), (c), and (d), were diffraction patterns respectively taken at ~25°C, ~450°C, ~550°C, ~600°C during specimen heat up; (e) was taken after the specimen were cooled back down to ~25°C.
Figure 5.9  A typical XRD pattern corresponding to Fig. 5.8(b), showing diffraction intensity vs. the scattering angle. The relatively small scattering angles are due to the shorter X-ray wavelength and higher photon energy used.

deposited Al/Cu bilayer specimen at different temperatures. In order to simulate the aforementioned Cu/Al/Cu TLP bonding conditions, the Al/Cu specimen was heated from room temperature, ~25°C, to the target temperature of ~600°C within 30min, then kept at this temperature for another ~30mins, followed by cooling to room temperature in ~120mins. Figure 5.8(a) shows the diffraction lines of the as-deposited Al/Cu specimen, which can be indexed to the (111) and (200) reflections of fcc Al and Cu, respectively. Solid state interdiffusion and reaction occurred between the Al film and the Cu substrate as the specimen temperature increases, leading to the formation of IMCs. Concomitant acquisition of diffraction patterns as the specimen temperature increases showed that the $\theta$-Al$_2$Cu phase was formed first, followed by the $\eta_2$-AlCu phase and the $\gamma_1$-Al$_4$Cu$_9$ phase. An excerpt of the diffraction patterns is shown in Fig. 5.8(b), acquired during heat up as the specimen temperature reached ~450°C. The present in-situ XRD experiments
observed the $\theta$-Al$_2$Cu -> $\eta$-AlCu -> $\gamma_1$-Al$_4$Cu$_9$ phase sequence during specimen heat up, and are in agreement with previous studies on Cu-Al solid state diffusion couples by Hentzell et al. [21] and Hamm et al. [22]. However, emergence of the $\zeta_2$ and $\delta$ phases during specimen heat up was not observed. Figure 5.9 shows diffracted intensity vs. the scattering angle 2$\theta$ corresponding to Fig. 5.8(b). Due to the much higher X-ray energy used in the present experiment, the 2$\theta$ values are much compressed as compared to a more conventional diffraction pattern using Cu K$\alpha$ radiation. Once the eutectic temperature and composition were reached at the interface, interfacial melting occurred rapidly. The interfacial melting incorporated more Al and Cu from the solids into the interfacial liquid. Diffraction lines from fcc Al, $\theta$-Al$_2$Cu, and $\eta$-AlCu disappeared with the occurrence of interfacial melting. A new line indexable to the $\epsilon_2$ phase formed. The $\gamma_1$-Al$_4$Cu$_9$ and Cu diffraction lines became fainter but could still be identified in Fig. 5.8(c) at ~550°C. The diffraction pattern in Fig. 5.8(d) was taken at ~600°C as the specimen heat up continued after interfacial melting. At this moment, all non-Cu diffraction lines can be indexed to $\gamma_1$-Al$_4$Cu$_9$, with one remnant line from the $\epsilon_2$ phase. As the specimen cool down occurred, the diffraction line from the $\epsilon_2$ phase disappeared and only lines from the $\gamma_1$-Al$_4$Cu$_9$ phase remained, as evidenced in Fig. 5.8(e) taken at ~25°C after cool down. In-situ XRD results, excerpted in Fig. 5.8, thus show that the remaining solid phase immediately after interfacial melting and re-solidification is the $\gamma_1$-Al$_4$Cu$_9$ phase.

5.3.3 Annealing after TLP Bonding

To further investigate the relationships between the three different types of structures observed within the bonding interface region, solid state annealing post TLP
bonding was carried out on specimen M2. This specimen was first polished and lightly etched after bonding, and then annealed for 20min at 600°C in a vacuum tube furnace with a base pressure of ~10^{-6} Torr. A position marker, in the form of a thin and deep slot made by micro electrical discharge machining, was placed close to the location at which

![ISE images of the bonding interface region at the same location after several annealing treatments:](image)

Figure 5.10  ISE images of the bonding interface region at the same location after several annealing treatments: (a) the as-bonded interface structure of specimen M2; (b) the interface region broadened after a 20min anneal at 600°C; (c) the $\gamma_1$-Al$_4$Cu$_0$ layer disappeared completely after 1 hour anneal at 600°C.

ISE imaging of the interface region, shown in Fig. 5.10(a), was performed. After annealing, the top surface layer, ~30µm in thickness, was removed from the specimen through mechanical polishing to eliminate any surface induced artifacts. The mechanically polished surface was etched with a ~5% iron nitrate solution. By locating
the same position marker after polishing and etching, structural characterization was made at the same bonding interface region location, before and after annealing.

Figure 5.10(b) shows an ISE image across the bonding interface region of specimen M2 after the first annealing. Image features of the bonding interface region are qualitatively similar to those present in Fig. 5.10(a), exhibiting the E/γ₁/E structure. Comparing Figs. 5.10(a) and 5.10(b), it is evident that the width of the entire bonding interface region increased slightly to ~60µm after annealing. The E layers increased in width, while the width of the γ₁ layer decreased significantly to ~10µm. Corroborating evidence was obtained from EDS line scans across the bonding interface regions. Al Kα intensity profiles as a function of location is superimposed on Figs. 5.10(a), 5.10(b), and 5.10(c). In Fig. 5.10(a), the two E layers correspond to two plateaus with lower Al Kα intensity as compared to the γ₁ layer in between them. After the first annealing, two much wider plateaus corresponding to the E layers are observed in Fig. 5.10(b). It is suggested that annealing at 600°C led to the formation of additional β-AlCu₃, which subsequently underwent eutectoid decomposition upon cooling. Formation of β-AlCu₃ led to further disappearance of the γ₁-Al₄Cu₉ phase and increased the E layer width.

The annealed specimen M2 was annealed a second time for an additional 40min at 600°C. Figure 5.10(c) shows an ISE image of the bonding interface region after the second anneal. The entire interface region, with a total width of ~68µm, appears to have transformed to the E structure while the γ₁ layer disappeared completely. The Al Kα intensity profile now exhibits one single plateau, signaling a uniform average composition across the entire bonding interface region. Results of the annealing study
indicate that the E/γ₁/E structure is a transitional structure between the γ₁ structure and the E structure.

5.3.4 Formation Mechanisms for Different Bonding Interface Structures

Three different types of bonding interface structures were found to be composed of only the γ₁-Al₄Cu₉ and (Cu) phases. Formation of the γ₁-Al₄Cu₉ phase is of great importance. In-situ XRD on sputter deposited Al/Cu bilayer specimens revealed that:

1) \(\theta\)-Al₂Cu, \(\eta\)-AlCu, and \(\gamma\₁\)-Al₄Cu₉ phases formed sequentially at the Al/Cu interface through solid state interdiffusion and reaction during heat up;

2) the bonding interface melted quickly after the interface reached the eutectic temperature and composition;

3) the \(\theta\), \(\eta\), and \(\gamma\₁\) phases formed during heat up were either completely dissolved into the interfacial liquid (\(\theta\) and \(\eta\)) or partially dissolved into the interfacial liquid (\(\gamma\₁\)). This process pushed the average composition of the interface toward the Cu-rich side;

4) the first solid phase formed from the interfacial liquid is the \(\varepsilon\₂\) phase, which subsequently transformed into the \(\gamma\₁\) phase upon cooling.

Combining the above information with results of structural examination from specimens M1, M2, and M3, it is suggested that formation of solid phases from the Al/Cu interfacial liquid follows this sequence: interfacial liquid \(\rightarrow\) \(\varepsilon\₂\) phase \(\rightarrow\) \(\gamma\₁\)-Al₄Cu₉. The remaining phase after specimen cool down is the \(\gamma\₁\)-Al₄Cu₉ phase.

The main difference between the bonding protocols used for specimens M1, M2, and M3 lies in the maximum bonding temperature: M1 was bonded below the eutectoid temperature of 567°C while M2 and M3 were bonded above 567°C. At temperatures
below 567°C, there is no thermodynamic driving for formation of the $\beta$-AlCu$_3$ phase at the $\gamma_1/(\mathrm{Cu})$ interface. When there is no further transformation for the $\gamma_1$ phase into the $\beta$ phase, a “$\gamma_1$ structure” bonding interface region forms, as in specimen M1.

If the specimen stays above the eutectoid temperature of $\sim$567°C for longer durations, the $\beta$-AlCu$_3$ phase forms at the $\gamma_1/(\mathrm{Cu})$ interface. In the case where $\beta$ formation completely consumes the $\gamma_1$ phase, the “E structure” subsequently forms through a eutectoid decomposition of the $\beta$-AlCu$_3$ phase upon cooling, $\beta$-AlCu$_3$ \(\rightarrow\) $\gamma_1$-Al$_4$Cu$_9$ + (Cu), as in specimen M3. Contrast modulations observed in ISE images of the “E structure” result from the (Cu)/$\gamma_1$-Al$_4$Cu$_9$ phase modulation following the eutectoid decomposition of $\beta$-AlCu$_3$. The eutectoid decomposition process produced much smaller grains as compared to those in the Cu bulk.

The “E/$\gamma_1$/E structure”, as in specimen M2, is a transitional structure between the “$\gamma_1$ structure” and the “E structure”. When the formation of $\beta$-AlCu$_3$ at $\gamma_1/(\mathrm{Cu})$ interfaces does not consume $\gamma_1$ completely, an “E/$\gamma_1$/E structure” will result upon cooling, with a $\gamma_1$ layer sandwiched in between two E layers. The annealing studies confirm that, given longer durations at temperatures above 567°C, the $\gamma_1$-Al$_4$Cu$_9$ layer will be consumed completely through $\beta$-AlCu$_3$ formation, with the entire bonding interface region subsequently transformed into a uniform E structure.

### 5.3.5 Relevance to TLP Bonded, Cu-based, Microchannel Devices

Enclosed Cu microchannel devices were fabricated through TLP bonding of Cu coupons containing microchannel arrays with mating Cu sheet metals with thin Al foil intermediate bonding layers. Figure 5.11 shows a cross-sectional ISE image of one such Cu microchannel device, bonded at $\sim$580°C with a $\sim$3min hold. The ISE image was
taken near a corner of one typical microchannel, and shows that TLP bonding led to well-formed microchannel corners, with no leakage across adjacent channels [20]. The ISE image shows ion channeling contrast from differently oriented polycrystalline grains from the Cu bulk and the mating Cu sheet metal. Processing of the commercial Cu sheet metal gave rise to its much smaller grain size as compared to the Cu coupon containing the microchannel array. Figure 5.11 further illustrates an extended bonding interface region with an $E/\gamma_1/E$ structure. The three separate layers are delineated with three black arrows in Fig. 5.11. The interface region has a total thickness exceeding 50 $\mu$m.

Additional examinations of a number of TLP bonded Cu microchannel devices showed interfacial structures consistent with what are described in Section 5.3.1. These observations indicate that mechanisms responsible for structure development within the bonding interface region, elucidated through characterization of TLP bonded Cu/Al/Cu
coupon assemblies and summarized in Section 5.3.3, remain operative in TLP bonded Cu microchannel devices. Thus understanding of the structure development within the Cu/Al/Cu TLP bonding interface region provides guidance to engineering development of Cu-based microchannel devices.

5.3.6 Tensile Strength of TLP Bonded Cu/Al/Cu Coupon Assemblies

For functional metal-base microchannel devices, mechanical properties of the bond are of interest. Tensile testing was performed on specimens prepared from TLP bonded Cu/Al/Cu sandwich-like coupon assemblies, T1, T2 and T3. At least four rectangular tensile specimens were made from each assembly. The bonding protocols for T1, T2 and T3 were correspondent to those used for M1, M2 and M3, except for decreased holding duration at the maximum bonding temperature. Because of the higher thermal masses of specimens T1, T2 and T3, the shorter hold durations were necessary to achieve similar interfacial structures. Post TLP bonding, structural examinations confirmed that specimens T1, T2 and T3 had respectively the $\gamma_1$ structure, the $E/\gamma_1/E$ structure, and the E structure in their bonding interface regions. Groups of tensile specimens made from T1, T2, and T3 were tested on the MTS858 system until fracture occurred across the bonding interface region.

Figure 5.12 shows a typical raw data set of tensile load force versus total extension, obtained from a T1 specimen with the $\gamma_1$ interfacial structure. It should be noted that the measured extension was that of the entire tensile testing system, including the connecting bolts and local deformation around the hole areas on the tensile specimen. In addition, the width of the bonding interface region was much smaller than the total
length of the tensile specimen. Therefore, this extension does not represent the extension of the bonding interface region.

![Graph showing total load force vs. total extension](image)

**Figure 5.12** A typical total load force vs. total extension curve obtained from one Cu/Al/Cu tensile specimen with the $\gamma_1$ interfacial structure.

Observation of the tensile specimens showed that, invariably, tensile fractures were confined within the bonding interface region. Fractured specimens showed little sign of area reduction across the fracture surfaces, independent of the bonding interface structure. This is consistent with observed force-extension curves, which invariably showed a monotonically increasing load force and an abrupt breaking point once a maximum load value was reached. In the absence of area reduction across the fracture surfaces, an average tensile stress on the bonding interface region was calculated by normalizing the total tensile force with the nominal specimen cross-sectional area. The most prominent feature exhibited by Fig. 5.12 is that the average tensile stress rises monotonically and that specimen fracture occurs in an abrupt manner once a maximum tensile stress is reached. It is therefore concluded that tensile testing with the present
protocol cannot distinguish any difference in ductility of the bonding interface, and that the only useful information yielded by this test is an average interfacial tensile strength. With at least four repeat specimens in each test group, measured average tensile strengths of TLP bonded Cu/Al/Cu interfaces with the $\gamma_1$ structure, the $E/\gamma_1/E$ structure, and the $E$ structure were $15.5\pm2.0$MPa, $21.8\pm1.5$MPa and $17.6\pm1.9$MPa, respectively. It should be noted that measuring an average tensile strength of TLP bonded Cu/Al/Cu sandwich-like coupon structures is only a first step toward a quantitative evaluation of the mechanical integrity of TLP bonded, Cu-based, microchannel devices, for which suitable testing protocols remain to be developed.

5.3.7 Examination of Tensile Fracture Surfaces

Tensile fractured specimens were immediately loaded into the FIB instrument and examined with no mechanical contact made to the fracture surface. Figure 5.13(a) shows a typical plan-view SE image of a fracture surface from specimen T1, with a $\gamma_1$ interfacial structure. A significant fraction of the fracture surface exhibited faceted morphological features. At the bottom of those faceted structures, rough ridges and voids were present. Further examination was made by FIB sectioning. Figure 5.13(b) shows a typical ISE image of the FIB cross section from the same general area on the fracture surface. The exposed grains had an average size of $\sim10\mu$m, and were confirmed to be $\gamma_1$-Al$_4$Cu$_9$ IMCs. The grain with a faceted fracture surface, delineated by opposing white arrows in Fig. 5.13(b), is seen to have broken in a brittle and trans-granular manner. In contrast, the rougher surface adjacent to the trans-granularly fractured grain, delineated by opposing black arrows, may have resulted from inter-granular fracture. Voids were present on the fracture surface, as indicated by the additional white arrows in Fig. 5.13(a) and (b). The
fracture surfaces of specimen T2 and T3 were examined in the same way. Figure 5.14 shows a typical plan-view SE image of a fracture surface from specimen T2, with an E/γ1/E interfacial structure. Faceted features on the fracture surface were again observed, suggestive of brittle trans-granular fracture. Voids are observed on the fracture surface as well, a few of them are delineated by white arrows. Additional FIB cross-section examination confirms that tensile fracture occurred within the γ1-Al4Cu0 layer of the E/γ1/E interface region. Figure 5.15 shows a typical plan-view SE image of a fracture surface from specimen T3, with an E interfacial structure. The fracture surface exhibited ridges almost vertical to the fracture surface and dimple morphologies typical of void growth and coalescence, suggesting the occurrence of localized plastic deformation. Voids were also found at the bottom of the ridges, a few are delineated by black arrows. Further FIB cross-sectional examination shows that the tensile fracture was contained entirely within the eutectoid layer, and did not go into bulk Cu.
5.3.8 Instrumented Nanoindentation across TLP Bonding Interface regions

The IMC $\gamma_1\text{-Al}_4\text{Cu}_9$ is expected to have higher strength than the terminal solid solution (Cu). Figures 15(a), 15(b), and 15(c) show SE images of a series of indents across the bonding interface region of the specimen M1, M2 and M3 respectively. The triangular indents started from a location within bulk Cu, traversed across the bonding interface region, and ended in the opposing bulk Cu region. The bars and the corresponding numbers next to the indents show measured hardness values from the corresponding indent location. The average value of hardness measured from the eleven indents outside the bonding interface region is $\sim$1.4GPa in Fig. 5.16(a). The average hardness within the $\gamma_1\text{-Al}_4\text{Cu}_9$ region is $\sim$9.3GPa. Figure 5.16(b) shows an SE image of indents across the E/$\gamma_1$/E interfacial structure of specimen M2. Hardness values obtained from indents placed within the (Cu) region, the eutectoid layer, and the $\gamma_1$ layer of the bonding interface region are in the range of 1.0-1.5GPa, 1.9-2.6GPa, and 6-10GPa,
Figure 5.16  Instrumented Berkovich indentation across bonding interface regions of TLP bonded Cu/Al/Cu specimens: (a), (b), and (c) are respectively plan-view SE images of indents across specimen assemblies M1, M2, and M3. The numbers on images (a), (b), and (c) denote measured hardness values while the bars have lengths proportional to the hardness values.

respectively. Figure 5.16(c) shows an analogous SE image summarizing results of indentation across the bonding interface region of specimen M3, with the E interfacial structure. The average value of hardness measured from the thirteen indents outside the bonding interface region is ~1.4GPa. Hardness values obtained from indents placed within the eutectoid interface layer are above 1.8GPa.

Data in Fig. 5.16 show that the hardness of the $\gamma_1$-Al$_4$Cu$_9$ layer exceeds significantly that of the (Cu)/$\gamma_1$-Al$_4$Cu$_9$ eutectoid layer, and is higher than that of the Cu base material by ~6-10 times. The indentation data thus confirm the expectation that $\gamma_1$-
Al₄Cu₉ has the highest hardness, and by inference, the highest strength within the bonding interface region.

5.3.9 Impact of Void Formation on Tensile Bond Strength

Results of nanoindentation across the bonding interface regions are not in direct accord with the measured average tensile bond strength. If intrinsic strength of the various phases within the bonding interface region were the sole determining factor, the γ₁ structure would be expected to possess the highest tensile bond strength. In contrast, two observations from the present experiments need to be rationalized. First, the measured average tensile bond strength for the γ₁ structure is the lowest of the three structures examined. Second, tensile fracture occurred across the γ₁-Al₄Cu₉ layer within the E/γ₁/E interface region despite its higher strength. To rationalize these two observations, it is believed that the presence of voids, formed during the TLP bonding process and distributed randomly within the interface region, needs to be taken into account. Voids serve as potential initiation sites for tensile fracture. The measured average tensile strength is suggested to depend on the detailed void configuration as well as the toughness of relevant phases within the bonding interface region, and not a sole function of the intrinsic strengths of the various phases. The presence of voids and their effects on fracture initiation provide a rational for the fact that the measured average tensile bond strengths are clustered together, from 15 to 22MPa, despite significant differences in the hardness, and by inference, the intrinsic strength of various phases within the bonding interface region. Details on the spatial distribution of voids and how it depends on the TLP bonding process have not been fully characterized, and remain to be studied in the future.
Formation of voids during TLP bonding has been observed previously. Extensive pore formation along the mid-plane of the intermediate bonding layer was attributed to its consumption due to interdiffusion during the heat up stage, before interfacial melting can commence. Alleviation of such pore formation can thus be achieved by increasing the thickness of the intermediate bonding layer to above a critical value [35]. Morphological observations, such as those shown in Figs. 5.4, 5.10 and 5.13, suggest that the present thickness of Al foils exceeded this critical thickness. Additional voids may be formed as further diffusional intermixing of the bulk and the bonding interface region occurs in the solid state, after the transient interfacial melt layer has solidified. Such Kirkendall voids arise from asymmetry of solid-state interdiffusion [36], and may serve to lower the overall tensile strength by providing failure initiation sites within the bonding interface region.

5.4. Summary

We have conducted a detailed study of Cu-Al-Cu TLP bonding interface regions. Cu/Al/Cu TLP bonding has been demonstrated to be a feasible approach to fabricate completely enclosed, Cu-based, microchannel devices. In-situ XRD showed that the first solid phase remaining within the bonding interface region after the Cu-Al-Cu specimens were cooled after interfacial melting is \( \gamma_1 - \text{Al}_4 \text{Cu}_9 \), and that the bonding interface structure then evolves from a \( \gamma_1 \) structure through an \( E/\gamma_1/E \) structure to an \( E \) structure, as the system moves closer to overall thermodynamic equilibrium. The mechanisms responsible for structure development within the bonding interface region of Cu/Al/Cu bulk coupon assemblies are shown to remain operative within TLP bonded Cu-based microchannel devices. Nanoindentation across Cu/Al/Cu bonding interface regions
showed that the $\gamma_1$-Al$_4$Cu$_9$ phase has the highest hardness, ~6-10 times higher than that of the Cu base material. The average tensile strength of TLP bonded Cu/Al/Cu specimens is shown to range from 15MPa to 22MPa, and suggested to be dependent on details of void distribution within the bonding interface region. The present study supplies data for guiding the development of an effective manufacturing protocol for Cu-based microchannel devices.

5.5 References


CHAPTER 6
SUMMARY

This dissertation concentrated on fabrication and assembly of metal-based MEMS, especially metal based microchannel devices. The so called “size effect” in micro & nano scale molding and indentation is studied with indenters of different geometries, including long rectangular blades and triangular wedges with different included angles. The adhesion between thin ceramic films and substrates is experimentally evaluated through proposal and execution of a new microscale testing protocol. To form functional microchannel devices, such as Cu based microchannel heat exchangers, a TLP bonding technique is employed to assemble the core parts of the device. Both the mechanical integrity and structural evolution of the bonding interface region have been studied.

Micro to nano scale compression molding to large plastic strains has been performed in single crystal Al specimens at room temperature. A series of long rectangular diamond punches with widths ranging from 5µm to 550nm were machined by FIB milling. Micro-/nano-scale compression molding creates deep plastic imprints in Al that are faithful in shape to that of the mold insert, and therefore offers a potential avenue for rapid fabrication of micro-/nano- scale metal-based structures. A detailed comparison was made between indentation size effects in one single crystal Al specimen in the pyramidal indentation geometry and the long rectangular strip punch geometry. Experimentally, the presence of significant indentation size effects in both the pyramidal indenter and the strip punch geometries was observed, but with a distinctly different dependence of the characteristic pressure on the corresponding characteristic length. The observation of a significant dependence of the micro/nano scale indentation response on indenter geometry suggests that this characteristic length is not a unique function of the
indented material, but is dependent on the stress/strain distribution underneath the indenter.

Micro/nano scale 2D wedge indentation experiments were conducted on a single crystal Al specimen at room temperature at three different included wedge angles, ~33°, ~53°, and ~93°. A method for obtaining the actual contact widths from analysis of experimental unloading curves in combination with imaging of wedge indent impressions made at high loads is proposed. This method, based on 2D elastic contact mechanics solutions, was used to obtain the hardness as a function of the contact width or depth. The present results show clear evidence of an indentation size effect over the range of wedge angles studied. The observed dependence of the projected contact pressure on the contact depth is consistent with the Nix-Gao relationship. A significant dependence of the characteristic length on the indentation angle is observed, and shown to be consistent with a 2D extension of the Nix-Gao model to the wedge indentation situation. Such an extension, however, over estimates the magnitudes of the characteristic length as compared to values deduced from experimentation. Quantitatively analyzed 2D wedge indentation offers another experimental test configuration for size-dependent plasticity theories.

A new protocol is proposed for testing coating/substrate interfacial failures through direct compression loading of micro-pillars containing an inclined interface region. A previous method for testing the limiting interfacial shear strength incurs relative large scatters, ~50%. In contrast, the present micro-pillar compression test yields more reproducible failure stresses, with typical data scatter ~15%. A large number of micro-pillar test specimens can be fabricated from a relatively small specimen. With
scripted FIB milling, pillar fabrication can become automated and quite rapid. The failure surfaces can also be made accessible to high-resolution structural and chemical analysis, and thus conducive to correlating interfacial structure and chemistry with mechanical failures within the interfacial region.

We have conducted a detailed study of Cu-Al-Cu TLP bonding interface regions. Cu/Al/Cu TLP bonding has been demonstrated to be a feasible approach to fabricate completely enclosed, Cu-based, microchannel devices. In-situ XRD showed that the first solid phase remaining within the bonding interface region after the Cu-Al-Cu specimens were cooled after interfacial melting is $\gamma_1$-$Al_4Cu_9$, and that the bonding interface structure then evolves from a $\gamma_1$ structure through an E/$\gamma_1$/E structure to an E structure, as the system moves closer to overall thermodynamic equilibrium. The mechanisms responsible for structure development within the bonding interface region of Cu/Al/Cu bulk coupon assemblies are shown to remain operative within TLP bonded Cu-based microchannel devices. Nanoindentation across Cu/Al/Cu bonding interface regions showed that the $\gamma_1$-$Al_4Cu_9$ phase has the highest hardness, ~6-10 times higher than that of the Cu base material. The average tensile strength of TLP bonded Cu/Al/Cu specimens is shown to range from 15MPa to 22MPa, and suggested to be dependent on details of void distribution within the bonding interface region. The present study supplies data for guiding the development of an effective manufacturing protocol for Cu-based microchannel devices.
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