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**MECHANISMS OF MICROSTRUCTURE DEVELOPMENT AT METALLIC-
INTERLAYER/CERAMIC INTERFACES DURING LIQUID-FILM-
ASSISTED BONDING**

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A thesis submitted in partial satisfaction of the requirements for the degree of

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Mechanisms of Microstructure Development at Metallic-Interlayer/Ceramic Interfaces During
Liquid-Film-Assisted Bonding

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by

Joshua Daniel Sugar

ABSTRACT

Mechanisms of Microstructure Development at Metallic-Interlayer/Ceramic Interfaces During
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by

Joshua Daniel Sugar

Master of Science in Engineering-Materials Science and Engineering

University of California at Berkeley

Professor Andreas M. Glaeser, Chair

Alumina has been bonded *via* copper/niobium/copper interlayers, and correlations have been made between various processing conditions (applied load, processing temperature, copper film thickness, surface roughness, *etc.*) and strength. Four-point bend strengths and micrographs of fracture surfaces have been used to determine the relationship between processing, microstructure, and properties. Transparent sapphire substrates bonded with copper/niobium/copper interlayers were used in model experiments to track the microstructural development of these ceramic/metal interfaces and to identify the important mechanisms that contribute.

High interfacial strengths were generally associated with small unbonded regions, extensive breakup of the copper film into isolated particles, ceramic pullout, and regions of niobium/alumina contact where the grain boundary grooves of the alumina are visible on both sides of the fracture surface. Experiments with sapphire substrates showed that asperities in the niobium and grain boundary grooves in the niobium play an important role in the initiation and growth of sapphire/niobium contact. The presence of a liquid film can enhance the kinetics of sapphire/niobium contact and growth by providing a low-temperature high-diffusivity path.

The breakup of the copper film was described using two models that were in fairly close agreement. The breakup of the copper film depended on the asperity density in the niobium, niobium grain boundary density, liquid film redistribution, and the breakup of liquid patches *via* Rayleigh instabilities. The redistribution of the liquid was affected by defect geometry, local film thickness, and local interfacial crystallography.

Thermal grooving effects of liquid copper on alumina and niobium were studied using conventional sessile drop experiments. The thermal grooving of one particular grain boundary in alumina when in contact with copper and niobium was studied using a fabricated bicrystal. Both diffusion mechanisms and the dissolution-precipitation reaction of alumina in niobium limited the kinetics of thermal grooving.

Andreas M. Glaeser

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For Grandma...

She was proud of me when I took my first step away from home,
and is proud today.

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I. INTRODUCTION

Few modern devices are based on monolithic structures comprised of a single phase or material. Instead a structure might incorporate several different phases and/or kinds of materials with vastly different properties and functionally distribute the various properties to specific locations in the structure. Modern structural alloys are often multiphase and contain interphase interfaces. Modern microelectronic components contain multiple phases, and in some cases, an intergranular phase. Materials used at elevated temperature can contain interphase interfaces that develop during thermal processing (e.g., precipitation of a second phase during age hardening), and can have heterophase interfaces that are introduced during later stages of processing as well. An example of the latter type of interface is that between a high-temperature structural alloy and an oxide thermal barrier coating designed to extend the component's temperature capability and lifetime. Structural concrete contains reinforcing steel rebar that increases the tensile strength by compressing the concrete and locally reducing the driving force for crack tip extension. Composites used in dental implants often contain acrylic resins and stiff inorganic fillers. Modern sporting equipment is often made from composite materials to have lightweight and high strength. Surfboards have a fiberglass reinforced plastic shell to make them stronger, lighter, and faster on the ocean. Thus, the seam between two phases/materials has become an important topic of study to ensure that interfacial properties do not degrade the desired properties of the bulk structure.

Ceramic materials have many beneficial properties, creating an appealing substitute to metal alloys in many applications. Ceramics have a relatively low density and high strength, making them good options for applications where the strength/weight ratio might be important, *i.e.*, vehicle frames. The chemical stability and inertness of ceramics create possibilities for uses at high temperatures, *i.e.*, internal combustion engines, or in applications where byproducts of chemical

degradation might be deleterious to one's health—biomedical implants. Lastly, excellent wear resistance of ceramics makes them a compelling choice for cutting tools, nozzles used at high pressures, or for ink-jet printing.

Often ceramics are not cost-effective because of the processing difficulties that arise. Crystalline ceramics cannot be cast or wrought like metals can. Usually ceramic parts are made from fine powders formed into green compacts and sintered to form high-density, fine-grained bulk material. This process does not lend itself well to forming large objects of complex shape. Ironically, the high strength and hardness of ceramic materials also makes it quite difficult, laborious, and expensive to machine them into useful parts with complicated shapes. A possible alternative is to process much smaller parts with simple geometry and join them together, effectively resulting in the desired final structure.

Brazing and diffusion bonding are two methods of joining ceramics that have proven to be successful. Brazing is closely related to soldering; a metal is melted and used as “glue” when it solidifies to hold two pieces of ceramic together. In order for the braze metal to work as a strong glue it must wet (see **BACKGROUND** section for a definition of wet) the ceramic and bond to it. Most braze alloys are based on Cu, Ag, and Au, and because of their relatively high excess liquid surface energies (γ_{LV}) and small oxidation potentials they neither wet nor react with ceramics to form strong bonds. This limits their usefulness.¹ Additions of reactive metals such as chromium and titanium to the braze metal have been shown to improve bond strength characteristics,²⁻⁴ but the service environments of these types of bonds are still limited by the melting temperature of the metal interlayer. The necessity for surface cleaning prior to joining to increase the surface tension of the free surfaces and increase the driving force for the braze to wet the ceramic also places limitations on brazing. Further complications arise from the rejection of solute atoms that occurs during solidification, which could cause the formation of an inhomogeneous microstructure that

may be particularly susceptible to intergranular corrosion, causing the interface to have an unexpectedly low strength.

Solid-state diffusion bonding uses a refractory metal as the interlayer between the two ceramics. Rather than melting this metal interlayer, diffusion bonding subjects an assembly to a pressure at high temperatures and activates diffusion in the metal interlayer. The pressure required for diffusion bonding is relatively higher than the pressure required to form a strong bond using the brazing technique. Activated diffusion drives metal atoms to the interface to eliminate voids and pores, which promotes the formation of a strong bond between the metal and the ceramic. It has been shown that diffusion bonds can be formed at half the absolute melting temperature, T_m , but typically temperatures as high as $0.8 - 0.9 T_m$ are required for strong ceramic/metal joints.⁵ The arrangement of bonded assemblies is limited to simple geometries that can withstand the pressures used to process diffusion-bonded joints. Although wetting is not as important for diffusion-bonded assemblies as it is for brazed assemblies, the contact angle that the metal makes with the ceramic affects the geometry of flaws at the interface.⁶ Thermal stresses must be considered from expansion mismatch between the metal and the ceramic material. Surface cleaning is important for diffusion bonding for reasons similar to brazing, but flattening and polishing of surfaces to decrease the size of pores and voids at the interface must also be performed prior to diffusion bonding. The difficulties and limitations associated with brazing and diffusion bonding have prompted efforts to develop new joining methods that combine the convenience afforded by utilizing a liquid phase (e.g., lower bonding pressure, less stringent surface preparation requirements, and mass production compatibility) with the performance advantages, specifically high-temperature use capability, more easily achieved by solid-state diffusion bonding approaches. Methods of joining exploiting interlayers that form a transient liquid phase have been developed in an effort to achieve this desirable combination of process and performance characteristics. Transient liquid phases

disappear because they are chemically unstable when in contact with the materials to be joined. The constituents of the liquid can dissolve in the adjoining materials to form a solid solution, or can react with the adjoining materials to form a stable refractory compound. Both processes lead to the isothermal disappearance or consumption of the liquid. A variation on this theme employs a liquid film that is chemically stable, but not morphologically stable. During joining, an initially continuous liquid film evolves into a collection of discrete particles or liquid droplets along the interphase interface.

Commercially, niobium/alumina diffusion bonds are used to seal arc tubes in sodium vapor lamps. Because the coefficient of thermal expansion (CTE) of niobium ($78 \times 10^{-7} / ^\circ \text{C}$) closely matches that of alumina ($81 \times 10^{-7} / ^\circ \text{C}$), this “pressure” bonding technique has been effective for this application. Previous studies have shown that a thin film of copper deposited on the alumina substrates can increase the kinetics of the niobium/alumina interface formation.^{5,7-9} In some instances the liquid phase can fill voids along the interface that could otherwise act as stress concentrators and crack initiation sites. By providing a high diffusivity path for the niobium and dissolving a small amount of niobium, the presence of a liquid copper film during processing greatly enhances the mass transfer kinetics of niobium to the metal/ceramic interface, producing stronger bonds in equal or reduced processing times and at lower temperatures than required for diffusion bonding.

During processing the copper film dewets the ceramic substrate and forms isolated droplets *via* Rayleigh instabilities.¹⁰ After cooling and solidification, a uniform dispersion of copper particles acts as a ductile second phase and toughens the metal/ceramic interface. The mechanisms that contribute to the initial breakup of the copper film exploit asperities or irregularities at the niobium and/or alumina surface, grain boundary grooving of either the ceramic or metal surface, and surface faceting caused by the presence of non-equilibrium surfaces at the interface. In addition

to aiding in the breakup of the copper film, grain boundary grooving and surface faceting can roughen the surfaces at the interface creating a more tortuous interfacial crack path and adding further toughness to bonded assemblies.

The general problem of joining ceramic components to themselves and to metals by mass production methods remains an area of research in which there is significant room for improvement. The present study employs a bonding technique that utilizes a non-equilibrium liquid film that persists during processing; the liquid film redistributes into a collection of discrete particles. This bonding technique is referred to as liquid-film assisted joining. Mechanisms that explain the interfacial microstructure development in bonded assemblies are explored and an attempt is made to understand the processing-microstructure-property relationship in alumina joined with copper/niobium/copper interlayers.

2. BACKGROUND

A strong ceramic/metal interface plays a vital role in structural composites based on metals and ceramics and in other structures intended for microelectronic, thermal, catalytic, biological, and other applications. A strong interface allows the chemical and thermal stability of ceramic materials to be paired with the ductility and toughness of metals to produce structures that are useful in a plethora of demanding environments. As a result of the widespread applicability of such structures, the fracture community has put significant effort into trying to understand crack growth behavior in ceramic/metal composite systems.¹¹⁻¹⁶ For high-temperature engine and energy conversion applications, processing methods that provide an ability to form bonds that retain their strength at temperatures close to or ideally higher than the joining temperature are especially appealing. Low-temperature, transient-liquid-based methods of forming ceramic/metal bonds will be discussed, and specific emphasis will be placed on materials relevant to this study and the associated mechanisms of interface formation.

2.1 Wetting and Work of Adhesion in Metal/Oxide Systems

When three phases, such as a liquid, a solid, and a vapor come into contact with one other along a line, a specific triple-junction geometry will develop that minimizes the surface energy of the system. If the solid is rigid, then a potential equilibrium geometry is illustrated in **FIGURE 2.1 (a)**.

The equilibrium geometry can be determined by a surface energy minimization procedure, or in isotropic systems, by balancing the surface tensions. The surface/interfacial energies are treated as forces acting parallel to the surface or interface with a magnitude given by γ_{ij} where γ_{ij} is the energy per unit area of the interface between the i and j phases. When the substrate is rigid, the

balance of forces is only in the horizontal direction (parallel to the substrate surface) and the resulting relationship is sometimes referred to as the Young equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_v \cos \theta \quad (2.1)$$

where γ_{sl} , γ_{sv} , and γ_v are the energies per unit area of the solid-liquid, solid-vapor, and liquid-vapor interfaces, respectively. A liquid is said to “wet” the solid surface when the contact angle, θ , is less than 90° , and when θ is greater than 90° the liquid is said to be nonwetting. If a continuous liquid film coats the surface, and $\theta > 0^\circ$, the film can “dewet” the substrate to reduce energy while conserving volume. The work of adhesion is defined as the energy change when one destroys a unit area of solid-liquid interface and forms a free liquid surface and a free solid surface.

$$\begin{aligned} W_{ad} &= \gamma_v + (\gamma_{sv} - \gamma_{sl}) \\ &= \gamma_v (1 + \cos \theta) \end{aligned} \quad (2.2)$$

Low values of θ are thus associated with a high work of adhesion; as θ approaches 180° , W_{ad} goes to zero and the tendency for film breakup and dewetting increases. The interfacial fracture energy scales with W_{ad} when plasticity effects are neglected, and thus improved wetting characteristics (decreasing θ) lead to a non-linear (cosine dependent) increase in the interfacial fracture resistance.

Oxygen additions to liquid metals have the potential to alter γ_v and γ_{sl} . If the system is in complete equilibrium, the ambient oxygen partial pressure, $p(O_2)$, will adjust, which in turn can affect γ_{sv} . Consequently, for liquid metals on substrates, the contact angle can depend strongly on the $p(O_2)$. For the specific case of liquid metals on solid oxides, two limiting $p(O_2)$ values arise, one corresponding to the $p(O_2)$ that would cause the oxide to reduce, and the other to the $p(O_2)$ that would cause the metal to oxidize. At the extreme $p(O_2)$ values, oxygen adsorption onto the metal surface or oxygen desorption from the oxide surface causes drastic changes in the contact angle. Over an intermediate range of $p(O_2)$, the contact angle is relatively insensitive to $p(O_2)$; a “plateau” region exists.¹⁷ For several metal/alumina systems “plateau” values of θ fall between 110°

and 130° and at the extreme $p(\text{O}_2)$ s they decrease to values as low as 90° . Specifically, the copper/alumina system at 1150°C has a contact angle that plateaus at approximately 118° , and the value of γ_v is 1400 mJ/m^2 , a relatively high liquid surface energy. Considerable effort to model the effect of $p(\text{O}_2)$ on surface/interface energies and work of adhesion has been performed for the copper/alumina interface that neglects the effects of melting, and also for the solid-state niobium/alumina interface, and the results agree with experiment.¹⁸⁻²¹

When bonding copper to alumina it is possible to form strong bonds by increasing the $p(\text{O}_2)$ in the bonding environment. This has the effect of reducing γ and increasing W_{ad} . At sufficiently high oxygen contents, a $\text{CuO-Cu}_2\text{O}$ eutectic melt that wets alumina well forms. However, at such high oxygen contents, copper oxides and/or copper aluminates could form. The formation of brittle oxide particles combined with voids at the ceramic/metal interface reduces the area of bonded region at the interface and causes a decrease in peel strength.²² Variable $p(\text{O}_2)$ studies showed that the improved wettability of copper on alumina at higher $p(\text{O}_2)$ may not be due to the formation of copper aluminate at the interface, but to the adsorption of copper-oxygen complexes at the solid/liquid interface.²³ Although copper aluminate does form at some higher values of $p(\text{O}_2)$, it does not seem to improve the wettability. A continuous copper aluminate layer did not form at the copper-alumina interface at 1300°C with a $p(\text{O}_2)$ of 10^{-4} bar, but contact angles $<90^\circ$ were reached.

Small additions of “active” elements like titanium, chromium, and yttrium, for example, can greatly enhance the wetting characteristics of copper on alumina and reduce the contact angle.^{2,24-26} Although interfacial reaction layers form in some instances and may cause the decreased contact angle, it is possible that a reaction layer is not needed to reduce γ , as observed with oxygen additions. The contact angle depends on the time the droplet is held above its melting temperature, and in general, the longer the drop is held at elevated temperature the lower the contact angle. In

some cases evidence^{27,28} suggests that formation of a ridge at the triple-line (in response to achieving a vertical force balance) and the migration of the ridge limits the rate of liquid redistribution and contact angle adjustment at the surface.

2.2 Wetting at Bimaterial Interfaces

When two materials such as a metal and a ceramic are separated by a thin liquid film, capillary forces will pull them into direct contact when the condition:

$$\cos \theta_1 + \cos \theta_2 \geq 1 \quad (2.3)$$

is met, where θ_1 and θ_2 are the contact angles for the liquid on the ceramic and metal, respectively (depicted in **FIGURE 2.1** (b)). Spatial variations in the film's morphological evolution may be explained by: local differences in grain boundary misorientation and grain boundary energy in either the metal or the ceramic that can affect the grooving kinetics; differences in θ_1 and θ_2 caused by local differences in surface crystallography or chemistry; and local variations in liquid film thickness.

2.3 Solid-State Diffusion Bonding: The Niobium/Alumina Interface

The niobium/alumina interface has been studied extensively as a model metal/ceramic system. The coefficient of thermal expansion closely matches for these two materials (a difference of $3 \times 10^{-7} / ^\circ\text{C}$ for temperatures ranging from 25°C to 1000°C), which minimizes the formation of thermal stresses at the interface. Niobium has a high melting temperature (2469°C) providing a large range of bonding temperatures that could potentially be studied. The relationship between a variety of processing parameters and the strength of the niobium/alumina interface has been studied. A collection of all of these relationships could help to predict the properties of many other metal/ceramic interfaces that are not appealing choices as model systems. The four-point-bend-method has been used to measure fracture energies of polycrystalline-niobium/sapphire interfaces in which the orientation of sapphire has been varied. Values of 26 J/m^2 and 55 J/m^2 have been

reported for polycrystalline niobium bonded to (0001) and (1 $\bar{1}$ 00) sapphire respectively (high vacuum, 1750°C, 10 MPa, 2h).²⁹ When samples are fabricated with sputter-cleaned surfaces and in ultra-high vacuum (UHV), fracture resistances similar to those observed from high-vacuum samples are produced at substantially lower temperature, $\sim$ 1000°C, and fracture energies as high as 110 J/m² have been achieved in samples bonded at 1500°C.³⁰ This increase in strength is in part due to the “activation” or roughening that occurs from sputter cleaning, the reduced number of impurities at the interface (oxygen, carbon, sulfur, and chlorine),³¹ and also as a result of the reduced uptake of oxygen and aluminum into the niobium at the lower bonding temperatures in the UHV environment. Observations have shown that impurities with larger atomic radii and lower heats of sublimation than the bulk material that segregate to grain boundaries can lead to a decrease in cohesion at the boundary.³² This model seems to apply for interfaces between dissimilar materials as well in some cases, as was seen with silver (and to a lesser extent with sulfur), which adhered completely to the metal side of the interface and caused a substantial decrease (in some cases a decrease of more than 50 J/m² with silver impurities) in the fracture energy of the niobium/sapphire interface.³³

The strength of the niobium/alumina interface is also largely dependent on the thickness of the niobium foil used in the bond. Large decreases in the Young’s modulus and the yield stress for niobium/sapphire compression test samples with thicker niobium foils have been attributed to the geometric constraint placed on the niobium foil from adhesion to the alumina.³⁴

Niobium/sapphire has served as a model system for studies seeking to determine the factors and mechanisms that lead to the formation of strong metal/ceramic interfaces. The increase in interface fracture energy with decreased metal grain size after bonding and with increased difference between final and initial grain size is explained by superimposing two competing effects of niobium grain growth during processing.²⁹ 1) Samples with large initial and larger final grain

sizes demonstrated decreased fracture energies when sweeping of metal grain boundaries over the sapphire surface left unbonded and/or regions of weak interface behind because unfavorable interface orientations predominated the interface due to the restricted grain growth of the large grains. 2) Samples that experienced a large change in grain size during processing had higher fracture energies when selective grain growth of increased the area density of low-energy niobium/sapphire orientation relationships along the niobium/sapphire interface. Further investigation³⁵ into the mechanisms of sapphire/niobium interface formation at 1447°C with an applied load of 2 MPa showed that grain boundary groove ridges in niobium provided initial points of interfacial contact, from which faceted bonding fronts grew in directions that depended on the crystallography of the niobium. The meeting of two bonding fronts resulted in a cylindrical void that breaks up according to volume-diffusion-controlled kinetics in the niobium.

Significant dissolution of the sapphire occurs at elevated temperature; in regions of contact the sapphire topography adjusts to conform to that of the niobium surface. The introduction of lithographically processed cavities into the sapphire surface by Rühle *et al.*³⁶ provided the basis for a model study for the mechanisms of niobium/sapphire interface formation. The formation of alumina precipitates at a distance from the interface confirmed that a dissolution reaction due to the thermodynamic considerations of Schulze *et al.*³⁷ must occur. At the bonding temperature, the sapphire is dissolved, aluminum diffuses substitutionally³⁸ while the oxygen diffuses interstitially³⁹ at a much faster rate in the niobium lattice. During cooling, sapphire reprecipitates in the lithographically processed flaws, which contributes to the closure of flaws at the interface.

TEM studies^{36,40-42} proved that the interfacial oxide layer seen by Moruzumi *et al.*⁴³ was actually preferential etching near the interface that occurred during TEM sample preparation, leading to a shadow effect that caused a contrast seam incorrectly interpreted to be a NbO_x layer. These TEM studies also showed that faceting can occur to accommodate small misorientations

between the close-packed planes of the alumina and the close-packed planes of the niobium in oriented bicrystals.

2.4 The Copper/Alumina Interface

Because the ensuing work focuses on the copper/niobium/alumina system, and the niobium/alumina interface has already been discussed, the copper/alumina interface deserves some attention. Early studies on the copper/alumina interface report tensile strengths between 74 and 84 MPa when calculated from experimentally measured push-off bond strengths of 0.200 g metal cylinders annealed on alumina discs at temperatures ranging between 1120°C and 1390°C for times ranging from 5 to 30 minutes (not respectively).⁴⁴ The strengths were largely dependent on copper purity—high-conductivity copper interfaces were 14% stronger than spectroscopically pure copper interfaces—and contact angle; lower contact angles (achieved by holding the sample at the wetting temperature for longer times) increased interfacial strength. The strength of copper/alumina interfaces is not attributed to a reaction layer as is the case in the tantalum/sapphire interface,⁴⁵ but rather to cation vacancies at the sapphire surface being replaced with metal ions and filling free surface states. TEM and EELS studies showed that a charge transfer at the copper/alumina interface (prepared using molecular beam epitaxy in ultra-high vacuum conditions) leads to the Cu⁺¹ oxidation state and the formation of copper-oxygen bonds across the interface. These results were consistent with multiple scattering calculations.⁴⁶ The stresses that develop at copper/alumina interfaces due to thermal expansion mismatch ($\alpha \approx 12 \times 10^{-6}/^{\circ}\text{C}$) can be quite significant and cause debonding.⁴⁵ These thermal stresses can be calculated accurately from simple models.⁴⁷ Significant relief of mismatched thermal contraction stresses is achieved by low-temperature annealing of copper/alumina interfaces after bonding (at 250°C), which can increase tensile fracture stresses from 10 MPa to values greater than 80 MPa.⁴⁸

Annealed polycrystalline copper foils that were single crystalline over the thickness of the foil were diffusion bonded to sapphire at 1067°C for 1 h in a reducing environment under an applied load of 20 MPa with the <100> direction of the foils parallel to the <0001> direction of sapphire.⁴⁹ After bonding, TEM analysis showed that the grains in the copper foils had reoriented themselves such that the <0001> direction of the sapphire was parallel to the <111> direction of copper, which is not necessarily what one would expect from surface energy considerations, but it seems that minimization of the lattice mismatch dominates the atomic arrangements at the interface.⁴⁹ Similar results have been found for niobium thin films (150 nm) grown on c-plane sapphire using MBE techniques at 800°C, and may be useful in explaining the mechanism of film reorientation.⁵⁰ After film deposition the orientation relationship found between the niobium film and the sapphire using Reflection High Energy Electron Diffraction (RHEED) showed the (111) planes of niobium parallel to the (0001) planes in the sapphire. During anneals at 1500°C for times ranging between 1 min and 4 h small grains of niobium embedded in the film with the (110) planes parallel to the (0001) planes in sapphire completely consumed the film. This is consistent with the thermodynamic analysis, which shows that above a critical film thickness (<12 nm) the Nb(111) film becomes thermodynamically unstable and Nb(110) grain growth is favored.

The chemistry of the interface gets increasingly more complicated as more oxygen is introduced into the system. Various chemical reactions occur and preferred orientation relationships exist between copper, copper oxide, copper aluminates, and the alumina at the interface.⁵¹ Sufficient evidence exists to suggest that there is a critical concentration of copper aluminate, perhaps related to the critical oxygen concentration, above which the 4-point bend strength of the copper/alumina interface decreases because the alumina is weakened by the CTE mismatch with randomly oriented copper aluminate ($\alpha_{a\text{-axis}} = 11.0 \times 10^{-6}/^{\circ}\text{C}$ and $\alpha_{c\text{-axis}} = 4.1 \times 10^{-6}/^{\circ}\text{C}$).⁵²

The mechanism for interface formation in the copper/alumina system is similar to that in the niobium/alumina system. Initially, metal creep occurs at the elevated bonding temperature and closes voids at the interface. Once creep has occurred, further void closure occurs by diffusion processes and/or an evaporation/condensation phenomena, which require extended times at elevated temperature. The amount of copper-oxygen eutectic liquid present at the interface greatly reduces the time required for an increase in the bonded area because a sufficient amount of liquid can fill interfacial voids.⁵¹ Sputter cleaning can increase the reliability and flexural strength of copper/alumina interfaces in a similar manner seen in the alumina/niobium system.³¹

2.5 Bonding Using Interdiffusing Metal Multilayers

Interdiffusion in the solid state has also been shown to produce strong bonds in the silicon nitride/nickel/niobium system at temperatures much lower than brazing temperatures required for this system.⁵³ This bonding technique requires a thin film interface metal (foil or film) and an adjacent metal, which interdiffuses to the ceramic/metal interface. No clear explanation of a bonding mechanism is provided, but the closure of pores at the ceramic/metal interface due to imbalanced vacancy fluxes that usually occur during metal interdiffusion (the Kirkendall effect) is one possibility. This method of bonding is a precursor to a technique using multilayer copper/niobium/copper interlayers that will be discussed shortly. First, bonding methods that utilize a nonequilibrium liquid phase must be discussed.

2.6 Bonding in the Presence of a Transient Liquid Phase

The presence of a liquid phase can reduce bonding times. Van Houten provided a survey of ceramic-to-metal bonding techniques used prior to 1959 of which those that utilized a liquid phase were labeled “of greatest current interest.”⁵⁴ Solid-liquid interdiffusion (coined SLID in 1965) is a bonding technique that utilizes a liquid phase that isothermally solidifies during

processing. At temperatures higher than the processing temperature the interlayer did not reliquefy.⁵⁵ This technique was originally developed for use in integrated circuits.

In 1972 a technique was developed for joining heat-resistant alloys (nickel superalloys) wherein a thin interlayer alloy of specific composition and melting point temporarily melts during processing and isothermally solidifies to produce a bond whose thermal and chemical characteristics resemble those of the base metals.⁵⁶ This type of bonding technique is called transient liquid phase (TLP) bonding.

Several efforts have been to adapt this technique to ceramic joining. TLP bonding in the silicon nitride system with an oxynitride glass liquid interlayer produced bonds with strengths roughly half those of the sintered silicon nitride material (ranging between 376 MPa and 310 MPa for SRI-sintered silicon nitride and as high as 555 MPa at 1000°C for AS800 silicon nitride), but higher than those obtained by other joining techniques.^{57,58}

Another technique involving multilayer interlayers in which a transient liquid phase is formed only near the interface, and the homogenization occurs within the interlayer has been termed partial transient liquid phase (PTLP) bonding.⁵⁹ Using titanium/nickel/titanium interlayers to join silicon nitride, this technique produced bonds that retained their strength at temperatures higher than the bonding temperature. The titanium “cladding” layer diffused into the nickel to cause local concentrations of titanium that fell below the liquidus line in the nickel/titanium phase diagram, which prevented melting of the interlayers at temperatures higher than the bonding temperature. PTLP bonding is a good candidate for bonding in other systems provided that there is adequate wetting between the liquid layer and the ceramic, and that an excessively thick brittle intermetallic phase does not form. The PTLP bonding technique has been used with copper/platinum, copper/nickel, and copper/nickel-chromium metal interlayers to form strong bonds with alumina^{60,61} as well as with copper/gold/nickel, titanium/copper, and

titanium/copper/palladium interlayers to form strong bonds with silicon nitride.^{62,63} Post-bonding anneals in air and argon of alumina assemblies joined by PTLP bonding generally seemed to decrease the strength, but for copper/platinum interlayers the strength increased after a post-bonding anneal in air because of reaction layer formation.

Another bonding technique exploits reactive metal penetration (RMP), which relies on chemical reactions between silicates and molten aluminum.⁶⁴⁻⁶⁶ RMP converts a monolithic ceramic preform into a ceramic/metal composite but can also be used as a bonding technique. Molten aluminum simultaneously reacts and penetrates a dense aluminosilicate, like mullite, leaving behind a metal/ceramic composite.

2.7 Prior Work on the Copper/Niobium System

In contrast to the copper/platinum and copper/nickel interlayers, which exhibit complete mutual solubility at elevated temperature, the copper/niobium system behaves as a simple eutectic system with the eutectic composition at approximately 2 at % niobium and a maximum solubility of approximately 1 at % niobium in copper at 1080°C.⁶⁷ The phase diagram is shown in **FIGURE 2.2**. Due to the low solubility of copper in niobium and sluggish solid-state interdiffusion, the copper films do not disappear during bonding.

Solid-state bonding of single crystalline copper foils to sapphire with a thin film of niobium (<200 nm) deposited on the sapphire has been performed at 900°C in UHV conditions for 2 h with an applied load of 8 MPa.⁶⁸ Bond fracture energy was greatly improved as compared to copper/alumina and niobium/alumina bonds because of the strong adhesion of niobium to alumina combined with the large plastic deformation in the metal side of the ceramic/metal interface during fracture. The processing temperature is also greatly reduced compared to niobium/sapphire diffusion bonds produced in high vacuum.

Alumina assemblies with copper/niobium-based interlayers have also been fabricated that utilize the lower melting temperature of copper compared to niobium and take advantage of the liquid state. Shalz *et al.* found that copper/niobium/copper interlayers could be used to fabricate strong alumina joints (processed at 1150°C, $0.2 \times 10^{-5} < p(\text{O}_2) < 2 \times 10^{-5}$ torr, 6 h, 5.1 MPa applied load) with strengths ranging between 119 and 255 MPa and with an average of 181 MPa.⁵ A significant number of failures occurred in the ceramic suggesting that the bond was stronger than the ceramic material.

The microstructure of these interlayer/alumina interfaces contained continuous and discrete second phase precipitates that resulted from a reaction between copper, alumina, and additional oxygen that was either dissolved in the copper or the niobium (this differs from the microstructure that developed in assemblies processed in a lower $p(\text{O}_2)$ environment^{7-9,69} and is to be discussed later). The continuous precipitate was usually found at niobium grain boundaries and fracture often occurred through these precipitates. The morphology of the precipitate phase resulted from the redistribution of the liquid copper cladding layer as capillary forces pull the niobium and alumina into direct contact as discussed previously. Previous wetting studies^{70,71} suggest that for the oxygen levels in this study, EQUATION (2.3) would certainly be met. Because of the low rate of incorporation of copper into niobium the copper is available for reaction for extended periods of time, and copper retains a high activity as a copper-rich liquid stays in equilibrium with the niobium at the processing temperature, thus making the reaction between copper and alumina probable. The reaction between the copper, alumina, and oxygen would then proceed until all of the copper has been consumed and the small amount of niobium present in the liquid has precipitated onto the niobium foil or ceramic, leaving regions with no detectable amounts of copper on either side of the interface. A strong correlation exists between the fracture

strength and degree of precipitate development at the interface. In general, areas of interface with extensive precipitate coverage had higher strengths and a greater tendency toward ceramic pullout.

A study by Marks *et al.*^{9,72} assessed the effects of processing conditions on the fracture strength of alumina bonded with copper/niobium/copper interlayers. These samples were prepared using a range of bonding pressure (2.2, 2.9, 6.8–8.2 MPa), temperature (1150°C and 1400°C), and $p(\text{O}_2)$ (the graphite hot press in Marks' study had a much lower $p(\text{O}_2)$ than the molybdenum hot press used by Shalz *et al.*⁵).

The mechanism of niobium/alumina contact formation was studied using transparent sapphire substrates. Niobium deformation contributed to some of the contact. However, micrographs suggested that initial contact occurred primarily along niobium grain boundaries. Above the melting point of copper, niobium grain boundaries were “etched” by liquid copper. Concurrently flanking grain boundary groove ridges developed, which grew in height and made contact with the sapphire (a three dimensional schematic of this is shown in Marks *et al.*, pg. 5617⁷). The contact zone grew, ultimately localizing the liquid layer atop individual niobium grains. Capillary instabilities occurred along the edges of the liquid film and formed “cylindrical” ligaments of copper-rich liquid. These ligaments subsequently underwent Rayleigh instabilities and formed isolated copper droplets at the interface in a process that resembles crack healing and thin-film breakup. Other studies have suggested that interface asperities can also play a large role in the formation of niobium/alumina contact.⁷

In samples with films that have undergone extensive dewetting, the majority of the interlayer/sapphire interface is dominated by niobium/sapphire contact. High-temperature fracture studies showed that the copper/niobium interlayers can retain a significant fraction of their room temperature strength to temperatures as high as 900°C.⁹ Above this temperature the strength decreased, however, and a majority of failures occurred in the ceramic. The decrease in

strength could then be attributed to degradation of the alumina properties at high temperatures rather than the properties of the metal interlayers. When a smaller-grained, higher-purity alumina was used, the bond retained roughly 42% of its strength above 1200°C (above the melting temperature of copper), and in some cases, test specimens plastically deformed to the limit of the testing jig without fracturing.⁷

The effect of copper film thickness and alumina surface finish have been studied as well.^{8,73} The copper film provides a high transport rate path for dissolved niobium and fills interfacial voids. Increasing the copper film thickness from 0 μm to 1.4 μm to 3.0 μm on polished alumina surfaces led to progressive improvements in average strength and Weibull modulus, which then decreased when the film thickness was increased further to 5.5 μm . For film thicknesses of 3.0 and 5.5 μm the copper suppresses the formation of a brittle niobium silicide phase, a prominent feature of fracture surfaces in diffusion-bonded samples and samples processed with a 1.4 μm thick copper film.⁷³

The fracture and fatigue behavior of alumina bonded with copper/niobium/copper interlayers was studied by Kruzic *et al.*⁶⁹ Under monotonic loading at ambient temperatures fracture largely occurred in a brittle manner with a mean fracture toughness of 39 J/m^2 ; the fracture toughness decreased at elevated temperatures. The failures are associated with niobium/alumina interfacial separation and small regions of interfacial copper deformation in a ductile manner. Quantitative EDS identified the same niobium silicide phase seen in an earlier study⁸ as Nb_5Si_3 . Comparison of the fracture and fatigue properties of liquid-film assisted bonded joints to bulk alumina proved that as long as flaw sizes are in a reasonable regime for brittle materials (<1 mm), the joint did not have a detrimental effect on the crack growth resistance properties of the ceramic structure.

2.8 Surface Structures in Single Crystal Sapphire

The development of the microstructure in the copper/niobium/alumina system is largely dependent on the duration that the liquid film stays in a particular region. Wetting, grain boundary grooving, and local film thickness variations have already been mentioned as factors that affect the breakup of the liquid film. Another consideration is changes in surface structure that occur to lower the total surface energy. As the surface planes reorient themselves, the shape of a crystal will change. Kinetic and equilibrium considerations are both important when determining the shape that a crystalline structure will ultimately take. The equilibrium considerations that minimize the surface free energy of a small crystal were outlined by Wulff,⁷⁴ and further described by Herring.⁷⁵ The circumstances are described under which an initially flat surface would rearrange its atoms into a more thermodynamically stable hill-and-valley structure. Mullins described the origination of these hill-and-valley structures as the nucleation and growth of individual facets.⁷⁶ Facet nucleation and growth was experimentally seen by Heffelfinger *et al.* for **c**(0001) plane and **m**(10 $\bar{1}$ 0) plane sapphire substrates.⁷⁶⁻⁷⁹ The **m**-plane substrates developed a hill-and-valley surface morphology while the **c**-plane substrates developed a terrace-and-step surface morphology. The steps in **c**-plane substrates seemed to nucleate with heights equal to $c/6$ ($c=1.3$ nm, the unit cell height) and then coalesce to heights of c and larger. These studies indicated that the time required for facet nucleation seemed to depend inversely on the angle separating the original unfaceted surface and the stable (simple) surface that would develop at the surface. The mechanism for facet coarsening whereby facet domains meet and coalesce to produce larger facets is also described in these studies. Further studies on the evolution of lithographically induced pores in sapphire^{80,81} demonstrated that the **m**-plane was not stable and disappeared during pore-shape equilibration. Interpretation of the shape change kinetics as surface diffusion controlled yielded widely varied and time-dependent values of surface diffusivity, and thus, surface-attachment-limited kinetics or

nucleation-limited kinetics seemed to play an important role in the morphological evolution of the pores.

Other methods that do not use lithography have been developed that probe the equilibrium shapes and orientation dependent surface energies of crystalline metals using scanning tunneling microscopy (STM). These methods have been used to study nickel and gold.⁸² One such study with gold found that extra or “magic” facets occurred at 3.7° and 11.7° from Au{111}<112> and at 8.0° from Au{100}<110>.⁸³ These nonequilibrium facets are believed to be a result of surface reconstruction. The Au atoms at the surface rearrange themselves into a more stable configuration that does not conform to the normal fcc unit cell. The nonequilibrium facets are thus a result of the different crystal structure at the surface stabilizing crystallographic planes not normally in the Wulff shape.

Surface structure, chemistry and cooling rate can all affect the morphology of a solidified liquid drop on a ceramic substrate.⁸⁴ The orientation-dependent surface structure of sapphire (terrace-and-step or hill-and-valley) can cause different pinning behavior around the periphery of a drop and thus lead to drop morphologies that deviate from circular cross-sections. Slow cooling rates gives ample time for equilibrium conditions to be met at triple junctions and liquid spreading can occur along one type of facet on a reconstructed surface (analogous to secondary wetting). Liquid morphologies will prove to play an important role in the formation of niobium/alumina contact when liquid copper is present.

2.9 Grain Boundary Grooving

The kinetics of grain boundary grooving have been developed for grooves that develop by evaporation-condensation, volume diffusion, and surface diffusion, and the linear dimensions of the groove are proportional to $t^{1/2}$, $t^{1/3}$, and $t^{1/4}$ respectively.⁸⁵⁻⁸⁷ One characteristic of grooves developed by diffusion is that they have a clear maximum in the groove height profile close to the

boundary compared to grooves developed by evaporation-condensation, which have a maximum height far from the grain boundary. The similarity in the groove profiles for surface and volume diffusion makes it quite difficult to distinguish between the two diffusion-controlled mechanisms.

Experimental studies are consistent with the theory and show that surface diffusion is the dominant mass transport mechanism for groove development in copper.⁸⁸ Experiments that measured grain boundary grooving rates of alumina substrates under sessile drops of various metals (Ni, Cu, Au, and Al) exhibited larger groove widths in regions of substrate in contact with the liquid compared to regions in contact with the vapor. This indicated that transport rates near the metal/ceramic interface were two to four orders of magnitude faster than on the pure alumina surface.⁸⁹ The results showed that groove growth under liquid Ni, Cu, and Au was controlled largely by volume diffusion through the liquid metal with a small interface diffusion contribution.

The same metal/ceramic systems have also been used to study the effect of triple junction grooving and ridging on wetting behavior. Ridging arises to balance the force in the vertical direction, a consideration neglected in Young's equation.^{27,28} Ridging can affect the spreading kinetics of the liquid drop and cause pinning. Another study that utilized liquid copper drops on alumina found that at $0.5 T_m$ of alumina (roughly the same temperature as the temperatures used in the grain boundary grooving studies), surface diffusion was rapid enough for shape changes to occur on the alumina surface, which affected the spreading behavior of the liquid drop.⁹⁰ The morphologic changes were dependent on the orientation of the substrate and the presence of impurities.

A model for the effects of surface energy anisotropy on grain boundary grooving has been developed that assumes surface diffusion as the dominant mass transport mechanism.⁹¹ This model assumes that the grain boundary is always perpendicular to the original surface and does not move during annealing, thus neglecting interfacial energy anisotropy that might arise from different grain

boundary plane orientations. A stability diagram was developed in this study that outlines the stability regions for different types of grain boundary grooves in grain boundary energy–surface energy anisotropy space. For the grooving of a polycrystalline material this type of map could prove to be quite useful in determining the types of grain boundaries that are present. The energetic selection criteria for different thermal groove morphologies developed with the model agreed with experimentally measured grain boundary grooves (using AFM) in a nickel-rich nickel-aluminum alloy.

2.10 Rayleigh Instabilities and Capillarity-Induced Morphological Changes

When the chemical potential of an atomic species varies nonlinearly over a surface, there is a driving force for atoms to move, thus adjusting the shape of that surface. These shape changes, referred to as capillarity-induced shape changes, can be important in the microstructural development of a liquid at a bimaterial interface. When a thin film dewets the interface, the film breaks up into cylindrical ligaments, which can then experience capillarity-induced instabilities and decompose further into discrete particles. The kinetics that govern capillarity-induced morphological changes for simple shapes were outlined by Mullins as surface- and volume-diffusion-controlled mechanisms.^{92,93}

At elevated temperatures polycrystalline materials generally experience grain growth whereby the large grains grow at the expense of the small grains. The atoms in the smaller grains have a higher chemical potential due to the higher curvature of the grain surface, and thus these atoms will migrate to the larger grain to lower their chemical potential. The kinetics that describe orientation and impurity effects on the grain boundary mobility and grain growth of alumina have been studied.^{94,95}

Microfabrication techniques made experiments possible that study the breakup of cylindrical pore channels. The breakup of microlithographically processed pore channels in

sapphire and silicon carbide have been studied extensively.^{10,96-102} The effects of crystallographic orientation, surface energy anisotropy, perturbation amplitude and wavelength, impurity content, and temperature on the breakup of the pore channels were all areas of interest in the various studies. The transition from diffusion-controlled evolution kinetics to surface-attachment and nucleation-limited kinetics has proven to cause difficulties when using these studies to extract diffusivity information.

To a much lesser extent the effects of capillarity on the morphology of a thin film have also been studied. Vilenkin *et al.* have described and modeled the kinetics that lead to the grain growth and the eventual break up of a small grained polycrystalline thin film on a rigid substrate.¹⁰³ An extension of Mullins work has been performed by Génin.¹⁰⁴ It included the effects of thin film stresses and capillary forces on thermal grooving to build an accurate description of the surface morphological evolution of a polycrystalline thin film.

(a)

(b)

FIGURE 2.1: (a) Illustration of equilibrium at a triple-junction in a solid-liquid-vapor system and (b) illustration of condition for liquid spreading $\theta_1 + \theta_2 < \pi$.

(a)

(b)

FIGURE 2.2: (a) Phase diagram for the copper–niobium system and (b) the copper-rich region shown at higher magnification.

3. EXPERIMENTAL PROCEDURES

3.1 Polycrystalline Alumina

Polycrystalline alumina blocks (COORS AD995, COORS TECHNICAL CERAMICS CO., GOLDEN, CO) $\geq 98\%$ dense, of dimensions 19.5 mm $\times$ 19.5 mm $\times$ 22.5 mm, and 99.5% purity were first glued to a magnetic steel plate using a thermal resin (BUEHLER, LAKE BLUFF, IL). Then, the blocks were ground with a diamond wheel on a surface grinder (K.O. LEE CO., ABERDEEN, SD) to obtain flat surfaces. The surface of largest area on the blocks was always ground. The surfaces were polished using successively finer diamond suspensions (SOUTH BAY TECHNOLOGIES, SAN CLEMENTE, CA) including 9 μm and 6 μm grit on a cast iron plate and 3 μm and 1 μm grit on respective solder plates using a Logitech (LOGITECH, SCOTLAND) mechanical polisher. After a 1 μm diamond suspension, a colloidal silica suspension (STRUERS, WEST LAKE, OH) on a polyethylene plate was used for the final polishing step. The blocks were then ultrasonically cleaned in various solutions (soap plus distilled water, distilled water, acetone, and isopropyl alcohol) for 15 min each. The blocks were dried under a hot air gun. The final cleaning step consisted of an air anneal (CM ELEVATOR FURNACE, BLOOMFIELD, NJ) in an alumina crucible at 1000°C for 1 h to burn off any residual organics that could be present.

3.2 Sapphire

Single crystal sapphire (MELLER OPTICS INC., PROVIDENCE, RI) of dimension 2" $\times$ 2" $\times$ 0.001" of various orientations (**c**-plane or **m**-plane) with a miscut of $\pm 1^\circ$ and an optical finish on both sides was cleaned using the same procedures as the polycrystalline alumina. The sapphire was not ground or polished because the finish provided by the supplier was sufficient. Prior to cleaning, the sapphire was cut with a diamond blade on a low-speed saw (BUEHLER, LAKE BLUFF, IL) to dimensions that depended on the desired applied load during processing. Mechanical strength data

for metal/sapphire interfaces were obtained from bonded samples produced using sapphire cylinders 1" in diameter and 1" tall (*INSACO INC., QUAKERTOWN, PA*). The cleaning procedures for the sapphire plugs were equivalent to those of the sapphire plates described previously, however, the final anneal was performed at 1600°C for 20 h in air to heal potential strength-limiting microscopic cracks in the material.

3.3 Copper Evaporation

Samples that were to be coated with copper were loaded onto a rotating table in a bell-jar-type physical vapor deposition system (*MIKROS INC., PORTLAND OR*). Copper wire (*CONSOLIDATED COMPANIES WIRE AND ASSOCIATED, CHICAGO, IL*) was cut into pieces approximately 0.5 cm and 1.5 cm long. The longer pieces were bent into a U-shape because previous experiments have shown that this is the most efficient way to load the copper into the system. The amount of copper used depended on the desired thickness of the copper layer. It has been shown previously that 1.0 g of copper deposits approximately 3 μm of copper on the surface with an approximate linear relationship between the mass of copper evaporated and the thickness of the copper layer deposited. The copper was ultrasonically cleaned in isopropyl alcohol for 15 min. The copper was then rinsed in distilled water, dipped in a solution 5 parts by volume nitric acid: 1 part by volume distilled water for 10 sec to remove surface oxides, rinsed in distilled water, and then left to soak in isopropyl alcohol. The copper pieces were dried with a hot air gun, and then placed into tungsten baskets inside the chamber. A chamber pressure of 2×10^{-6} torr was obtained using a diffusion pump with a roughing mechanical pump before evaporation commenced. Voltage was applied to the tungsten baskets until the copper was completely evaporated from the baskets. A glass slide with a 25 mm diameter cover slip on top of it placed inside the chamber during evaporation served as a means for measuring the thickness of the copper coating by profilometry alpha-step measurements (*TENCOR INSTRUMENTS, INC., SAN JOSE, CA*). The glass slide and cover slip were

cleaned prior to being placed in the chamber by ultrasonic cleaning in isopropyl alcohol and drying with a hot air gun.

3.4 Niobium Foil

Niobium foil, 125 μm thick and 99.99% pure (*GOODFELLOW CORP., MALVERN, PA*) was cut to the same dimensions as the surface with which it would bond using scissors. It was successively ultrasonically cleaned in soap plus distilled water, distilled water, isopropyl alcohol, and ethanol for 15 min. The niobium was finally dried with a hot air gun. The niobium was not flattened because early work showed that the flattening procedures resulted in a much rougher surface.⁸

3.5 Photolithography

It was desired for some of the sapphire samples to have surface features that resembled cracks, grain boundaries, or reservoirs of locally increased copper film thickness. Photolithography was an efficient and clean way of introducing surface features into the sapphire while minimizing the amount of damage and dislocations produced. All of the photolithographic processes were performed in a Class 100 clean room (*MICROFABRICATION LABORATORY, EECS DEPARTMENT AT UC BERKELEY*).

The first step in the photolithographic process was cleaning the samples in the clean room. Sapphire plates and/or plugs were ultrasonically cleaned for 15 min in a 5:1:1 by volume $\text{H}_2\text{O}:\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$ solution (known as SC1) and in a second solution 6:1:1 by volume $\text{H}_2\text{O}:\text{HCl}:\text{H}_2\text{O}_2$ (known as SC2) for 15 min. The sapphire was rinsed in distilled water, blown dry with a nitrogen gun, and baked in air at 150°C for 20 min.

Sapphire was then spin-coated with positive photoresist (*SHIPLEY 1818, SHIPLEY Co., INC., SUNNYVALE, CA*) for 30 sec at a spin rate between 4000-5500 rpm, giving a resist thickness of approximately 1.6 μm . Sapphire with photoresist on the surface was baked at 90°C for 20 min, and

then the sapphire surface was selectively exposed to *uv* light in a projection printer (CANON, SAN JOSE, CA) using various masks.

Masks were designed on a computer using various software and transferred onto a glass plate with a pattern generator (PATTERN GENERATOR, GCA CORPORATION, BEDFORD MA). Mask patterns included channels bounded by sinusoidal waves, rectangular channels, and rectangular holes. It was possible to create a grid-like pattern by exposing the rectangular channel mask once, rotating the sample 90°, and then exposing the same pattern a second time. After exposing the photoresist with the projection printer, the samples were soaked in developing fluid (SHIPLEY MICRODEPOSIT DEVELOPER, SHIPLEY CO., INC., SUNNYVALE, CA) for 30 sec, which dissolved the exposed photoresist and left a pattern on the sapphire surface identical to that on the mask, but reduced in size by a factor of 4. The sapphire was rinsed in distilled water, blown dry with a nitrogen gun, and baked in air at 120°C for 20 min.

Ion-beam etching transferred the pattern from the photoresist to the surface of the sapphire. An ion mill (VEECO MICROTCH SYSTEM, VEECO INSTRUMENTS INC., NEW YORK, NJ) using a perpendicular incidence argon ion beam etched the surfaces. The thickness of the photoresist together with the etch rate of the photoresist under the given conditions produced surface features approximately 0.5 μm deep. Prior to bonding sapphire that was lithographically processed was cleaned, using the procedures previously described.

3.6 Bonding

The substrates were removed from the deposition chamber and loaded into a graphite element hot press with the niobium sandwiched between them. Graphite dies with Graphoil® (UCAR CARBON COMPANY INC., CLEVELAND, OH) pieces between each piece were stacked below and above the sample in such a way that the metal interlayer of the sample sat in the center of the hot zone of the heating elements. Thin pieces of boron nitride (ADVANCED CERAMICS CORP.,

CLEVELAND, OH) were placed between the sample and the dies so that they did not react with each other. A desired load was applied to the sample using a hydraulic pump and the graphite die apparatus. The hot press was pumped down to a pressure below 8×10^5 torr and then a voltage was applied to the elements to heat the chamber. The temperature was increased at $4^\circ\text{C}/\text{min}$ to the processing temperature of either 1400°C or 1150°C , held for 6 h, and then cooled at $2^\circ\text{C}/\text{min}$ to room temperature. Occasionally, while heating, the pressure inside the chamber would increase to $\geq 8 \times 10^5$ torr. When this occurred the temperature was held until a pressure $< 8 \times 10^5$ torr was reached. Usually the program was held for 30 min at approximately 400°C and again for 30 min at approximately 800°C . If the program was above 1000°C , holding the temperature program was avoided because the temperature was very near the melting temperature of copper, 1085°C . It was desired to have liquid copper for the same amount of time in all of the experiments.

3.7 Mechanical Testing

The as-processed samples were removed from the hot press and machined into regular beams $3 \text{ mm} \times 3 \text{ mm} \times 3 \text{ cm}$. The rectangular samples were first cut into 3 mm thick plates using a diamond blade (NATIONAL DIAMOND LAB INC., LOS ANGELES, CA) on a K.O. Lee surface grinder. The plates were ground flat, and striation marks left on the plate surfaces by the surface grinder were removed by polishing with $15 \mu\text{m}$ diamond paste on a large piece of glass. The plates were polished on vibratory polishers (SYNTRON FMC CORPORATION, HOMER CITY, PA). A nylon cloth with adhesive backing was placed on the Syntron surface, the flat plates were loaded into weighted polishing jigs that rest on the nylon cloth and slowly circle the perimeter of the cloth as a result of the vibratory action of the Syntron. Successively smaller grit diamond pastes: $15 \mu\text{m}$, $6 \mu\text{m}$, $3 \mu\text{m}$, and $1 \mu\text{m}$ (SOUTH BAY TECHNOLOGIES, SAN CLEMENTE, CA) were applied to the nylon surface along with lapping oil (BUEHLER INC, LAKE BLUFF, IL) to achieve a smooth surface with a minimal amount of defects. A high-speed saw (STRUERS, WEST LAKE, OH) with a diamond blade cut the plates into

beams of the desired dimensions. The edges of the beams adjacent to the polished surface were beveled on a 6 μm diamond wheel to minimize sharp edges and defects that could decrease the beam strength. By grinding the corners of the beams it was possible to label them with a scheme that was permanent and would not come off during cleaning, and that differentiated their location relative to the bulk sample during processing. Prior to testing, the beams were ultrasonically cleaned for 15 min in the following: soap plus tap water, distilled water, acetone, isopropyl alcohol, and denatured HPLC grade ethanol (*ALDRICH CHEMICAL COMPANY INC., MILWAUKEE, WI*). The beams were blown dry with a hot air gun and then mechanically tested.

Room-temperature strength tests were performed with an Instron mechanical tester (*INSTRON, CANTON, MA*). A four-point bend testing jig with an inner span of 9 mm and an outer span of 25 mm was utilized. A displacement controlled flat-crosshead was lowered until it just contacted a steel sphere that rested on top of the jig. The crosshead was then lowered at a rate of 0.05 mm/min until the beam fractured. The load was measured with a 100 kG load cell and sent to a strip chart recorder that plotted the load versus the displacement. The mode of fracture was recorded and the strength was calculated using the load at failure and accurate measurements of each beam's cross sectional area made with a micrometer.

3.8 Microstructural Evolution

Many of the experiments with sapphire windows were performed to monitor the morphology of the copper layer during processing. Therefore, the time the sample was at the processing temperature is always indicated with the corresponding micrograph. The time these samples were processed may vary from the time previously mentioned in the bonding section because it was desired to see the morphology of the copper at intermediate times. A marker was usually placed on the surface of the sapphire either by using a microhardness indenter (*MARK V LABORATORY, EAST GRANBY, CT*) or by scratching with a diamond scribe so that the same location

on the sample could be found after each anneal. The samples were annealed at the processing temperature in a vacuum furnace (CENTORR INC., SUNCOOK, NH) at pressures typically lower than 5×10^{-5} torr. The furnace had tungsten mesh elements and molybdenum shields. The temperature was increased at $10^{\circ}\text{C}/\text{min}$ and held at the processing temperature for variable amounts of time; the samples were cooled at $30^{\circ}\text{C}/\text{min}$. Often, once at temperature, the pressure in the furnace reached values below 7×10^{-6} torr. After each anneal, numerous micrographs of the specified locations of the samples were taken at various magnification and recorded on digital media.

3.9 Bicrystal Fabrication

One sample was fabricated that had two single crystals misoriented by a tilt angle, making it possible to study the grooving of a single asymmetric tilt boundary. An asymmetric tilt boundary was used because of its relative ease of fabrication in an attempt to see if the expected grooving result would occur for alumina in contact with liquid copper and a niobium foil. A schematic that illustrates the fabrication steps for the bicrystal sample is shown in **FIGURE 3.2**.

First a piece of *c*-plane sapphire was cut randomly into two pieces on a slow-speed saw. These two pieces would eventually act as the seed crystals. The edges that resulted from the cut were polished on a nylon cloth using successively smaller-grit diamond pastes ($15\text{ }\mu\text{m}$, $6\text{ }\mu\text{m}$, and $1\text{ }\mu\text{m}$). The two seed crystals were ultrasonically cleaned in soap plus distilled water, distilled water, acetone, and isopropanol for ≥ 15 min. The seeds were rotated relative to their original orientation, and then diffusion bonded to a polished piece of undoped polycrystalline alumina fabricated by Robert Marks¹⁰⁵ in the graphite hot press at 1300°C for 5 h with an applied load of 10 MPa. The diffusion-bonded assembly (seeds and polycrystalline material) was sandwiched between *c*-plane sapphire windows for structural support. Prior to diffusion bonding, additional anneals in low oxygen partial pressures were performed to grow the grain boundary into the polycrystalline

material (1500°C for 24 h, 1600°C for 24 h, 1700°C for 24 h, 1700°C for 92 h, 1750°C for 92 h, 1800°C for 24 h, 1850°C for 74 h, and 1600°C for 4 h). Once the grain boundary had extended sufficiently by growth of the seeds into the polycrystalline material, the sample edge was ground using 15 μm diamond paste on glass to expose the grain boundary at the surface. **FIGURE 3.3** shows the grain boundary at various stages of growth. The grain boundary shown in (a) does not resemble the grain boundary shown in (b), but a sufficient amount of material has been removed at the surface from polishing between these two steps, which caused the difference. The bicrystal surface was hand-polished using 15, 6, and 1 μm diamond paste on nylon cloth. Then the bicrystal was bonded using metal interlayers with an applied load of 2.2 MPa at 1400°C for 6 h. The grain boundary was in contact with the metal during bonding. Slices were taken at various times after post-bonding anneals to study the grain boundary topography.

3.10 Grain Boundary Grooving

It was possible to measure the extent to which grain boundaries grooved when liquid copper was in contact with them using simple wetting experiments. Small amounts of copper wire were cleaned (following the same procedures described in the BONDING section) and bent into a U shape. The copper wire was placed on niobium and polycrystalline alumina substrates from the same source as the material used in bicrystal fabrication. These samples were placed into an argon environment furnace (CENTORR INC., SUNCOOK, NH) and annealed for various times at 1400°C. The copper was etched away in a 5:1 $\text{H}_2\text{O}:\text{HNO}_3$ by volume solution and then AFM was performed on the region in contact with the liquid drop.

3.11 Atomic Force Microscopy

Surface topography measurements of various samples were performed using an atomic force microscope (PARK INSTRUMENTS, SUNNYVALE, CA). In some cases it was necessary to etch the metal interlayer to allow the characterization of the ceramic surface only. The metal was etched in

70% by volume HNO_3 and 30% by volume HF. Typical etch times were 3-4 days to remove all of the metal interlayer. Unannealed sapphire substrates were soaked in the etchant solution for the same time, and the surface topography was unaffected by etching. Using the software package that controls the AFM, images were made in contact mode of the surface topography. Both line profiles and three-dimensional images obtained from the AFM data were used. AFM was done with a typical gain value of about 0.15 and a frequency of 1 Hz or less.

(a)

(b)

(c)

(d)

FIGURE 3.1: Illustration of (a) bonded assembly with sapphire as the substrate and (b) polycrystalline alumina as the substrate. In (c) the sample from (b) has been machined into plates, and in (d) these plates have been machined into beams, which can be tested using the 4-point bend test method.

FIGURE 3.2: Schematic showing (a) the seeding and growth of the bicrystal, and (b) the bonded assembly.

(a)

(b)

20 μm

FIGURE 3.3: The bicrystal sample (a) before the grain boundary has grown extensively into the polycrystalline material and (b) after the grain boundary has grown significantly and the remaining polycrystalline material has been removed leaving the grain boundary exposed at the free surface.

4. RESULTS AND DISCUSSION

Before discussing the details of microstructure development in the copper/niobium/alumina system, a brief discussion of joint strength is used to show that this system can produce strong and reliable bonds. These characteristics provided the motivation for studying the microstructural evolution.

The strength of polycrystalline samples was found from the four-point bend technique. For the geometry of the particular four-point bend tester used, the fracture stress is found from (Appendix I):

$$\sigma_f = \frac{24gP_f}{bd^2} \quad (4.1)$$

g = gravitational acceleration

P_f = load at failure

b = beam width

d = beam height

Usually, the mechanical reliability of samples is determined from fracture energy measurements. The four-point bend stress is not a good substitute for fracture energy measurements for the purpose of fracture prevention. The four-point bend stress, however, provides a method of correlating the processing conditions of a bonded assembly to its strength. The size and distribution of defects in a bonded assembly will be the critical factors that limit strength. When failure occurs from a crack that has completely propagated in the ceramic, improvements made at the ceramic/metal interface will not increase strength, and any attempts to increase strength need focus on the processing of the ceramic material. Failure from a crack that has completely propagated along the ceramic/metal interface suggests that improvements in strength

could be made by using a different set of bonding/processing parameters with the intent of reducing the severity and frequency of defects at the ceramic/metal interface. Four-point bend strength measurements of the bonded assemblies give usable data to make connections between flaw size, severity, and location (ceramic or interface) for assemblies processed differently. A more severe or larger flaw will tend to cause the assembly to fail at a lower stress. Analysis of micrographs of the fracture surfaces then allows further correlation between microstructure and strength. Strength data combined with micrographs of fracture surfaces facilitate the determination of the relationship between microstructure, processing, and properties, the crux problem for the materials scientist.

4.1 Strength Data

4.1.1 Diffusion-Bonded Samples

Polycrystalline alumina blocks were solid-state diffusion bonded to a niobium foil at 1400°C for 6 h with an applied load of 2.2 MPa and were tested for mechanical strength (**FIGURE 4.1**). These samples were weaker than any samples that contained copper and all of them failed at the ceramic/metal interface. These samples had an average strength of 94 MPa with a standard deviation of 18 MPa and a Weibull modulus of 5.5, suggesting a significant amount of scatter in the data. When diffusion-bonded plates were annealed at 1400°C for 12 h in vacuum with no applied load, the strength decreased and became unmeasurable; beams failed during the machining process. The flaws in diffusion-bonded beams must have become larger and/or more severe when no load was applied at elevated temperature. Increasing the processing time for diffusion-bonded samples does not significantly improve strength, and may even degrade the strength characteristics of the bonded assemblies.

Data from studies⁸ using the same materials showed that the average roughness of the polished alumina and the as-received niobium are 30 nm and 100 nm, respectively. It seemed

plausible that by depositing a thin film ($1.3\text{ }\mu\text{m}$ thick) of copper onto the alumina surfaces the strength characteristics might be significantly improved. Both roughness values are less than the copper film thickness ($1.3\text{ }\mu\text{m}$), and thus it seems reasonable that the amount of liquid formed could fill many interfacial gaps and reduce the area fraction and severity of unbonded regions along the niobium/alumina interface. The combination of the dissolution of $1.3\text{ at. \%}$ niobium in liquid copper at 1400°C and the diffusion coefficient of niobium in liquid copper, which is expected to be orders of magnitude higher than the self-diffusion coefficient for niobium, should enhance the rate of niobium redistribution relative to that when no liquid is present. The filling of interfacial voids by the liquid, transport of the niobium through the liquid to shrink and eliminate interfacial voids, and dewetting of the liquid film all contribute to a higher area fraction of alumina-niobium contact and a decrease in the quantity and severity of interfacial flaws, which could lead to higher strengths compared to samples processed without a liquid.

4.1.2 Samples Processed With a Copper Film at 1150°C and 1400°C

Samples processed with a $3\text{ }\mu\text{m}$ thick film of copper deposited on the alumina surfaces were also tested for mechanical strength. The effects of various processing conditions including temperature and pressure on the strength of the alumina–copper/niobium interlayer interface were desired. These results have been published previously.^{7,72} From the strength data shown in **FIGURE 4.1** it appears that it is possible to produce interfaces at 1150°C with an applied load of 7 MPa that match the strength of bonds produced at 1400°C with an applied load of 2.2 MPa . However, samples processed with higher load at lower temperature had a lower average strength than those bonded at lower load and higher temperature. Samples processed at 1400°C had a mean fracture strength of $235 \pm 15\text{ MPa}$ while samples processed at 1150°C had a mean fracture strength of $188 \pm 52\text{ MPa}$. 71.4% of the beams processed at 1400°C failed in the ceramic compared to 33.3% that failed in the ceramic for beams processed at 1150°C . This suggests that at the higher processing

temperature inherent flaws in the ceramic were less severe than the interfacial flaws in the majority of the beams. In most cases, strength was limited by the ceramic material of the assemblies processed at 1400°C, and thus varying other processing conditions at 1400°C would probably not increase the strength any further. Comparison with previous studies^{5,7,9} suggests that increasing the applied load at lower processing temperatures can lead to increased strength, however, it seems that the highest strengths are obtained by bonding at higher temperatures. The increased applied load during processing can accelerate the breakup of the copper film, which leads to more niobium/alumina contact and fewer large patches of copper at the interface. Since copper does not adhere to alumina as well as niobium does, large patches of copper at the interface could lead to decreased strengths. Evidence exists to suggest that increased copper thicknesses would decrease the strength of bonded assemblies due to the decreased W_{ad} of the copper/alumina interface compared to the niobium/alumina interface and the increased amount of copper/alumina interfacial contact.¹⁰⁶ The breakup of the continuous liquid copper film into a dispersion of particles at the interface is beneficial to the mechanical properties of the bonded assemblies because the particles can plastically deform and increase the toughness of the ceramic/metal interface. Mechanistically, the increased load causes the niobium foil to deform as it is placed in more intimate contact with the alumina. More initial niobium/alumina contact leads to smaller and more infrequent regions of liquid coverage at the ceramic/metal interface. The edges of the sample also showed evidence that more liquid was extruded when the higher load was used; small droplets (0.5–1 mm in size) of copper were visible around the edges of the sample (this has also been seen in a previous study⁵). This decreased the amount of liquid copper at the interface. One droplet with a radius of 0.5 mm could decrease the copper film thickness as much as 0.8 μm . The breakup of liquid patches into discrete particles *via* Rayleigh instabilities is faster for patches that are initially smaller.

More thorough studies on the effect of copper thickness suggest that as film thickness is increased the Weibull modulus increases, and that when a 13.0 μm thick copper film is used the mean fracture strength and standard deviation of the interfacial failure data are essentially indistinguishable from the ceramic failure data.^{8,73} Bonds processed at 1400°C with 5.5 μm thick film of copper experienced almost no change in bend strength compared to samples with a 3 μm thick film, but the Weibull modulus decreased from 15 to 6 when the copper film thickness was increased from 3 μm to 5.5 μm .⁷³ The increased scatter in the strengths of samples processed with a thicker copper film indicates that perhaps the extent of breakup of the copper film varied greatly from beam to beam and suggests significant irregularity in the film morphology and microstructure of the samples with the thicker copper film.

Temperature and pressure play an important role in joint characteristics of assemblies that are processed with a copper film. At a fixed bonding temperature of 1150°C, increasing the applied load during vacuum bonding from 2.2 MPa to 5.1 MPa to 7 MPa increased the average strength in four-point bend tests from $78 \pm 22 \text{ MPa}$ ^{7,72} to $181 \pm 45 \text{ MPa}$ ⁵ to $188 \pm 52 \text{ MPa}$ ^{7,72}. Failures primarily occurred along the alumina-niobium interface. At a fixed bonding pressure of 2.2 MPa, increasing the bonding temperature from 1150°C to 1400°C increased the four-point bend strength from $78 \pm 22 \text{ MPa}$ to $235 \pm 15 \text{ MPa}$,^{7,72} and approximately 75% of the samples failed in the ceramic. Ceramic failures were also observed in high-temperature fracture tests up to 1100°C for samples processed at 1400°C, which suggests that a strong interface with potential for use at elevated temperature is formed.^{7,72} Increasing the bonding pressure does lead to increased strengths, but does not fully duplicate the increased strengths that occur when samples are processed at a higher temperature. This suggests that pressure and temperature increases lead to fundamentally different paths of interfacial microstructure development, one possibly dictated by deformation and creep and the other by diffusional processes.

4.1.3 Single Crystal Samples

Sapphire wafers and cylindrical sapphire plugs spanning a range of surface finish/roughness were produced and bonded using copper/niobium/copper interlayers in an effort to examine and characterize the effects of surface roughness on ultimate joint properties. The effect of surface roughness on the strength and failure characteristics of polycrystalline samples is discussed elsewhere.⁷³

Two samples were roughened using UV lithography to introduce controlled roughness without damaging the sapphire. A series of trenches that were 10 μm wide, separated by 20 μm , that covered the surface in two orthogonal directions were etched onto the surface of the sapphire samples. These samples failed to survive all of the fabrication steps of specimens prepared for mechanical strength testing. In one case, it was desired to introduce lithographic cavities in sapphire plugs, but the lithographic tools and equipment could not accommodate samples thicker than 1 mm, which are too thin to test on the four-point bend tester. Attempts to modify the mask aligner to accommodate larger samples were not effective. In the other case, a thin lithographically processed sample was successfully diffusion bonded to polycrystalline alumina to make the sample large enough to span the outer span of the jig on the four-point bend tester, but all of these samples failed at the sapphire/polycrystalline alumina diffusion bonded interface during machining of test specimens, yielding no useful information about the lithographically processed sapphire/niobium interface.

One sample that did yield mechanical test specimens was a sample of sapphire cylinders with bonding surfaces roughened on the surface grinder and then processed at 1400°C with 2.3–3 μm of copper present on the sapphire surface and an applied load of 2.2 MPa. The strength of these samples is compared with samples with polished sapphire surfaces (FIGURE 4.2).⁷² Of the roughened samples that survived to mechanical testing, the average strength was 166 MPa with a

standard deviation of 22 MPa compared to polished surfaces which had a mean strength of 130 MPa with a standard deviation of 21 MPa. Some of the roughened samples displayed stable crack growth behavior during mechanical testing. In these samples the load-displacement curves had many peaks and valleys, due to loading of the crack and then slight extension of the crack tip, causing unloading to occur. Half of the samples failed by stable crack growth, and half of the samples failed in a normal catastrophic failure mode. The samples that failed catastrophically seemed to follow the same strength trend as samples with polished surfaces and were unaffected by the roughened surface. It seems that the surface grinder introduced significant damage into the surface of the ceramic, and in some cases caused the samples to be cracked at the interface before a load was ever applied. After the beams failed, the ends on either side of the interface hit the surface of the testing jig, but usually there was not enough force to cause any further damage to the samples. One sample that failed along the interface shattered into many pieces when it hit the surface of the testing jig, probably as a result of surface damage and crack branching that might have occurred during testing. Microscopic cracks at the interface, as a result of roughening, provided area of no metal/ceramic contact and a low resistance crack path that caused these samples to fail by very slow stable crack growth at low fracture strengths.

4.2 Fractography

An attempt to correlate strength characteristics to microstructure was made by analysis of micrographs of fracture surfaces fabricated using various processing parameters.

4.2.1 Samples containing Copper

Fracture surfaces from bonds processed at 1400°C with an applied load of 2.2 MPa have been discussed previously,^{5,7-9} and a typical micrograph is shown in **FIGURE 4.3**. Matching regions of the fracture surface for the metal and the ceramic side are shown such that points equidistant from the line marked “Mirror Plane” were adjacent to each other and at the interface in the bonded

assembly. In the micrograph, regions where the ceramic grains have imprinted themselves onto the metal surface are thought to be regions of intimate contact between the metal and the ceramic. Other regions where the metal surface has a featureless area corresponding to an area containing grain boundaries on the ceramic side are thought to be unbonded regions at the interface. The remaining regions of the fracture surface include torn copper particles that can be matched with their mirror image on opposite sides of the interface and regions of ceramic pullout. Ceramic pullout and tearing of copper particles indicate regions of contact and relatively strong adhesion at the interface.

Fracture surfaces from samples processed at 1150°C with an applied load of 7 MPa are shown in **FIGURE 4.4** and **FIGURE 4.5**. **FIGURE 4.4** is a typical fracture surface for samples that failed at relatively high strength. Features similar to those in the sample processed at 1400°C can be seen such as ceramic pullout and copper tearing. Upon inspection there do not appear to be unbonded regions similar to those seen in the sample processed at 1400°C. There is a relatively large region of ceramic pullout, which indicates that although failure occurred at the interface, flaws in the ceramic played a role in limiting the strength of the assembly and providing a crack path of least resistance. There is also a significant decrease in the amount of copper tearing and “balling-up” that occurs in samples processed at 1150°C compared to samples processed at 1400°C. It has been shown previously that the interfacial fracture energy of thin-film interconnect structures can increase 1500% due to plastic dissipation when copper film thickness is increased from 0.3 μm to 16.4 μm .¹⁰⁷ A similar effect could be occurring as the copper morphology changes to more of a “ball” like structure at 1400°C, which experiences more plastic work during fracture than the film or “pancake” morphology seen at 1150°C and increases the interfacial fracture toughness. Increased solubility of niobium in liquid copper at 1400°C could aid the copper/alumina adhesion by producing a fine dispersion of niobium precipitates at the metal/alumina interface (like those seen

in **FIGURE 4.25** (b)). The copper could then adhere to the niobium precipitates, and the niobium precipitates adhere well to the alumina surface, which could lead to increased fracture strengths. **FIGURE 4.5** shows a sample that failed at a relatively low load. The metal side of the fracture surface is almost completely covered in copper. The low strength of this sample can probably be attributed to a low area fraction of niobium/alumina contact as previous studies suggest the trend for lower strengths to occur in samples with increasing amounts of copper/alumina contact.^{7,9,106} There are isolated regions where it appears that copper has dewetted the niobium surface. In some of these cases the ceramic side of the fracture surface in this region is missing a grain or has a hole in it. It is likely that the copper cannot be seen in these regions because pullout occurred and alumina grains are still adhered to the metal surface, but this only occurred in 3.5% of the fracture surface area shown in **FIGURE 4.5**.

4.2.2 Single Crystal C-Plane Cylindrical Samples

It was not possible to image the bonded interface of the single crystal cylindrical samples because the focal length of the optical microscope cannot accommodate samples that are 1" thick. There is also much greater difficulty in determining bonded and unbonded regions of the fracture surfaces in the cylindrical sapphire samples because there are no alumina grain boundaries to locate on opposite sides of the fracture surface. However, it is possible to match torn copper particles on both sides of the interface. **FIGURE 4.6** shows a typical example of a fracture surface in a sample that failed catastrophically. Large featureless unbonded regions similar to those seen in the polycrystalline sample processed at 1400°C can be seen. It seems that the unbonded region on the metal side of the fracture surface corresponds to a region of the sapphire that has increased roughness. The smoother region seems to look the same on both sides of the fracture surface. Non-uniformity in the roughness of the sapphire surface and local irregularities in the sapphire surface morphology combined with localized depressions in the surface of the niobium could have induced

liquid flow. Some regions at the interface would thus be depleted of liquid while others would have an excess of liquid. Substantial rearrangement of mass by solid-state diffusion mechanisms would have to occur in regions that lacked liquid to initiate sapphire/niobium contact. These regions could subsequently form strong bonds by solid-state diffusion-bonding mechanisms. However, solid-state contact growth requires extended times at elevated temperatures, and it would seem that it does not occur after 6 h at 1400°C. The absence of the liquid in rougher areas of the interface caused large unbonded regions to be present after bonding, and therefore, low failure strengths.

FIGURE 4.6 (c) shows a region of fracture surface from a sample that failed at 48.2 MPa. Instead of failing catastrophically as expected, the sample failed very slowly and the load-displacement curve during fracture followed the loading and unloading cycle that occurs during stable crack growth. This image shows two unbonded regions labeled *a* and *b*. In *a*, the unbonded region closely resembles regions from other samples. In *b* the unbonded region has a slight yellow-brown discoloration. If this unbonded region were to extend all the way to the edge of the sample then it is possible that ink, water, and glue used during machining could have penetrated into this unbonded region and caused this discoloration. This unbonded region could then act as an interfacial crack that becomes more compliant as the sample is loaded, creating stable crack growth-failure conditions and causing the sample to eventually fail at a very low load, which was observed in half of the single-crystal samples that survived to mechanical testing.

Fracture surfaces from single-crystal cylindrical samples with polished surfaces⁷² were quite different from the fracture surfaces shown from the roughened surface. The unbonded regions in the samples with polished surfaces are much smaller and more uniformly distributed than the unbonded regions in roughened samples. This could be a direct result of a longer wavelength roughness (peak-to-peak width on the surface of the sapphire) that results from the roughening

method. Polished surfaces might have a much smaller roughness amplitude and wavelength, which produces more uniformly distributed unbonded regions that are smaller in size.

4.2.3 Samples not containing copper

Polycrystalline samples prepared without copper were comparable in strength to the sapphire samples with copper. Samples without copper exhibited fracture behavior unlike any other sample. In these samples the crack sometimes deviated into the niobium foil and caused it to tear. This can be seen by regions of shiny metal appearing on the ceramic side of the fracture surface. A region where the torn niobium foil can be seen on both sides of the fracture surface is marked **a** in **FIGURE 4.7**. Chemical analysis of these regions using EDS prove that niobium appears on both sides of the fracture surface. Inspection of the EDS map suggests that the niobium is more prone to tear in regions adjacent to the smaller sized grains in the alumina. An EDS scan of these regions also shows that silicon is present in regions where the niobium has torn. It is likely that the silicon present in the alumina could easily be transported from the glassy phase in the alumina to the metal where the alumina grain boundary density is high because the grain boundaries act as a high diffusivity path. A sufficiently low diffusivity of silicon in niobium would then cause a higher concentration of silicon in regions of the ceramic/metal interface where the ceramic had a fine grain structure. This increases the likelihood that the silicon could react with the niobium and form a brittle phase that precipitates at regions having a high density of grain boundaries. Prior work has identified the brittle phase as Nb_5Si_3 .⁶⁹

Fractography of the diffusion-bonded samples shows featureless unbonded regions (**b** in **FIGURE 4.8(d)**) as seen in polycrystalline samples, and areas of faceted boundaries between unbonded and bonded regions (**a** in **FIGURE 4.8(d)**) as previously seen by Reimanis.³⁵ These faceted features are also evident when sapphire is diffusion bonded to niobium as seen in **FIGURE 4.8(e)**. Polycrystalline alumina/niobium interfaces are discussed in further detail in previous work.⁸ The

featureless unbonded regions are regions that probably were not in contact with the alumina, and the bonding front did not grow through these regions.

Another feature shown in **FIGURE 4.8(d)** is the mottled black region labeled **c**. This feature is not seen when niobium is diffusion-bonded to sapphire (**FIGURE 4.8 (e)**). It is also not seen in unannealed niobium foil or niobium foil that has been annealed in vacuum for 6 h at 1400°C, but it is seen when niobium is diffusion-bonded to polycrystalline alumina (**FIGURE 4.7 (a)** and **FIGURE 4.8(d)** labeled **c**). The polycrystalline alumina contains small amounts of a glassy phase, which could supply a liquid phase at 1400°C when copper is not present at the interface. It is believed that the silicon in this glassy phase reacts with the niobium to form a brittle silicide that has been shown to tear during fracture of the diffusion bonded samples.^{8,69} It is possible that the oxygen from the glassy phase also reacts with niobium to leave an oxide that has the appearance of the mottled black region on the niobium surface seen in **FIGURE 4.8(d)** labeled **c**. Usually, regions of niobium tearing that can be found on ceramic sides of diffusion-bonded fracture surfaces correspond to regions of this oxide formation on the metal side of the fracture surface, which should be expected if this chemical reaction is occurring.

Anneals at 1400°C in vacuum for 12 h with no applied load caused the strength of diffusion-bonded samples to decrease to values so low that samples did not survive preparation of mechanical test specimens. Results found by Reimanis³⁵ show that the bonded area grew after anneals at elevated temperatures, which seems to contradict the decrease in strength found in this study. The alumina and niobium are both polycrystalline. It is possible that certain regions of niobium/alumina contact had high interface energy compared to the sum of the alumina and niobium free surface energies. In these regions bonding was not favored, and these regions grew at elevated temperature. It seems unlikely that the alumina and niobium would have bonded in the first place, however, if the interface energy was higher than the sum of the free surface energies.

Another more likely possibility is that the extended anneals allowed for more silicon to segregate to the interface. This produced a greater fraction of glassy phase and brittle silicide precipitates at the interface. The greater abundance of brittle silicides at the interface could have caused the bonds to exhibit the decreased strengths after annealing and fail during machining.

Comparatively, polycrystalline samples with copper present formed the strongest bonds. Also, these samples had much less unbonded region compared to samples without copper.⁸ Samples processed at lower temperatures often had regions of large copper coverage, which has been shown to correlate with lower average strengths in earlier studies.⁷ It seems that samples with high strength all had significant breakup of the copper film into isolated droplets, a minimum amount of area of unbonded region,⁸ and a large amount of niobium in contact with the alumina such that mirror images of features on the alumina surface were visibly imprinted on the niobium foil after fracture. Therefore, there is an interest in examining the factors that lead to film breakup including: time, crystallography, and thermal grooving.

4.3 Microstructure Evolution in Model Samples

The breakup of the copper film in alumina bonded *via* copper/niobium/copper interlayers has proven to be an important factor in the development of the interfacial microstructure, which ultimately affects the strength of bonded assemblies. The transparency of sapphire substrates allowed the possibility to follow and track the development of the interfacial microstructure at the processing temperature with time. It has been shown that some crystallographic planes of sapphire are unstable when in contact with vapor.⁷⁷⁻⁸¹ Specifically, the *c*-plane is a stable plane and the *m*-plane is an unstable plane. When *c*-plane sapphire is annealed in air, a terrace-and-step morphology develops on the surface (the terraces are parallel to the *c*-plane), and when *m*-plane sapphire is annealed in air, the instability causes a saw-tooth morphology to develop on the surface. The fabrication of samples with different crystallographic planes allowed not only the

determination of how surface crystallography might affect the breakup of the film, but also the determination of whether the instability still exists for sapphire in contact with copper/niobium, and if the instability does exist, the determination of how surface topography might effect the breakup of the copper film.

The problem of liquid redistribution at a bimaterial interface is complicated. When a liquid is between two materials that it wets, it will spread. When a liquid is between two materials that it does not wet it tends to form a somewhat spherical particle at the interface, effectively minimizing the area of high-energy interface. When the liquid is between one material that it wets and one material that it does not wet, as is the case for liquid copper between niobium and alumina, the condition for liquid spreading, as discussed previously, is $\gamma_1 + \gamma_2 < \gamma$. In the alumina/copper/niobium system the energy of the copper/niobium interface is considerably lower than the energy of the copper/alumina interface. One would expect that liquid copper would be pulled out of chasms, grain pullouts, and V-shaped cracks in alumina to reduce the area of high energy interface. Capillary forces would cause the liquid to flow from larger interfacial gaps into smaller ones. As the liquid flows out of an interfacial region it leaves behind a new gap, which could act as a defect. During liquid redistribution there is a constant dynamic process of generation and removal of interfacial defects. The local film thickness, local surface topography of both the sapphire and the niobium, crystallography of niobium grains, and defect geometry are all going to play competing roles in attracting the liquid from one interfacial region to another. Snapshots of the interfacial microstructure at different stages in development show the competing effects of these factors as the liquid is redistributed and migrates from one region to another at different times.

The interfacial microstructure of samples processed at 1400°C has been shown in previous work.⁹ After 6 h the breakup of the copper film was at very different stages of development at

different locations in the sample and there was considerable microstructural variability. It was desired to watch the breakup more closely and follow microstructure as it develops through the different stages of film breakup. It seemed reasonable that using a lower processing temperature (1150°C), much closer to the melting temperature of copper (1085°C), would decrease solubilities and diffusivities, facilitating the careful tracking of the microstructural development.

4.3.1 *C-plane samples*

Previous work describes how the points of contact between the niobium and the sapphire that initiate the breakup of the copper film are niobium grain boundaries and asperities in the niobium foil.^{8,9} The interfacial microstructure and liquid breakup affects the defect structure, and ultimately the strength of samples. Samples fabricated using transparent sapphire as the ceramic substrate allowed nondestructive investigation of microstructural development at the niobium/alumina interface. Images taken at the same location at various times during processing allowed the mechanisms and processes by which the metal/ceramic interfacial microstructure develops to be identified and characterized. Images of *c*-plane sapphire are shown in **FIGURES 4.9–4.12**. These samples were processed at 1150°C just above the melting temperature of copper (1085°C) in an attempt to document the breakup of the copper film. Also, lithographically processed cavities (sinusoidally shaped) were introduced in the samples shown in **FIGURES 4.11** and **4.12** to create localized regions of increased copper thickness. This further aided the ability to obtain micrographs showing significant events in the breakup of the copper film. **FIGURES 4.9** and **10** show interfacial microstructures after a 6 h bonding cycle with an applied load of 2.2 MPa, and then additional anneals in vacuum (no applied load) such that the total time at 1150°C is 15 h, 22 h, 29 h, 36 h, and 43 h in a), b), c), d), and e) respectively. There is very little indication of interfacial porosity, but in both cases the area fraction of niobium/alumina contact is low, 59% and 45% in **FIGURES 4.9** (a) and **10** (a) respectively. The sequence shown in **FIGURE 4.9** shows lines of

niobium/sapphire contact that develop and persist, which indicates that niobium grain boundaries play the major role in initiating film breakup, and copper remains trapped in the grain boundary groove, thereby outlining the niobium grains.

The sequence in **FIGURE 4.10** shows points of contact that develop with time, which suggests that irregularities in the surface, probably asperities in the niobium foil also provide sites of contact initiation. After a total of 43 h at 1150°C, the niobium/alumina contact area fraction has increased to 77% and 75% in **FIGURES 4.9** and **4.10** respectively. Although the general trend is for alumina/niobium contact to grow with time it is not true that all regions of initial asperity contact will grow. In some cases, a high-energy surface of the niobium could be exposed or the crystallography of the niobium/alumina interface could have a very high energy at the asperity surface. A driving force would thus transport mass to smooth the asperity causing it to disappear, which does occur in the micrographs, but is far less noticeable than the asperities from which contact expands. The differences in evolution patterns may reflect statistical differences in the crystallography, roughness, and/or texture of the niobium foil. Surface roughness may increase the number of contact points and accelerate the growth of niobium/alumina contact area, and grain boundaries and other irregularities in the surface of polycrystalline alumina substrates may also contribute to a higher degree of film breakup after bonding than is observed with sapphire.

Samples that have lithographically processed cavities facilitated the following of grain boundary groove ridge growth. When a ridge intersected a cavity, contact between the groove ridge and the sapphire initiated in the unetched region, and eventually the ridge grew through the etched region to the sapphire surface. Asperities in the niobium will also initiate contact in unetched regions. In **FIGURE 4.11** an area of a lithographically processed sample is shown. In the 0.5 μm deep cavity it is evident that a grain boundary of the niobium is grooving and rising to the sapphire surface at the location marked **a**. A triple point associated with that particular grain boundary is

first visible after 7 h and it continues to grow and groove more until it is filled with copper between 15 and 63 h. In the 63 h micrograph the shape of the grain boundary is still visible because the copper at the surface has taken its shape in the width of the grain boundary groove. After 127 h the liquid has drained from the grain boundary groove and the grain boundary groove is visible again. **FIGURE 4.12** shows a region of the sample that has asperities in the niobium foil initiating the contact with the sapphire. In this sample it is also apparent that the asperities play a much more important role than the grain boundaries. A grain boundary marked **a** is visible early on in the development of the microstructure, but becomes overwhelmed by asperities in the niobium foil and is no longer evident even after 7 h.

The disappearance and rearrangement of niobium grain boundaries will become a recurring theme in many of the following micrographs. Previous studies have shown that rapid grain growth of niobium can occur in the presence of liquid copper.⁵ In a bonding cycle of 6 h at 1150°C (conditions very similar to the present study), it was found that niobium grains grew from an average size of 115 μm to an average size of 160 μm in the presence of liquid copper. In this study, measurements showed that the niobium grains grew from an average size of 25 μm to 54 μm when in contact with liquid copper at 1150°C. At 1400°C, the niobium grains grew to an average size of 123 μm when no copper was present, and to an average size of 146 μm when liquid copper was present. Grain growth at 1400°C probably experiences a much more rapid decay in kinetics once the grain size approaches the foil thickness (125 μm) because grain boundary migration is then limited to two dimensions.

The intimate contact of a niobium grain boundary groove ridge with the sapphire can cause pinning of the grain boundary. In order for migration to occur, significant redistribution of mass in both the niobium and the sapphire by solid-state diffusion mechanisms is required, which is not very active at the processing temperatures used. The presence of the liquid can facilitate

boundary migration because diffusion through the liquid is much faster than solid-state diffusion. As the grain boundaries move, the crystallography of the niobium at the interface changes and the liquid copper redistributes. The energetics and balance of surface energies at the triple-point could cause the appearance and disappearance of grain boundaries at the surface. Liquid copper could get trapped inside grooved regions and remain there, leading to the appearance of a persisting grain boundary, in contrast to other regions where the grain boundary may seem to disappear altogether when the boundary groove migrated.

The grain structure of the niobium below the visible surface can also affect the morphology of the grain boundary groove ridges that are visible by affecting the direction that the grooves will migrate. The delicate balance that occurs between the driving force to lower the chemical potential by grain growth, and the minimization of interface and surface energies especially at grain boundary grooves, leads to substantial interfacial morphological changes in the time scale presented in this study. Regions of fine-grained niobium will experience rapid changes early on, and then the kinetics of these changes will decay as minimization of surface energies become more important than the reduction in chemical potential that occurs by grain growth. The disappearance of grain boundaries is likely due to fine-grained regions of niobium experiencing rapid grain growth at short anneal times, and causing the substantial changes in the interfacial microstructural morphology.

Using the grain size information previously mentioned it is possible to calculate the change in grain size that would occur after 120 h for various rate law kinetics. For $t^{\frac{1}{n}}$ kinetics:

$$\bar{d}_t^n - \bar{d}_{t=0}^n = kt \quad (4.2)$$

Where $\bar{d}$ is the average grain size of a material. If the grain growth of niobium follows $t^{\frac{1}{2}}$ kinetics then the average grain size would experience an increase of 160 μm in 120 h. This suggests major migration of grain boundaries. For $t^{\frac{1}{3}}$ and $t^{\frac{1}{4}}$ kinetics, the average grain size would increase 90 μm and 88 μm , respectively. These increases in grain size are sufficient to explain some of the

differences in microstructure caused by niobium grain growth seen between 1 h and 120 h at the processing temperature.

4.3.2 *M-plane sapphire*

M-plane sapphire has also been used as the substrate in similar time-evolution experiments to study the effect of crystallography and stability because it has been shown that *m*-plane sapphire is unstable when in contact with vapor. In **FIGURE 4.13** a typical interfacial region is shown. In this region, it is asperities in the niobium foil that play an important role in the initial contact of the niobium to the sapphire. The final microstructure of the interface shows that grain boundary grooving is important to formation of niobium/sapphire contact. It seems that asperities play a more important role in the early development of the microstructure, but at extended times the grooving of the grain boundaries finalizes the regions of contact between the niobium and the sapphire. Some regions that appear to have niobium/sapphire contact in **FIGURE 4.13** (a) seem to be covered in copper in **FIGURE 4.13** (b).

One region of particular interest is enlarged and shown in **FIGURE 4.13.1**. At first glance, it appears that this region might initially be a gap between the niobium and sapphire that eventually fills with copper; niobium/sapphire contact appears to grow through this region at extended anneal times. Closer inspection seems to indicate that a ridge has formed around the edge of this feature. There are two possibilities that could explain ridge formation. One possibility is that the ridge formed as a result of a triple-point force balance at the liquid copper/sapphire/vapor interface. Previous work has shown that with liquid copper on sapphire ridges can develop after 0.75 h at 1100°C,⁹⁰ so it seems likely that ridges could have formed after 1 h at 1150°C. As more sapphire/niobium contact develops more liquid is liberated to fill these types of interfacial voids. However, if this is the case, then the interfacial contact area analysis and modeling that is presented

in a later section is subject to greater uncertainty (which could in part explain why fitting the data was not entirely successful).

Another possible explanation for the formation of the ridge is that it developed as a result of sapphire/niobium contact. An asperity on the niobium surface could have initially made contact with the sapphire, then debonded, allowing liquid to flow into that region. During later stages of annealing, a bonding front from elsewhere in the sample almost completely grows through this region. Because the niobium/sapphire interfacial energy is relatively low it seems unlikely that a bonded region would debond, but perhaps as grain growth occurred and the crystallography of the niobium in contact with the sapphire changed, the interfacial energy increased causing debonding. It seems unlikely that a niobium grain would grow at the surface if that particular niobium/sapphire interface was unstable, but there is the possibility that the surface grain that formed the initial contact was consumed by a subsurface niobium grain. Growth of another grain that yields a stable niobium/sapphire interface was impeded by the ridge, which had to smooth sufficiently before the stable niobium/sapphire interface could grow through this particular region.

Coarsening could also cause larger patches of sapphire/niobium contact to grow at the expense of smaller ones as the larger patches have a lower potential along their perimeter, but there are three regions of quite different size in **FIGURE 4.13**, and they all seem to initially have contact and then become debonded. These three regions are close enough together that it is possible that as grain growth occurred they were all consumed by one grain beneath the niobium surface during early stages of annealing, and became debonded as they were consumed. These features are seen often enough in the micrographs that uneasiness ensues with this type of explanation because it seems unlikely that there would be many instances of this particular type of grain growth.

Another possibility to explain the phenomena seen in **FIGURE 4.13.1** relates to mechanical debonding. A load was applied for the first hour of bonding, which probably aided in forming the

initial contact between the sapphire and the niobium. However, during all subsequent anneals, no load was applied, and thus, the relaxation of the interface may have contributed to the debonding of a region of niobium/sapphire interface. There also may have been patches of liquid copper trapped between regions of contact of sapphire and niobium, and upon heating and cooling the thermal expansion mismatch of the copper with the niobium and the sapphire could have additionally contributed a driving force for the debonding of small regions of sapphire/niobium interface.

The region adjacent to the area marked **b** in **FIGURE 4.13** (e) has vertical lines resembling the lines seen earlier in **FIGURE 4.11** (b). These lines are due to the faceting of the **m**-plane surface. Both the facets of the **c**-plane and **m**-plane substrates will be discussed in more detail later.

A region of the **m**-plane sample containing a lithographically processed cavity (0.5 μm deep) is shown in **FIGURE 4.14**. Near the centerline of the cavity some niobium grain boundaries are visible during the early anneals. These particular grain boundaries are not present in the final microstructure. In the early stages of annealing, the liquid copper could have dewetted that particular region of the interface because there may have been a gap from a depression in the niobium foil in that region. With no niobium in the immediate vicinity, the liquid copper would flow out of the gap in an attempt to reduce the surface area of high-energy liquid copper/sapphire interface. The niobium surface microstructure then evolves into a state that lowers its energy when it is in contact with the vapor; grain boundary grooves develop. The rainbow pattern present in this region could be caused by the refraction of visible light as it travels through media of different indexes of refraction (sapphire and vapor) and suggests that a gap exists between the sapphire and the niobium. At some time between 15 and 32 h, the liquid copper migrated over these particular grain boundaries in the niobium. As the contact area of sapphire/niobium interface increases, it would seem that there is more “free” liquid to go around. Capillary forces could cause liquid to flow

into the region that was not in contact with the liquid initially. The niobium grain boundaries became more mobile in contact with the liquid because the diffusivity of niobium in liquid copper is much higher than the solid-state diffusivities, facilitating movement of the grain boundary grooves. The final microstructure of the interface has a different grain boundary in contact with the sapphire surface and does not include the grain boundaries that were seen in contact with the vapor at earlier anneal times. The striking change in grain structure that occurs at intermediate times once the liquid was drawn into the region of void is probably due to the increased mobility of the grain boundaries in the presence of liquid copper. Previous calculations showed that one would expect the average grain size of the niobium to increase at least $88\text{ }\mu\text{m}$ based on $t^{\frac{1}{4}}$ kinetics, which seems reasonable based on the observed change in grain structure.

Another feature that appears as black spots labeled **d** in **FIGURE 4.14 (a)** disappear progressively at later anneal times. It is unclear what these features are, but they may be asperities in the surface of the sapphire that resulted from ion milling. It is possible that the photoresist in this region of the sample was almost completely etched away, which left small regions of sapphire surface that were exposed to the ion beam during milling. This led to a roughening of the surface and caused the black spots seen in the figure. Eventually the surface smoothed, which is evident after 32 h at 1150°C . Ridges that resemble the ridge seen in **FIGURE 4.13.1** are visible in **d** and **e** of **FIGURE 4.14 d)**. The ridge shown near **e** is very similar because the niobium/sapphire contact that caused the formation of this ridge starts to debond after the applied load is removed from the sample. The ridge near **d** formed from niobium/sapphire contact that initiated in the absence of an applied load and could perhaps be explained using the grain growth arguments mentioned previously in conjunction with **FIGURE 4.13.1**.

FIGURE 4.15 shows another example of an early grain structure in the niobium that was not present after extended time anneals and is completely different than the final grain structure seen in

the micrographs. Although the micrographs did not capture a time when liquid copper was in contact with the center region of this part of the sample, the difference in microstructure at various times could be due to the increased ease of groove migration when liquid copper migrates over boundaries and wets them some time between 15 and 31 h at 1150°C, when the most notable change in microstructure occurred. If this region was never in contact with the liquid, the kinetics of grain growth by solid-state diffusion mechanisms are still rapid enough to cause the observed changes in microstructure. Assuming “slow” kinetics ($t^{\frac{1}{4}}$), the niobium foil is predicted to experience a change in the average grain size of 56 μm after 31 h at 1150°C. The grain structure that is visible at the surface at early times in **FIGURE 4.15** appears to be smaller than the average grain size and thus it is to be expected that these grains would change shape rapidly as grain growth and grain boundary migration occurs. The rainbow pattern in the early stages of this region’s microstructural development once again suggests a gap between the niobium and the sapphire that disappears once the niobium grain boundary groove ridges contact the sapphire surface.

4.3.3 *M-plane processed at 1400°C*

Series of micrographs for *m*-plane samples processed at 1400°C show similar features to *c*-plane samples processed at 1150°C. **FIGURE 4.16** shows the evolution for a typical region of the sample. In this particular sample a triple-point region in the niobium provides a point of initial contact of the niobium/sapphire interface. There are regions that early on are covered in copper and then appear to become unbonded regions when the liquid copper migrates leaving a rainbow-like pattern (labeled *b*) at the interface (which occurs for reasons aforementioned). It is possible that copper is still present on the niobium side of these voids, but it is difficult to see because the void distorts the color and makes it difficult to tell. It is also possible that the liquid flowed out of these voids through regions that had not made complete niobium/sapphire contact yet or along niobium grain boundaries. After an anneal at 1700°C for 12 h there seems to be no copper left at

the interface and all unbonded regions appear to have formed contact between the sapphire and niobium. The solid-state diffusivities of niobium at 1700°C are probably high enough that these voids could have closed after 12 h, and if liquid is present in the voids, it would only have the beneficial effect of shortening the required anneal times.

FIGURE 4.17 shows another region of the *m*-plane sapphire that was processed at 1400°C. Again a grain boundary groove of the niobium and asperities in the niobium foil appear to have been important in the formation of initial niobium/sapphire contact. An important feature in this set of micrographs is that after short anneal periods features that resemble facets (horizontal black lines) appear. After more extended periods of annealing, these facets disappear. Between 1.75 h and 3.75 h the lines are completely gone even in regions where the copper is still in contact with the sapphire. At extended times when all of the copper is gone there appears to be contact everywhere between the niobium and the sapphire, and there is no evidence of any faceting on the surface. The disappearance of facets could be a result of the niobium stabilizing the *m*-plane surface, or an effect of a change in oxygen activity that occurs as oxygen diffuses out of the copper during annealing and into the niobium or the furnace ambient. Once the niobium comes into contact with the sapphire, mass transport becomes very difficult because solid-state diffusion must occur in both the niobium and sapphire for the facets to grow. A spatially varying misorientation relationship between the niobium grains and the sapphire further complicates things in contrast to the case when liquid copper was present. Once regions of niobium/sapphire contact were formed perhaps it became energetically favorable in terms of interfacial energies and kinetically faster for these regions to grow at the expense of the facets. Mass transport occurred to move atoms from the facets to niobium/sapphire bonding fronts, and the facets were sacrificed in order to form more regions of niobium/sapphire contact. Perhaps, at 1150°C for extended times (longer times than this study shows) the niobium/sapphire contact of *m*-plane samples would grow and the facets would smooth

as the samples processed at 1400°C did. Usually, little faceting occurred in regions of niobium/sapphire contact, and facets were more commonly found in regions of extended liquid copper contact. The difficulty of finding regions of faceting for AFM analysis both at 1150°C and at 1400°C may be a result of the facets disappearing at extended anneal times, suggesting that niobium does in fact stabilize the *m*-plane sapphire surface.

4.3.4 Interfacial Area Analysis

Micrographs have shown that the redistribution of the liquid plays an important role in the development of the microstructure at the sapphire/niobium interface. As the liquid copper breaks up into isolated particles, regions of copper/sapphire interface are generally replaced with regions of sapphire/niobium contact. Investigation into the breakup of the copper film allows for the determination of the kinetics that govern the formation of niobium/sapphire interface. Fractography has shown that higher strengths result from samples that exhibit more complete breakup of the copper film. An understanding of the time scale required for complete breakup to occur would enable an optimization of processing conditions that produce strong bonds.

An attempt to analyze the kinetics of sapphire/niobium interface formation was made using software to analyze the area fraction of copper coverage in micrographs similar to those shown in **FIGURES 4.9–4.17**. The breakup of the liquid copper film at the interface was analyzed using a Macintosh computer and the public domain NIH ImageJ program (developed at the U.S. National Institute of Health and available on the Internet at <http://rsb.info.nih.gov/nih-image/>). With this software package it was possible to take grayscale images of the interface and analyze the % area fraction of copper at the interface at various times. **FIGURE 4.18** shows a scatter plot of all the data that have been analyzed from samples processed at 1150°C. No discernable difference seemed to exist between *c*-plane samples and *m*-plane samples, thus they are included in the same figure. The data is irregular and scattered. From the plots it seems that the copper film breaks up

faster at short times when there is a higher area fraction of copper/sapphire contact present. Assuming first order kinetics and that the rate of area copper film breakup is proportional to the area fraction of copper/sapphire interface available, it is possible to perform a kinetic analysis of film breakup. Defining A as the area fraction of copper/sapphire interface, t as time, A_0 as the equilibrium value of copper/sapphire interface (the solubility of copper in niobium at 1150°C prevents the copper from completely disappearing), and k as the rate constant:

$$\frac{dA}{dt} = k(A - A_0) \quad (4.3)$$

which, after integration, becomes:

$$\int_{A_0}^A \frac{dA}{(A - A_0)} = \int_0^t k dt \quad (4.4)$$

$$\ln \frac{A - A_0}{A_0 - A_0} = kt$$

The general curve fit option on the application *Kaleidagraph* was used to fit this model to 16 data sets at 1150°C and 2 data sets at 1400°C of % area fraction of copper/sapphire interface versus time. The software solved for the parameters k and A_0 when determining the equation for the curve. It was not possible to fit every data set to this model. Mathematical singularities occurred in 6 of the data sets as a result of the iterative process by which the software package calculates the kinetic parameters. In these cases, the value of A_0 approached the value of A , producing a singularity in EQUATION (4.4) and leading to unusable kinetic parameters. The data sets at 1150°C for which the model produced useable kinetic parameters are shown in **FIGURE 4.19**. The curves from the model curve fit and the corresponding kinetic parameters are shown for the data set that had the shortest time (the model lower bound) and the longest time for film breakup (the model upper bound). For these data sets, values of k and A_0 ranged between 0.020886–0.14842 and

2.4778–7.7464 %, respectively, and an average value for k of .0788648 and an average value for A_0 of 12.84856 describe the data from experiments conducted at 1150°C.

FIGURE 4.20 shows the data sets from samples processed at 1400°C. The values of k and A_0 ranged between 1.1703–1.46563 and 1.8988–2.1888, respectively. At 1400°C, it seems that the model does not fit as well as for samples processed at 1150°C. It is not as meaningful to call these curves the upper and lower bounds for data processed at 1400°C because there are only two data sets.

Other models were explored because it was desired to model the copper-film breakup without encountering mathematical singularities. Another model often used for phase transformations utilizes the Johnson-Mehl-Avrami equation, which has the form:

$$f = 1 - \exp(-kt^n) \quad (4.5)$$

where f is the volume fraction of transformed material, k is a kinetic parameter, t is time, and n is an exponent typically between 1 and 4. In this case, regions of sapphire/copper contact transforming into regions of sapphire/niobium contact is interpreted as the phase transformation and f is then the area fraction of sapphire/niobium contact. The curves generated from fitting the data to this model are shown in FIGURE 4.19.I and FIGURE 4.20.I for samples processed at 1150°C and 1400°C, respectively. Samples processed at 1150°C had values of k and n that ranging from .045254–1.0102 and 0.253385–0.78828, respectively. An average of a majority of the data sets that had comparable values of k and n , yielded values of k and n equal to 0.4062 and 0.417399, respectively. At 1400°C values of k and n ranged from 1.3645–2.3082 and 0.47525–0.71082, respectively. The large variation in n is cause for concern when using the Johnson-Mehl-Avrami equation because this parameter has significance in the dimensionality of the transformation being modeled, and it largely affects the shape of the model curve. The large variation in n for data at one temperature suggests

that the mechanisms contributing to film breakup at different regions in the same sample could be different.

In general, it is valid to assume that:

$$J \propto D \cdot C_{\max} \quad (4.6)$$

where J is a flux, D is a diffusion coefficient and $C_{\max}$ is the solubility limit at the processing temperature. In this case, the relevant diffusion coefficient and solubility limit refer to those parameters for niobium in liquid copper. For the first-order kinetic models the ratio of diffusivities can be found because $k \propto J$, in the Johnson-Mehl-Avrami equation, however, some algebraic manipulation shows that $k^n \propto J$. Taking the relevant ratios from both models, and taking the solubility limits from the phase diagram (3 at. % at 1400°C versus 0.81 at. % at 1150°C), it is possible to calculate that the ratio of diffusivities (D_{1400}/D_{1150}) is 6.51 for the Johnson-Mehl-Avrami model and 4.51 for the model that assumes first-order kinetics. It is expected that the ratio of the diffusion coefficients (D_{1400}/D_{1150}) would be on the order of 1.33 based on viscosity data for liquid copper and the assumption that $D \propto 1/\text{viscosity}$. A large increase in the diffusivity is not expected because the activation energy for diffusion in liquids is generally quite small compared to activation energies for solid-state diffusion mechanisms. The discrepancy between the ratio of diffusivities calculated from the models versus the value obtained from viscosity data could be due to the effects of other diffusion mechanisms besides diffusion through the bulk liquid. An interfacial diffusion mechanism could be active at these temperatures. Also, 1400°C is roughly half the melting temperature of niobium, (2469°C) and at this temperature it would be expected that other low-temperature diffusion mechanisms would be active (grain boundary diffusion and dislocation pipe diffusion, for example) causing the marked difference in film breakup at 1400°C versus 1150°C.

Qualitatively, micrographs (**FIGURES 4.9–4.17**) show that sapphire/niobium contact initiates at grain boundary grooves or asperities in the foil. Grain boundary initiation depends on grain boundary density, which is dependant on grain size. Different regions of the niobium foil have different grain sizes, and the grain size changes fairly rapidly at the processing temperature. In general, it is observed that the initial contact at grain boundary grooves leads to increases in contact area by growing inward towards the center of the grain. The origins of surface asperities are not known, and their density varies widely along the interfacial area of the sample. Contact from an asperity generally grows radially outward from the asperity. Further breakup of the copper film occurs *via* Rayleigh instabilities when “finger-like” liquid channels breakup into spherical particles. To further complicate analysis of the processes, the liquid redistributes itself often, and depending on local capillary forces can rapidly and completely drain from a specific interfacial region. A complete model would have to take into account grain size and inward growth of contact from boundary grooves, asperity density and outward radial growth rate, Rayleigh finger spacing and channel breakup, and capillary forces that cause liquid flow to fully describe the film breakup presented here. It is quite surprising that the simple models used are in a fairly close agreement and are only a factor of 3–5 different from simple approximations using viscosity. Although these models are not complete and/or sufficient in predicting the breakup of the copper film, they could be useful in an industrial situation for back-of-the-envelope estimates.

4.3.5 Sapphire Interfacial Morphology

Previous investigators have found that certain crystallographic planes of sapphire are not stable when in contact with air at elevated temperatures.⁷⁷⁻⁸¹ Unstable planes then form facets to expose stable planes at the surface. These facets can have topographies resembling a terrace-and-step structure (as is the case for the *c*-plane) or a saw-tooth structure (as is the case for the *m*-plane). This type of surface topography could lead to increased mechanical strengths of bonded

assemblies by deflecting interfacial cracks in a torturous manner. One study found that when *c*-plane sapphire is diffusion-bonded to niobium in high vacuum, facets can develop to accommodate small deviations from the exact orientation of the interface.⁴² There is no mention of the development of facets when *m*-plane sapphire is diffusion bonded to niobium in UHV.^{33,34} The effect of copper on the interface topography of the sapphire/niobium interface has not been studied previously.

After the series of optical micrographs were taken, showing the breakup of the copper film and the interfacial microstructure for times extending to 127 h at 1150°C, sections of the samples were taken and left to soak in an acid solution to dissolve the metal interlayers. Then, AFM was performed on the samples to assess the morphology of the sapphire surface that had been in contact with the metal interlayer. The entire surface of the sample did not facet, but particular regions faceted into a terrace-and-step morphology in *c*-plane sapphire, and a hill-and-valley morphology for *m*-plane sapphire. The AFM images are shown in **FIGURE 4.21** and **4.22**. The *c*-plane sapphire steps are likely due to the miscut of the sapphire ($\pm 1^\circ$) since the step spacing and height are consistent with a miscut of 0.8° (within the tolerance limit specified by the manufacturer). The *m*-plane hill-and-valley structure could be due to an instability of the *m*-plane surface of sapphire when in contact with metal, which is similar to what is seen for *m*-plane in contact with vapor.⁸¹ An attempt to index the facets comprising the hill-and-valley structure using the measured interplanar angle measurements was attempted, but the results were inconclusive. It seems that the facets seen here are not parallel to crystallographic planes that have been proven stable in air or vacuum. Some step features in **FIGURE 4.22** suggest that step-bunching could be occurring. Measurements in silicon have shown that step-bunching can occur on vicinal surfaces, where bands of steps form the appearance of large unstable planes that are actually composed of many small steps with faces parallel to stable planes.¹⁰⁸ Tran discusses the stability of various

crystallographic planes of sapphire when these planes are in contact with liquid metals; these planes are not present in the Wulff shape when sapphire is in contact with vapor.¹⁰⁹

The varying size of the hills and valleys in the AFM image of the *m*-plane sapphire suggests that the facets are coalescing and coarsening, which is expected for these types of facets.⁷⁷ Since this topography does not occur everywhere on the sapphire surface it seems that the niobium contact greatly affects the formation and size of the facets. The optical micrographs of the interfacial microstructures suggest that the facets form in regions that are in contact with the liquid copper for extended periods of time. It is possible that the *m*-plane of sapphire is unstable when in contact with liquid copper. Since the liquid copper can be displaced with ease, and the *m*-plane of sapphire might be unstable at high-temperature, energetically it might be favorable for the sapphire to form facets when in contact with pools of liquid copper. This would explain the observations. No previous evidence exists to suggest that the *m*-plane sapphire/niobium interface is unstable. The energetics of the polycrystalline niobium/*m*-plane sapphire interface is further complicated because each niobium grain defines a different interface crystallography. The absence of a hill-and-valley structure suggests that most niobium/*m*-plane combinations are stable. Optical micrographs taken after anneals at 1700°C for 12 h do not show any evidence of facet formation (FIGURES 4.16 (e) and 4.17 (e)), and one would expect diffusion to be sufficiently active at 1700°C to produce facets at an unstable interface. It would seem that the niobium/*m*-plane alumina interface is stable at high temperatures, and in some cases, facets that may have formed in contact with liquid copper may smooth as more regions of alumina/niobium contact develop.

Previous studies⁷⁷⁻⁷⁹ of sapphire samples annealed in air at 1400°C showed that the *m*-plane surface formed facets after 2 h parallel to the $(1\bar{1}02)$ plane with heights equal to 6 nm. Samples annealed for up to 8 h in air at 1400°C had facet heights as large as 15 nm. Facets in *m*-plane samples processed at 1150°C with liquid copper present were not visible in optical

micrographs until after 127 h and were approximately 80 nm in height. Only one data point was obtained for the facet height in contact with copper/niobium interlayers after 127 h at 1150°C, so it is not possible to fit the data to a growth model.

No accurate measurements of facet height were made for samples in contact with copper/niobium interlayers at 1400°C. This data makes it impossible to fit data to a model to predict facet height time dependence and compare the rates at two temperatures in terms of relevant kinetic parameters. After 0.25 h at 1400°C facets were visible in regions in contact with liquid copper (FIGURE 4.17). These facets were approximately parallel to one edge of the sapphire substrate. The *m*-plane substrates are bounded by the *c*- and *a*-directions. Therefore, the facet axis (line of intersection) is parallel to either the *c*- or *a*-direction. Previous studies for sapphire substrates annealed in air found that the facet axis in facets on *m*-plane substrates ran parallel to the *a*-direction.⁷⁷⁻⁷⁹ This suggests that the facets seen for sapphire annealed in air, and annealed in contact with copper/niobium interlayers may align along the same crystallographic direction. These facets (seen in FIGURE 4.17) smoothed and were no longer visible after 3.75 h at 1400°C. No evidence from previous work has suggested that the *m*-plane sapphire/niobium interface is unstable, and it is possible that the facets that formed in contact with liquid copper after 0.25 h at 1400°C smoothed after 3.75 h at 1400°C to create larger regions of niobium/sapphire contact.

Features will not be visible in the optical microscope unless they are larger than the resolution limit, which is on the order of 100 nm, and facets 80 nm in height were visible in samples processed at 1150°C with copper/niobium interlayers. The visible facets after such a short anneal time (0.25 h) at 1400°C suggest that the liquid copper increases the kinetics of facet formation for *m*-plane samples at higher temperature. Typical step heights after 8 h in air at 1400°C for *c*-plane samples were 2.6 and 3.9 nm.⁷⁸ In *c*-plane samples processed at 1150°C in the presence of copper/niobium interlayers, facets were visible after 7 h (FIGURE 4.11 and 4.12) in optical

micrographs further supporting the view that the liquid may promote more rapid facet formation at 1150°C than in air at 1400°C.⁸⁹ After 127 h at 1150°C the facets in c-plane samples in contact with copper/niobium interlayers had heights that were approximately 5–7 times as large as heights observed after 8 h at 1400°C in air, which again supports the hypothesis that the presence of a liquid can greatly enhance the kinetics of diffusion-controlled morphological transformations.

4.4 Wetting and Grain Boundary Grooving

Single-crystal sapphire substrates in contact with copper/niobium interlayers have revealed the importance of thermal grooving in the polycrystalline niobium foil on the breakup of the copper film, redistribution of the liquid, and the overall development of the interfacial microstructure. The effects of using polycrystalline alumina substrates on the interfacial microstructural development have yet to be discussed. It is desired to know how thermal grooving in the alumina affects the interfacial microstructure, and also whether the presence of a liquid can enhance kinetics in alumina as much as it can in niobium. First, an experiment that deals with the thermal grooving of polycrystalline alumina in contact with copper/niobium interlayers will be discussed, then thermal grooving of both niobium and alumina when in contact only with liquid copper will be discussed. This attempts to fully understand the factors affecting interfacial microstructural development in the alumina/copper/niobium system.

4.4.1 Bicrystal

In order to study one particular alumina grain boundary and how it grooved during processing with the copper/niobium system a bicrystal sample was fabricated. Before thermally etching the alumina grain boundary groove, the surface of the alumina was polished by hand on a nylon cloth with successively smaller diamond grit pastes (15 µm, 6 µm, 1 µm, and 0.25 µm). This polish should have produced a sufficiently smooth surface such that scratches would not be misinterpreted as grain boundary grooves. The AFM results (FIGURE 4.23 – 4.25) show that the

width of the grain boundary groove is increasing with time. The width of a grain boundary groove is defined as the distance between the maximum heights of the humps (ridges) on either side of the grain boundary groove. The width after 50 h at 1400°C is 4.47–8.05 μm (depending on where it is measured in **FIGURE 4.23**), then the width increases to about 10.07 μm (average of height profile B and C **FIGURE 4.24**) after an additional 100 h at 1400°C, and then the width increases to 45.3 μm after an additional 20 h at 1700°C. This widening with extended anneal times is expected.⁸⁷ Once again a lack of data prevents the determination of a relevant kinetic parameter. It is not possible to determine the time exponent in the kinetics of the grain boundary groove widening because there are two data points at 1400°C and one at 1700°C, which is insufficient to compare to a model and obtain a relevant kinetic parameter.

Due to rounding of the AFM probe tip⁸⁹ it was necessary to change the AFM probe tip often to ensure that the grain boundary groove was imaged accurately. Accurate images of the grain boundary groove seem to show that the groove root rounded between 50 and 150 h at 1150°C. The shape of the groove after 20 h at 1700°C was drastically different than it was after the lower temperature anneals. It has a very large dihedral angle, and it did not have the expected shape of a grain boundary groove. The groove was very wide and bounded by straight rather than curved surfaces, and in at least two of the height profiles the root looks quite rounded. This does not resemble the shape of a grain boundary groove predicted by Mullins.⁸⁷ As copper atoms diffuse down the alumina grain boundary, area of alumina/vapor and/or alumina/niobium interface can be left behind, which would have a lower interfacial energy than the copper/alumina interface, and could lead to a larger dihedral angle. As the liquid copper redistributes itself and the microstructure of the interface develops, the materials in contact with each other change, thus changing the interfacial energies that must equilibrate. The large differences in the topography of the grain

boundary groove at different times and temperatures are in part due to the equilibration of different interfacial energies.

Based on the sapphire experiments it is expected that after 50 h at 1400°C a large fraction of the interface should be sapphire/niobium. It is not expected that the dihedral angle should change much at such extended anneal times as a result of changing interfacial energies because the sapphire/niobium interface seems to be relatively stable, and 50 h should be enough time to form large regions of sapphire/niobium interface. Once sapphire/niobium interface is formed, that interface should persist. When the liquid copper is no longer present, the alumina grain boundary could take much longer to equilibrate since 1400°C is a fairly low temperature compared to the melting temperature of alumina (12046°C but dependent on purity). The morphological changes that occur to the grain boundary groove might result from grain boundary migration. It is expected that the undulating grain boundary formed in this bicrystal sample would experience migration as atoms migrate to regions of the boundary with lower chemical potential (smaller radius of curvature). After 50 and 150 h at 1400°C the shape of the grain boundary groove has what appears to be humps on either side of the grain boundary, which suggests that a diffusion mechanism is controlling the kinetics.⁸⁹ The humps are not clear and easy to find after the 50 h anneal. Instead of one clear hump, saddle points exist on the surface on either side of the grain boundary. This could be a result of grain boundary migration, which requires the nucleation of a second groove. The image shown after 50 h at 1400°C may show the groove after it has migrated quite a bit, and the saddle points are a result of the deterioration of the original location of the groove. These saddle points obscured the groove maxima, and caused of the factor of 1.6–1.7 variation in the grain boundary groove width measurements made in the height profiles in **FIGURE 4.23**.

Another important factor that could have caused the appearance of saddle points on the alumina surface is grain boundary grooves in the niobium. If the region shown in **FIGURE 4.23**

happened to be a region of alumina grain boundary that crossed a niobium grain boundary, a grain boundary groove in the niobium could have caused features that appear to be saddle points on the surface of the alumina. An example of a niobium grain boundary that left visible features on the surface of the alumina is shown in **FIGURE 4.26** (c).

It is not possible to say if after 150 h at 1400°C the grain boundary groove reached equilibrium, but it certainly does not have a uniform profile along its length, which is expected for an equilibrated grain boundary groove. The additional 100 h at 1400°C should have been sufficient time for active diffusion mechanisms to cause some morphological changes to occur between 50 h and 150 h. The profile of the groove after 150 h at 1400°C has a morphology that is more reminiscent of the grooves that Mullins described with clear maxima on either side of the boundary groove in at least one of the height profiles. The root rounding that occurred and the apparent shallowing could be a result of the low sapphire/niobium interface energy causing a large dihedral angle and rounding the root tip to maximize the sapphire/niobium contact area.

The large difference in the grain boundary groove shape at 1400°C versus that at 1700°C could be a result of a change in the limiting mechanism of groove shape change kinetics. In the early stages of annealing the liquid copper enhances the ability of the alumina grain boundary to equilibrate *via* diffusion. At 1700°C, alumina should be much more soluble in niobium than it is at 1400°C. The grooving kinetics of the alumina grain boundary could be controlled by the dissolution of alumina in niobium rather than surface or volume diffusion, which might explain the large difference in groove shape. The absence of humps on either side of the boundary, and the much more linear profile on the sides of the grain boundary groove might indicate a dissolution/precipitation-controlling mechanism rather than a diffusion-controlling mechanism. The straight edges on the sides of the boundary also might be facets that have formed on the

surface of the alumina. It is unclear which crystallographic planes the facets lie parallel to because the angular measurements suggest that these surfaces are 2.7–3.8° from the c-plane.¹¹⁰

Regions of the bicrystal surface away from the grain boundary after the 50 h anneal at 1400°C are shown in **FIGURE 4.26**. The surface of the alumina is not flat in regions away from the grain boundary and does not facet in ways that might be expected on the basis of **FIGURE 4.21**. The AFM images seem to suggest that the surface of the niobium and the surface of the sapphire conform to one another and make contact even in regions with surface defects to maximize the niobium/sapphire interfacial contact area. Pores that exist at the surface of the alumina as a result of processing could coarsen to form large surface holes or pits (**FIGURE 4.26 (a)**). Some of the surface defects in the AFM images seem too big to occur as a result of polishing with 0.25 μm diamond grit paste. This would seem to support the presumption that coarsening occurred. The surface of the niobium has a strong effect on the topography of the alumina surface. Large protrusions resembling mountains on the surface of the alumina could also form as a result of holes or pits in the niobium (**FIGURE 4.26 (b)**) as the alumina could dissolve in the niobium and then precipitate inside the pit.

Niobium grain boundaries can also largely affect the surface topology of the alumina. **FIGURE 4.26 (c)** and **(d)** show a region of the alumina surface that was in contact with a niobium grain boundary and shows that it has left a large print on the surface of the alumina. This type of behavior has been observed in prior studies,¹¹¹ and is possible because of the dissolution reaction of niobium in alumina. The line profiles do not seem to suggest the existence of a ridge in this particular boundary groove. The development of this groove was dependant on mass transport of alumina towards the groove root and niobium away from the groove root. Similarly, the development of a groove in alumina is dependant on mass transport of niobium towards the groove root and alumina away from the groove root. It would seem likely that the kinetics of these groove

morphologies at some temperature should be similar since they are both dependant on the transport of the same atomic species. The niobium grain boundary groove is very roughly the same size as the alumina grain boundary groove after 50 h at 1400°C (5.27 μm wide and 0.550 μm deep compared to 4.47–8.05 μm wide and 0.3–0.4 μm deep in the alumina), which is to be expected since both grooves are limited by the same mechanisms (diffusion and the dissolution reaction). The flat portion at the top of the protrusion caused by the niobium grain boundary shown in **FIGURE 4.26** (c) could be a result of AFM tip rounding.⁸⁹ Careful investigation of the AFM image suggests that the AFM tip broke halfway through the image scan. There seems to be a clear feature where the tip could have broken off resulting in the flatter parts of the scan in the grain boundary groove tip.

This method of fabricating bicrystals is not ideal for systematic studies of interfacial energies in the copper/niobium/alumina system because of the anisotropy present. It was possible to obtain data showing the grooving of this particular boundary, but for a systematic study of this type, fabrication of symmetric tilt boundaries (described in PhD thesis by Robert Marks¹⁰⁵) would be preferred. Also, single crystal niobium foil would help eliminate the variability of the alumina/niobium interfacial energy, and niobium grain boundary grooves would not interfere with the surface topography of the alumina. Alternatively, a coarse grained niobium foil ($d \sim 1$ mm) would allow for the opportunity to study mass transport and grooving kinetics at a number of crystallographically different niobium/sapphire interfaces in one bicrystal sample. This study seems to at best show a proof of concept that this method could be used for the systematic study of interfacial energies and interfacial transport in the copper/niobium/alumina system (and perhaps in other systems as well), which could significantly broaden the current knowledge of metal/ceramic interfaces.

4.4.2 Liquid Copper on Niobium

A wetting experiment was performed in an attempt to better understand the wetting behavior of liquid copper on niobium. A short piece of copper wire was placed on a niobium foil substrate, and annealed at 1400°C for 6 hours. This was an attempt to see how the copper and niobium behave during the bonding cycle when alumina is not present. **FIGURE 4.27** (a) shows a micrograph of the as-received niobium foil, and (b) shows a schematic of the niobium foil after annealing with the solidified drop on the surface. The expected result of a copper-colored drop (with a spherical cap shape) was not found, but the drop was closer in color to the niobium foil. In order to locate the copper, the sample was mounted in an epoxy resin and cut in cross-section near the drop center. Then a micrograph of a cross section of the drop was taken, as shown in **FIGURE 4.27** (c). Approximately 3 at % of niobium dissolves in the liquid copper at 1400°C. Upon cooling, the solubility of niobium in liquid copper decreases, and the drop surface is enriched with niobium precipitates. De Lima *et al.* reported that the surface enrichment of niobium precipitates is due to their density,⁷¹ but data from Crawley¹¹² and Armstrong *et al.*¹¹³ suggests that at all temperatures above the melting temperature of copper solid niobium is actually more dense than copper. These precipitates could have heterogeneously nucleated at the drop surface. A calculation of Stoke's velocity for particles between 5 μm and 40 μm in diameter (measured values of size) yields values that range between 0.02 m/s and 0.002 m/s. It would take the particles between 2 min and 20 min to settle from the surface of the drop to the solid-liquid interface if they had a constant size and were perfect spheres. At a cooling rate of 30°C/min, the liquid drop completely solidified in approximately 11 min, and the precipitates probably coarsened during cooling as the solubility of niobium in copper decreased, which suggests that the larger particles might not have grown to a relatively large size until near the end of the solidification process. It seems reasonable that the settling velocity of these particles was slow enough during cooling that they did not have time to

settle to the solid-liquid interface and they were frozen in nonequilibrium positions at the drop surface. **FIGURE 4.27 (c)** shows that the precipitates are concentrated near the drop surface with some just below the drop surface, but the center of the drop does not contain any precipitates. At lower temperatures, the eutectic liquid solidifies and additional niobium-rich particles are produced. The micrograph supports this hypothesis because there are niobium-colored precipitates near the surface of the drop. A surface enrichment of niobium particles has been seen by previous investigators.^{71,114} When the copper was liquid, it is possible that the niobium particles formed a three-dimensional interconnected network on the drop surface. The thermal contraction that occurred when the copper solidified probably caused this film to collapse and produce the uneven surface seen at the perimeter of the drop. After complete solidification, the copper-rich nature of the drop was probably not evident because the niobium-rich precipitates were covering the surface of the drop.

After a nitric acid rinse to dissolve the copper, micrographs were taken of different regions of the niobium foil that had different colorations. The region under the drop is shown in **FIGURE 4.27 (d)**. In this region the niobium grain boundaries have thermally grooved in the presence of the liquid copper (they are not the result of the nitric acid etch because the whole sample was in contact with nitric acid, but niobium grain boundary grooves are not visible everywhere in the sample). The surfaces of the grains also appear shiny and smooth. These grain boundary grooves at the metal/liquid interface are much wider than grain boundary grooves at the metal/vapor interface, which are not visible. This suggests that grooving is much faster at the niobium/liquid copper interface than it is at the niobium/vapor interface. Grain size measurements showed that the grains under the drop had an average size of 160 μm , and regions away from the drop had an average size of 105 μm , which suggests that grain growth was more rapid under the liquid drop than it was for region in contact with vapor. In **FIGURE 4.27 (e)** a region near the center of the

niobium foil is shown. In this region, the niobium surface is shiny and smooth, but there are asperities on, and holes in, the surface. EDS analysis showed that this region is not chemically different from the bulk niobium foil. It is believed that the liquid drop spent some time over this area of the niobium foil, but because the foil was not flat, the drop migrated at temperature and did not spend extended time periods in this region. There might have been enough time for some surface smoothing to occur, but not time for niobium grain boundaries to groove.

A region of the foil that had a different texture after etching and was slightly darker in color was found near the edge of the niobium foil and is shown in **FIGURE 4.27 (f)**. In this region there are features that closely resemble the features marked **c** in **FIGURE 4.8 (d)**. It seems that this is the appearance of the niobium foil that is not in contact with liquid copper at all after annealing for 6 h at 1400°C. Chemical analysis using EDS showed that there was no significant difference in oxygen levels in regions similar to those in **FIGURE 4.27 (e)** compared to regions similar to **FIGURE 4.27 (f)**. There was no significant difference in chemistry at different regions in this sample to draw any conclusions about chemical species causing the differences in surface appearance. The mottled black regions could just be regions of the niobium foil that did not contact the liquid and never smoothed. Grain size measurements showed no difference in grain size between regions like those in **FIGURE 4.27 (e)** and **(f)**. One other possibility is that small droplets of liquid copper could have migrated to the edges of the niobium foil. Ridges could have formed around these small droplets. Then, these small droplets might evaporate and leave behind small pits at the niobium surface. This could cause a very rough niobium surface that appears as a mottled black region in the micrographs. It is uncertain why the micrographs show features very similar to those seen in diffusion-bonded fracture surfaces.

One interesting feature that was found near the perimeter of the drop after etching in nitric acid was that there were still remnants of copper. Interestingly enough, the remaining copper

seemed to take on the morphology of nanowires. An SEM micrograph showing the copper nanowires is shown in **FIGURE 4.26 (g)**. These nanowires are not relevant to anything. Micrographs taken near the triple-point of this interface did not yield the information that was desired. Normally, a useful contact angle could be found, but because the shape of the drop is so irregular it was not possible to obtain the measurement from this sample. Other investigators have shown that the contact angle of copper on niobium is $\approx 67^\circ$ at 1090°C and decreases to less than 2° at 1500°C .^{71,114} It is unclear what caused the nonequilibrium morphology of this drop. It is possible that gravitational effects combined with the large size of this particular drop caused the contact angle to deviate from the equilibrium value. Clearly, this sample did not yield the expected or desired results.

4.4.3 Liquid Copper on Coors AD995 Alumina

The topography of sapphire in contact with copper and niobium has been discussed. Previous investigators have discussed the wetting behavior and surface topography of sapphire in contact with liquid copper.^{84,90} It was desired to see the effect of liquid copper on the topography of the alumina material used to prepare joints made with copper/niobium/copper interlayers. The effect the liquid copper has on the topography of the surface of the Coors alumina was investigated by depositing a copper film ($2.87\text{ }\mu\text{m}$ thick) on a Coors alumina substrate. The sample was then annealed for 0.5 hr at 1100°C .

The micrographs show that the copper morphology varies greatly on the surface of the alumina substrate (**FIGURE 4.28 (a)** and **(b)**). In some regions the copper film has developed into isolated particles (a), but in other regions the copper film is almost continuous except for some regions of dewetting and has developed a visible grain structure during cooling and solidification (b). It seems as though all of the regions where dewetting occurred have small surface defects or

pits in them (some of them are shown and enlarged in **FIGURE 4.28** (e)–(g)). It is possible that these defects acted as dewetting initiation sites.

No other experiments have shown the copper film to have a grain structure. The regions of large copper coverage in sapphire experiments (**FIGURES 4.9–4.17**) do not show a copper grain structure and fracture surfaces with regions of large copper coverage from polycrystalline alumina samples (**FIGURES 4.3–4.6**) do not show a copper grain structure. Polycrystalline samples show that the alumina grain structure is visible in the copper film, but not a copper grain structure (**FIGURE 4.5** (a)). Because the grain structure of the copper film seems very similar to the grain structure characteristic of the alumina used, see **FIGURE 4.28** (c), it seemed possible that the grain structure was a result of alumina grains being etched by the liquid and then patches of copper solidifying in a way that revealed the underlying alumina grain structure. Regions similar to those shown in **FIGURE 4.28** (b) were etched in nitric acid and then examined under the optical microscope. Alumina grain boundaries were not visible in regions that were under large patches of liquid copper film. This seems to suggest that the liquid copper did not etch the alumina grain boundaries “enough” at 1100°C for 30 min to make them visible in an optical microscope and the grain structure is from the copper solidification. This experiment also seems to suggest that the kinetics for film break-up on a surface are very rapid, and that at temperatures very close to the melting temperature (1100°C is $\approx 15^\circ$ above the melting temperature of copper) a significant amount of dewetting can occur, which is perhaps not surprising since a factor of 10^3 increase in diffusivity is expected when the temperature is raised above T_m . The relative magnitude of the driving force for this type dewetting to occur to minimize surface/interfacial energies is examined in Appendix II.

Another anneal at 1400°C for 6 hr was performed to simulate the bonding cycle on the copper/alumina system. The copper film was uniformly distributed as isolated droplets shown in

FIGURE 4.28 (c). The alumina grain structure is well defined and is shown in the micrograph. Another micrograph shown in **FIGURE 4.28** (d) shows the alumina substrate after etching the copper in nitric acid solution. A faint ring is left from the edge of the copper particles, but the micrographs do not show a significant difference in the grain structure of the alumina in contact with the liquid compared to that in contact with the vapor. It was desired to compare the widths of grain boundary grooves in contact with liquid to ones in contact with vapor. It was not possible to locate clear boundaries between alumina/liquid and alumina/vapor contact in the AFM because the silicon AFM tips rounded and broke too quickly to ever measure a ridge (circles shown in **FIGURE 4.28** (d) caused by the drop) on the surface. Groove widths ranged from 0.917 μm to 2.3 μm with an average of 1.83 μm , and there did not seem to be a correlation between the locations of the wider grooves or the locations of the narrower grooves. Although it is expected that groove widths should be larger in regions in contact with the liquid after short times (5 min at slightly higher temperatures with 99.997% pure alumina),⁸⁹ perhaps at 1400°C there is enough glassy phase present in the grooves of this alumina (99.5% pure) that all grooves are essentially in contact with a liquid, and thus experience the same enhancement kinetics.

4.4.4 Liquid Copper on Alumina Fabricated by Robert Marks

The thermal grooving of one particular grain boundary in a pure alumina was studied with the bicrystal experiment. It was desired to determine the thermal grooving characteristics of the bulk polycrystalline material used to fabricate this bicrystal experiment when in contact with liquid copper at equivalent time and temperature conditions. Copper droplets were placed on the undoped alumina fabricated by Robert Marks for anneal times and temperatures similar to those used in the bicrystal experiment. One anneal for 50 h at 1400°C and one anneal of 150 h at 1400°C were performed. Initially, the grain size of this alumina is so small that grooving is difficult to study. Rapid grain growth occurs and the grain boundary grooves interact with one another too

much to get an accurate image of the grain boundary grooves. An initial anneal of the alumina substrate for 30 h at 1600°C sufficiently enlarged the grains so that it was possible to study the grain boundary grooving of this material without significant further grain growth. The resulting grain structure after annealing for 30 h at 1600°C is shown in **FIGURE 4.29** (a). After this anneal, the grain size of this alumina is much finer than the grain size of the Coors alumina. This alumina has an average grain size of approximately 5 μm , compared to Coors, which has a bimodal distribution of grain sizes with averages of approximately 5 μm and 20 μm .

A piece of copper wire was then placed on the alumina substrate and it was annealed at 1400°C for 50 h in a gettered argon environment (the same environment used for the bicrystal experiment and the grooving experiments with Coors alumina). An AFM image that shows the triple-line ridge that developed at the solid-liquid-vapor boundary is shown in **FIGURE 4.29** (b). Line scans of this region are then shown in **FIGURE 4.29** (c). The line scans do not show a significant difference in the grain boundary groove widths for regions in contact with the liquid compared to regions not in contact with the liquid, 2.46 versus 2.77 μm . These results are contradictory to the expected ones because the groove width is wider in the region in contact with the vapor, but two data points are not enough data to make an accurate comparison. Also, due to the fine grain structure of this alumina it is possible that the grain boundary grooves from adjacent grains are affecting the kinetics of the grooving. The maxima of the groove heights occur near the centers of the grains. The groove profiles have a maximum, but the grains are not big enough for a minimum to occur between adjacent grooves. This causes a groove morphology that is different from the problem that Mullins treated for one single grain boundary. It is hard to draw a conclusion about the grooving of this material after 50 h at 1400°C because the groove morphology is not the expected or desired one. It is interesting to note that the groove in the bicrystal experiment, resulting from niobium/alumina contact, was significantly wider after 50 h at 1400°C.

This might suggest that the dissolution of alumina in niobium plays a more crucial role in the alumina grain boundary grooving kinetics than the presence of liquid copper does. It could alternatively be an effect of the adjacent groove interactions slowing the kinetics of groove widening. When the grain structure of a material is relatively large, there is going to be a large difference in chemical potential between the region near the groove height maxima (large radius of curvature and high chemical potential) compared to the grain center (radius of curvature is approximately zero and low chemical potential). If the location of the groove maxima and grain centers are the same, then there is no driving force for mass transport because there is no chemical potential gradient along the surface of the grain, which could lead to slower widening kinetics. This effect is illustrated in **FIGURE 4.29** (c).

FIGURE 4.30 shows AFM line scans after an anneal of 150 h at 1400°C was performed with a copper droplet on the alumina surface. Again, no significant difference was seen in groove widths in contact with the liquid compared to groove widths not in contact with the liquid. The groove widths were all between 3–4 μm , but the average of the groove widths shows that the grooves in contact with the liquid copper were slightly wider than the grooves in contact with the vapor, 3.70 μm versus 3.45 μm , which is to be expected. The groove width in the bicrystal sample was significantly wider after 150 h than the groove widths in this sample. It seems that the liquid copper is very important in accelerating the kinetics of grain boundary grooving in the niobium, but for the processing times used to fabricate these metal/ceramic interfaces the dissolution of alumina by niobium plays a much more crucial role in accelerating the kinetics of alumina grain boundary grooving. No faceted grooves similar in shape to that seen after the 1700°C anneal in the bicrystal sample (**FIGURE 4.25**) were found. All of the grooves measured from the polycrystalline alumina sample had humps on either side, and thus were probably kinetically limited by diffusion. It seems that profile C in **FIGURE 4.30** (b) is the only groove measurement where the groove height maxima

are not at the grain centers, and the grain above that particular groove in the AFM image is a relatively large grain.

FIGURE 4.1: Fracture strength data for various polycrystalline alumina samples.

FIGURE 4.2: Fracture strength data for various sapphire samples.

FIGURE 4.3: Typical fracture surface from a bond processed at 1400°C with an applied load of 2.2 MPa that failed at 206 MPa. The metal side of the fracture surface is shown in a) and the ceramic side is shown in b).

- a)* featureless regions on the metal surface where ceramic grains have not imprinted on the metal surface corresponding to unbonded regions
- b)* matching triple point on both sides of the fracture surface corresponding to a bonded region
- c)* torn copper particle that appears on both sides of the interface in mirror image
- d)* a region of ceramic pullout

FIGURE 4.4: Fracture surface of a bond processed at 1150°C with an applied load of 7 MPa; this sample failed at 237 MPa. The metal side of the fracture surface is shown in a) and the ceramic side is shown in b).

- a) matching regions of ceramic pullout
- b) corresponding mirror image parts of a torn copper particle
- c) triple point that occurs on both the metal and ceramic sides of the fracture surface

FIGURE 4.5: Fracture surface of a sample processed at 1150°C with an applied load of 7 MPa. This sample failed at 98.4 MPa. The metal side of the fracture surface is shown in a), and the ceramic side is shown in b).

a) and **b)** regions of copper dewetting that are missing imprints of grain boundaries present in the corresponding region on the ceramic side of the fracture surface.

a)

20 μm

20 μm

b)

c)

FIGURE 4.6: Metal (a) and ceramic (b) side of a fracture surface from a sapphire plug sample processed at 1400°C with an applied load of 2.2 MPa. The sample failed at 157 MPa. In (c) a cropped micrograph is shown from a sample that failed at 48.2 MPa. Two unbonded regions are shown, *a* and *b*. One is discolored (*b*) probably because the unbonded region extended all the way to the edge of the sample leaving this region open to contamination during machining.

FIGURE 4.7: Fracture surface from a diffusion bonded sample processed at 1400°C with an applied load of 2.2 MPa. This sample failed at 119 MPa. The metal side is shown in a) and the ceramic side is shown in b).

FIGURE 4.8: a) SEM image and corresponding EDS map with niobium shown in blue and aluminum shown in yellow. EDS shown in c) suggests that embrittlement caused by presence of silicon could lead to fracture through the niobium foil. In d) a high magnification of a fracture surface (metal side) from a diffusion bonded sample shows both the faceted front between bonded and unbonded regions of the interface *a* and a featureless unbonded region *b*. Features that more closely resemble the facets seen by Reimanis are reproduced again in e) a micrograph taken from a region of sapphire diffusion bonded to niobium for 1 hr at 1400°C with an applied load of 2.2 MPa.

FIGURE 4.9: A sequence of interfacial microstructures for sapphire/copper/niobium/copper couples initially bonded at 1150°C with an applied load of 2.2 MPa and after successive anneals in vacuum for a) 15 h b) 22 h c) 29 h d) 36 h and e) 43 h. In this region, grain boundary groove ridges appear to play a prominent role in the initial dewetting of the copper.

FIGURE 4.10: A series of interfacial microstructures for sapphire/copper/niobium/copper couples initially bonded at 1150°C with an applied load of 2.2 MPa and after successive anneals in vacuum for a) 15 h b) 22 h c) 29 h d) 36 h and e) 43 h. In this region asperities seem to play a more prominent role in the initial dewetting of the copper film.

FIGURE 4.II: A series of micrographs showing the breakup of the copper film on *c*-plane sapphire after a) 1 h b) 7 h c) 15 h d) 63 h, and e) 127 h at 1150°C. The lithographically processed feature is 0.5 μm deep. Inside the feature first contact to the sapphire is made by the niobium grain boundary marked as *a*. After 15 h facets start to appear on the surface of the sapphire (the vertical lines in the vicinity of *b*). The grain boundary is filled with liquid copper between 15 and 127 h, but then the liquid disappears again before 127 h is reached.

FIGURE 4.12: A series of micrographs of c-plane sapphire with a lithographically processed feature that is $0.5\ \mu\text{m}$ deep. Images are taken after a) 1 h b) 7 h c) 15 h d) 31 h, and e) 127 h at 1150°C . In this series asperities in the niobium foil are the points of initial sapphire contact inside the lithographically processed groove. The niobium grain boundary marked *a* seems to not be as important as asperities as it disappears from the interface between 1 and 7 h. Again facets are visible as vertical black lines.

FIGURE 4.13: A sequence of micrographs for an m-plane sapphire sample processed at 1150°C for a) 1h b) 15 h c) 31 h d) 63 h and e) 127 h. Although asperities seem to be important to the initial contact of the niobium to the sapphire, a grain boundary effects the final microstructure of the niobium/sapphire interface. A triple point is labeled *a* and a region of facets (vertical lines) is labeled *b*.

FIGURE 4.13.1: An enlarged region from **FIGURE 4.13** that shows a feature that lacked copper originally and then later filled with copper. These images are shown after a) 1 h, b) 3 h, c) 7 h, d) 15 h, e) 31 h, and f) 63 h at 1150°C. Notice that a ridge around the edge of the feature seems to persist, but appears to become more diffuse with time.

FIGURE 4.14: A sequence of micrographs of m-plane sapphire after anneals of a) 1h b) 3 h c) 15 h d) 32 h and e) 127 h at 1150°C. In the lithographically processed cavity, it seems that the grain boundaries grooved but did not contact the sapphire early on. The spotty features marked *a* and the grain boundary marked *b* seem to disappear at extended anneal times. The grain boundary marked *c* in c) seems to be more permanent and in contact with the sapphire as it is present at 127 h. Features that resemble ridges like those seen in **FIGURE 4.13.1** are seen in the vicinity of *d* and *e* in d). Another region of facets is visible at *f* in e).

FIGURE 4.15: Sequence of micrographs for m-plane sapphire with a 0.5 μm deep lithographically processed cavity after anneals of a) 1 h b) 15 h c) 31 h and d) 127 h at 1150°C. At times less than 31 h the grain structure of the niobium marked *a* is visible in the cavity. Between 15 and 31 h the grain boundaries move and do not resemble the grain boundaries visible earlier. The redistribution of liquid copper could cause this drastic change in the niobium grain structure.

FIGURE 4.16: A series of micrographs for an m-plane sample taken after anneals of a) 0.25 h b) 0.75 h c) 1.75 h d) 7.75 h at 1400°C and e) after an additional anneal at 1700°C for 12 h. The grooving of a niobium grain boundary seems to be the initiator of niobium/sapphire contact at 1400°C. After annealing at 1700°C for 12 h no copper is present at the interface. A triple point that is likely a point of initial contact is marked *a* and an unbonded region with a rainbow pattern caused by the refraction of light is marked *b*.

FIGURE 4.17: A series of micrographs from an m-plane sample after anneals at 1400°C of a) 0.25 h b) 0.75 h c) 1.75 h d) 3.75 h and e) an additional anneal of 12 h at 1700°C. Early on facets that appear as horizontal lines are present, but they disappear completely after 1.75 h. This can be seen in the region marked *a*. A grain boundary that was likely an initial point of contact is labeled *b* and a region with asperities is marked *c*. Once again no copper is evident after annealing at 1700°C

FIGURE 4.18: Area analysis of copper coverage for several samples (c- and m-plane) processed at 1150°C. The data is quite irregular and scattered. Copper film thicknesses varied between 2–4 μm for all samples. For example, **FIGURES 4.9** and **4.10** are from a sample that had a copper thickness that ranged between 2.05 and 3.02 μm . **FIGURES 4.11–4.13** are from a sample that had a copper thickness ranging between 2.07 and 3.15 μm .

FIGURE 4.19: Kinetic models for the breakup of the copper film using **EQUATION (4.4)** at 1150°C are shown. Some data from **FIGURE 4.18** were omitted because mathematical singularities occurred when calculating the kinetic parameters. A more sophisticated software package with capabilities to determine the kinetic parameters for these data would avoid this issue.

FIGURE 4.19.1: A model for the formation of niobium/sapphire interface of samples processed at 1150°C using a Johnson-Mehl-Avrami type equation.

FIGURE 4.20: Area analysis and kinetic models for the breakup of the copper film at 1400°C in contact with m-plane sapphire are shown. These data are from the regions of ceramic/metal interface shown in FIGURES 4.16 and 4.17. The copper thickness in these regions of sample ranged between 1.86 and 3.10 μm .

FIGURE 4.20.1: A model for the formation of niobium/sapphire interface for samples processed at 1400°C using a Johnson-Mehl-Avrami type equation.

(a)

FIGURE 4.21: (a) An AFM image of the surface topology of c-plane sapphire in contact with copper and niobium and after being annealed at 1150°C for 127 h and the corresponding line profile (b). The metal layers were etched in an acid solution to expose the sapphire surface, which has developed into a terrace-ledge morphology.

(b)

FIGURE 4.22: An AFM image showing the (a) three-dimensional surface morphology of m-plane sapphire after being in contact with copper and niobium for 127 h at 1150°C and (b) the corresponding line profile. The image was taken after the metal layers were etched in an acid solution to expose the sapphire surface that has developed into a saw-tooth morphology.

(a)

(b)

FIGURE 4.23: Corresponding AFM image (a) and line profile (b) for the bicrystal sample after annealing for 50 hr at 1400°C in contact with copper and niobium. The arrows point to saddle points, which could features of a grain boundary groove present before migration occurred.

(a)

(b)

FIGURE 4.24: Corresponding AFM image (a) and line profile (b) for bicrystal sample after annealing for 150 hr at 1400°C in contact with copper and niobium.

(a)

(b)

FIGURE 4.25: Corresponding AFM image (a) and line profile (b) for bicrystal sample after a total of 150 hr at 1400°C plus an additional 20 hr at 1700°C while in contact with copper and niobium.

FIGURE 4.26: AFM images of bicrystal sample in regions away from the grain boundary after 50 h at 1400°C are shown in (a) and (b). The topology of the bicrystal surface is affected by the niobium asperities. In (a) there appears to be pits in the bicrystal surface perhaps corresponding to protrusions in the niobium surface, and in (b) protrusions in the bicrystal surface could be caused by pits in the niobium surface. The AFM image in (c) and the corresponding line profile in (d) are from a region that was in contact with a niobium grain boundary.

FIGURE 4.27: A micrograph of the as received niobium is shown in (a) at a 40 x magnification. (b) A schematic of what the wetting experiment with copper and niobium looked like after annealing for 6 h at 1400°C. In (c), a micrograph of the cross section of the drop is shown, and (d), (e), and (f) show micrographs of the regions marked *d*, *e*, and *f* in (b) respectively on the surface of the niobium. The micrographs shown in (c)–(f) were taken at a 20 x magnification. In (g) (next page) a region near the perimeter of the drop is shown in high magnification, it seems as though copper nanowires have formed as an artifact of the etching.

(g)

FIGURE 4.27 (continued)

FIGURE 4.28: A copper film 2.87 μm thick was deposited on a Coors alumina substrate and annealed first for 0.5 hr at 1100°C. Two regions showing different copper morphologies are shown in (a) and (b); the alumina grain boundaries are not visible in either. The sample was then annealed at 1400°C for 6 hr and the copper morphology was fairly uniform on the surface and resembled the region shown in (c). The copper particles were etched in nitric acid prior to the micrograph taken in (d) and faint rings were left at the edges of the particles marked with arrows. In (e), (f), and (g), enlargements of the regions labeled e, f, and g in (b) are shown. Surface defects that may act as film dewetting initiation sites are indicated.

FIGURE 4.29: (a) Micrograph showing the grain structure in the polycrystalline material fabricated by Robert Marks after an initial anneal of 30 h at 1600°C. In (b) an AFM image shows the triple line ridge that developed at the solid-liquid-vapor interface. The line scan in (c) shows that there was not a significant difference in the grain boundary widths for regions in contact with liquid compared to regions not in contact with the liquid. The schematic in (d) illustrates how the reduced driving force for mass transport in a small-grained material might lead to slower kinetics of groove widening.

FIGURE 4.30: Line scans of a region of polycrystalline alumina fabricated by Robert Marks that was (a) not in contact with liquid copper and (b) in contact with liquid copper during an anneal for 150 h at 1400°C.

5. CONCLUSIONS

The mechanisms that contribute to the microstructure development in alumina assemblies bonded using copper/niobium/copper interlayers were examined. In particular, the enhancement in kinetics due to the presence of a liquid film and the effects of liquid-film morphology were studied. Microstructure/strength relationships were developed from strength data combined with micrographs of corresponding microstructures. Stronger interfaces were generally characterized by extensive breakup of the liquid film into droplets that plastically deformed and tore during fracture and were present on both the metal and ceramic side of the fracture surface. Fracture surfaces also contained few small featureless unbonded regions, regions of ceramic pullout, and large regions of niobium/alumina contact in which the alumina grain boundaries were visible on both sides of the fracture surface.

The chronology of the microstructural development at these metal/ceramic interfaces was recorded using transparent sapphire substrates in model experiments. Observations of the transformation of copper/sapphire interface into niobium/sapphire interface allowed for the identification of the mechanisms that contributed to the initiation and growth of sapphire/niobium contact. Asperities in the niobium foil and grain boundary grooves in the niobium foil were major sites of niobium/sapphire contact initiation. Other mechanisms that contributed to contact growth and further liquid-film breakup include liquid film redistribution, which depends on defect geometry, local film thickness, and interfacial crystallography, and breakup of liquid patches *via* Rayleigh instabilities. Microlithography techniques made it possible to locally vary the liquid film thickness and establish that sapphire/niobium contact growth occurred more slowly in locally thicker regions of liquid.

Kinetic models were developed to describe dewetting kinetics at 1150°C and 1400°C. These models predict the area fraction of copper/sapphire or niobium/sapphire contact at increasing times during processing. One model uses simple first-order kinetics and the other model utilizes a Johnson-Mehl-Avrami equation. Neither model accurately predicted the extent of breakup for all samples, and kinetic parameters at constant temperature varied considerably. However, it was possible to compare the two processing temperatures using average kinetic parameters and there was reasonable agreement (a factor of 1.44). It is expected that other diffusion mechanisms besides bulk niobium diffusion through the liquid are active at the processing temperatures. Given the large number of factors and mechanisms contributing to the microstructural development, the agreement of the simple kinetic models is quite surprising.

Simple wetting experiments allowed for the investigation of the effects of liquid copper on the thermal grooving of alumina and niobium. Wetting experiments showed that a dispersion of niobium precipitates on the surface of a liquid copper drop might play an important role in the adhesion of liquid copper to alumina and high fracture strengths. The fabrication of an alumina bicrystal also facilitated the study of the grooving of one particular grain boundary in the copper/niobium/alumina system. The grain boundary grooves in alumina have humps on either side of the groove, which indicates that the kinetics of grooving are limited by diffusion. The dissolution and precipitation reaction of alumina in niobium can also be an important mechanism contributing to the morphology of grain boundary grooves when alumina is bonded to copper/niobium/copper interlayers. The presence of a liquid can enhance kinetics of grooving, ridging, and surface faceting in alumina. Difficulties arise when trying to measure the kinetics of grain boundary grooving in small-grained materials because grooves from adjacent grains interfere with mass transport and alter the grooving energetics and kinetics.

REFERENCES

1. R.E. LOEHMAN AND A.P. TOMSIA, "Joining of ceramics." *American Ceramic Society Bulletin*, 1988. **67**(2): p. 375-80.
2. R.M. CRISPIN AND M. NICHOLAS, "The wetting and bonding behaviour of some nickel alloy-alumina systems." *Journal of Materials Science*, 1976. **11**(1): p. 17-21.
3. P. KRITSALIS, B. DREVET, N. VALIGNAT, AND N. EUSTATHOPOULOS, "Wetting transitions in reactive metal/oxide systems." *Scripta Metallurgica et Materialia*, 1994. **30**(9): p. 1127-32.
4. P. KRITSALIS, V. MERLIN, L. COUDURIER, AND N. EUSTATHOPOULOS, "Effect of Cr on interfacial interaction and wetting mechanisms in Ni alloy/alumina systems." *Acta Metallurgica et Materialia*, 1992. **40**(6): p. 1167-75.
5. M.L. SHALZ, B.J. DALGLEISH, A.P. TOMSIA, R.M. CANNON, AND A.M. GLAESER, "Ceramic joining III bonding of alumina via Cu/Nb/Cu interlayers." *Journal of Materials Science*, 1994. **29**(14): p. 3678-90.
6. M.R. LOCATELLI, "Partial transient liquid phase brazing of alumina via microdesigned Ni-based interlayers." M.S. Thesis in Department of Materials Science and Mineral Engineering at University of California at Berkeley in 1997.
7. R.A. MARKS, J.D. SUGAR, AND A.M. GLAESER, "Ceramic joining IV. effects of processing conditions on the properties of alumina joined via Cu/Nb/Cu interlayers." *Journal of Materials Science*, 2001. **36**(23): p. 5609-5624.
8. J.D. SUGAR, J.T. MCKEOWN, R.A. MARKS, AND A.M. GLAESER, "Liquid-film-assisted formation of alumina/niobium interfaces." *Journal of the American Ceramic Society*, 2002. **85**(10): p. 2523-2530.
9. R.A. MARKS, D.R. CHAPMAN, D.T. DANIELSON, AND A.M. GLAESER, "Joining of alumina via copper/niobium/copper interlayers." *Acta Materialia*, 2000. **48**(18-19): p. 4425-38.
10. J.S. STOLKEN AND A.M. GLAESER, "The morphological evolution of cylindrical rods with anisotropic surface free energy via surface diffusion." *Scripta Metallurgica et Materialia*, 1992. **27**(4): p. 449-54.
11. H.C. CAO, M.D. THOULESS, AND A.G. EVANS, "Residual stresses and cracking in brittle solids bonded with a thin ductile layer." *Acta Metallurgica*, 1988. **36**(8): p. 2037-46.
12. A.G. EVANS, B.J. DALGLEISH, M. HE, AND J.W. HUTCHINSON, "On crack path selection and the interface fracture energy in bimaterial systems." *Acta Metallurgica*, 1989. **37**(12): p. 3249-54.
13. A.G. EVANS, M.C. LU, S. SCHMAUDER, AND M. RÜHLE, "Some aspects of the mechanical strength of ceramic/metal bonded systems." *Acta Metallurgica*, 1986. **34**(8): p. 1643-55.

14. A.G. EVANS, M. RÜHLE, AND M. TURWITT, "On the Mechanics of Failure in Ceramic/Metal Bonded Systems", in *International Conference on the Structure and Properties of Internal Interfaces*. 1985, Les Editions de Physique: Les Ulis Cedex. p. 613-25.
15. R.O. RITCHIE, R.M. CANNON, B.J. DALGLEISH, R.H. DAUSKARDT, AND J.M. McNANEY, "Mechanics and mechanisms of crack growth at or near ceramic-metal interfaces: interface engineering strategies for promoting toughness." *Materials Science & Engineering A-Structural Materials Properties Microstructure & Processing*, 1993. **A166**(1-2): p. 221-35.
16. B.J. DALGLEISH, M.C. LU, AND A.G. EVANS, "The strength of ceramics bonded with metals." *Acta Metallurgica*, 1988. **36**(8): p. 2029-35.
17. E. SAIZ, A.P. TOMSIA, AND R.M. CANNON, "Wetting and Work of Adhesion in Oxide/Metal Systems", in *Ceramic microstructures : control at the atomic level*, A.P. Tomsia and A.M. Glaeser, Editors. 1998, Plenum Press: New York. p. 65-82.
18. W. ZHANG, J.R. SMITH, AND A.G. EVANS, "The connection between *ab initio* calculations and interface adhesion measurements on metal/oxide systems: Ni/Al₂O₃ and Cu/Al₂O₃." *Acta Materialia*, 2002. **50**: p. 3803-16.
19. X.-G. WANG AND J.R. SMITH, "Adhesion of Copper and Alumina from First Principles." *Journal of the American Ceramic Society*, 2003. **86**(4): p. 696-700.
20. I.G. BATYREV, A. ALAVI, AND M.W. FINNIS, "Equilibrium and adhesion of Nb/sapphire: The effect of oxygen partial pressure." *Physical Review B*, 2000. **62**(7): p. 4698-706.
21. W. ZHANG AND J.R. SMITH, "Stoichiometry and adhesion of Nb/Al₂O₃," *Physical Review B*, 2000. **61**(24): p. 883-9.
22. Y. YOSHINO, "Role of oxygen in bonding copper to alumina." *Journal of the American Ceramic Society*, 1989. **72**(8): p. 1322-7.
23. M. DIEMER, A. NEUBRAND, K.P. TRUMBLE, AND J. RÖDEL, "Influence of Oxygen Partial Pressure and Oxygen Content on the Wettability in the Copper-Oxygen-Alumina System." *Journal of the American Ceramic Society*, 1999. **82**(10): p. 2825-32.
24. M.G. NICHOLAS, T.M. VALENTINE, AND M.J. WAITE, "The wetting of alumina by copper alloyed with titanium and other elements." *Journal of Materials Science*, 1980. **15**(9): p. 2167-206.
25. P.R. CHIDAMBARAM, A. MEIER, AND G.R. EDWARDS, "The nature of interfacial phenomena at copper-titanium/alumina and copper-oxygen/alumina interfaces." *Materials Science & Engineering A-Structural Materials Properties Microstructure & Processing*, 1996. **A206**(2): p. 249-58.
26. H. MATSUMOTO, M.R. LOCATELLI, K. NAKASHIMA, A.M. GLAESER, AND K. MORI, "Wettability of Al₂O₃ by liquid Cu as influenced by additives and partial transient liquid-phase bonding of Al₂O₃." *Materials Transactions Japan Institute of Metals*, 1995. **36**(4): p. 555-64.
27. E. SAIZ, A.P. TOMSIA, AND R.M. CANNON, "Ridging effects on wetting and spreading of liquids on solids." *Acta Materialia*, 1998. **46**(7): p. 2349-61.

28. E. SAIZ, A.P. TOMSIA, AND R.M. CANNON, "Triple line ridging and attachment in high-temperature wetting." *Scripta Materialia*, 2001. **44**(1): p. 159-64.
29. M. TURWITT, G. ELSSNER, AND G. PETZOW, "Manufacturing and Mechanical Properties of Interfaces Between Sapphire and Niobium", in *International Conference on the Structure and Properties of Internal Interfaces*. 1985, Les Editions de Physique: Les Ulis Cedex. p. 123-7.
30. H.F. FISCHMEISTER, G. ELSSNER, B. GIBBESCH, K.H. KADOW, F. KAWA, D. KORN, W. MADER, AND M. TURWITT, "Solid-state bonding of accurately oriented metal/ceramic bicrystals in ultrahigh vacuum." *Review of Scientific Instruments*, 1993. **64**(1): p. 234-42.
31. B. GIBBESCH AND G. ELSSNER, "Ultra high vacuum diffusion bonded Nb-Al₂O₃ and Cu-Al₂O₃ joints-the role of welding temperature and sputter cleaning." *Acta Metallurgica et Materialia*, 1992. **40**: p. S59-66.
32. M.P. SEAH, "Adsorption-induced interface decohesion." *Acta Metallurgica*, 1980. **28**(7): p. 955-62.
33. D. KORN, G. ELSSNER, H.F. FISCHMEISTER, AND M. RÜHLE, "Influence of interface impurities on the fracture energy of UHV bonded niobium-sapphire bicrystals." *Acta Metallurgica et Materialia*, 1992. **40**: p. S355-60.
34. G. SOYEZ, G. ELSSNER, M. RÜHLE, AND R. RAJ, "Constrained yielding in niobium single crystals bonded to sapphire." *Acta Materialia*, 1998. **46**(10): p. 3571-81.
35. I.E. REIMANIS, "Pore removal during diffusion bonding of Nb-Al₂O₃ interfaces." *Acta Metallurgica et Materialia*, 1992. **40**: p. S67-74.
36. M. RÜHLE, M. BACKHAUS-RICOULT, K. BURGER, AND W. MADER. "Diffusion Bonding of Metal/Ceramic Interfaces - A Model Study at the Nb/Al₂O₃ Interfaces". *Proceedings of the 22nd University Conference on Ceramics, and the International Materials Symposium* **21**. 1986. Berkeley, CA: Plenum Press 295-305.
37. K. SCHULZE, B. RICKES, AND G. PETZOW, "Reactions of Nb-Al powder mixtures during sintering." *Journal of the Less-Common Metals*, 1984. **100**: p. 429-41.
38. N.V. BODROV AND G.I. NIKOLAEV, "Application of atomic absorption spectroscopy to the study of an aluminium oxide carbon interaction and to the investigation of the high temperature evaporation and diffusion of aluminium in refractory metals." *Zhurnal Prikladnoi Spektroskopii*, 1974. **21**(3): p. 400-4.
39. E. FROMM AND E. GEBHARDT, eds. *Gase in Metallen*. 1978, Springer Verlag.
40. K. BURGER, W. MADER, AND M. RÜHLE, "Structure, chemistry and diffusion bonding of metal/ceramic interfaces." *Ultramicroscopy*, 1987. **22**(1-4): p. 1-13.
41. M. RÜHLE, K. BURGER, AND W. MADER, "Structure and chemistry of grain boundaries in ceramics and of metal/ceramic interfaces." *Journal de Microscopie et de Spectroscopie Electroniques*, 1986. **11**(3): p. 163-77.
42. M. FLORJANCIC, W. MADER, M. RÜHLE, AND M. TURWITT, "HREM and Diffraction Studies of an Al₂O₃/Nb Interface", in *International Conference on the Structure and Properties of Internal Interfaces*. 1985, Les Editions de Physique: Les Ulis Cedex. p. 129-33.

43. S. MOROZUMI, M. KIKUCHI, AND T. NISHINO, "Bonding mechanism between alumina and niobium." *Journal of Materials Science*, 1981. **16**(8): p. 2137-44.
44. M. NICHOLAS, R.R.D. FORGAN, AND D.M. POOLE, "The Adhesion of Metal/Alumina Interfaces." *Journal of Materials Science*, 1968. **3**: p. 9-14.
45. G. HEIDT AND G. HEIMKE, "A study of the nature of solderless metal-ceramic bonds by reflectivity measurements." *Journal of Materials Science*, 1975. **10**(5): p. 887-95.
46. G. DEHM, C. SCHEU, G. MOBUS, R. BRYDSON, AND M. RÜHLE, "Synthesis of analytical and high-resolution transmission electron microscopy to determine the interface structure of Cu/Al₂O₃." *Ultramicroscopy*, 1997. **67**: p. 207-17.
47. M. WITTMER, C.R. BOER, P. GUDMUNDSON, AND J. CARLSSON, "Mechanical properties of liquid-phase-bonded copper-ceramic substrates." *Journal of the American Ceramic Society*, 1982. **65**(3): p. 149-53.
48. R.M. CRISPIN AND M. NICHOLAS, "Alumina-Copper Diffusion Bonding." *Ceramic Engineering and Science Proceedings*, 1989. **10**(11-12): p. 1575-81.
49. C.A.M. MULDER AND J.T. KLOMP, "On the Internal Structure of Cu- and Pt-Sapphire Interfaces", in *International Conference on the Structure and Properties of Internal Interfaces*. 1985, les Editions de physique: Les Ulis Cedex. p. 111-16.
50. T. WAGNER, M. LORENZ, AND M. RÜHLE, "Thermal stability of Nb thin films on sapphire." *Journal of Materials Research*, 1996. **11**(5): p. 1255-64.
51. C. BERAUD, M. COURBIERE, C. ESNOUF, D. JUVE, AND D. TREHEUX, "Study of copper-alumina bonding." *Journal of Materials Science*, 1989. **24**(12): p. 4545-54.
52. K. SUNG TAE AND K. CHONG HEE, "Interfacial reaction product and its effect on the strength of copper to alumina eutectic bonding." *Journal of Materials Science*, 1992. **27**(8): p. 2061-6.
53. Y. IINO AND N. TAGUCHI, "Interdiffusing metals layer technique of ceramic-metal bonding." *Journal of Materials Science Letters*, 1988. **7**(9): p. 981-2.
54. G.R. VAN HOUTEN, "A Survey of Ceramic-to-Metal Bonding." *Ceramic Bulletin*, 1959. **38**(6): p. 301-7.
55. L. BERNSTEIN AND B. BARTHOLOMEW, "Applications of Solid-Liquid Interdiffusion (SLID) Bonding in Integrated-Circuit Fabrication." *Transactions of the Metallurgical Society of AIME*, 1966. **236**: p. 405-12.
56. D.S. DUVAL, W.A. OWCZARSKI, AND D.F. PAULONIS, "TLP Bonding: A New Method for Joining Heat Resistant Alloys." *Welding Journal*, 1974. **53**: p. 203-14.
57. R.E. LOEHMAN, "Transient Liquid Phase Bonding of Silicon Nitride Ceramics", in *Surfaces and interfaces in ceramics and ceramic-metal systems*, J.A. Pask and A.G. Evans, Editors. 1981, Plenum Press: New York. p. 701-11.
58. S.J. GLASS, F.M. MAHONEY, B. QUILLAN, J.P. POLLINGER, AND R.E. LOEHMAN, "Refractory oxynitride joints in silicon nitride." *Acta Materialia*, 1998. **46**(7): p. 2393-9.

59. Y. IINO, "Partial transient liquid-phase metals layer technique of ceramic-metal bonding." *Journal of Materials Science Letters*, 1991. **10**(2): p. 104-6.
60. M.L. SHALZ, B.J. DALGLEISH, A.P. TOMSIA, AND A.M. GLAESER, "Ceramic joining II. Partial transient liquid-phase bonding of alumina via Cu/Ni/Cu multilayer interlayers." *Journal of Materials Science*, 1994. **29**(12): p. 3200-8.
61. M.L. SHALZ, B.J. DALGLEISH, A.P. TOMSIA, AND A.M. GLAESER, "Ceramic joining. I. Partial transient liquid-phase bonding of alumina via Cu/Pt interlayers." *Journal of Materials Science*, 1993. **28**(6): p. 1673-84.
62. B.J. DALGLEISH, A.P. TOMSIA, K. NAKASHIMA, M.R. LOCATELLI, AND A.M. GLAESER, "Low temperature routes to joining ceramics for high-temperature applications." *Scripta Metallurgica et Materialia*, 1994. **31**(8): p. 1043-8.
63. M. PAULASTO, G. CECONE, AND S.D. PETEVES, "Joining of silicon nitride via a transient liquid." *Scripta Materialia*, 1997. **36**(10): p. 1167-73.
64. E. SAIZ AND A.P. TOMSIA, "Kinetics of metal-ceramic composite formation by reactive penetration of silicates with molten aluminum." *Journal of the American Ceramic Society*, 1998. **81**(9): p. 2381-93.
65. R.E. LOEHMAN, K. EWSUK, AND A.P. TOMSIA, "Synthesis of Al_2O_3 -Al composites by reactive metal penetration." *Journal of the American Ceramic Society*, 1996. **79**(1): p. 27-32.
66. E. SAIZ, S. FOPPIANO, W. MOBERLY-CHAN, AND A.P. TOMSIA, "Synthesis and processing of ceramic-metal composites by reactive metal penetration." *Composites - Part A: Applied Science & Manufacturing*, 1999. **30A**(4): p. 399-403.
67. T.B. MASSALSKI, ed. *Binary Alloy Phase Diagrams*. Vol. 1-3. 1990, ASM International: Metals Park, OH.
68. L. WEIPING, G. ELSSNER, AND M. RÜHLE, "Effects of thin film Nb interlayer in Cu/sapphire bonds." *Materials Science & Engineering A-Structural Materials Properties Microstructure & Processing*, 2001. **A317**(1-2): p. 153-62.
69. J.J. KRIZIC, R.A. MARKS, M. YOSHIYA, A.M. GLAESER, R.M. CANNON, AND R.O. RITCHIE, "Fracture and fatigue behavior at ambient and elevated temperatures of alumina bonded with copper/niobium/copper interlayers." *Journal of the American Ceramic Society*, 2002. **85**(10): p. 2531-2541.
70. M.R. LOCATELLI, A.P. TOMSIA, K. NAKASHIMA, B.J. DALGLEISH, AND A.M. GLAESER, "New strategies for joining ceramics for high-temperature applications." *Mechanical & Corrosion Properties, Series a (Key Engineering Materials)*, 1995. **111-112**: p. 157-90.
71. O.F. DE LIMA, M. KREHL, AND K. SCHULZE, "Wetting characteristics of copper on niobium." *Journal of Materials Science*, 1985. **20**(7): p. 2464-70.
72. R.A. MARKS, "Effects of processing conditions and ambient environment on the microstructure and fracture strength of copper/niobium/copper interlayer joints for alumina." M.S. Thesis in Department of Materials Science and Mineral Engineering at University of California, Berkeley in 2000.

73. J.T. McKEOWN, "Processing and Characterization of Alumina-Niobium Interfaces Produced by Liquid-Film-Assisted Joining." M.S. in Materials Science and Engineering at University of California at Berkeley in 2003.
74. G. WULFF, "Zur Frage der Geschwindigkeit des Wachstums und der Auflösung der Krystallflächen." *Zeitschrift für Krystallographie*, 1901. **34**: p. 449.
75. C. HERRING, "Some Theorems on the Free Energies of Crystal Surfaces." *The Physical Review*, 1951. **82**(1): p. 87-93.
76. W.W. MULLINS, "Theory of Linear Facet Growth During Thermal Etching." *Philosophical Magazine*, 1961. **6**: p. 1313-41.
77. J.R. HEFFELFINGER, M.W. BENCH, AND C.B. CARTER, "On the faceting of ceramic surfaces." *Surface Science*, 1995. **343**(1-2): p. L1161-6.
78. J.R. HEFFELFINGER, M.W. BENCH, AND C.B. CARTER, "Steps and the structure of the (0001) α -alumina surface." *Surface Science*, 1997. **370**(1): p. L168-72.
79. J.R. HEFFELFINGER AND C.B. CARTER, "Mechanisms of surface faceting and coarsening." *Surface Science*, 1997. **389**(1-3): p. 188-200.
80. M. KITAYAMA, T. NARUSHIMA, W.C. CARTER, R.M. CANNON, AND A.M. GLAESER, "The Wulff shape of alumina: I. Modeling the kinetics of morphological evolution." *Journal of the American Ceramic Society*, 2000. **83**(10): p. 2561-71.
81. M. KITAYAMA, T. NARUSHIMA, AND A.M. GLAESER, "The Wulff shape of alumina. II. Experimental measurements of pore shape evolution rates." *Journal of the American Ceramic Society*, 2000. **83**(10): p. 2572-83.
82. H.P. BONZEL, "Surface morphologies: transient and equilibrium shapes." *Interface Science*, 2001. **9**(1-2): p. 21-34.
83. H.P. BONZEL, U. BREUER, B. VOIGTLANDER, AND E. ZELDOV, "Temperature-dependent morphologies of gold surfaces." *Surface Science*, 1992. **272**(1-3): p. 10-16.
84. N. RAVISHANKAR, S.R. GILLISS, AND C.B. CARTER, "Dewetting of liquids on ceramic surfaces at high temperatures." *Microscopy & Microanalysis*, 2002. **8**(4): p. 257-67.
85. W.W. MULLINS, "Theory of Thermal Grooving." *Journal of Applied Physics*, 1957. **28**(3): p. 333-9.
86. W.W. MULLINS, "The Effect of Thermal Grooving on Grain Boundary Motion." *Acta Metallurgica*, 1958. **6**: p. 414-27.
87. W.W. MULLINS, "Grain Boundary Grooving by Volume Diffusion." *Transactions of the Metallurgical Society of AIME*, 1960. **218**: p. 354-61.
88. W.W. MULLINS AND P.G. SHEWMON, "The Kinetics of Grain Boundary Grooving in Copper." *Acta Metallurgica*, 1959. **7**: p. 163-70.
89. E. SAIZ, R.M. CANNON, AND A.P. TOMSIA, "Energetics and atomic transport at liquid metal/ Al_2O_3 interfaces." *Acta Materialia*, 1999. **47**(15-16): p. 4209-20.

90. V. GHETTA AND D. CHATAIN, "Morphologies adopted by Al_2O_3 single-crystal surfaces in contact with Cu droplets." *Journal of the American Ceramic Society*, 2002. **85**(4): p. 961-4.
91. L. KLINGER AND E. RABKIN, "Effects of surface anisotropy on grain boundary grooving." *Interface Science*, 2001. **9**(1-2): p. 55-63.
92. W.W. MULLINS AND F.A. NICHOLS, "Surface- (Interface-) and Volume-Diffusion Contributions to Morphological Changes Driven by Capillarity." *Transactions of the Metallurgical Society of AIME*, 1965. **233**: p. 1840-8.
93. W.W. MULLINS, "Capillarity-induced surface morphologies." *Interface Science*, 2001. **9**(1-2): p. 9-20.
94. A.M. GLAESER, "Microstructure development in ceramics: the role of grain growth." *Yogyo-Kyokai-Shi*, 1984. **92**(10): p. 537-46.
95. J. RÖDEL AND A.M. GLAESER, "Anisotropy of grain growth in alumina." *Journal of the American Ceramic Society*, 1990. **73**(11): p. 3292-301.
96. J.D. POWERS AND A.M. GLAESER, "High-temperature healing of cracklike flaws in Mg- and Ca-ion-implanted sapphire." *Journal of the American Ceramic Society*, 1992. **75**(9): p. 2547-58.
97. J.D. POWERS AND A.M. GLAESER, "High-temperature healing of cracklike flaws in titanium ion-implanted sapphire." *Journal of the American Ceramic Society*, 1993. **76**(9): p. 2225-34.
98. L. KULINSKY, J.D. POWERS, AND A.M. GLAESER, "Morphological evolution of pre-perturbed pore channels in sapphire." *Acta Materialia*, 1996. **44**(10): p. 4115-30.
99. M. KITAYAMA, J.D. POWERS, L. KULINSKY, AND A.M. GLAESER, "Surface and interface properties of alumina via model studies of microdesigned interfaces." *Journal of the European Ceramic Society*, 1999. **19**(13-14): p. 2191-209.
100. J.D. POWERS AND A.M. GLAESER, "Orientation effects on the high-temperature morphological evolution of pore channels in sapphire." *Journal of the American Ceramic Society*, 2000. **83**(9): p. 2297-304.
101. A.M. GLAESER, "Model studies of Rayleigh instabilities via microdesigned interfaces." *Interface Science*, 2001. **9**(1-2): p. 65-82.
102. T. NARUSHIMA AND A.M. GLAESER, "High-temperature morphological evolution of lithographically introduced cavities in silicon carbide." *Journal of the American Ceramic Society*, 2001. **84**(5): p. 921-8.
103. A.J. VILENKIN, R. KRIS, AND A. BROKMAN, "Breakup and grain growth in thin-film array." *Journal of Applied Physics*, 1997. **81**(1): p. 238-45.
104. F.Y. GENIN, "Surface morphological evolution of thin films under stress and capillary forces." *Interface Science*, 2001. **9**(1-2): p. 83-92.

105. R.A. MARKS, "Fabrication of Controlled-Misorientation Alumina Grain Boundaries and Implications of the Triple-Junction Equilibrium Conditions." Ph.D. Thesis in Materials Science and Engineering at University of California, Berkeley in 2003.
106. W. LIU, G. ELSSNER, AND M. RÜHLE, "Effects of thin film Nb interlayer in Cu/sapphire bonds." *Materials Science & Engineering A-Structural Materials Properties Microstructure & Processing*, 2001. **A317**(1-2): p. 153-62.
107. M. LANE, R.H. DAUSKARDT, A. VAINCHTEIN, AND G. HUAJIAN, "Plasticity contributions to interface adhesion in thin-film interconnect structures." *Journal of Materials Research*, 2000. **15**(12): p. 2758-69.
108. K. YAGI, H. MINODA, AND M. DEGAWA, "Step bunching, step wandering and faceting: self-organization at Si surfaces." *Surface Science Reports*, 2001. **43**(2-4): p. 45-126.
109. K. TRAN, "Evolution of Geometrically Controlled Metallic Particles in Single Crystal Alumina." Master's Thesis in Materials Science and Engineering at University of California at Berkeley in 2003.
110. W.E. LEE AND K.P.D. LAGERLOF, "Structural and Electron-Diffraction Data for Sapphire (α -Al₂O₃)." *Journal of Electron Microscopy Technique*, 1985. **2**(3): p. 247-258.
111. M. RUHLE, M. BACKHAUS-RICOULT, K. BURGER, AND W. MADER. "Diffusion Bonding of Metal/Ceramic Interfaces - A Model Study at the Nb/Al₂O₃ Interfaces". *Proceedings of the 22nd University Conference on Ceramics, and the International Materials Symposium* **21**. 1986. Berkeley, CA: Plenum Press 295-305.
112. A.F. CRAWLEY, "Densities of liquid metals and alloys." *International Metallurgical Reviews*, 1974. **19**: p. 32-48.
113. P.E. ARMSTRONG, J.M. DICKINSON, AND H.L. BROWN, "Temperature Dependence of the elastic stiffness coefficients of niobium (columbium)." *Transactions of the Metallurgical Society of AIME*, 1966. **236**: p. 1404-8.
114. E.N. HODKIN, M.G. NICHOLAS, AND D.M. POOLE, "The surface energies of solid molybdenum, niobium, tantalum and tungsten." *Journal of the Less-Common Metals*, 1970. **20**(2): p. 93-103.

APPENDIX I: TENSILE STRESS EXPERIENCED BY A BEAM IN THE 4-POINT BEND TEST

When a beam experiences bending, the stress it experiences is given by:

$$\sigma = -\frac{My}{I} \quad (\text{A.1})$$

where M is the bending moment experienced by the beam at position y from the neutral axis for a beam with a moment of inertia I . The geometry of a beam experiencing bending in a 4-point bend test is depicted below.

It is possible to calculate the moment, M , that the beam experiences from the relation:

$$\frac{dM}{dx} = V \quad (\text{A.2})$$

where V is the shear force experienced by a volume element in the beam. It is possible to construct a plot of the shear experienced by a volume element at position x using the method of sections and summing the forces to zero starting at the left end of the beam. A sketch of the shear V as a function of x is shown below.

It is possible to now integrate to find the moment M . The constant of integration is zero because no moment can be applied by the rods applying the forces. A plot of the moment is shown below.

From the plot it is clear that the maximum moment the beam experiences is equal to $\frac{Pa}{2}$. So the maximum tensile stress is going to be experienced on the bottom edge of the beam when x is a position that is half of the length of the beam. Combining equations:

$$\begin{aligned}
 M &= \frac{Pa}{2}; y = -\frac{d}{2}; I = \frac{bd^3}{12} \\
 \sigma &= -\frac{Pa}{2} \cdot -\frac{d}{2} \cdot \frac{12}{bd^3} \\
 \sigma &= \frac{3Pa}{bd^2}
 \end{aligned} \tag{A.3}$$

If P is given in kg, then it is necessary to multiply by g to obtain P in N. For a testing jig with an inner span of 9 mm and an outer span of 25 mm, $a=8$ mm, and thus the equation for the maximum tensile stress experienced by the beam is obtained:

$$\sigma_{\max} = \frac{24P_{\max}g}{bd^2}.$$

APPENDIX II: DRIVING FORCE FOR THIN-FILM DEWETTING

The microstructure of sapphire joined using copper/niobium/copper interlayers has been shown to develop into large regions of niobium/sapphire contact with isolated particles of copper dispersed along the interface. A thin-film of copper deposited onto an alumina substrate will also dewet the surface and form many isolated particles. For the case of the thin-film at the bimaterial interface, it has been shown that many factors can affect the formation of the isolated droplets including thermal grooving, surface defects, and crystallographic orientation dependent surface energies. The formation of isolated droplets from a thin liquid film on a surface is completely driven by the minimization of surface energies. It is desired to determine the relative values of this driving force for the formation of one isolated drop on a surface, compare it to the driving force for the formation of multiple drops, and determine how the film thickness affects these driving forces.

Young's equation describes the equilibrium contact angle, θ , that develops at solid/liquid/vapor interfaces to minimize surface energies. For all but the lowest contact angles, a film that completely covers a substrate surface must contract from the edges of the substrate if volume is to be conserved in the film material, and if equilibrium is to be reached. The schematic below illustrates a continuous film that dewets to either one drop or multiple drops of equilibrium shape.

The geometry of the isolated drops is that of a spherical cap. Thus, it is important to define the important geometric parameters in a spherical cap. Those parameters are defined in the schematic below.

Some relevant geometric relationships between the parameters in the schematic above are given below.

$$h = R - R \cos \theta$$

$$a = R \sin \theta$$

$$V_{cap} = \frac{1}{3} \pi h^2 (3R - h)$$

$$A_{cap} = 2\pi R h$$

where V_{cap} and A_{cap} are the volume and surface area of the spherical cap, respectively. Notice that when θ is defined this way, these geometric relationships are valid for all values of θ between 0° and 180° .

Using this geometric description it is possible to calculate the change in free energy when a continuous film contracts to form a drop at various equilibrium contact angles for given values of interfacial energies. The initial geometry of the system to be dealt with was determined from two basic assumptions. The film thickness had to be much less than the length and width dimensions. Also, it was assumed that the film's volume was unity, and unit volume was conserved as the film would contract and form one or many drops. For different equilibrium contact angles, the radius of the spherical segment was always back calculated by assuming conservation of volume. Arbitrary units were used for all of the calculations. The initial condition with the relevant dimensions is shown in the schematic below. The change in free energy is always calculated relative to this initial state.

The change in free energy for the film dewetting the substrate and forming a spherical cap for different values of equilibrium contact angle is given by:

$$\Delta G = nA_{cap}\gamma_{lv} + n\pi(R(\theta)\sin(\theta))^2\gamma_{sl} + [1000^2 - n\pi(R(\theta)\sin(\theta))^2]\{\gamma_{sl} + \gamma_{lv}\cos(\theta)\} - \left\{[1000^2 + 4 \cdot 1000 \cdot 1 \times 10^{-6}]\gamma_{lv} + 1000^2\gamma_{sl}\right\}$$

where:

n = the number of drops

$R(\theta)$ = a function that calculates the radius of a spherical cap

that conserves the volume of the film for a given equilibrium contact angle and n

γ_{lv} = liquid/vapor interfacial energy

γ_{sl} = solid/liquid interfacial energy

$\frac{\gamma_{sl}}{\gamma_{lv}} = 2$ for the purposes of this calculation

t = the thickness of the film (does not appear here, but will be used later)

The change in free energy can then be plotted for various equilibrium contact angles. The plot below compares the free energy change for the continuous film transforming into 1 drop and transforming into 1000 drops.

Upon inspection it appears as though the driving forces for these two processes are equivalent. The plot below shows that this is not the case.

It is clear from the plot that $G_{1000 \text{ drops}} - G_{1 \text{ drop}} > 0$. This means that the driving force for the film transforming to one drop is always more negative than the driving force for a transformation to multiple drops. The difference is not large, which implies that perhaps the morphology of a thin-film on a surface is very sensitive to nucleation sites for drop formation. It emerges that the shape of this plot is insensitive to relative values of interfacial energies and number of drops. The scale of the vertical axis changes to accommodate different number of drops and relative values of interfacial energies, but the shape of the curve remains the same. As the number of drops the film breaks up into increases (n), the value of $G_{n>1 \text{ drops}} - G_{1 \text{ drop}}$ becomes more positive. One would expect that if a film were to initially break up into multiple drops for kinetic reasons that these drops would coarsen to eventually form one big drop given enough time because thermodynamically, a single-drop morphology minimizes the interfacial energy.

The question that remains is the effect of film thickness on this driving force. The plot below shows the effect of increasing film thickness on the driving force for the formation of one drop. A film thickness 10 times the thickness originally used for this calculation has been used, and the volume of the film material has been adjusted accordingly.

In this case the thicker film has a less negative change in free energy and therefore a smaller driving force for dewetting. For a given area of substrate and a constant volume of film material, a scaling law exists between the radius of the drop and the film thickness:

$$At = \frac{4}{3}\pi R^3 \cdot \text{scaling factor for a spherical cap}$$

$$\therefore R \propto t^{\frac{1}{3}}$$

The curvature contribution of the chemical potential of the drop scales with the radius of curvature:

$$\mu \propto \frac{2}{R}$$

A thicker film would therefore lead to a larger drop radius and a decreased curvature increment to the chemical potential, which explains why the driving force for a thicker film to form a drop is smaller.

The next plot compares $\Delta G_{1000 \text{ drops}}$ for a film thickness of 1×10^{-5} to $\Delta G_{1000 \text{ drops}}$ for a thickness of 1×10^{-6} .

It seems as though there is also a greater driving force for the thinner film to breakup into multiple drops, similar to the case for one drop, but the difference is greater for multiple drops. Volume conservation requires that the sum of the volume of all of the drops is equal to the film volume, thus the scaling law becomes:

$$At = \frac{4}{3}\pi R^3 n \cdot \text{scaling factor for a spherical cap}$$

$$\therefore R \propto \left(\frac{t}{n}\right)^{\frac{1}{3}}$$

The thicker film is going to reduce the curvature increment to the chemical potential, but the greater number of drops is going to increase the curvature increment to the chemical potential. Thicker films have a smaller driving force for drop formation, and the driving force for transformation increases with decreasing number of drops.

Finally, the last plot shows a comparison of a transformation to 1000 drops versus 1 drop for a film with thickness 1×10^{-5} .

It would seem that as film thickness increases, there is a greater difference in driving forces for the formation of one drop and multiple drops, but the minimum energy still occurs with the formation of one drop. The results of these calculations can be summarized into three important conclusions:

1. As film thickness decreases, the driving force per unit volume for dewetting increases.
2. The driving force is greater (more negative) for the formation of fewer drops.
3. As film thickness increases, the difference between the driving force for the formation of one drop and the formation of multiple drops increases.

The plots below summarize the results in graphical form.