# METALLIZATION OF AIN

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To Allah,

my mother

&

my wonderful family .....

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## ABSTRACT

Heat dissipation from silicon chips is becoming critical as a result of increasing circuit density and power applied to these chips. In this regard, aluminum nitride (AIN) is the most promising candidate to be used as a substrate since it possesses high a thermal conductivity and thermal expansion coefficient close to that of silicon. In addition, metal-ceramic interfaces determine the heat dissipation through a circuit. In order to minimize the effect of interfaces, direct bonding (DB) of AlN to Cu was studied. DB process has been reported to provide a low thermal barrier and an interface which is free of thermal fatigue.

In this work process parameters of DB were optimized based on time, temperature and thickness of the Cu-foil for Cu-Al<sub>2</sub>O<sub>3</sub> system in a N<sub>2</sub> atmosphere containing 500 ppm O<sub>2</sub> in a temperature range of 1065 to 1075°C. These conditions were then applied to the Cu-AlN system. Wettability of AlN by Cu was studied and improved through oxidation of AlN and modification of Cu by adding 1 at. % O<sub>2</sub>. The activation energy for oxidation of AlN was found to be 94 kJ/mol. It was then shown that direct bonding of Cu to AlN can be performed without any intermediate layer. The average peel strength of AlN-Cu, Al<sub>2</sub>O<sub>3</sub>-Cu and AlN-Al<sub>2</sub>O<sub>3</sub>-Cu systems were measured to be 42, 49 and 14.7 MPa, respectively.

# <u>RÉSUMÉ</u>

Dù à l'augmentation de la densité des circuits électroniques ainsi qu'à l'accroissement de la puissance appliquée aux puces de silicium, la dissipation thermique des circuits électroniques est devenue un facteur critique. Considérant ceci, le nitrure d'aluminium (AlN) offre de grandes promesses comme substrat puisque ce matériau possède une haute conductivité thermique ainsi qu'un coefficient d'expension thermique près de celui du silicium. L'interface métalcéramique est un autre facteur important qui détermine la dissipation thermique dans un circuit. Dans le but de minimiser les effets d'interfaces, la méthode de lien direct (LD) ou "direct bonding" (DB) de AlN au cuivre (Cu) a été étudiée. Il a été démontré que le procédé LD permet d'obtenir un interface libre de fatigue thermique et offrant peu de résistance thermique.

Dans ce travail, différents paramètres du procédé LD ont été optimisés. Ceux-ci incluent le temps, la température (1065 - 1075°C) et l'épaisseur de la feuille de cuivre (Cu) pour le système Cu-Al<sub>2</sub>O<sub>3</sub> dans un atmosphère d'azote contenant 500 ppm O<sub>2</sub>. Ces conditions ont ensuite été appliquée au système Cu-AlN. La mouillabilité du cuivre sur le nitrure d'aluminium a été étudiée et améliorée grâce à l'oxydation de AlN et à l'ajout de 1 at.% O<sub>2</sub> au cuivre. L'énergie d'activation pour l'oxydation de AlN a été évaluée à 94 kJ/mol. Il a ensuite été démontré qu'un lien direct entre le Cu et AlN peut être effectué sans aucune couche intermédiaire. La force d'adhésion moyenne des systèmes AlN-Cu, Al<sub>2</sub>O<sub>3</sub>-Cu et AlN-Al<sub>2</sub>O<sub>3</sub> a été calculée comme étant 42, 49 et 14,7 MPa respectivement.

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## **1. INTRODUCTION**

The combination of materials of different types, such as ceramics, metals, glass fibers-organic polymers, is of ever increasing technical importance. Due to such combinations it is possible to make full use of the best properties of all materials concerned. In order to be able to do this in an optimum way, it is necessary to obtain a good bonding between these materials.

Aluminum nitride is emerging as an attractive substrate material in microelectronic packaging applications because of its superior thermal and mechanical properties. Moreover the trend to high density circuitry has prompted increased use of copper materials. Copper conductors have the conductivity of pure gold or silver conductors, combined with the solder leach resistance and migration resistance of high-performance Pd-Ag conductors.

Metallization of aluminum nitride by copper is, therefore, an important technological concern. Numerous methods can be used to metallize the surface of aluminum nitride. Some methods consist of electroless plating techniques, conventional evaporating and sputtering methods to form thin films, and direct bonded copper (DBC) processes whereby aluminum nitride surface is pre-oxidized to alumina for subsequent spinel formation. This pre-oxidation technique has also been utilized to improve the bonding adhesion for the thick film process. Direct bond copper substrates are chiefly used for high power applications such as high speed switching modules, audio and microwave power amplifiers, opto-electronic IC's, and power supply modules, because of the extremely low electrical resistances of the

#### **INTRODUCTION**

Cu material, which guarantee extra large currents in the conductors. Thick film techniques have also been developed. The majority of the thick film materials suffer from poor adhesion to the aluminum nitride substrates. This is mostly because the surface chemistry of substrates varies and depends on the manufacturer.

Among all of these processes, direct bonded copper is very promising. As its name implies there is no intermediate layer between the conductor and the substrate. When a low thermal resistance of the substrate is required the direct copper bond method is very advantageous since the low thermal conductivity solder layer between copper metallization and aluminum nitride substrate is avoided. Besides having a low thermal resistance, the direct bonded substrates are virtually free of thermal fatigue since no plastic deformation occurs on temperature cycling below 100 °C.

Thus the need to bond AIN to Cu is clear, and this work is concerned with the direct bonding of Cu to AIN. The following chapter reviews the various metallization processes which are commonly used in microelectronic applications. Then the experimental procedure will be presented and finally the results obtained from the direct bonding experiments will be discussed.

### 2. LITERATURE REVIEW

2.1. Packaging; The way in which the components of a circuit are arranged to perform a logic function plays a key role in microelectronic industry. A usual packaging hierarchy can be illustrated by using the card-on-board (COB) structure for an electronic system. Figure 1. shows a typical COB structure for packaging. Such a structure is three-dimensional, allowing interconnections in all three directions.

The chip, containing many circuits, is attached to a ceramic substrate (chip carrier). The substrate is, in turn, attached to the card that is plugged into the board (back panel). The levels shown in Figure 1. are referred to as the packaging hierarchy. The first-level package is the substrate (sometimes called a module), the second level is the substrate on the card, and the third level is the card on the board.





## 2.2. Chip

Most electronic circuits today are based on devices created on silicon. Single crystals of silicon are grown from the melt of silicon at 1420 °C, and a rod of silicon is produced with a diameter of about 10 centimetres or even larger. It is then sliced to about 1 mm thick plates called wafers. Each wafer is ground and polished mechanically and chemically. Then an epitaxial layer of silicon of either p or n type is grown on the surface. This is followed by an oxidation step. The oxide is then etched by photographic processes to form a mask pattern in the oxide, exposing the area where doping is required. Exposure to gaseous phosphorus compounds, for example, at high temperatures produces a doping of the semiconductor according to the mask pattern, to a depth determined by the diffusion conditions. This is one of the simplest device structures. Metallization and patterning at this point can produce field effect transistors. Metal evaporation and etching for an interconnection pattern follow to produce circuits and interconnections between circuits (integration). Typical integrated circuits today require multiple diffusion steps and several layers of interconnection.

#### 2.3. Chip Carrier

A silicon chip is attached to a substrate that contains the wiring structure for the power and signal connections. The substrate may also provide a path for heat transfer from the chip. The wires on the substrate are produced by the so called thin-film or thick-film technology. The substrate is often made of ceramic. Details of these technologies and materials will be discussed in the following sections. There are a variety of methods for connecting the chip to a substrate. One common method of interconnecting the chip and substrate is through a process called wire bonding. This wire bonding consists of attaching flexible wires from the bonding pads on the top of the chip to the substrate. Gold-plated wires are typically used, and the bonding pads on both the chip and substrate are also plated with gold. The bonds are formed through thermal compression bonding with a heated tool. The other method which is extensively used for bonding is known as C-4 (controlled-collapse chip connections). The C-4 connections are made by very small solder balls formed during the sequence of process steps for the wafer. Later, when the chip is placed on a substrate, the solder balls contact and melt onto an array of metal pads on the substrate.<sup>1</sup>

#### 2.4. Thermal Management in Electronic Packaging

In order to achieve performance in data processing equipment, trends in electronic package designs have moved toward larger circuit chips, higher I/O (input/output), increased circuit density, and improved reliability. Increases in chip size, I/O, and circuit density bring about improved performance by reducing electrical line lengths and therefore, point-to-point signal flight times. Greater circuit density means increased power density (W/in<sup>2</sup>).

Reliability at all levels of packaging is directly related to operating temperature. Higher operating temperatures accelerate various failure mechanisms such as creep, corrosion, and electromigration. In addition, temperature differences that occur as a system is cycled between power-off and power-on conditions have a significant effect on electronic component reliability. This effect is related to fatigue in composite structures.<sup>2</sup>

Having the importance of heat dissipation of the circuit in mind, a variety of cooling methods such as natural and forced air cooling, single-phase liquid cooling,<sup>3</sup> heat pipes,<sup>4</sup> thermoelectric cooling,<sup>5</sup> microchannel cooling,<sup>6</sup> have been used to improve the chip power dissipation. A variety of materials have also been developed to meet performance, density, and cost objectives. Aluminum nitride as a substrate combined with direct copper bonding are two methods of improving the heat dissipation from circuit. These two cases will be discussed in more details in the following sections.

### 2.5. SUBSTRATE

The substrate serves as the supporting structure for microelectronic circuitry and also acts as a surface for the deposition of the conductive, dielectric, and resistive materials that form the passive circuit elements.<sup>7</sup> Additionally, the substrate is the mechanical support of all active and passive chip components. Therefore, various materials can serve as substrate materials such as ceramics, metals, plastics and composites. This study deals with AlN ceramic substrates.

Substrate materials should possess certain properties necessary for microelectronic circuit applications. These include: high thermal conductivity, low thermal expansion mismatch with respect to silicon, high temperature resistance,<sup>8</sup> moderate mechanical strength, high electrical resistivity and dielectric strength. Among them, high thermal conductivity and close thermal expansion relative to other components in the circuit play key roles in choosing a substrate material and will be briefly discussed below.

#### 2.5.1. Thermal Conductivity

The frequent need to conduct heat away from hot spots such as transistor chips makes high thermal conductivity an essential property of substrate materials. In ceramics, high thermal conductivity is only realized in highly crystalline, single phase and high purity substrates. Due to the addition of sintering aids to promote densification of crystalline ceramics, such as  $Al_2O_3$ , an intergranular vitreous bonding phase usually forms and acts as an intergranular thermal barrier since glass is a poor thermal conductor. The latter is one reason glas, has not found wide acceptance as a substrate material.<sup>7</sup>

#### 2.5.2. Thermal Expansion

A substrate in a microelectronic circuit should work beside other components such as the silicon chip, tin-lead solders, organic adhesives, conductors and so on. Thermal expansion mismatch between the substrate material and other circuit components becomes important in applications designed for operation at temperature extremes. In such a cases, stresses can be generated during thermal cycling if large differences in thermal expansion exist between the various materials, often resulting in failure of one or more of the components.<sup>9</sup>

## 2.5.3. Substrate Materials

In view of the required properties for a substrate, various materials can be used for this purpose. Alumina, berylia, aluminum nitride, SiC, glass-ceramic, and metal core substrates are among the most commonly used substrate materials.

2.5.3.1.Alumina is the most widely used substrate material due to a combination of electrical, mechanical and economic advantages. The 96%  $Al_2O_3$  composition has become the industry standard and is used in approximately 90% of all circuits. The remaining 4% of the substrate compositions are usually in the form of sintering aids, added for complete densification without significant grain growth and to maximize electrical properties. The most common additives are magnesia and silica. Magnesia inhibits grain growth of alumina crystals by segregating to the grain boundaries and preventing grain boundary movement.<sup>10</sup> Silica is used because it forms a liquid phase with alumina at a temperature lower than melting point of alumina and this promotes more rapid sintering.<sup>11</sup>

*3.5.3.2. Berylia* has a thermal conductivity of approximately half that of copper at room temperature. The high-strength, high thermal conductivity combination also gives berylia good thermal shock resistance (Table 2.1). The main drawback of berylia is its high toxicity.<sup>12</sup>

3.5.3.3. Metal Core Substrates: The need for improved thermal conductivity, combined with the requirement for good mechanical strength in harsh environments, has led to the development of a variety of Metal Core Substrates. Early systems were based on porcelain-coated steel.<sup>13</sup> However these materials suffer from a serious coefficient of thermal expansion (CTE) mismatch between the metallic and ceramic components. Since that time, copper-clad molybdenum and copper-clad Invar substrates have been developed. The major advantage of the coated clad metal

core approach is the ability to modify the CTE, while providing the superior thermal conductivity possessed by Cu.<sup>14</sup>

2.5.3.3. Aluminum Nitride has recently been intensely studied for electronic ceramic packaging applications because of its high theoretical thermal conductivity value and non-toxic nature. The estimated theoretical value of its thermal conductivity at room temperature is  $320 \text{ Wm}^{-1}\text{K}^{-1.15}$  However, measured values vary from 30 to 260  $\text{Wm}^{-1}\text{K}^{-1}$ .<sup>16,17</sup> The primary heat transport mechanism of AlN is phonon propagation.<sup>18</sup> It is stated that impurities or other lattice and microstructural defects, such as vacancies, interstitials, dislocations, and grain boundaries, can cause phonon scattering and thus lower the thermal conductivity, it is necessary that the substrates be composed of high-purity, low additive content materials.

AlN has a coefficient of thermal expansion (CTE) between 4 and  $4.5 \times 10^{-6} K^{-1}$ , (Table 2.1)<sup>19</sup> and is close to that of the silicon (2.7  $\times 10^{-6}$ ) and thus suitable for direct attachment to very large scale integration (VLSI) dies. The combination of high thermal conductivity and low CTE gives AlN good thermal shock resistance<sup>20</sup>. Moreover AlN possesses a higher flexural strength value than alumina or berylia. The lower hardness of AlN compared to Al<sub>2</sub>O<sub>3</sub> also facilitates machining processes of the substrate.

Densification of AlN plays a key role in its thermal conductivity. In order to achieve high density and optimize properties, submicron powders with a wide

Substrate	CTE, 10 <sup>-6</sup> K <sup>-1</sup>	Thermal Conductivity, Wm <sup>-1</sup> K <sup>-1</sup>	Bending strength, MPa	Dielectric constant (1 MHz)
AIN	3.1(a)-4.6	60-230, 320(c)	275-345	8-10
Al <sub>2</sub> O <sub>3</sub> ,96%	6.3-9.1	12-26	205-345	8-10
SiC(b)	2.5(a)-4.7	33-270, 330(c)	275-490	40-100
BeO,99.5%	5-7	200-280,330(c)	140-275	5.8-6.7
S1(c)	2.7(c)-3.6	130-1240	14	12-100

Table 2.1. Properties of Alternative Electronic Substrate.<sup>9</sup>

(a) At 50°C. (b) Hot Pressed, alpha. (c) Single Crystal.

particle size distribution are used. Sintering aids such as  $Y_2O_3$ ,<sup>21</sup>  $YF_3^{22}$ , CaO, and CaC<sub>2</sub> <sup>23</sup> improve densification through the formation of liquid phases. These liquids crystallize on cooling to calcium aluminates for CaO or CaC<sub>2</sub> additives<sup>24</sup> and yttrium aluminates for the  $Y_2O_3$  additives<sup>25,26</sup>. The thermal conductivity of AlN is strongly dependent on oxygen content<sup>27</sup>. The achievement of high thermal conductivity is possible if the grain boundaries are relatively free of the sintering aids and the AlN lattice is free of oxygen. It is suggested that the this is accomplished by heat treatments that lead to liquid removal by evaporation or migration of sintering aids and oxygen impurities at grain boundary triple points<sup>24,26</sup>. The addition of carbon (C) from CaC<sub>2</sub> also reduces the oxygen content, improving the thermal conductivity<sup>28</sup>. CaC<sub>2</sub> powder is well-known to be a strong reducing agent, furthermore, the onset temperature of densification with CaC<sub>2</sub> is close to the lowest liquid-formation temperature (1400°C) in the CaO-Al<sub>2</sub>O<sub>3</sub> phase diagram. It is suggested that most oxygen impurities in the initial AIN powder are removed from the AIN lattice by the CaO-Al<sub>2</sub>O<sub>3</sub> liquid phase. It is also suggested that part of the oxygen content disappears as CO or CO<sub>2</sub> gas.

# 2.5.3.4.1. STRUCTURE OF AIN

Aluminum nitride has a hexagonal wurtzite crystal structure of space group of P6<sub>3</sub>mc and lattice parameters of a=3.111 Å, c=4.978 Å, and c/a=1.600.<sup>29</sup> A wurtzite structure *AB* can be regarded as being composed of two interpenetrating hexagonal close packed lattices, of Al and N atoms (Figure 2.2). It has been



Figure 2.2 Wurtzite crystal structure.

concluded from the above crystallographic studies that there are two distortions in the AlN lattice when compared to the ideal wurtzite structure (i e. c/a=1.633). The first is a compression along the hexagonal axis of each individual lattice and the second is a shift of one lattice with respect to the other such that an atom of one lattice is no longer at the centroid of the tetrahedron of the four nearest neighbours of the other lattice. This gives rise to a dipole in the centre of each tetrahedron containing an atom of the opposite kind. The effect of the c/a compression is to shorten the Al-N bond along the c axis relative to the other lattice. The measured Al-N bond length in the direction of the hexagonal axis and c direction are 1.917 and 1.885 Å, respectively. The bond angles in the direction of the hexagonal axis and c direction are 107.7° and 110.5°, respectively. The Pauling electronegativity gives AlN 33% ionic character showing that the AlN is predominantly a covalently bonded material.

### 2.6. CONDUCTORS

Conductors are materials of low resistivity used primarily to transmit signals from one circuit location to another. Other uses include: resistor terminations, crossover connections, low value resistors, wire bond attachments, capacitor electrodes and many other applications.

The choice of a suitable conductor depends upon several factors, which may include some or all of the following: resistivity, solderability, solder leach resistance, wire bondability, migration resistance, thermal-aged adhesion, thermalcycled adhesion, line resolution, compatibility with other components and finally cost. It is obvious that not all properties can be obtained in a single conductor, therefore several metallurgies exist. Among all of conductors which can be used Au, Pt-Au, Ag, Ag-Pd, Ag-Pt, Cu and Ni are the most attractive.

The metallurgy of a conductor has a strong influence on many of the factors that determine the choice of materials. Pure gold has high conductivity, excellent wire bondability, and migration resistance making it suitable for several applications in electronic circuits. However, pure Au conductors are not easily solderable using conventional tin-lead solders because of its poor solder leach resistance, i.e. Au dissolves readily in this kind of solder alloy. This problem can be solved by the addition of platinum to the Au at the expense of conductivity. For the same reason, palladium is added to Ag alloys to minimize the silver migration resistance and to improve solder leach resistance. In addition to this, Au conductors are extremely expensive.

The tendency to higher circuit densities and the need to accommodate advanced IC requirements have led to a need for high electrical conductivity materials<sup>(30)</sup>. Suitable choices of conductor and metallization depend on the application. To utilize the high speed capabilities of current IC's, the propagation delay time between chips should not become the limiting factor in the system performance. Therefore connections with minimum resistance are required. In costsensitive applications the use of Au conductors is obviously not possible. This limits the choice to Cu or compositions close to pure silver, as it shown in Table 2.2 where typical thick-film conductor resistivities are compared.

In comparison with Au and Ag, alloying is unnecessary for Cu conductors because pure Cu possesses many desirable properties such as conductivity, solderability, solder leach resistance, migration resistance, and cost effectiveness. More over Cu is able to form a spinel with alumina resulting in  $CuAlO_2$  phase. This ability makes Cu suitable for direct bonding to alumina.

Copper has historically been the most common thin-film conductor material.

In this category copper is compared with aluminum and gold. Copper has lower bulk resistivity, but needs an extra corrosion protection layer on its surface such as a thin gold flash. Copper corrosion can cause adhesion

Composition	Resistivity at printed thickness $m\Omega/square$
Pt-Au	50-100
Ag-Pd	15-40
Au	3-5
Cu	2-4
Ag	1.5-3.0

Table 2.2. Typical Thick-film Resistivities.<sup>12</sup>

loss, thereby reducing overall circuit reliability.

Thick film copper conductors are becoming important both economically and for their properties<sup>(31)</sup>. The use of Cu in the form of thick film paste has the common advantage of using Cu in microelectronic applications. However, copper may present some drawbacks, one of which is the added cost of processing in nonoxidizing atmospheres. Another drawback of nitrogen fired copper conductor is poor compatibility with resistor or dielectrics of commercial thick film paste which are generally fired in air. During recent years there have been remarkable improvements in computer processing speed. These improvements have been achieved by a variety of means and mounting the devices more densely, thus reducing the wiring separation between them. To increase the wiring density, circuits must be produced which have fine wiring patterns. This means that the conductor used in the wiring has a smaller cross-section, and the electrical resistance of the wiring is therefore higher. This in turn means that fewer electrical signals are propagated, and distortions occur in the waveform. If superconductive substances could be used as wiring materials in place of ordinary conductors such as Cu, this problem could be greatly alleviated.

#### 2.7. METALLIZATION

Metallization processes are used to deposit a thin metallic layer on the surface of the integrated circuit chip for its electrical or protective properties. This kind of metallization is used both for interconnection on the chip and to define a place for the attachment of bond wires. Printed and microelectronic circuits from their beginnings have depended heavily on the techniques of metallizing to render insulating surfaces conductive, modify conductor characteristics, and create circuit elements.

Various methods can be used to metallize a ceramic material. These methods include (1) thick film, (2) thin film process, (3) electroplating, (4) direct bonding, (5) molybdenum-manganese process, (6) titanium hybrid process. These methods will each be described briefly.

Bonding Mechanisms; Generally speaking, bonding mechanisms in metallizing of ceramics by metal can be divided in three major groups:

(i) Mechanical cohesion caused by the creep of the metal. Surface diffusion and evaporation/condensation phenomena have also to be considered in the filling of porosity and defects resulting from polishing,<sup>(32)</sup>

(ii) Physical adhesion related to surface energies <sup>(33)</sup> is mainly responsible for bonding with noble metals <sup>(34)</sup> and non-oxidized metals,

(iii) Chemical reaction between elements especially with reactive metals (Zr, Ta, Nb)<sup>(35)</sup> occurs through a redox reaction. Chemical reactions also take place between different oxides.

2.7.1. Thick-film Process can be defined as sequential printing and firing of conductor, resistor, and dielectric paste formulations onto a substrate. Generally speaking, thick-film pastes consist of three distinct phases: a functional phase, a permanent binder phase, and a vehicle phase. Functional phases, depending on the role that they play in circuits, consist of conductor, resistor, and dielectric materials. The permanent binder phase is generally composed of mixtures of glass powders (frits) and oxides. The vehicle phase itself contains two components, a volatile solvent and a nonvolatile resin. The vehicle phase serves the function of dispersing the thick-film inorganic phases and making them screen printable. The vehicle phase also determines the drying rate, the bond between the unfired film and the substrate, and the burnout characteristics.

2.7.1.2. Printing is done by forcing the paster through a screen onto a substrate. Figure 2.3 shows the sequential of printing process.

The appropriate paste to be printed is placed on one side of the screen. Pressure is applied by the action of a squeegee. The squeegee traverses the screen, forcing the paste through the open holes. Finally, the desired pattern is printed onto the substrate.

2.7.1.2. Firing is performed after the paste is screened onto the substrate. Firing consists of several stages (Figure 2.4). The first stage is oven drying at 100

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to 150°C for 5 to 15 min to remove solvents. The next stage is firing at about 200 to 500°C. In this stage burned off. organic resins are Depending on the kind of thick-film materials, it may be fired in air or a atmosphere. air-fired nitrogen In systems, the polymer decomposes by simple oxidation. In nitrogen-fired system, organic resins undergo a thermal dissociation. At the higher temperatures, the peak firing temperature, glass frits begin to soften and flow, metal particles begin to sinter, and a film is formed. The content and chemistry of binder has strong effect on the performance and adhesion of thick-

film. Adhesion of the film to substrate is achieved by a combination of mechanical and chemical means. Glasses such as lead-



Figure 2.3. Sequential of printing processes.<sup>(12)</sup>





bismuth-silicate or lead-borosilicate chemistry wet the surface of the substrate providing mechanical adhesion  $^{12}$ . Additives such as Cu<sub>2</sub>O and PbO often are added

4

to the binder to provide a chemical bond between the film and substrate.

During the firing process, functional phase particles sinter by means of a combination of solid-state diffusion and reactive liquid phase sintering. Solid state diffusion starts at low temperature by neck formation between metal particles. Near peak temperature the oxide layers on the surface of particles dissolve in the liquid glass phase and rapidly transport themselves. This accelerates the sintering process, allowing full densification to be achieved.

2.7.2.Thin film; This is formed by either evaporating or sputtering the desired materials onto the substrate in a vacuum. The films are then patterned using photolithography and  $etching^{(36)}$ . This technique is applicable to conductors, resistors, and dielectrics<sup>(37),(38)</sup>.

The thin film technology is adaptable to both single-layer and multilayer applications. A typical thin film structure consists of an interface adhesion, a resistor and a conductive layer. Adhesion layers are usually chromium, titanium, or nickel. Tantalum, tantalum nitride, nichrome, or a chromium silicon dioxide composite are often used as resistor materials. Copper, aluminum, and gold are common conductor materials. Conductive layers are typically 1 to 10  $\mu$ m thick, and the other layers range from 5 to 100 nm thick.<sup>(39)</sup>

Two important metallization processes for thin-film applications are . evaporation and sputtering.

2.7.2.1 Evaporation; Deposition of a metal by evaporation in its simplest form involves heating a metal, in a vacuum chamber, to a temperature at which it

changes from either a solid or liquid phase to a gaseous phase. This gaseous phase travels from the source to a cooler surface where it condenses back again to form the deposited film.

2.7.2.2. Sputtering: Deposition of metal by sputtering is a somewhat more complex and interesting process. It involves the establishment of a glow discharge (plasma) in a low-pressure inert gas within a vacuum chamber, the acceleration of ions from the glow discharge across a voltage gradient and transfer of energy from these accelerated ions to atoms of a solid metal surface of a target. The target is the source of the metal to be deposited. Energized atoms of target metal are ejected and travel through the space in front of the target to the cooler surface of the substrate where they condense to form the deposited film.

2.7.2.3. Electroless Copper Plating: The purpose of electroless plating in manufacturing of printed circuit is to provide a means of initiating metallization on insulating substrate surface. Two methods are used to metallize a substrate by electroless plating process. These include subtractive and additive processes.<sup>(40)</sup> In the former, i.e. subtractive process, an insulating substrate with surface copper layers and drilled holes is coated with a thin layer of electroless copper. The circuit board then is finished by a masking or etching process to create surface circuitry. In the additive process the entire copper layer is deposited by electroless plating. The surface circuitry is defined by a mask applied before plating, and the lines and holes are plated simultaneously.

### 2.7.3. Direct bonding copper

This process is categorized differently than thin-film and thick-film processes. There are more similarities to metal-ceramic joining than any other process. The direct bonding process essentially was developed for bonding copper to alumina. This process is also categorized among the major joining methods of oxide ceramics to metals. These include (1) solid state diffusion bonding,  $^{(41)}$  (2) active metal method,  $^{(42)}$  (3) Refractory-metal metallizing method,  $^{(43)}$ 

In hybrid power electronics, each circuit element electrically isolated and internally connected to perform a electrical function. Conventionally this was achieved by the thick-film and moly-manganese processes. Strong bonding between metals and ceramics in the thick film and moly-manganese process is achieved by the presence of an intermediary layer. The intermediary layer is a poor electrical conductor at high frequencies, where the current flows in a thin skin at the metal ceramic boundary. This thin layer generates heat if high current is passed through it. For these reasons, the applications of these conventional methods are limited. In the direct copper bonding process, the metal is bonded directly onto the ceramic and only a few monolayers of transition layer occur between the copper and the ceramic. Therefore the thermal contact resistance between copper and ceramic is low. As a result, high power and high frequencies operation is possible. Another advantage of direct bonding copper is the elimination of low thermal conductivity solder between the Cu-metallization and the ceramic substrates. In addition to a low thermal resistance, the directly bonded substrates are almost free of thermal

fatigue, since no plastic deformation occurs on temperature cycling below 100°C.

The basic concept of the direct bonding is to form a liquid skin around the copper to be bonded. The liquid must wet both the copper and the ceramic and form a strong bond after cool-down. The melting point of this liquid should be near the melting point of the copper so that the copper becomes soft and can form easily to the shape of the substrate surface. Moreover, the predominant constituent of this liquid should be copper, so that the high electrical and thermal conductivity can be maintained. The thickness of the liquid layer should be small compared with the copper to maintain its structural integrity.

Fortunately, the above requirements can be achieved by utilizing the oxygen copper eutectic melt which wets and bonds to the ceramic. Figure 2.5 shows the phase diagrams of the Cu-O system on the Cu-rich side.<sup>(44)</sup> It can be seen that the melting temperature decreases as the amount of oxygen in the Cu increases.

It can also be seen that the amount of oxygen which can form a solid solution with Cu is exceedingly small (100ppm). Whenever the oxygen content in copper exceeds the solid solubility limit, the oxygen will appear in the form of copper oxide (Cu<sub>2</sub>O). By heating copper containing oxygen to above 1065 °C, some eutectic liquid will be present in the material. The eutectic melt formed is basically Cu rich (95.32 percent Cu and 4.68 percent Cu<sub>2</sub>O). The relative amount of solid and liquid and their composition, can be obtained by the lever principle. The amount of the calculated Cu-Cu<sub>2</sub>O eutectic liquid as a function of temperature using the "lever principle" in the Cu-O binary system is shown in Figure 2.6. It can be seen that the liquid volume



Figure 2.5. Cu-O binary phase diagram

increases rapidly when the temperature is above 1070°C. It is clear that a slight change of temperature can drastically alter the volume of liquid phase.Two procedures have been suggested for controlling the eutectic skin layer. These include preoxidation of copper and heating the assembly, copper foil and ceramic, in oxidizing atmosphere with a given partial pressure of oxygen<sup>(45)</sup>. The liquid volume generated at the surface of this oxidized copper can be calculated as follows:

.



Figure 2.6 Amount of  $Cu-Cu_2O$  eutectic liquid as a function of temperature.

$$\frac{V_{L(T)}}{V_{Cu_2O}} = \frac{33.3(at. \% \text{ of oxygen for } Cu_2O)}{at. \% \text{ of oxygen at } L \text{ at temperature } T \text{ (T>1065° C)}}$$
(2.1)

Where  $V_L$  is the volume of the liquid (L),  $V_{Cu2O}$  is the volume of the Cu<sub>2</sub>O, and T is the temperature.

The process parameters of diffusion bonding in  $\text{Cu-Al}_2\text{O}_3$  system were studied by Crispin *et al.*<sup>(46)</sup> The reported results for average strength versus temperature are in accord with the work of Bailey and Borridge<sup>(47)</sup> and Heidt and Heimke.<sup>(48)</sup> The results obtained on the effect of decreasing the pressing time differs from other work and Heidt and Heimke.<sup>(49)</sup> The improvement of joint strength as a result of decreasing the pressing time is attributed to decreased stress induced crack growth.

The effect of alumina composition on interfacial chemistry and strength of direct bonding of copper-alumina has been studied by Holowczak *et al.*<sup>(50)</sup> It was found that calcium and magnesium together promote adherence where increasing the silica content appeared to reduce the bond strength. It has been also concluded that aluminas which contain both calcium and silica have lower bond strength. It is possibly due to the formation of interfacial phases other than copper aluminates. The effect of composition and crystal size of alumina ceramics on metal to ceramic bond strength bas been also studied by Floyd<sup>(51)</sup>.

Mulder *et al.*<sup>(52)</sup> studied the Cu-Sapphire interface resulting from solidstate bonding. It has been concluded from TEM studies that the Cu metal oriented (111) on basal (0001) sapphire. Although this metal orientation is not the most favourable from the point of view of the lowest surface energy, the results are in agreement that the system strives towards a situation with a low lattice mismatch. This indicates that Fletcher's work<sup>(53)</sup>, stating that interfacial energy decreases with decreasing mismatch of lattices, also applies to more complex crystal structures.

Yoshino *et al.*<sup>(54)</sup> applied a layer of CuO powder on the surface of alumina before direct bonding of copper. It has been suggested that cupric oxide
reacts with alumina to form porous copper aluminates. It has been also concluded that the porous CuAlO<sub>2</sub> absorbs thermal stresses and consequently it shows better resistance to thermal cracking than does the directly bonded substrate.

It has been shown by Courbiere *et al.*<sup>(55)</sup> that by hot pressing of alumina and oxidized copper,  $CuAlO_2$  forms at the beginning of the treatment. After prolonged heat treatment, it is destabilized in favour of  $Al_2O_3$  and  $Cu_2O$  by diffusion of oxygen. This has been correlated to the decrease of bond strength with time in this system.

Naka *et al.*<sup>(56)</sup> studied the joining of alumina to copper using amorphous Cu-Ti filler metal. It is reported that isothermal solidification process takes place during joining, and copper dissolves into Cu-Ti filler metal, and then, a copper solid solution containing Ti precipitates form from the Cu-Ti filler metal. The strengths in this study are among the highest reported in this system. On the other hand, the formation of titanium oxide TiO<sub>x</sub> and (Al,Ti)<sub>2</sub> O<sub>3</sub> solid solution oxide is attributable to the strong joint between alumina and Cu-Ti filler alloy. In addition the electrical conductivity of the system would decrease drastically.

In the case of bonding AIN to refractory metals Westwood *et al.*<sup>(57)</sup> studied the microstructure and microchemistry of tungsten and its compound reactions with AIN. It has been found that the adhesion in this system is due to both a mechanical interlocking and a chemical precipitation reaction, and no reaction occurs between W powder and AIN.

# 2.8. Interface of Cu-AlN

Ohuchi<sup>(58)</sup> studied the electronic structure and adhesion of Cu-AlN interface. AlN, in his study, was made "in-situ" by bombarding the surface of pure Al with  $N^{2+}$  ion beam. Copper were then sputtered and the changes in valence electron distributions were measured using Ultraviolet Photoelectron Spectroscopy (UPS). It has been concluded that the adhesion strength of Cu to AlN is strongly influenced by the surface crystallographic orientations. The semi-quantitative adhesion measurements also showed that Cu adhered to AlN (0001) surface stronger than to AlN (1012) of Al (1011) surface and the origin of adhesion was attributed to the intrinsic bonding nature of Cu-AlN interface, where Cu prefers to bond to Al.

# 2.9. Wettability

One of the primary requirements of bonding metals to ceramics, in liquid state bonding, is the ability of the molten metal to wet the surface of ceramic. The main thermodynamics relations of wetting theory are the equations for wetting angle ( $\theta$ ) and adhesion ( $W_a$ ):

$$\gamma_{l\nu} \cos\theta - \gamma_{s\nu} - \gamma_{sl} \tag{2-2}$$

$$W_a = \gamma_{lv} \cdot (1 + \cos \theta) \tag{2-3}$$

Where  $\gamma_{sv}$ ,  $\gamma_{sl}$ , and  $\gamma_{lv}$  are interfacial surface energies at the interfaces of solid body-gas, solid body-liquid and liquid-gas, respectively (Fig.2.7).

Equations (2.2) and (2.3) are derived from equilibrium conditions. Both of the above equations were proposed by Young.<sup>(59)</sup> These equations were then derived by others using different methods(60), (61)ranging from the mechanical equilibration of forces at the three-phase boundary to the use of variational methods<sup>(59),(62)</sup> and thermodynamics concepts.<sup>(63),(60)</sup> Oliver et  $al.^{(64)}$  studied the effect of surface roughness and the texture of substrate and concluded that these two factor strongly affect the contact angle.

 $(Y_{Sv} - Y_{Sl}) = (Y_{Sv} - Y_{Sl})$  (b) (b) (b) (b) (b) (c) (b) (c) (c)

Β,

8 B

(a)

In the case of non-equilibrium Figure 2.7. Configurations for (a) wetting condition, it is assumed that system is and (b) non-wetting conditions. in thermal and mechanical equilibrium but not in chemical equilibrium. Levin<sup>(65)</sup> studied the stability of refractories in liquid steel and formulated conditions for vigorous wetting of the solid phase by

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Β,

liquid, considered that it is necessary for the liquid and solid phases to be as far as possible from equilibrium contact conditions. In the work of Kingery et al.<sup>(66)</sup> and in the work of Eremenko <sup>(67)</sup>, it has been found that a metallic liquid will wet a solid metallic body if a sufficiently intensive chemical reaction is taking place between them.

Various systems have been considered to study the non-equilibrium wetting conditions. Jordane and Lane<sup>(68)</sup> studied the wetting of solid metal by a liquid phase and concluded that interfacial energy decreases as a result of a chemical reaction and dissolution. Ono and Kondo<sup>(69)</sup> have applied the thermodynamics of irreversible processes and obtained the generalized Gibbs formula for interfacial tension under non-equilibrium systems. Zhukhovitsky  $\exists t al.^{(70)}$  calculated variations of interfacial tension for stationary processes where a constant difference of the components' chemical potentials ( $\mu$ ) in the solid and the liquid phases is maintained, such that  $\Delta G = M \Delta \mu$ , where M is a constant.

The possibility of applying equations (2.2) and (2.3) in non-equilibrium systems where  $\gamma_{sl}$ ,  $\Theta$  and  $W_a$  are the functions of time is discussed in Naidich's work.<sup>(71),(72)</sup>

The work of adhesion between the two phases (1), (2) in the general case may be presented in the form of:

$$W_a = W_{a(equil.)} + W_{a(non-equil.)}$$
(2-4)

Interfacial tension is expressed as

$$\gamma_{1,2} = \frac{\gamma_1 + \gamma_2 - W_{a(equil.)}}{\gamma_{equil.}} - \frac{W_{a(non-equil)}}{\Delta \gamma_{non-equil.}}$$
(2-5)

$$\mathbf{\gamma}_{1,2} = \mathbf{\gamma}_{\text{equil.}} - \mathbf{\Delta}\mathbf{\gamma}_{\text{non-equil.}}$$
(2-6)

where  $\gamma_{equil}$  is a function of the difference in the nature and properties of contacting phases P<sub>1</sub> and P<sub>2</sub>: and  $\gamma_{non-equil}$  is the function of the systems' deviation from the equilibrium state (the differences of the component chemical potentials)  $\Delta \gamma_{non-equil} = \phi(\mu_i^{-1} - \mu_i^{-2}).$ 

2.9.1.The wettability of predominantly ionic compounds by metals. The wettability ionic compounds molten metals have been extensively of by studied.<sup>(65),(73),(74)</sup> High melting metal oxides are, as a rule, are poorly wetted by liquid metals. However, chemically oxygen-active metals such as Ti, Zr, Br, Al, Mg, Li etc. wet and form small contact angles and spread completely over certain oxides,  $Al_2O_3$ , BeO, SiO<sub>2</sub>, MgO, surfaces. <sup>(71),(75),(76)</sup> On the basis of the above works, it can be stated that wettability of oxide by a metal and adhesion in such a system increases with growing affinity of the liquid phase metal for oxygen. It can be also concluded that interaction of any substance with a chemical compound will be less intensive the stronger the interatomic bonds, i.e. a tendency towards covalent bond formation. In other words, the weaker the bonds between the metal and oxygen in the oxide (ionic solids), the greater the chemical interaction and wetting of oxides by liquid metals should be.

The surface tension, reported by Rhee,<sup>(77)</sup> of liquid Cu at its melting point (1083°C) is 1.168 N/m, and slightly higher than the 1.157 N/m predicted by the Kunin<sup>(78)</sup>, somewhat higher than the 1.100 N/m predicted by Zadumkin formula<sup>77</sup>; values reported in the literature vary from 1.085 to 1.355 N/m.<sup>(79)</sup> The temperature coefficient of surface tension of liquid Cu was -2.3 x 10<sup>-4</sup> N/m°C reported by Pawlek *et al.*<sup>(80)</sup>, compared with -2.7 x 10<sup>-4</sup> N/m°C reported by Rhee<sup>76, 2</sup>

The effects of oxygen on the contact properties of metals was studied in detail.<sup>(81),(82),(83)</sup> In these works, the surface tensions of melts of such systems as Fe-O, Ni-O, Cu-O, Ag-Cu-O have been studied together with their wetting characteristics on aluminum and manganese oxides. It has been reported that oxygen causes an abrupt decrease of the surface tension of the melt and improvement in the ability of the melt to wet the oxide surface. The contact angle for copper on aluminum oxide at 1100°C is equal to 130° but drops to 60° with an oxygen content of 1-2% in copper-oxygen melts (alloys of copper and copper oxide), and completely wets corundum monocrystals and manganese oxide, as well as some other ceramic oxide phases.<sup>(84),(82)</sup>

Naidich<sup>(85)</sup> pointed out the following for the action of oxygen dissolved in the liquid metal on the metal adhesion properties:

(a) Neutral atoms at the liquid metal surface can not be bound by strong chemical bonds with an oxide surface formed by negatively charged ions of oxygen.

(b) A metal-oxide bond is formed when the atoms of the metals move their valence

electrons and give them up to the oxygen. Positive metal ions are then bound by strong ionic bonds to the oxygen ions at the oxide surface.

2.9.2. The Wettability of Covalent Solids by Metals. Covalent solids are characterized by closed stable electron configurations of atoms with high strength interatomic bonds. Interaction and high adhesion energy (and wettability) are possible only at the expense of bond dissociation in the solid phase and chemical reaction between the metal and the solid body. The metal should possess high chemical affinity to any kind of solid phase atoms.

The wettability of graphite and diamond by Cu, Si, Au, Ga, Sn, Bi has been studied. (86),(87),(88),(89) and these metals do not wet diamond or graphite. Inactive metals such as copper, silver, and gold do not wet the surface of boron nitride and low adhesion is also observed. (70, 89),(90),(91)

Data on the wettability of aluminum nitride by lead (wetting angle is 143° at 540°C) and silver-aluminum nitride (wetting angle is 133° at 1000°C) were also reported.<sup>(92),(93)</sup> Wetting conditions have been reported for  $Si_3N_4$  and AlN by Ag-28Cu-2Ti alloys.<sup>(94)</sup> The degree of wettability of solid carbides, borides or nitrides depends on the relative values of the heats of formation of metal-solid compounds and of the solid compound itself. The contact angles of boron nitride wetted by aluminum and silicon are 60 and 90°, respectively,<sup>(70, 89)</sup> i.e. aluminum wets boron nitride better in accordance with the higher heat of formation of aluminum nitride (-632.2 kJ.gmol<sup>-1</sup> of nitrogen).<sup>(95)</sup> The wettability of AlN by

Al and Cu-Ag-Ti has been also reported by Tomsia *et al.*<sup>(96)</sup> Good adhesion has been reported for these systems and attributed to the formation of TiN and Al which are thermodynamically favoured.<sup>(97)</sup>

### 2.10.Oxidation of AlN

Pure AlN is not wetted by Cu. In order to improve chemical reactivity of AlN and to increase chemically compatibility with other components in circuits, an oxidation process can be used.<sup>(98)</sup> Kubaschevski and Evans<sup>(99)</sup> have reported that AlN decomposes when heated in air at 940 to 950°C whereas Lyutaya *et al.* <sup>(100),(101)</sup> stated that AlN oxidizes when heated in air above 800°C. In addition, the oxidation of single crystal of AlN has been studied by Slack and Chelly<sup>(102)</sup> who found that at room temperature a protective oxide layer, about 10 nm thick, formed on single crystals of AlN in one day. Larrenka *et al.*<sup>(103)</sup> showed that the oxidation rate of sintered AlN in oxygen at 800°C to 1100°C was very low and that at 1100°C only 8% was oxidized. In water, an AlN surface decomposes to a porous surface film of a hydrated alumina phase at 100°C.<sup>(104)</sup> Jones *et al.*<sup>(105)</sup> attributed the effect of the thickening of the Al<sub>2</sub>O<sub>3</sub> surface film in slowing oxidation kinetics. It has also concluded that the water in the residual furnace gas plays a more important role than the oxygen in controlling the weight gain of AlN.

### **OBJECTIVES**

# **3.OBJECTIVES**

The objectives of this study are as follows:

1) To optimize the process parameters of the direct bonding of Cu to  $Al_2O_3$  in terms of temperature, atmosphere, and thickness of the copper foil and to understand the mechanisms of direct bonding of copper to  $Al_2O_3$ .

2) To study the metallization techniques of ceramic substrates, specifically AIN, for microelectronic applications and to investigate the possibility of applying the same procedure to the AIN-Cu system.

3) To study and modify the wettability behaviour of AlN by Cu through the surface modification of the AlN and compositional modification of Cu and to metallize AlN by Cu a using direct bonding process and study the chemical compatibility of this system.

4) To eliminate the pre-oxidized layer from the direct bonding process of AlN to Cu and finally to study the effect of oxygen content of Cu on reaction with AlN and understand the mechanism of bonding in this system.

# 4. EXPERIMENTAL PROCEDURES

# **4.1. STARTING MATERIALS**

Aluminum nitride was used in the form of both substrates and powder. The substrates were used for copper bonding experiments whereas the powder was used to investigate the reaction which takes place between AlN and  $Cu_2O$ . The specifications of the hot-pressed AlN substrate and the chemical analysis of the powder are shown in Tables 4.1 and 4.2, respectively.

Table 4.1 Specification of AlN substrates.\*

Density g/cm <sup>3</sup>	3.3
Thermal conductivity W/m.K	180
Surface roughness (Ra) µm	0.3-0.8
Thermal expansion coefficient $(10^{-6}/ °C)$	4.4
Modulus of elasticity (GPa)	300
Average grain size µm	9

COMPONENT	CONTENT
Ca	87 ppm
Fe	<10 ppm
Si	<22 ppm
С	340 ppm
0	0.87 wt.%
S.S.A**	$3.4 \text{ m}^2/\text{g}$

Table 4.2 Chemical analysis of AlN powder.\*

\*\*Specific Surface Area

<sup>\*</sup>Tokuyama Soda Co.,Ltd.

The  $Cu_2O$  powder was supplied by Aldrich<sup>\*\*\*</sup> and had the general specification given in Table 4.3.

CHEMICAL IMPURITIES		POWDER CHARACTERISTICS	
Р	0.012%	Average	7
Ni	<0.01%	particle size (µm)	
Fe	0.028%		0.3 m <sup>2</sup> /g
Zn	0.021%	S.S.A	

Table 4.3 General specification of Cu<sub>2</sub>O powder.

Conventional copper powder used for thick-film applications, was used to make the various Cu-O compositions. This copper powder was supplied by Sherritt Gordon Inc.<sup>\*\*\*\*</sup>. The impurity content of this powder is listed in Table 4.4.

Table 4.4 Chemical analysis of copper powder.

IMPURITIES %	С	02	S
	0.082	0.18	0.007

Oxygen free high conductivity copper (OFHC) copper foil, supplied by Aldrich, was used for direct bonding of copper to AlN.

Two different kinds of nitrogen gas were used during this research,

<sup>\*\*\*\*</sup>Aldrich Chemical Company, Inc.

<sup>\*\*\*\*</sup> Grade: 2M, Organic Treated

commercial and pre-purified nitrogen<sup>\*</sup>. The former contains 500 ppm oxygen and 25 ppm moisture and was used for direct bonding. The latter contains only 1 ppm oxygen and was used as an inert gas for simulating the reaction which takes place at the interface.

# 4.2. Furnace Equipment

A horizontal tube furnace was used for both wettability and bonding experiments (Figure 4.1). A temperature controller, Omega CN8610TC, with a type K thermocouple and accuracy of  $\pm$  3°C was used to control the temperature of the process. Both ends of the mullite tube were water cooled making the chamber vacuum tight. The chamber of the furnace was connected to a rotary vacuum pump and an inert gas source. At one end of the tube a quartz window was installed to take photographs of sessile drops at the temperature of experiment. A D-shaped was designed for supporting and levelling the sample inside the furnace.

# 4.3. Surface Modification of AlN

In an attempt to improve the wettability of AlN by Cu, an oxidation process was used to change the surface chemistry to  $Al_2O_3$ . Hot pressed AlN substrates with small quantities of additives and with a bulk density of 3.25 g/cm<sup>3</sup>, were cut into square coupons 12 x 12 x 2 mm, and weighed. The specimens were placed in a

<sup>\*</sup>Lindegas products UN No.: UN 1066

horizontal tube furnace regulated at the desired temperature. Air flowed into the furnace at the rate of 15 mL/min. After maintaining the samples at the desired temperature and for the specified time, the samples were furnace cooled to room

### Horizontal Tube Furnace





temperature and then weighed. The resultant weight gain, due to the oxidation process, was then used to study the oxidation kinetics of AlN, and calculating the thickness of the oxide layer.

# 4.4. Wettability Tests (Sessile Drop Test)

The sessile drop method was used to measure the contact angle between copper and AlN. In brief, the sessile drop apparatus was a controlled atmosphere, horizontal resistance tube furnace. The specimen was placed on an  $Al_2O_3$  D-shaped tube inside the furnace. The furnace was operated at  $10^{-2}$  mbar or less.

Different kinds of substrates were used to investigate the wetting behaviour of copper on ceramics. Substrates in this study were divided into three categories; AlN,  $Al_2O_3^*$  and pre-oxidized AlN. AlN and  $Al_2O_3$  substrates were used in the asreceived condition and degreased ultrasonically in acetone.

Pure copper powder (Table 4.4) was used to measure the wettability of each of the above substrates by copper. The powder was mixed with isopropanol to form a paste and applied on the substrate. The amount of paste used in the experiments was always the same, to avoid varying the conditions of each test. The wetting experiments were carried out at temperatures ranging from 1085 °C to 1200 °C. The drop size was kept as small as possible (5 mg) to minimize the effect of gravity on the sessile drop. These experiments were performed under pre-purified N<sub>2</sub> for

\* Coors

different times at the desired temperature.

In order to study the effect of oxygen content in the copper on the wettability of the various ceramic substrates, samples were prepared by fusing pure copper powder with cupric oxide. In this way, copper-oxygen alloys were formed which were then chemically analyzed for oxygen using infrared absorption method.<sup>\*</sup> In this method powder samples are weighed out directly into the crucible. As the sample melts nitrogen and hydrogen in the sample are released, oxygen reacts with the crucible material to form carbon monoxide. It is then passed out of the furnace together with the helium carrier gas. The Co content is then measured by a infrared detector.

These experiments were carried out under steady-state (non-flow) conditions in a protective atmosphere (prepurified nitrogen). The procedure for a wetting test consisted of first flushing the chamber with pre-purified N<sub>2</sub>, pumping the system down to  $<10^{-2}$  mbar, heating to the test temperature (e.g. 45 minutes to 1100°C), holding 1 ir a specified test time, thus forming a drop, which was then photographed at a magnification of 5-6X, and furnace cooling. The dimensions of the metal drop, from which the contact angle was calculated, were then measured on the negatives by a general-purpose measuring microscope. Some of the samples were cut through the centre of the drop and contact angles were measured using a Scanning Electron Microscope (SEM).

<sup>\*</sup> ON-mat 822, supplied by STROHLEN INSTRUMENT Co., West Germany.

### 4.5. Bonding Procedure

Cu foil was bonded to as-received AlN, alumina and pre-oxidized AlN. As can be seen schematically in Figure 4.2, substrates were cleaned ultrasonically. OFHC copper foils were cut into shape and degreased ultrasonically. The copper foils were then etched in a 15% nitric acid solution, rinsed under tap water and dried. The substrates were then bonded to Cu by heating the assembly to temperatures between 1065-1075°C. The tube was first evacuated to  $10^{-2}$  mbar. The Chamber was then filled with commercial N<sub>2</sub> gas and heated. During the experiment a 15 ml/min. flow of commercial N<sub>2</sub> gas was running through the chamber.

The time required to reach the temperature of the experiment (1065-1075°C) was 35 minutes. After holding the sample for different times at the bonding temperature, it was furnace cooled to room temperature.

The lack of reproducible joints confirmed the importance of the position of the sample inside the furnace while other variables such as the gas flow and cooling water flow at both ends of the tube were kept fixed. In order to establish a stable condition for all experiments, a temperature profile was measured along the tube. The results are shown in Figure 4.3. As it is clear from this Figure, the hot zone is about two centimetres. In comparison with the size of the sample which was about 1 centimetre, a slight change of position can change the temperature considerably and may explain the discrepancy in the results.



Figure 4.2 Bonding procedure of Cu to AlN.



Figure 4.3 Temperature profile along the tube.

#### 4.6. Simulation of Interfacial Reaction

Chemical simulation of the interfacial reaction, resulting from bonding of two materials, can be done by using the powders of the parent materials. In order to determine the effect of oxygen content on the interaction of Cu and AlN, mixtures of AlN and Cu<sub>2</sub>O powder were prepared. In this way, the interfacial surface area between these two materials is much larger and therfore larger quantities of reaction product are formed and are then detectable by X-ray. In addition further investigation can be carried out using SEM equipped with quantitative Electron Dispersive Spectroscopy (EDS).

Powder processing; The powders of AlN and  $Cu_2O$  were chosen with almost the same particle size and shape. Figure 4.4 shows the powder processing sequence. The powder mixtures of 100 mg of  $Cu_2O$  and AlN were attrition milled in iso-propyl alcohol at a speed of 150rpm for 30 minutes in a plastic container of 4 L capacity. The ratio of liquid to powder was 5 to 1, by weight.  $Si_3N_4$  media having a diameter of 4mm was used. The proportion of media weight to that of powder was 2 to 1. The slip was then passed through a 212µm sieve to separate it from the media and it was then dried in a microwave oven. The resulting powder was granulated through a 100 µm sieve. Green samples were formed by die-pressing approximately 2g of the powder mixture at a pressure of about 4MPa, forming pellets of 10mm in diameter and 30mm height. The pellets were then isostatically pressed at 300MPa. The green density of the pellets was then estimated by dividing the weight by the volume observed from the dimensions.



Fig. 4.4 Sequence of powder processing for interface simulation.

Firing; The green samples were fired in the furnace described in section 4.4. The firing conditions were identical to those of the bonding experiments (section 4.4.) so as to simulate the interfacial reaction as accurately as possible. The sintering temperature ranged from 700°C to 1200°C, and was maintained for 1 hour. All

experiments were carried out in a pre-purified nitrogen atmosphere at atmospheric pressure. The density of samples after firing were measured by using Archimedes method as described in ASTM C373-88.<sup>(106)</sup> X-ray and microstructural analyses were carried out on selected samples.

### 4.7. X-ray Diffraction (XRD)

The fired AlN and Cu<sub>2</sub>O powders were pulverized to a fine powder using a mortar and pestle. The powder were then analyzed with a Philips X-ray diffractometer using filtered CuK $\alpha$  radiation at an accelerating voltage of 40 kV (± 0.1%) and a beam current of 20mA (± 0.1%) with a scanning rate of 0.01 deg./sec. The intensity and the 2 $\theta$  data were measured by using the Philips APD 1700 diffractometer computer system. The peaks for the (100) hkl plane for AlN occur at 2 $\theta$ =33.2° and that of the (111) hkl plane for Cu at 48.5° were used to quantify the rate of reaction at different temperature. The details of this procedure are given in Appendix I.

# 4.8. Thermogravimetric Analysis (TGA)

In order to investigate the reaction kinetics of AlN with  $Cu_2O$  thermogravimetry was used. Measurements of changes in sample mass with temperature and time were made using a thermobalance<sup>\*</sup>. This is a combination of

\* CAHN D-100, CAHN Instruments., California, USA.

an electronic microbalance, which has a resolution of 1 microgram, with a furnace which has temperature accuracy of  $\pm 1^{\circ}$ C, and associated temperature programmer Figure 4.5.

By taking the following reaction into account, it is clear that by heating the AlN with  $Cu_2O$ ,  $Al_2O_3$  and elemental copper are formed, and  $N_2$  gas is released.

$$0.66AIN + Cu_2O - 0.33Al_2O_3 + 2Cu + 0.33N_2$$

The evolution of  $N_2$ , which causes a weight loss, was the parameter measured in the study of the kinetics of the above reaction.

Samples were prepared as described in section 4.5. They were then suspended inside the furnace using a platinum wire and basket. The balance was tared before starting the experiment. Weight losses during the experiment were registered and stored by a computer connected to the system and were used later to analyze the kinetics of the reaction. In order to confirm the results obtained from thermogravity analysis, X-ray analysis were also carried out on the powder mixtures treated.





# 4.9. Microscopy and Energy Dispersive Spectroscopy

Bonded samples and sections of the reacted powder mixtures were mounted in a cold-setting resin and polished down to a  $1\mu$ m diamond finish. The interfaces of the Cu bonded to AlN and microstructures resulting from chemical reaction of the interface were then examined using SEM<sup>\*</sup> analysis a ter carbon or Au-Pd coating. Microchemical analysis was carried out using Energy Dispersive spectroscopy (EDS).<sup>\*\*</sup> The detector, was able to operate with either a Be window (7.5µm thick) and an ultra-thin (0.1µm) Al window. The ultra-thin window was used to detect elements with low atomic number between 6 and 11 (i.e. C to Na). Both detectors were inclined at 40° to the plane of the stage. In order to analyze the interface a 10keV acceleration voltage was used in the spot analysis mode to minimize the excitation volume. The X-ray detector was then connected to a Tracor Northern TN 5400 EDS analysis system.

A standardless quantitative analysis program was used to calculate the ZAF correction factor. This program corrects the errors due to atomic number, absorption and fluorescence. The details of this correction method is given in Appendix II. High magnifications and low acceleration voltages were performed in the case of microanalysis of the interface. Since there was not any significant reaction zone at the interface, spot analysis was used to analyze the interface.

<sup>\*</sup>Type JEOL JSM-840A

<sup>\*\*</sup> Tracor Northern TN-96-606E3/513

# 4.10. Evaluation of mechanical strength

The peel test was used to evaluate the adhesion of the copper to the base materials after bonding. The basic direct copper bonding was conducted using a  $12 \times 12 \times 2 \text{ mm}^3$  AlN and  $10 \times 10 \times 1 \text{ mm}^3$  Al<sub>2</sub>O<sub>3</sub> ceramic substrates. Three strips of copper measuring  $5 \times 5 \times 0.1 \text{ mm}^3$  were placed parallel and equally spaced on the top of the substrates, and bonded as described in section 4.5. The peel tests were then made by holding the AlN and Al<sub>2</sub>O<sub>3</sub> along both edges, so that the copper to pulled perpendicular to the surface at a rate of 0.5 mm/min. using a tensile testing machine<sup>\*</sup>. The resulting loads of the peel tests were then used to evaluate the mechanical strength of the interface.

<sup>\*</sup> Instron Model 1362

# 5. RESULTS AND DISCUSSION

In this chapter, the results of the wetting behaviour of AIN,  $Al_2O_3$ , and the pre-oxidized AIN by Cu will be presented, and the effect of the oxygen content on the wetting behaviour of the aforementioned substrate will be also discussed. The influence of process parameters and the optimum condition for an acceptable bond in the direct bonding process will be established. The microstructures obtained from direct bonding of Cu to various substrates, the kinetic approach to the oxidation of AIN and a proposed reaction of AIN with copper containing oxygen at the interface, along with the results of mechanical strength of the interface will be presented and discussed.

# 5.1. WETTABILITY OF AIN BY COPPER

In joining metals to ceramics, the formation of an intimate interface is a primary requirement. An intimate solid/liquid interface can only be formed if the liquid wets and spreads at the solid surface. Consequently, wettability of a substrate by a liquid metal is the most important factor for liquid state bonding. The wettability study of AlN by Cu was therefore an obvious first step in this work.

The reason for choosing the hot-pressed AlN as a substrate was to decrease the effect of the surface roughness on the wettability results<sup>(107)</sup>. The extra surface area that a rough surface adds at the interface, in comparison with a ideal smooth surface, deviates the wetting conditions from thermodynamic equilibrium to one of non-equilibrium. It has been also reported that increasing the surface roughness improves wetting.<sup>106</sup>

The reason for selecting high purity copper was to eliminate the effect of alloying elements on the reaction of AlN with Cu. In fact, active elements which have a high affinity for nitrogen can react with AlN and substitute for aluminum in the AlN crystal structure thus reducing its thermal conductivity. The solid/liquid interfacial energy can be strongly affected by these kinds of reaction at the interface. The effect of the solid/liquid interfacial energy on the wetting contact angle can be deduced using Young's equation.

Two kinds of atmospheres were used to study the wettability of AlN by copper: (a) a flowing nitrogen gas and (b) vacuum of  $10^{-5}$  mbar. The reason for performing the experiment under vacuum was to remove the physically absorbed species and gases which have been absorbed on the substrate surface or in the open porosity. The gas absorbed at the interface might expand at higher temperatures, forming large bubbles. As a result of bubble formation at the interface the thermodynamic equilibrium will be changed (Equation 2.2). In this case the surface tension between the gas and liquid phase, and the pressure that the bubble exerts at the interface must be taken into account. The reason for performing the experiments under flowing and static nitrogen was to get comparable data with that obtained for the effect of impurities (mostly oxygen) on the wettability of AlN by Cu.

The contact angles between Cu/AlN at different temperatures under flowing nitrogen are shown in Figure 5-1. Contact angles reported in this graph are given for

zero time at melt. However this system indicated a decreasing contact angle with time, and this is shown in Figure 5-2.



Figure 5.1. Contact angles for AlN–Cu system under  $N_2$ .



Figure 5.2. Contact angle for AlN-Cu system in Vacuum, Nitrogen and Flowing Nitrogen at 1100°C.

The contact angles under the flowing nitrogen were smaller than those obtained in vacuum. This difference was obviously attributed to the impurity content of the nitrogen used. This assumption is confirmed by the results obtained under static nitrogen gas. The contact angles for the static condition were between those obtained in vacuum and flowing gas conditions. In comparison with static gas, flowing gas would provide more available impurities (e.g.  $O_2$ ,  $H_2O$ ,...) to be absorbed

by the melt. Further experiments were performed to demonstrate the effect of oxygen on this system.

No significant change in contact angle with time was noted for the experiments done under vacuum. Pure Cu did not wet the surface of AlN. Indeed, the contact angle between these two materials did not reach less than 145° up to 1200°C (see Figure 5.1). It can also be seen that increasing the temperature does not significantly effect the contact angle.

The long holding time for the wetting experiments ensured equilibrium, since no significant change occurred after longer times under vacuum. The 30 minutes holding time was found to be the best for the three kinds of experiments already mentioned. Indeed, the contact angle did not change after the first five minutes. The longer holding time was chosen to allow the system to equilibrate with the surrounding environment.

The result of the wetting experiments of pure copper and AlN show that there is no tendency of chemical interaction between these two components. The calculations of the work of adhesion and wettability in the Cu-AlN system carried out by the formulae cited in chapter 2 (equation 2.1 and 2.2) are presented in Table 5.1. The values of  $\gamma_{1v}$  of Cu were estimated by Rhee<sup>(108)</sup>, who found the relation between  $\gamma_{1v}$  and temperature to be:

$$\gamma_{IV}$$
 (Cu) (dynes/cm)-1462-0.27T (°C) (5.1)

Time (min.)	θ (N <sub>2)</sub>	γ <sub>ls</sub> (dynes/cm)	W <sub>a</sub> (dynes/cm)	
1	160	2084	70.2	
5	157	2062	92.6	
10	153	1928	127	
15	150	1998	156	
20	146	1956	199	
25	25 142		246	
30	136	1828	327	

Table 5.1. Effect of time on the wetting behaviour.

The decrease of the contact angle as a result of increasing temperature in Figure. 5.1 and 5.2 can be attributed to the decrease in  $\gamma_{lv}$  (equation 4.1, and 2.1). It can also be attributed to dissolution of  $O_2$  and other impurities in the Cu or physical bonding of Cu to the surface of AIN which shows its effect by decreasing the  $\gamma_{sl}$  values.

In order to investigate the variation of  $\gamma_{sl}$  with temperature and other additives, Young's equation can be applied (Equation 3.2). Equation 5.1 was used to calculate  $\gamma_{lv}$ . The  $\gamma_{sv}$  values for AlN were taken from Rhee<sup>(76, 2)</sup> in order to calculate the liquid/solid surface tension. The changes of contact angle ( $\theta$ ) for experiments done under flowing nitrogen at 1100°C is likely because of oxygen impurity of nitrogen since the amount of O<sub>2</sub> available would increase with time. This can effect the  $\gamma_{ls}$  and consequently the W<sub>a</sub> values as shown in Table 5.1.

In brief, the results obtained from wettability study showed that joining of

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pure copper to AIN is not possible. It was then concluded that the modification of either the surface of the AIN or the chemical composition of the copper were necessary to achieve a bond in this system. The latter case can be seen from the data obtained from the effect of time on wetting contact angle which is probably a result of gas impurities in the copper composition (Table 5.1).

In the former case *i.e.* surface modification of the AlN was studied by Iwasa *et al*  $^{(97)}$  and Chiang *et al.* They reported that the oxidation of AlN changes the system to AlN-Al<sub>2</sub>O<sub>3</sub>-Cu.

The second step of this work then focused on the study of the oxidation mechanism of AlN and direct bonding of Cu to  $Al_2O_3$ , in order to understand the mechanisms of bonding and to apply this to the AlN-Cu system.

# 5.2. Direct Copper Bonding

Several process parameters affect the direct bonding metallization process. Temperature, time, atmosphere, and the thickness of the copper foil are four key parameters in this regard.

#### 5.2.1. Effect of Temperature

The direct bonding process is possible in a limited range of temperature i.e. from 1065 to 1075°C. This narrow range of temperature requires a precise temperature control (see section 2.7.3). The CN8600 series of the Omega temperature controller was thus chosen. Based on the accuracy of the temperature controller and the temperature sensitivity of the process, 1070°C was chosen for the initial experiments.

# 5.2.2. Introducing the Oxygen at the Interface.

The basic concept of the direct copper bonding which, is to form a liquid skin around the copper, is partially fulfilled by choosing the proper atmosphere. The kind of oxidation atmosphere determines the thickness of the oxide layer on the surface of the copper foil and this affects the amount of eutectic layer at the interface. The latter is a function of temperature. Two procedures were used to introduce the oxygen at the interface;

(a) Pre-oxidation of the Cu-foil, and

(b) Bonding in an oxidizing atmosphere.

The relation between the thickness of the liquid which forms during bonding and the thickness of the oxide layer on the surface was determined using equation 3.2. It should be noted here that during the oxidation process the Cu foil was oxidized and this limited the thickness of the foil which could be used.

### 5.2.3. Pre-Oxidation of Cu Foil.

Cu foils with various thicknesses were prepared using a rolling mill, and oxidized in air at a temperature ranging from 50-300°C for few seconds, since only a few Angstroms were needed for this purpose. The dark orange oxide layer was clear for those samples oxidized above 100°C. The oxide layer was removed from

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one of the surfaces. Joining was performed by placing the oxidized layer in contact with the substrate. The direct bonding was carried out in a nitrogen atmosphere with 10 ppm impurity of oxygen. In order to understand the mechanisms of bonding and to apply this to the AlN-Cu system, a conventional  $Al_2O_3$  substrate was used in this series of experiments, as already explained in Chapter 3. The results of the bonding in terms of the thickness of the foil and the temperature of the process are summarized in Table 5.2.

Table 5.2. The effect of ...: idation temperature and thickness of Cu-foil on direct bonding.

Thickness of	Oxidation temperature (°C)					
the foil (mm)	50	75	100	125	175	200
0.1	<u>N</u>	М	M	M	M	M
0.2	N	N	В	<u>M</u>	M	M
0.3	N	N	В	В	В	M
0.4	N	N	В	В	В	<u>M</u>
0.5	N	В	В	В	В	М

N:Not bonded B:Bonded M:Melted

It can be concluded that the thinner the foil, the more difficult it is to get a satisfactory bond, which was expected from equation 3-2 and the Cu-O binary phase diagram, Figure 2.5. In thin foils the amount of the liquid which forms is considerably higher and consequently, foils could not keep their structural integrity.

The reason for poor bonding may be attributed to the low amount of liquid phase available to wet the surface at the interface with the substrate. It can also

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be concluded that the thicker the foil, the more chances of obtaining a satisfactory bond since the proportion of liquid to solid phase does not cause a problem. Two tests were carried out to check whether a bond was satisfactory. A visual check determined if the foil had kept its structural integrity. Qualitative peel tests were carried out to evaluate the strength at the interface. This was done using a sharp object peeling the Cu foil from the substrate. The results of the quantitative peel test will be reported later in this chapter.

The data reported for thicknesses ranging from 0.1 to 0.4 mm in this process were not reproducible. There was no such problem for the foil with the 0.4 mm thickness. Absorption of the oxygen, as an impurity from the nitrogen gas was another factor that complicated the control of the amount of liquid formed at the interface, this being attributed to the control of the thickness of the oxide layer during the oxidation and bonding process. It was difficult to establish a uniform condition for the same experiment since the required layer of oxide was so thin. These results led to the consideration of other alternative i.e. bonding in an oxidizing atmosphere.

#### 5.2.4. Bonding in an Oxidizing Atmosphere.

Introducing oxygen at the interface was accomplished by using a nitrogen gas containing about 500 ppm oxygen. Oxygen diffused and oxidized the surface of the copper foil. Because of the low partial pressure of oxygen (about  $5 \times 10^{-1}$  mbar), the oxidation process was slow and facilitated controlling the thickness of the oxide layer.



Figure 5.3. The heating cycle resulted in a satisfactory direct bond.

The heating rate to the set temperature of the experiment was found to be a major factor in this process: the slower the heating rate, the thicker the oxide layer and consequently the more extensive was liquid formation. It was also found that the heating rate at higher temperatures was more important than at the lower temperatures. The best heating cycle which resulted in a satisfactory bond is shown in Figure 5.3. A typical microstructure obtained by using these conditions is shown in. Figure 5.4. Region (A) is copper whereas the lower part i.e. region (B) is  $Al_2O_3$ . In between, there is a eutectic region (C) of  $Cu_2O$  particles in a copper matrix. The dark cavities at the interface are gas pores. The shape of these cavities distinguishes them from shrinkage cavities. Two reasons for the formation of these cavities are proposed.



Figure 5.4. The interface microstructure of direct bonding of Cu to  $Al_2O_3$ .

(a) During the solidification of the eutectic phase, the dissolved gas in the liquid comes out of the solution, as a result of the difference in gas solubility in the liquid and solid.

(b) Gas entrapment may occur at the interface. The reason for this may be:

1) Gases are trapped in the surface porosity of the alumina, and

2) the eutectic liquid forms initially at the edges of the foil and then develops towards the centre i.e. since the sample edges are heated faster than the rest of the copper foil, there would be no way for the gas to escape, and thus cavities are formed at the interface.

The lack of good contact between the copper foil and alumina increased the
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chance of gas entrapment at the interface. Evacuation of the substrate before bonding can significantly decrease the amount of the gas at the interface. Furthermore pressing of the parent joint before bonding can decrease the gap between the two materials. However, it would also decrease the diffusion rate of oxygen at the interface making the direct bond difficult. The former reason, i.e. gas entrapment in the surface porosity, is more likely to be responsible since the high thermal conductivity of copper decreases the possibility of the later reason to happen.

# 5.3. Bonding Mechanism in the Cu-Al<sub>2</sub>O<sub>3</sub> System.

In order to find out whether a reaction occurs at the interface, which could be responsible for bonding, the wettability of  $Al_2O_3$  by Cu was studied. The results of this study and that of AlN/Cu are shown in Figure 5.5. The non-wetting condition is obvious for the Cu-Al<sub>2</sub>O<sub>3</sub> system for temperatures ranging from 1085 to 1200°C. The difference between the data obtained for AlN-Cu and  $Al_2O_3$ -Cu systems can be ascribed by the difference in bonding structure of AlN and  $Al_2O_3$  which are covalent and ionic, respectively (see section 9.1 and 9.2 in chapter 2). In comparison with the results obtained from direct bonding it was then concluded that oxygen should play an important role in the AlN-Cu system. The effect of oxygen on the wettability of  $Al_2O_3$  by copper was then studied by adding different amounts of oxygen in the form of Cu<sub>2</sub>O powder, to the pure copper powder. These experiments were carried out at 1150 °C for 30 minutes to ensure that the Cu<sub>2</sub>O dissolved completely in the copper melt. The wettability results are plotted in Figure 5.6.



Figure 5.5. Contact angles for  $Al_2O_3\mbox{-}Cu$  and AlN–Cu system under  $N_2$ 

It is clear that the contact angle drops sharply with increasing oxygen content. Eremenko<sup>(64)</sup> also studied this system and obtained an abrupt decrease in the interfacial energy as a result of oxygen addition to the pure copper. It is suggested that the decrease in the interfacial energy could be a result of decreased surface tension of the liquid phase or a result of an increased work of adhesion. Oxygen in this system works as a surface active additive in liquid copper which causes a decrease in contact angle. It can thus be concluded that the wettability results



Figure 5.6. The Effect of oxygen content on wettability of  $Al_2O_3$  by copper.

confirm a chemical bond in the direct bonding of copper to  $Al_2O_3$ .

# 5.3.1. Interface Analysis of Cu-Al<sub>2</sub>O<sub>3</sub> Direct Bond.

There is widespread speculation that a reaction layer forms at the copperalumina interface, and was suggested by Chaklader and his co-workers (109), (110). Other reports,(111) however, contradict these findings and suggest that there is no apparent reaction phase at the interface between copper and alumina.

In order to establish whether a chemical bond was formed at the interface, Energy Dispersive Spectroscopy (EDS) analysis was performed. The details of this

Interface	Cu (atom%)	Al (atom%)
1	53	47
2	48	52
3	35	65
4	32	68

Table 5.3. Composition of  $Al_2O_3$ -Cu interface as shown in Figure 5.4.

analysis are explained in Appendix II. The results of the EDS analysis in Table 5.3 confirmed that a reaction occurred at the interface resulting in a spinel of copper and aluminum. A typical EDS spectrum of the interface is shown in Figure 5.7. As expected from the alumina-copper oxide phase diagram, Figure  $5.8^{(112)}$ , the metastable phases at the interface were identified as CuAlO<sub>2</sub> and CuAl<sub>2</sub>O<sub>4</sub>. No specific region of the interface were found to be either CuAlO<sub>2</sub> or CuAl<sub>2</sub>O<sub>4</sub> because the proportions of Al to Cu changed from point to point. The variation in the proportion of Al to Cu can be attributed to (a) the thin interface layer or (b) the following reactions that can take place at the interface, as proposed by Yoshino *et al.*<sup>(113)</sup>.

$$2CuAl_2O_4 - 2Cu + 2Al_2O_3 + O_2$$
(5.2)

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Figure 5.7. Typical EDS spectrum obtained from the  $Cu-Al_2O_3$  interface.

$$CuAl_2O_4 + Cu - 2CuAlO_2$$
(5.3)

## 5.4. Modification of the Wettability of AlN by Copper.

## 5.4.1. Oxidation of AlN

The results obtained from wettability studies of AlN-Cu and of  $Al_2O_3$ -Cu supported the idea of oxidizing AlN to achieve bonding in the AlN-Cu system. In this regard, oxidation kinetics of the AlN substrates and the microstructure of the oxide layer were studied. The goal was to determine the optimum thickness of the oxide layer in order to achieve direct bonding with a view to obtaining good contact and therefore high thermal conductivity. Oxidation of AlN was done in air over a

<u>65</u>



Figure 5.8.  $Al_2O_3$ -Cu<sub>2</sub>O phase diagram.

temperature range of 900 to 1300°C. Experimental oxidation curves of hot-pressed AlN samples as a function of time and temperature are given in Figure 5.9. As can be seen from this figure the oxidation rate of AlN is comparatively low, and after 6 hours at  $1200^{\circ}$ C only  $0.4 \text{ mg/cm}^2$  specific weight gain was recorded. The oxidation of sintered AlN is described by the parabolic rate equation;

$$\Delta g = K_p \sqrt{t} \tag{5.4}$$

where  $K_p$  is the parabolic rate constant, t is the time, and  $\Delta g$  is the weight gain per unit area of the sample. The parabolic shape of the curves confirms that the oxidation of AlN is a diffusion-controlled process through the oxide layer. The activation energy obtained experimentally (93 kJ/mol) was calculated from the plot of the rate constants  $K_p$  vs temperature Figure (5.10). Figure 5.11(a) shows the typical microstructure obtained from the oxidation of AlN. The microstructure of the oxide layer is completely different from that of AlN. The oxide layer consists of very fine, nanometre sized grains. This can be considered as an advantage for this process because it facilitates achieving a smooth surface finish, which is necessary for deposition of the other circuit components.

AlN conversion to  $Al_2O_3$  is accompanied by 2.19 vol% volume change (Appendix III). The stresses resulting from both this volume change and thermal stresses resulting from a difference in the Coefficient of Thermal Expansion (CTE)



Figure 5.9. Oxidation of AlN vs time and temperature.

of AlN and  $Al_2O_3$  caused cracking along the AlN-Al\_2O\_3 interface (Figure 5.11.(b)). The results of microstructural studies of the oxide layer revealed that samples with more than ~ 1 µm oxide layer on the surface showed cracking at the interface.

The results of XRD tests (Figure 5.12) on the substrate before and after oxidation confirmed that  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum) forms during the oxidation of AlN. The AlYO<sub>3</sub> phase was detected as a second phase in the AlN substrate itself. No other

phase was found as a second phase in the oxide layer but the results of EDS analysis confirmed the existence of about 1.5 -2 at.% yttrium in this layer. The existence of traces amount of nitrogen and yttrium in the oxide layer confirmed the presence of either yttrium oxy-nitride or polytype phases.



Figure 5.10. Rate constants of AlN oxidation vs temperature.







Figure 5.11. Microstructures obtained from the oxidation of AIN substrates, (a) microstructure of the oxide layer grown on the surface of AIN, (b) cracks due to the CTE mismatch between two materials, (c) cracks resulting from shrinkage during sintering.



Figure 5.12. X-ray pattern of the oxide layer on the surface of AlN substrate.

## 5.4.2. Compositional Modification of Copper

Although oxidation of aluminum nitride improves wettability and bonding of Cu to AlN, it introduces a thermal barrier at the interface. It also adds one more step to the bonding process. The thermal stress resulting from the difference in (CTE) of AlN and  $Al_2O_3$  is also another disadvantage of using the oxidation process to improve wettability.

Active metals are available (e.g. titanium) that possess a higher affinity for aluminum than nitrogen. Addition of these metals to copper can improve both wettability and bonding in the Cu-AlN system. <sup>(93)</sup> However the conductivity of copper should also be considered when these elements are added to copper in order to improve its bonding to ceramics for electronic applications. Unfortunately, active metals affect the electrical conductivity of copper when they are added in small quantities and exist in solid solution.<sup>(44)</sup> On the other hand, oxygen has less harmful effect on the conductivity of copper.<sup>(44),(114)</sup> It can also be directly introduced at the interface and forms stable compounds such as oxides and oxynitrides.

The thermodynamic calculations suggest that oxygen can react with AlN forming  $Al_2O_3$  and nitrogen. This was also confirmed by the results obtained from the oxidation studies of AlN. The overall reaction can be written as:

$$2AIN + \frac{3}{2}O_2 - Al_2O_3 + N_2 \tag{5.6}$$

By comparison between the free energy formation of AlN and  $Al_2O_3$ , it easily can be concluded that  $Al_2O_3$  is more stable than AlN in air.

Furthermore, copper can dissolve oxygen and form copper oxide as demonstrated by the Cu-O phase diagram Figure 2.5.

It can be concluded here that AlN might react with copper containing oxygen. In order to confirm this assumption, the reaction between AlN and  $Cu_2O$  were studied. The first step was to investigate the possible reaction at the interface. The thermodynamic calculations suggest that the reaction occurs as follows:

$$0.66AIN + Cu_2O = 0.33Al_2O_3 + 2Cu + 0.33N_2$$
(5.7)

The free energies ( $\Delta G^{\circ}$ ) of the reaction for a temperature range of 500 to 1200°C and in a nitrogen atmosphere was calculated as,

$$\Delta G^{\circ} = -178198 - 37.1 T \tag{5.8}$$

This equation shows that at higher temperatures AlN is unstable.

The second step in this study was to investigate the wettability of AlN by  $Cu_2O$ . Copper oxide powder ( $Cu_2O$ ) was used for this purpose. The wettability study of AlN by  $Cu_2O$  revealed that AlN is wetted by  $Cu_2O$ . This also confirmed that a reaction takes place at t...e interface. Figure 5.13 shows the microstructure obtained from wettability studies for this system. The formation of elemental copper at the interface, where  $Cu_2O$  is in intimate contact with AlN, is obvious and proves the formation of one of the products predicted by the thermodynamic calculations.

The experimental results using a mixture of the powders of the above reactants (AIN and  $Cu_2O$ ) also confirmed the formation of elemental copper. A typical microstructure obtained from heating of the aforementioned mixed powders in vacuum at 900°C is shown in Figure 5.14. The EDS analysis shown in Figure 5.15 confirms that the bright phase is copper. Although,  $Al_2O_3$  was not detected by EDS analysis but X-ray analysis confirmed the presence of this phase.  $Al_2O_3$  was identified on the X-ray pattern which is shown in Figure 5.16.

The amount of copper formed from the mixed powder in the temperature range 700 to 1000°C was used to optimize the reaction temperature (see section 4.6). The X-ray studies showed that this reaction is complete at about 900 °C. It was

# **RESULTS AND DISCUSSION**



Figure 5.13. Microstructure obtained from wettability study of AlN by  $\rm Cu_2O$ 



Figure 5.14 Typical microstructure obtained from heating the mixture of AlN and  $\rm Cu_2O$  powders in vacuum at 900°C.



Figure 5.15. EDS analysis of mixed powders of  $Cu_2O$  and AIN heated in vacuum at 900°C.



Figure 5.16. X-ray pattern resulted from chemical simulation of the interface.



Figure 5.17. Amount of the Elemental Copper Formed Versus Temperature. also employed to calculate the activation energy and the reaction constant using the Arrhenius equation. Figure 5.17 and 5.18 show copper formation and ln rate of copper formation vs. 1/T, respectively. The activation energy was approximately 117 kJ/mol. The reaction constant was about 3.92, and the following equation can be derived:

$$K = 3.92 \exp\left(-\frac{117}{RT}\right)$$
 (5.9)





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# 5.5. Wettability of AlN by Copper Containing Oxygen.

Based on the results obtained from simulation of the possible reactions at the interface between AlN and copper containing oxygen, a study was carried out to investigate the improvement in wettability of AlN by copper containing oxygen. Copper with various contents of oxygen in the form of  $Cu_2O$  were prepared and the wettability was assessed. The effect of oxygen content on the contact angle is shown in Figure 5.19.



Figure 5.19. The effect of oxygen on the wettability of AlN-Cu system.

#### **RESULTS AND DISCUSSION**

It is obvious from Figure 5.19 that oxygen strongly affects the solid-liquid interfacial energy, resulting in wetting. It can also be attributed to the decrease in surface cension of liquid copper. In fact, wettability experiments confirmed the reaction at the interface. It obviously can be attributed to the existence of oxygen since the addition of oxygen was the only variable in this system and is suggested that the reaction between AlN and Cu<sub>2</sub>O was responsible for this wettability improvement. However, the reaction between oxygen dissolved in the molten copper, not in the form of Cu<sub>2</sub>O, should also be considered. Reaction 5.6 can be considered as a simple oxidation reaction for AlN. Comparing the results obtained for oxidation of AlN in air and that of oxidation by  $Cu_2O$ , it can be concluded that the oxidation occurs at a lower temperature in the later case. This can be attributed to the high activity of oxygen when it is in the form of an oxide or is in solution in molten copper. The lower activation energy for this case also confirms a lower energy required for the oxidation process to take place in the presence of  $Cu_2O$ . The further increase in the contact angle can be explained by the increase of the liquidus temperature in the Cu-O phase diagram as the oxygen content increases. (see Figure 2.5)

### 5.6. Effect of Oxygen on the AlN-Cu Interface

A SEI micrograph of a typical AlN-Cu interface is shown in Figure 5.20 (a). As is clear from this figure there is no distinct reaction zone. The reaction zone should be very thin because even at high magnification no distinct phase was





b

#### **RESULTS AND DISCUSSION**

observed. One of the interesting points about this microstructure is that there are no flaws at the interface. Considering the reaction 5.6 in this chapter, it was expected that the cavities resulting from  $N_2$  evolution at the interface were one of the major sources of porosity. However, the results of microstructural studies did not confirm this. The possible reasons for this kind of structure may be (a) little or no reaction taking place at the interface thus resulting in no gas evolution, (b) oxidation of AlN may occur during heating of the sample to the bonding temperature and change the system to an  $Al_2O_3$ -Cu system, (c) the proposed reaction has occurred and the liberated gas has come out of the interface and molten copper. Among these possibilities the later is more likely to have occurred. The results of mechanical strength of the interface which will be reported later in this chapter confirmed this.

Another point about the microstructure obtained is the absence of cracks at the interface. The most common cracks in metal-ceramic interfaces occur due to the CTE mismatch between the metal and ceramic. The lack of this kind of crack in this system can be attributed to the high ductility of copper. In fact, thermal stresses are relieved by plastic deformation of copper during cooling from the bonding temperature. A backscatter image is also shown in Figure 5.20. The shape of the  $Cu_2O$  is completely different from the original, spherical,  $Cu_2O$  particles. They were almost spherical, confirming their complete solution during bonding.

### 5.7. Mechanical Evaluation of the Bond Strengths

The results of the peel test done on samples bonded at 1070°C for 5 minute under a flowing nitrogen containing 500 ppm oxygen are summarized in Table 5.4.

Table 5.4. The results of Peel test on Metallized substrates.

System	Average Peel Strength (MPa)	Max. Peel Strength (MPa)
۸۱ <sub>2</sub> 0 <sub>3</sub> -Cu-ú	49	66.6
AIN-Cu-O	42.1	58.8
AIN-Al <sub>2</sub> O <sub>3</sub> -Cu-O (Prooxidized)	14.7	39.2

The low strength for AlN-Al<sub>2</sub>O<sub>3</sub>-Cu-O system can be explained by the stresses existing between the Al<sub>2</sub>O<sub>3</sub> and AlN, owing to the thermal expansion mismatch between the various atom-layers. The thermal expansion coefficient of Al<sub>2</sub>O<sub>3</sub> (~ 9  $\times$  10<sup>-6</sup>°C<sup>-1</sup>) is almost double that of AlN (5  $\times$  10<sup>-6</sup>°C<sup>-1</sup>). The cracks produced at the AlN-Al<sub>2</sub>O<sub>3</sub> interface and on the surface of the Al<sub>2</sub>O<sub>3</sub> after oxidation suggest the existence of high thermal stresses, causing cracks resulting from shrinkage during the formation of the Al<sub>2</sub>O<sub>3</sub> phase through oxidation on the surface and differential contraction between AlN and Al<sub>2</sub>O<sub>3</sub> on cooling. The thermal stresses between Cu and CuAlO<sub>2</sub> and between Al<sub>2</sub>O<sub>3</sub> and CuAlO<sub>2</sub> in this system, as discussed in section 5.3, may also be responsible for weakening the interface. However this is not as effective as the former case because the latter exists in the Al<sub>2</sub>O<sub>3</sub>-Cu-O system, where high strength is observed.

The fracture surfaces obtained from peel tests are shown in Figure 5.21. In the case of  $AIN-Al_2O_3$ -Cu, (Figure 5.21 (a)), there is no evidence of copper at the interface by EDS analysis and only AIN was detected, confirming that fracture occurs at the  $AIN-Al_2O_3$  interface.

The high strength in the  $Al_2O_3$ -Cu-O can be attributed to the formation of a strong CuAlO<sub>2</sub> bonding phase at the interface. The fracture surface for this system is shown in Figure 5.21.(a) where relatively fine grains of copper are observed. The presence of these particle are attributed to the copper bonded to  $Al_2O_3$  by copper aluminate spinel formation at the interface. These grains are completely located at the reaction, eutectic layer zone. Larger grains of copper with a multi-faceted shape can also be seen. The shape of these grains confirm the pull out of copper grains from the copper foil. The reason for this can be explain by the formation of copper-oxygen eutectic at the grain boundary of copper, as observed in Figure 5.4. The existence of this layer strongly deteriorates the strength of copper and causes intergranular fracture.

The relatively high strength for AlN-Cu-O system can be explained by the integrity of the interface between copper and AlN, as shown in Figure 5.21(c). It should also be noted that this AlN-Cu-O system demonstrated the best wetting characteristics. The high strength in this system can be explained by the mechanism suggested by Scott,<sup>(115)</sup> who explains that chemical interactions on the microscopic scale resulting in the formation of new compounds at the ceramic-metal interfaces have a marked effect on bond strengths. It has been also con<sup>r</sup>irmed that



crack

Figure 5.21. Fracture surfaces of (a)  $Al_2O_3$ -Cu, (b) AlN- $Al_2O_3$ -Cu-O, and (c) AlN-Cu-O systems.

### RESULTS AND DISCUSSION

the reaction with active metals proceed by the nucleation and growth of islands of the product bridging the metal-ceramic interface. The optimum degree of interaction will be when the interface is first covered by the bridging compound, in a layer about 100 nm thick. As oxygen in the AlN-Cu-O system acts as an active elemei and can substitute for nitrogen in the AlN crystal structure, the above mechanism can be proposed here. The fracture surface of AlN-Cu-O system shown In Figure 5.20 (c) displays the fine dispersion of copper particles at the interface confirming the role of oxygen in this system. The fracture surface observed for AlN-Cu-O system was more covered than the one observed for  $Al_2O_3$ -Cu system expecting higher interfacial strength but the results of peel test did not confirm this. This might be attributed to the cracks seen on the fracture surface of Figure 5.21 (c) which are found propagating perpendicular to the interface. It might also be due to experimental error. This kind of bond had a very thin reaction layer at the interface (few nanometre) and the relatively high strength confirm the above proposed mechanism of bonding.

## **6.**Conclusions

The metallization of AIN by Cu was studied based on metal-ceramic bonding requirements. The direct bonding technique was chosen as the metallizing process. In this regard, the process parameters were established on  $Al_2O_3$ -Cu system and later applied to AIN-Cu system. In order to metallize AIN, the wettability of  $Al_2O_3$  and AIN by Cu, oxidation of AIN, effect of oxygen in these systems, and mechanical properties of the interface were studied. The following conclusions can be drawn from these studies;

1) AlN can not be wetten by pure copper. The non-wetting condition is not a strong function of time and temperature. It can be thus concluded from the wettability results, that a modification either of the surface of the AlN or by altering the chemical composition of copper is required to achieve a bond, and hence improve wettability. Surface modification of AlN can be done through oxidation, by changing the surface chemistry from a nitride ceramic to an oxide or oxynitride ceramic. Compositional modification can be done by adding an active element (oxygen) which possesses a higher affinity for aluminum than nitrogen.

2) The kinetic study of hot pressed AlN substrate showed that the reaction of AlN with oxygen obeys the parabolic rate law. The corresponding activation energy (93.4 k J/mol.) showed a low oxidation rate in a temperature range from 900 to 1200°C. The main oxidation product of AlN was  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The existence of trace amounts of nitrogen and yttrium in the oxide layer confirmed the presence of either yttrium oxy-nitride or polytype phases.

3) Pure copper cannot wet  $Al_2O_3$  as well. Addition of oxygen to copper effectively improves wetting. In fact, this forms the basis of the commercial direct bonding process. EDS chemical analysis showed that the CuAlO<sub>2</sub> is the most likely phase at the interface of  $Al_2O_3$ -Cu containing oxygen.

4) It was found that oxygen can be used as active element with copper. The oxygen content of copper reacts with AlN forming  $Al_2O_3$  which is more stable than AlN. Chemical simulation of the interface using powders of AlN and  $Cu_2O$  confirmed the formation of  $Al_2O_3$  at the interface. The proposed reaction can be written as;

$$0.66AlN + Cu_2O - 0.33Al_2O_3 + 2Cu + 0.33N_2$$
(4-13)

This reaction was experimentally verified within a temperature range from 700 to  $1000^{\circ}$ C. The activation energy (117 kJ/mol.) for this system is close to that of oxidation in air (94 kJ/mol.).

5) The addition of oxygen to AIN-Cu system (about 1-1.5 at.%) charges the system from a non-wetting to a wetting situation, making bonding of Cu to AIN possible. The microstructural examination of the interface did not show any phase

## CONCLUSIONS AND RECOMMENDATIONS

to be responsible for bonding. However, the mechanism proposed by Scott (see section 5.7) for active metals is the most likely one for AlN-Cu system.

6) The mechanical properties of the interfaces using a standard peel test showed that the strength of the bond for AlN-Cu (42.14 MPa) is between that of  $Al_2O_3$ -Cu (50 MPa) and pre-oxidized AlN-Cu (14.7 MPa) fulfilling the minimum required strength of 19.6 MPa for microelectronic application. The low strength for pre-oxidized AlN-Cu bond is a result of CTE mismatch between  $Al_2O_3$  and AlN. In contrast, the high strength for  $Al_2O_3$ -Cu bond was attributed to the formation of CuAlO<sub>2</sub> phase at the interface.

## 6.1.Recommendations

1) Sintering aids can affect the wettability, and hence bonding of ceramics to metals. Further work in order to study the effects of sintering aids currently used with AlN, specifically  $Y_2O_3$  and CaO, on metallizing of AlN by copper is suggested.

2) Transmission electron microscopy (TEM) study of the AlN-Cu interface and oxide layer on the surface of AlN are required to establish the presence of specific phases which are responsible for the formation of such a strong joint.

3) The idea of using oxygen as an active element in copper to bond to AlN

can be expanded to other metal-nitride ceramic systems. In this regard, the study of bonding  $Si_3N_4$  to metals, which possess less stable oxides than  $SiO_2$  is recommended.

4) A solution thermodynamic approach is required in order to understand the role of oxygen dissolved in copper in reaction with AlN.

5) Oxygen has two opposing effects in AIN-Cu system. It improves the bonding and it also deteriorates the electrical conductivity of copper. Thus the amount of oxygen needs to be optimized in terms of these two parameters.

## APPENDIX I

## QUANTITATIVE X-RAY DIFFRACTION ANALYSIS

The rate of reaction between AIN and Cu<sub>2</sub>O was calculated by measuring the amount of Cu formed at different temperature. The amount of Cu formed was determined by X-ray diffraction. In order to generate a calibration curve, mixtures of known rations of Cu and AlN were prepared and subjected to filtered. Cu Ka radiation using a Phillips X-ray diffractometer (APD 1700). The ratio of the intensities of the 100% (100) hkl X-ray peak for AlN, at  $2\theta$ =33.2°, and that of the 100% (111) hkl X-ray peak for Cu, at  $2\theta$ =43.29°, were used to plot the calibration curve. The resulting diffraction pattern was determined over 20 of 30-50° with a scanning rate of 0.01°/sec.

The heights of the relevant peaks were used to determine the amount of Cu formed via the following equation:

$$W_{Cu} = I_{Cu} / (I_{Cu} + I_{AlN})$$

Where  $I_{Cu}$  and  $I_{A1N}$  are the height of the X-ray peaks of Cu, and AlN, respectively and  $W_{Cu}$  is the weight fraction of Cu in the mixture.

The errors in measuring the peak heights and the minimum detectable peak height were the most significant errors in this analysis. (The calibration curve is shown in Fig. A.I).



Fig. A.I. XRD calibration curve for measuring the amount of Cu formed.

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### APPENDIX II

## ZAF method

It is known from Moseley's Law<sup>(116)</sup> that the wavelength or energy of characteristic X-rays is proportional to its atomic number of the element producing the X-ray. It is clear that the intensity of X-rays of a given element in the specimen should be proportional to the concentration of that element in the specimen. In his doctorial thesis, Castaing<sup>(117)</sup> actually carried out a series quantitative niteroanalyses using electron-generated X-rays: moreover, he initiated the various corrections that are needed to convert X-ray intensity data into weight percent. In the years that followed, others formulated and refined these corrections into the standard matrix correction procedures that we know of as the atomic number-absorption-fluorescence (ZAF) method. This method is usually used within an analytical software program.

Atomic Number Correction (Z). The atomic number factor, or Z factor, corrects for the difference between the X-rays that are generated in the sample compared to those generated in the backscatter coefficient and the electron stopping power between unknown and standard. It can be eliminated by using a high overvoltage; however, as we will see, that approach would increase the absorption effect. Z factor is a function of following parameters:

 $Z-f(E_o, E_c, Z, A, Q, J)$ 

#### APPENDIX II

where  $E_o$ =accelerating voltage

 $E_e$ =critical excitation potential

Z=atomic number

A=acomic mass

Q=ionization cross section

J =mean ionization potential

Fluorescence Correction. The characteristic fluorescence factor, or F factor, is usually the least significant. It corrects for those X-rays that are detected by the detector but were not generated by the electron beam. These X-rays are the result of secondary fluorescence by characteristic lines of other elements in the specimen. Because of its nature the F factor is always less than one, as a rule of thumb, for the transition m tals, fluorescence becomes significant 2, 3, and 4 atomic numbers below the fluorescing element; e.g., Cu fluoresces Co, Fe and Mn. The fluorescence correction a function of following parameters:

$$F-f(E_o, E_c, A, \frac{\mu}{\rho}, \Psi, \omega, r, P)$$

 $\mu/\rho$  = mass absorption coefficient

 $\Psi$ = take-off angle

 $\omega$  = fluorescence yield

r= absorption ratio

 $P = type of fluorescence, e.g. K<sub>L</sub>, K\alpha etc.$ 

Absorption Correction. The absorption factor is usually the most important

ore. It corrects for those X-rays that were generated in the sample but absorbed before they were able to escape and be detected. The A factor is a ratio of the absorption behaviour between the standard and the unknown. At some depth within the specimen, the number of X-rays generated reaches a maximum, and as overvoltage increases so does this depth and the volume from which X-rays are produced. On the other hand, X-rays produced deep within the sample are more likely to be absorbed than those produced near the surface. As a result, there is an optimum overvoltage. Absorption is affected by the absorption path length, which in turn is affected by the take-off angle. The higher the take-off angle, the shorcer the absorption path length. The absorption correction is a function of the following parameters:

$$A-f(E_o, E_c, Z, A, \frac{\mu}{\rho}, \psi)$$

The take-off angle and overvoltage are both under the analyst's control and can be used to minimize the magnitude of the matrix correction. It should be noted that each of the factor is a function of composition.

The ZAF factor then corrects for the difference in the X-ray peak intensities of standard and sample. The way that it works can be summarized by the following equation;

$$C_{i}^{\text{sum}} \sim (ZAF) \cdot \frac{l_{i}^{\text{sum}}}{l_{i}^{\text{std}}}$$

### APPENDIX II

where  $I_i$  is the peak intensity of a given X-ray energy line of element I in the EDS spectrum and  $C_i$  is the wt% concentration of element i, (sap) and (std) are referred to unknown and standard sample.

The X-ray lines for Al and Cu in Table I were used for quantitative chemical analyses and qualitative analyses were performed using the X-ray lines for oxygen and nitrogen chemica<sup>1</sup> analyses. An electron acceleration voltage of 20 KeV were used for all quantitative EDS analyses. In the case of the quantitative analyses an acceleration voltage of 5 KeV was employed to detect the oxygen and nitrogen. The low acceleration voltage was used to minimize the absorption and to obtain the minimum X-ray spatial resolution. Base on the data on Table I, it can be seen that, the analytical X-ray peaks employed were separated with no overlaps from any of the X-ray peaks of the other elements.

Element	X-ray Peak Energy	
	K <sub>α1</sub> (KeV)	$L_{\alpha 1}$ (KeV)
Al	1.486	
Cu	8.040	0.930
N	0.392	
0	0.523	

Three major possible source of errors in the EDS chemical analysis which can affect the results obtained in this work can be summarized as;

(a) Counting errors associated with the X-ray detection facility,

(b) errors in calculating the ZAF corrections and

(c) variance between the individual analyses, due to the thin layer of the reaction zone and interfaces and also due to the inhomogeneities in the microstructures being analyzed.

Errors associated with the error a and b were introduced by the X-ray signal facility. The evaluation of these two errors are out of this work, but various studies<sup>118</sup> in the case of errors associated with ZAF correction have shown that, in the region of take off angles  $30^{\circ} \le \Psi \le 60^{\circ}$  this error would have insignificant effect on the value of the A<sub>1</sub> correction.

McDermid<sup>119</sup> studied the propagation of X-ray detectors counting errors for a Ni-Cr-Si-Nb alloys in EDS area analysis. The X-ray detection system was the same as employed in the present work. It was found in his work that the propagation of the X-ray detector counting errors are relatively small. He also found that the confidence limit associated with the analysis variance was significantly larger than the X-ray detection errors. These conclusions were chosen as a basic assumptions in this analysis.

In the case of the present study the thin layer of the interface in comparison with excitation volume were the largest single source of error in the EDS chemical analyses performed. Because of the thin layer of the interface in the Cu-AlN and  $Cu-Al_2O_3$  system. variance in chemical compositions observed. The chemical analyses were based on at least four different locations and finally an average value were chosen as the chemical composition of the interface. The confidence limit for variance of the chemical analyses were determined using control limit theorem and
the student t-distribution.  $^{120}$ 

Inhomogenities of the ceramic materials, presence of the sintering aids, were also another source of error. In the case of existence of other elements such as Y and Ca the results obtained from that analysis were ignored.

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The volume change calculation resulted from oxidation of AlN

This calculation is based on the difference in densities of AlN and  $Al_2O_3$ . The density of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is 3.97 g/cm<sup>3</sup> and that of AlN is 3.26 g/cm<sup>3</sup>.

The following reaction was assumed for oxidation of AlN;

$$2AIN + 3/2O_2 = Al_2O_3 + N_2$$

1 mol. of AlN = 41 g.mol

1 mol. of  $Al_2O_3 = 101.96$  g.mol

 $\rho_{A1N}$  =  $W_{A1N}$  /  $V_{A1N}$  , 3.26 = ( 2 x 41 ) /  $V_{A1N}$  then  $V_{A1N}$  = 25.15  $\rm cm^3$ 

 $\rho_{A12O3}$  =  $W_{A12O3}$  /  $V_{A12O3}$  , 3.98 = 101.96 /  $V_{A12O3}$  then  $V_{A12O3}$  = 25.61  $\rm cm^3$ 

 $\Delta V\%$  = (V\_{A12O3} - V\_{A1N} )/ V\_{A1N} x 100 then  $\Delta V\%$  = 1.79

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