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Reaction kinetics and mechanical properties in the reactive brazing of copper to aluminum nitride

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Abstract Aluminum nitride (AlN) is an attractive substrate material for electronic packaging applications because of its high thermal conductivity and electrical resistivity. However, improved metallization of aluminum nitride is required for reliable conductivity and good adhesion to the ceramic substrate. In this study, the kinetics, microstructure, and mechanical strength of Ag–Cu–Ti/AlN reaction couples have been studied in the temperature range of 900–1,050 °C and hold time range of 0–1.44×10^4 s using a eutectic silver–copper filler alloy containing titanium within the range of 2–8 wt%. The product layer thickening kinetics has been observed to change from a linear to non-linear thickening mechanism with the increase in holding time and temperature. At shorter hold times at a fixed temperature, the interfacial product layer followed a linear thickening kinetics. With the increase in the hold time, the thickening kinetics of the interface followed a non-linear thickening behavior. The non-linear thickening mechanism has been approximated as a parabolic thickening mechanism. The interface has been found to be rich in the reactive metal (Ti) content. The mechanical strength of the brazed joints has been analyzed using four-point bend tests. The strength of the brazed joints initially increased and then decreased with an increase in the hold time at a fixed temperature. A maximum strength of 196 MPa has been obtained for a brazed joint heated at 1,000 °C for 2,700 s containing 2 wt% Ti in the filler alloy. It was observed that the sample with the maximum strength had a discontinuous interface.

Introduction

Joining a metal to a ceramic is required for many advanced applications, such as microchip substrates, capacitors, heat sinks, and structural materials at both ambient and elevated temperatures. However, problems such as thermal expansion mismatch between the metal and ceramics due to the development of residual stress at the interface deteriorate the joint quality. Aluminum nitride (AlN) is a ceramic material possessing a coefficient of thermal expansion (CTE) similar to silicon, along with high thermal conductivity and high electrical resistivity. Research regarding the brazing of AlN is presently being performed because it has the potential to replace alumina (Al_2O_3) and beryllium oxide (BeO) that are presently used as commercial substrate materials.

Aluminum nitride is a potential candidate for replacing alumina, which holds 96% of the commercial applications, because it has ten times higher thermal conductivity than alumina. The thermal conductivity and electrical resistivity of AlN are 320 W/m K at RT and 10^{13} ohm cm, respectively [1]. The thermal expansion coefficient of AlN (4.7×10^{-6} K^{-1} at RT-875 K) closely matches the expansion coefficient of silicon wafers (2.7×10^{-6} K^{-1}) hence the component supported on AlN substrate is less likely to fail due to thermal cycling than that supported on beryllium oxide or alumina substrates [2]. Aluminum nitride also has a low dielectric constant and loss, and is nontoxic in nature

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with a less temperature sensitive thermal conductivity (K = 320 W/m K at RT) compared to the thermal conductivity of beryllium oxide (K = 250 W/m K at RT). Beryllium oxide is also toxic in nature [1].

Among the various methods of metallization, brazing is preferred for mass production; and brazing can provide smooth and rounded fillets at the periphery of the joints. In brazing, the base material does not melt. Brazing is hence applicable in the joining of dissimilar materials that cannot be joined by fusion processes due to metallurgical incompatibility. Brazing produces less thermally induced stress and distortion because the entire component is subjected to the same thermal exposure [3].

In direct brazing, a chemical reaction takes place between the braze alloy and the ceramic substrate. Modern filler metals for brazing of ceramics contain active elements (Ti, Zr, Hf) that promote wetting by forming an interfacial product layer by a dissolution or reduction reaction. The extent of dissolution of the ceramic surface is usually at the microscopic level (<100 μm). The brazed joint strength is maximized if the gap is properly filled and embrittling phases have not been produced by reactions between the filler metal and the ceramic substrate [3]. To obtain a strong bond between the metal and ceramic, an optimum liquid contact angle (<90 °C) is required which depends on the type of the metal foil, the ceramic substrate, the composition of the liquid phase and the type of atmosphere [4].

Typically, when a reaction couple is heated to a particular temperature for relatively short hold times, the interface thickening follows a linear rate law and the system is interface reaction controlled. During this stage, the thickness of the interface increases and it tends to become continuous. Upon increasing the hold time at a given temperature, the thickness of the continuous interface continues to increases by reaction of the species diffusing through the interface. During the later stage, the system follows a parabolic or a non-linear thickening behavior and is diffusion controlled. This is, however, the most common behavior of the interface of a reaction couple when subjected to heating.

The governing equation for the linear rate law is:

$$X = K_{\mathrm{L}}t, \tag{1}$$

where X is the interfacial product thickness in typically μm, K_{L} is the linear rate constant and t is the time in seconds. In the initial stages, when the interface is thin and discontinuous, the reaction takes place in between the liquid metal and the solid substrate. The interface thickening is then expected to follow a linear rate law [5].

When the reaction time and temperature increases, the product layer becomes thicker and continuous covering the entire region of the ceramic substrate exposed to the liquid metal. During this stage, diffusion through the product layer becomes rate controlling. The reaction rate is likely to decrease progressively because of the gradual thickening of the product layer which results in an increase in the diffusion path through the layer. The system is then expected to follow a parabolic thickening mechanism. The governing equation for the parabolic mechanism is given by

$$X^2 = K_{\mathrm{P}}t, \tag{2}$$

where X is the interfacial product layer thickness in typically μm, K_{P} is the rate constant for the parabolic mechanism, and t is the time in seconds [5].

In this study, brazing of aluminum nitride has been analyzed. It is difficult to join aluminum nitride to copper because AlN has poor wettability to copper and a significantly lower thermal expansion coefficient than copper [6]. It has been reported by Colpetzer et al. that both the titanium and zirconium alloys exhibited a contact angle less than 90° on aluminum nitride and exhibited a good adhesion as well [7]. Hence, the present study aims at optimizing the brazing of copper to aluminum nitride using 72Ag–28Cu–Ti as a braze alloy.

The overall goal of the project is to better understand the microstructures developed during reactive brazing of copper foils to aluminum nitride using eutectic silver–copper braze alloys (72Ag–28Cu) with titanium as reactive metal addition to the braze alloy (as shown in Fig. 1) and to characterize the kinetics of the microstructural development and the resulting mechanical properties of the brazed joint. The CTE value of Ag–Cu–Ti braze alloy (14×10^{-6}/°C) is significantly higher than the CTE value of aluminum nitride (43×10^{-7}/°C) but is nearly same as that of copper (17×10^{-6}/°C). In addition, the joint between copper and the braze alloy is more ductile compared to

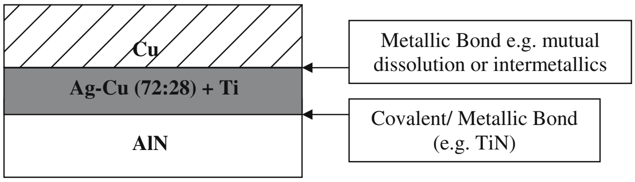

Fig. 1 Bonding arrangement of the Cu to AlN brazed joint using 72Ag–28Cu–Ti filler alloy (the current study focuses on the Ag–Cu–Ti/AlN interface)

the joint between the braze alloy and the aluminum nitride substrate. The probability of failure, therefore, is more likely due to the development of residual stresses at the AlN/braze alloy interface. The specific goal of the project is to study the interface between the braze alloy and aluminum nitride and analyze its mechanical properties. The reaction kinetics of eutectic silver–copper–titanium filler alloys on aluminum nitride substrates has been analyzed at various temperatures and hold times. The mechanical strength of the brazed joints has been measured using a four-point bend testing configuration and the mechanical properties have been correlated to the braze microstructures.

Experimental procedure

The experimental materials used in this study were aluminum nitride, silver–copper eutectic foils and high purity titanium powder. Cylindrical plates of aluminum nitride having a diameter of 25 mm and thickness of 1 mm were procured from St. Gobain Advanced Ceramics (Sunburn, NY) and were used to study the reaction kinetics and microstructure. The plates were prepared by hot pressing in a graphite die. The aluminum nitride samples had a purity of 96.5 wt% with 3.5 wt% Y_2O_3 addition. According to the vendor specification, the average grain size reported was 4.5 ± 0.5 μm. Cylindrical and rectangular bars of commercial grade AlN, obtained from Vactronics (Buffalo, NY) and ART, respectively, were used to study the mechanical properties of the brazed joint by a four-point bend test. The silver–copper eutectic foil obtained from Lucas Milhaupt has a melting temperature of 780 °C. The source and composition of the materials used to analyze the reaction kinetics and microstructural development have been summarized in Table 1. The strength of the AlN brazed joint has been tested using four-point bend test. Table 2 summarizes the source and shape of the aluminum nitride samples used for mechanical testing.

Table 1 Composition and sources of experimental materials for reaction

Materials	Composition (Vendor specification)	Source
Aluminum nitride (Commercial grade)	AlN with Y_2O_3, Al_2O_3 and SiO_2 as additives	St. Gobain
Titanium powder (325mesh)	99+%	Johnson Matthey Company
Ag–Cu foils (2.54×10^{-5} m)	71.46 Ag–28.51 Cu with 0.03% other (wt%)	Lucas Milhaupt

Table 2 Source and shape of the samples used for mechanical strength test

Source	ART, Buffalo, NY	Vactronics, Flushing, NY
Shape	Rectangular	Cylindrical
Dimension (mm)	Length = 20	Diameter = 12
	Width = 10	Length = 20
	Thickness = 10	
Thermal conductivity (W/m K)	170	140

The aluminum nitride substrates were polished on a series of silicon carbide papers of grit sizes (#120 down to #600) and diamond pastes (6 μm down to 1 μm) in order to achieve a smooth surface free of absorbed materials such as water vapor, dust and oxide surface film. The polished aluminum nitride substrates were cleaned in ethanol using ultrasonic vibration for approximately 1,200 s followed by a rapid drying using hot air. A given weight of high purity titanium powder was wrapped in a pre-weighed silver–copper eutectic foil and the metal sample was then placed on the polished and cleaned surface of an aluminum nitride substrate. The approximate weight of the metal foil placed on the aluminum nitride surface was 1–1.5 g. The samples were then placed in the heating chamber of an electric vacuum furnace from Thermal Technology Inc. Porous titanium sponge material were placed around the sample in the heating chamber in ceramic crucibles as an oxygen “getter”. The furnace had graphite heating elements, inert gas operational capabilities and programmable controller. An initial vacuum of less than 1×10^{-5} torr was obtained using mechanical and diffusion pump. The samples were initially heated in vacuum to 400 °C in order to out gas any residual moisture. The remainder of the thermal cycle was performed under ultra high purity argon (99.99%) under an over pressure of 7.2 kPa followed by furnace cooling under the same argon overpressure.

The samples thus prepared were then cross-sectioned. Cross-sections of the metal/ceramic interface were then mounted in bakelite and polished using silicon carbide papers of grit sizes (#120 down to #600) and diamond pastes (6 and 1 μm particle size). The samples were then sputter coated with a conductive layer of gold–palladium alloy. The polished and coated cross-sections were subsequently examined using a scanning electron microscope/Electron Dispersive Spectroscopy (SEM/EDS) to characterize the microstructure and microchemistry of the interfacial region.

The test variables used for the determination of the reaction kinetics of aluminum nitride and silver copper titanium diffusion couples are isothermal temperature, hold time and composition. In the current study, titanium additions have been varied in the range of 2–8 wt%. Aluminum nitride and eutectic silver–copper (nominal composition: 72Ag–28Cu wt%) diffusion couples containing 2%, 5% and 8% titanium by weight were heated at four different isothermal temperatures of 900, 950, 1,000 and 1,050 °C for five different hold times. A hold time of 0 s was performed at each temperature in order to account for the reactions that occur during the heat-up and cool-down cycle. The test matrix used to prepare the diffusion couples is summarized in Table 3. Additional details on the experimental procedure are available elsewhere [8].

The samples for the four-point bend test were prepared using two aluminum nitride bars. The bars were polished using silicon carbide papers of grit sizes (#120 down to #600) and diamond paste (6–1 μm particle size). The samples were then cleaned using ethanol in an ultrasonic vibrator for nearly 20 min and dried in hot air. A silver–copper eutectic foil with a thickness 2.54×10^{-5} m with a circular shape of diameter 12 mm was attached to cylindrical monolithic aluminum nitride bars of length 20 mm using an adhesive, Superglue^{TM}. The AlN bar was then placed in an upright position with the face bearing the silver–copper eutectic foil facing upwards. A pre-weight amount of high purity titanium powder was then spread on top of the eutectic silver–copper foil. Another cylindrical monolithic AlN bar of length 20 mm having Ag–Cu eutectic foil pasted on one side of it was then positioned on the former AlN bar holding the titanium powder as shown in Fig. 2. The total thickness of the silver–copper eutectic foil used was 5.08×10^{-5} m (5.08×10^{-2} mm). A graphite fixture containing the samples was then placed in the heating chamber of the vacuum furnace and was heated to a desired temperature and hold time under argon over pressure of 7.2 kPa. The test matrix for the mechanical test samples is presented in Table 4. The brazed samples were then cut and rough surface ground using silicon carbide grit papers. Using an optical microscope, it was confirmed that the polished samples were free of surface micro-cracks. The final samples had a length of 40 mm, a width 3–5 mm and a thickness 3–5 mm. The joint strength of the samples was then measured using a four-point bend test fixture in an Instron 8482 mechanical testing machine with a ramp rate of 0.5 mm/min and a load cell of 5 kN. The fixture used had an inner-span of 20 mm and an outer-span of 40 mm.

Table 3 Test matrix for the study of reaction kinetics of aluminum nitride and silver–copper–titanium diffusion couples

Hold time (s)	Isothermal holding temperature (°C)			
	900	950	1,000	1,050
0[a]	2,5,8	2,5,8	2,5,8	2,5,8
1,800	2,5,8	2,5,8	2,5,8	2,5,8
3,600	2,5,8	2,5,8	2,5,8	2,5,8
7,200	2,5,8	2,5,8	2,5,8	2,5,8
14,400	2,5,8	2,5,8	2,5,8	2,5,8

[a] Heat up and cool-down cycle only without any isothermal hold

2, 5, 8 = 2%, 5% and 8% titanium by weight (added to 72Ag–28Cu eutectic alloy)

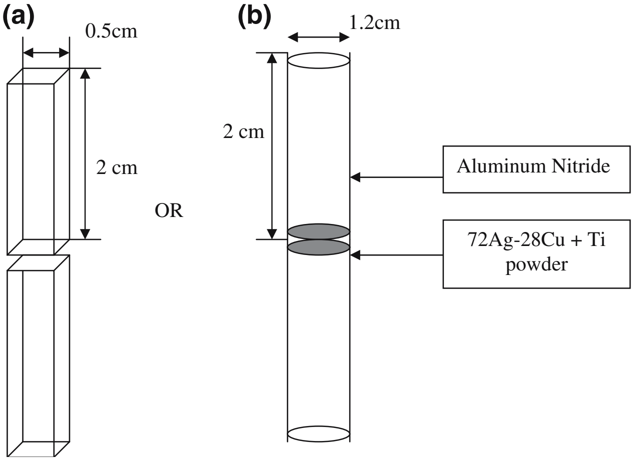

Fig. 2 The set-up of the square and cylindrical AlN samples has been demonstrate in **a** and **b**, respectively, in the graphite fixture before being placed into the heating chamber of the vacuum furnace. Titanium powder was placed in between the silver copper eutectic foil and the braze alloy was placed in between the two aluminum nitride test bars

Results and discussion

The results have been divided into three major sections: microstructural analysis, thickening kinetics and mechanical property evaluation.

Table 4 Test matrix used to prepare the samples in order to analyze the mechanical strength of the brazed joints

Temperature (°C)	Hold time (s)				
	0	1,800	2,700	3,600	5,400
1,000	C-2 C-5	C-2 A-5	C-2 C-5	C-2 A-5	C-2 C-5

2 = silver copper eutectic containing 2% Ti by weight

5 = silver copper eutectic containing 5% Ti by weight

A = sample source is ART, Buffalo, NY

C = sample source is Vactronics, Flushing, NY

Microstructural analysis

In this study, several typical microstructures have been compiled in Figs. 3 and 4 in order to explain the different stages of growth and thickening of the interface of AlN/72Ag–28Cu foils containing 2 wt% titanium reaction couples that have been heated at 900 and 1,000 °C for different hold times. The microstructures obtained on heating the samples for different hold times at a temperature of 900 °C have been compiled in Fig. 3. With the increase in the hold time, a change in the interface thickness can be observed in the microstructures presented in Fig. 3. Figure 4 summarizes typical microstructures of the AlN/eutectic silver–copper braze alloy containing Ti reaction couples heated at 1,000 °C for different hold times. Comparing Figs. 3 and 4, it can be observed that the interface growth and thickening kinetics obey similar trends at both low and high temperatures. When heated for 0 s at 900 or 1,000 °C (heat-up and cool-down cycle only), the interface between the aluminum nitride and eutectic silver–copper containing titanium is very thin and discontinuous. Upon increasing the hold time, the thickness of the interface increases and gradually becomes continuous covering the entire surface of aluminum nitride. The EDS analysis performed using the SEM indicates that the interface is rich in titanium. Based on the literature review, it can be concluded that the reaction product formed at the interface is titanium nitride (TiN) [6, 9, 10].

Discontinuous to continuous reaction product layer transition

The SEM has been used to analyze the microstructures of the samples obtained under various temperatures and hold times. For all temperatures, a transition from a discontinuous to continuous reaction product layer was observed.

Several microstructures (Figs. 5–12) have been compiled in order to support the different stages of growth and thickening of the interface. In Fig. 5, the most preliminary stage of interface thickening is presented. The reaction couple was prepared at 900 °C with a hold time of 0 s (heat-up and cool-down only). The interface is very thin and discontinuous. The average thickness of the interface was less than 0.3 μm.

As the reaction time and temperature increases, blocks of TiN nucleate and grow at the aluminum nitride/liquid metal interface (as shown in Fig. 6). Since the interface is discontinuous, and liquid diffusion is significantly faster than solid-state diffusion, the growth of the interface continues due to the reaction between the solid aluminum nitride and the liquid metal.

The change in microstructure from discontinuous to continuous reaction product layer correlates with a

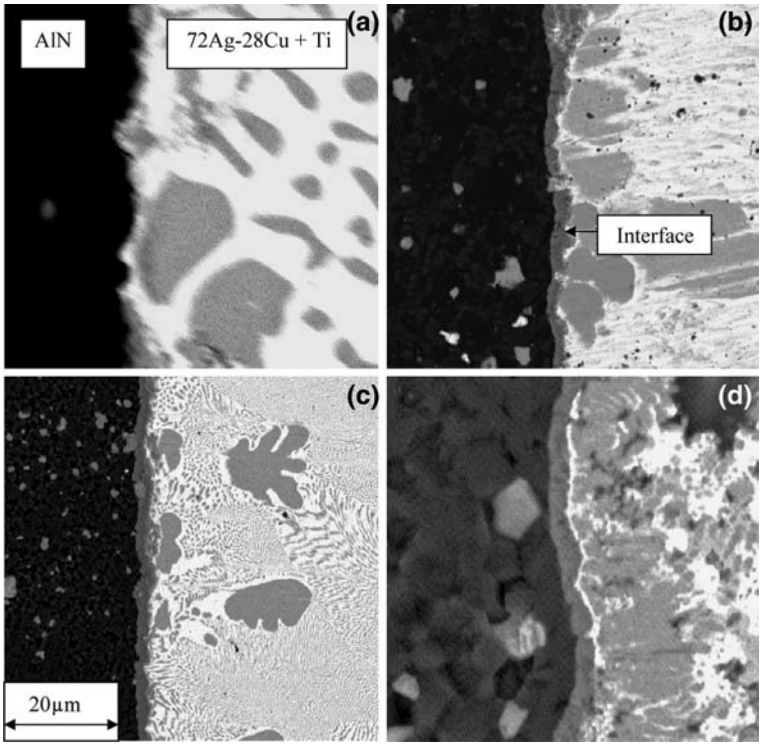

Fig. 3 Typical microstructures for AlN/72Ag–28Cu alloy containing 2 wt% Ti reaction couple heated at 900 °C for a hold times of (**a**) 0 s, (**b**) 3,600 s (**c**) 7,200 s, and (**d**) 14,400 s (~1,000×)

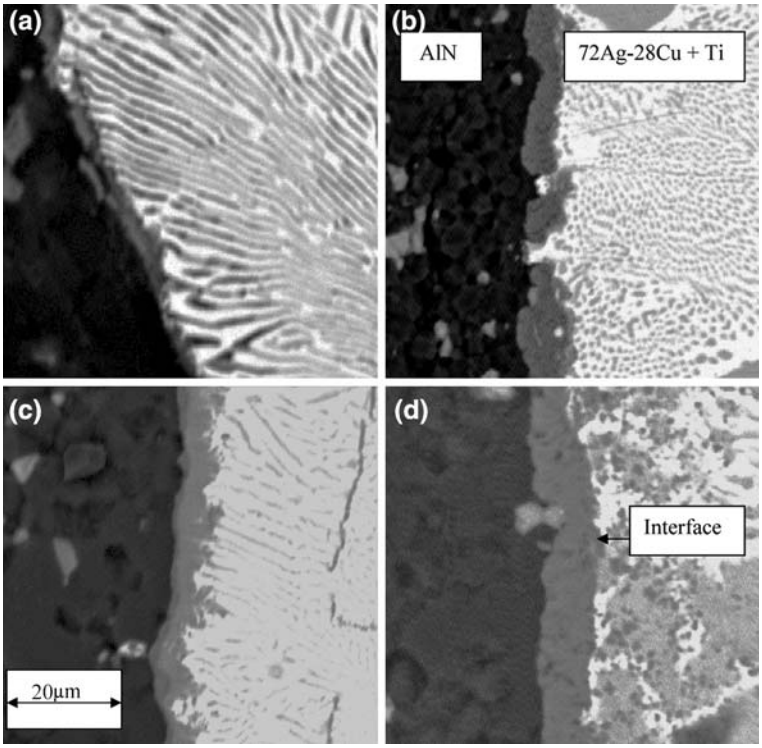

Fig. 4 Typical microstructures for AlN/72Ag–28Cu alloy containing 2 wt% Ti reaction couple heated at 1,000 °C for a hold times of (**a**) 0 s (**b**) 3,600 s (**c**) 7,200 s and (**d**) 14,400 s (~1,000×)

transition from a linear to a non-linear thickening mechanism. This will be discussed in detail in the thickening kinetics section (see Section Thickening kinetics).

As shown in Fig. 7, with further increases in the temperature or hold time, the titanium nitride interface increases in thickness and also grows linearly, covering larger regions of the aluminum nitride surface. With even further increases in temperature or hold time, the titanium nitride interface becomes continuous as shown in Fig. 8. The microstructure has a continuous but non-uniform interfacial reaction product layer which indicates that the system obeys a non-ideal thickening kinetics. The sample is said to follow a non-ideal thickening kinetics because the sample did not exhibit linear thickening behavior as predicted by classical linear thickening mechanism and the sample did not exhibit parabolic thickening mechanism as

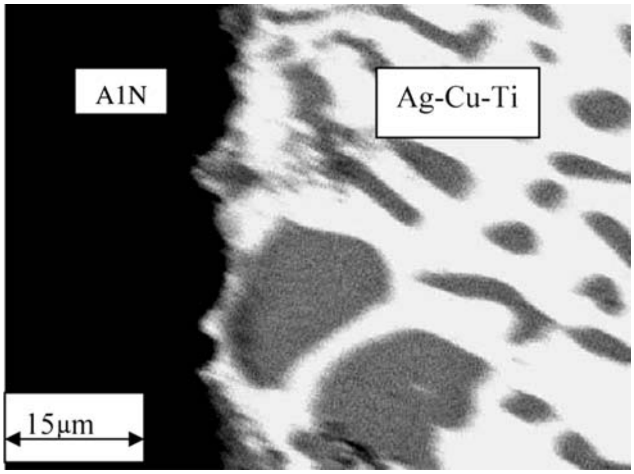

Fig. 5 Microstructure of the Ag–Cu eutectic with 8 wt% Ti addition/AlN reaction couple heated to 900 °C for a hold time of 0 s. The interface is thin (<0.3 μm) and discontinuous (~1,000×)

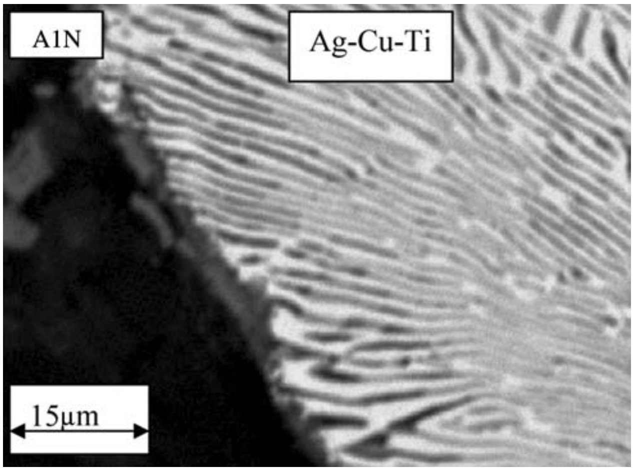

Fig. 6 Microstructure of the Ag–Cu eutectic with 8 wt% Ti addition/AlN reaction couple heated to 1,000 °C for a hold time of 0 s. The interface is thin (0.62 μm) and discontinuous (~1,000×)

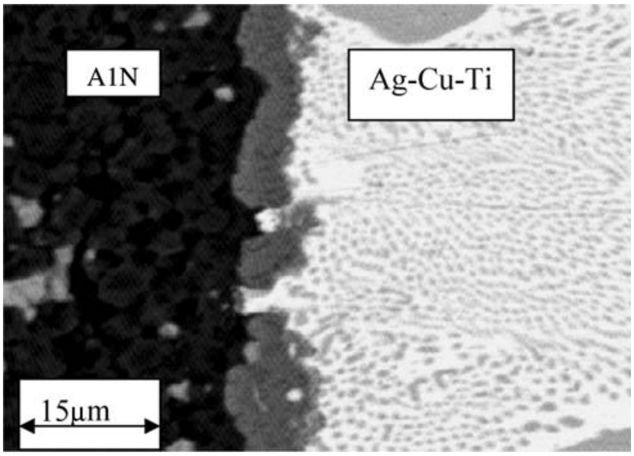

Fig. 7 Microstructure of the Ag–Cu eutectic with 2 wt% Ti addition/AlN reaction couple heated to 1,000 °C for a hold time of 3,600 s. The interface is thin (1.47 μm) and discontinuous (~1,000×)

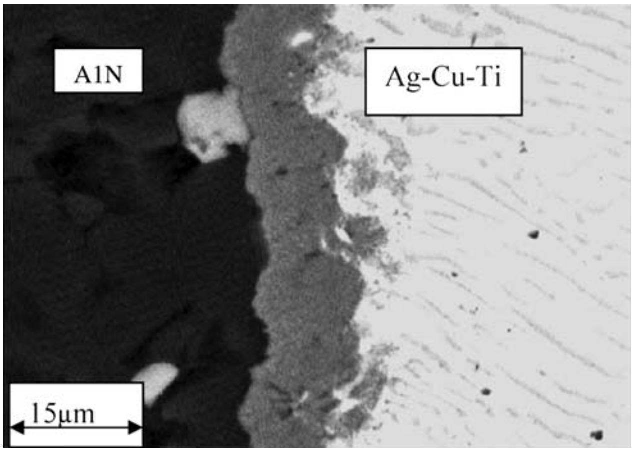

Fig. 9 Microstructure of the Ag–Cu eutectic with 5 wt% titanium additions/AlN reaction couple heated to 1,050 °C for a hold time of 7,200 s. The interface is continuous (~1,000×)

predicted by the classical interface controlled mechanism. At longer hold times, the interface thickens and remains continuous as shown in Fig. 9.

Formation of the reaction product is expected via a reaction between the solid aluminum nitride and liquid metal containing the reactive element, Ti [11]. Figure 10 presents a typical microstructure of a sample having a thick but porous interface. The system is expected to follow an interface-controlled mechanism because if the interface is porous, it is not continuous.

Thickening kinetics

The reaction couples of eutectic copper–silver alloys (72Ag–28Cu) containing 2, 5 and 8 wt% Ti/AlN have been heated at five different temperatures and hold times. The interfacial product layer thicknesses of the samples were measured and the interfacial product layer has been plotted as a function of hold time in Figs. 11–15 in order to determine if the data exhibit a linear thickening behavior.

In Fig. 11, the samples heated at 900 °C exhibit a linear thickening rate until a hold time of 3,600 s (60 min). Beyond an isothermal hold time of 3,600 s, a deviation from the linear mechanism is observed for each of the three groups of samples containing 2%, 5% and 8% titanium, respectively. Observing Figs. 11 and 12, it can be concluded that the three groups of samples obey similar thickening kinetics mechanisms between 900 °C and 950 °C.

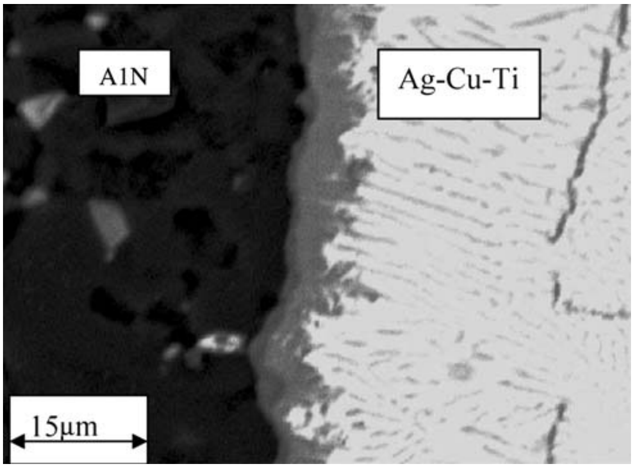

Fig. 8 Microstructure of the Ag–Cu eutectic with 5 wt% titanium addition/AlN reaction couple heated to 1,000 °C for a hold time of 7,200 s. The interface is thicker (2.4 μm), continuous and non-uniform (~1,000×)

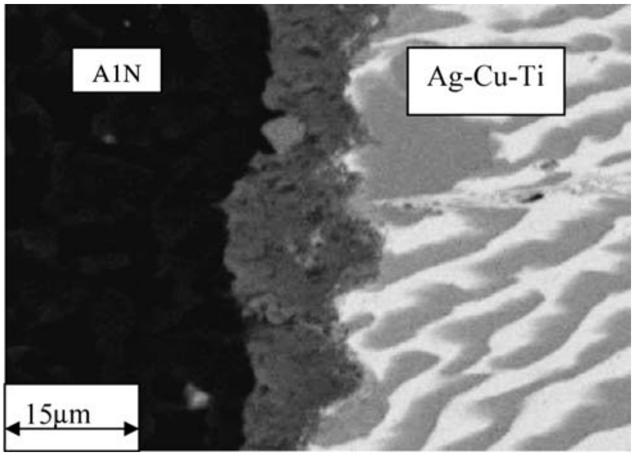

Fig. 10 Microstructure of the Ag–Cu eutectic with 5 wt% titanium additions/AlN reaction couple heated to 1,050 °C for a hold time of 14,400 s. The interface is thick (5 μm) and porous (~1,000×)

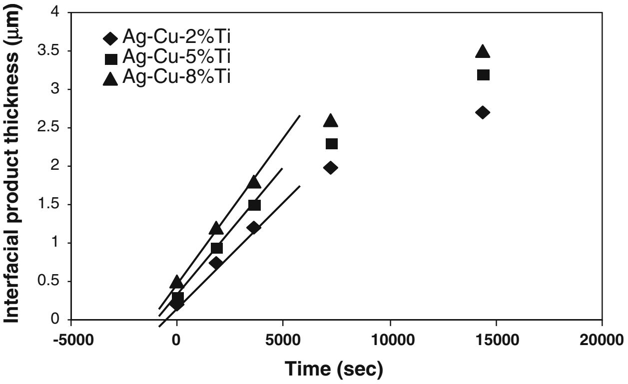

Fig. 11 Interfacial product layer thickness as a function of holding time at 900 °C for AlN in contact with 72Ag–28Cu eutectic liquid alloy with 2–8% titanium additions (wt%)

In Fig. 13, the interface thickness of the 2%, 5% and 8% Ti samples heated at 1,000 °C has been plotted as a function of five different hold times. The samples containing 2% and 5% Ti by weight show a similar trend as observed in Figs. 11 and 12. A deviation from the linear mechanism is apparent beyond a hold time of 3,600 s. However, the group of samples containing 8% Ti by weight shows a deviation from the linear behavior beyond a hold time of 7,200 s.

In Fig. 14, the thickening kinetics of the 2%, 5% and 8% Ti samples heated at 1,050 °C has been analyzed. The samples containing 2% Ti by weight, exhibit a similar trend relative to the 1,000 °C samples. A shift from the linear mechanism is observed beyond a hold time of 3,600 s. However, the samples containing 5% and 8% Ti by weight shows a deviation from the linear behavior beyond a hold time of 7,200 s.

The thickness values are an average of 10–15 random measurements along the cross-section of the sample. For discontinuous and continuous layers, the raw data of the interface measurements and standard deviations have been compiled elsewhere [8]. It has been observed that under certain conditions, typically at lower temperature and shorter hold times, the interfacial product formation proceeds at a constant rate and the mechanism is said to obey a “linear rate law”. At lower temperatures and hold time, the rate-determining step is the reaction between the reducing species (Ti) and the AlN surface. During this stage, the system follows an interface-controlled mechanism.

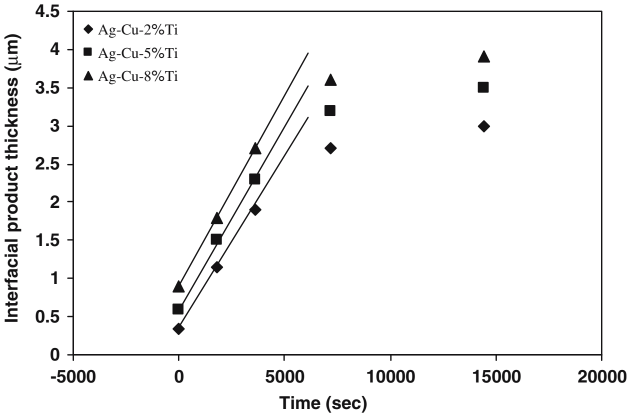

Fig. 12 Interfacial product layer thickness as a function of holding time at 950 °C for AlN in contact with 72Ag–28Cu eutectic liquid alloy with 2–8% titanium additions (wt%)

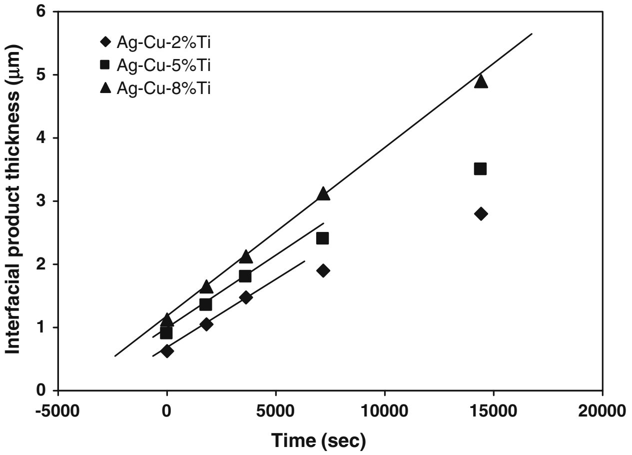

Fig. 13 Interfacial product layer thickness as a function of holding time at 1,000 °C for AlN in contact with 72Ag–28Cu eutectic liquid alloy with 2–8% titanium additions (wt%)

The data in the current study, however, suggest a possible two-step thickening mechanism. At the longer hold times, the data exhibit a deviation from the linear behavior. The second mechanism is a non-linear thickening behavior, possibly a parabolic rate law or mixed reaction kinetics.

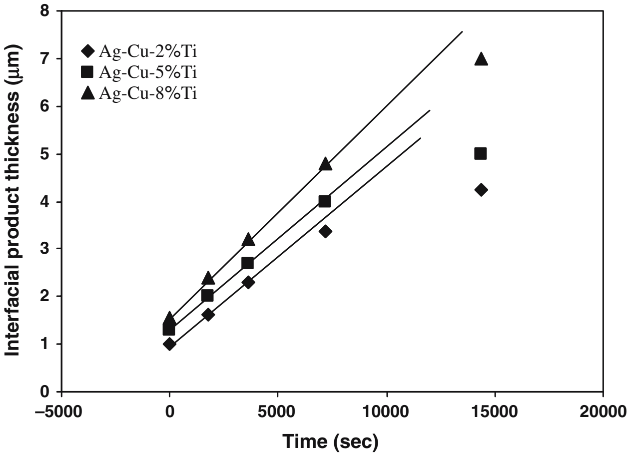

Fig. 14 Interfacial product layer thickness as a function of holding time at 1,050 °C for AlN in contact with 72Ag–28Cu eutectic liquid alloy with 2–8% titanium additions (wt%)

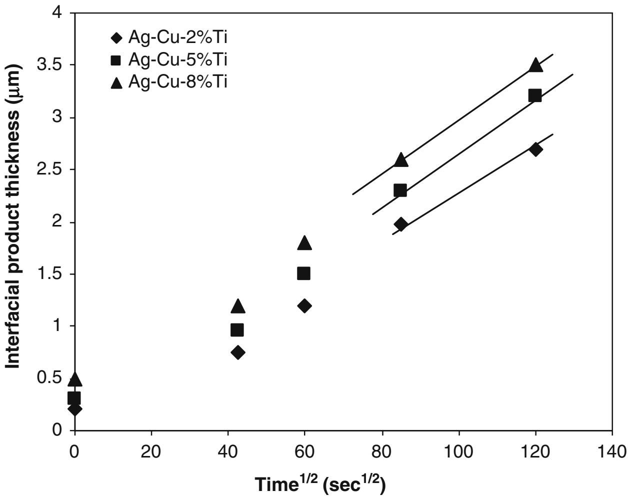

Fig. 15 Interfacial product layer thickness as a function of square root of holding time at 900 °C for AlN in contact with 72Ag–28Cu eutectic liquid alloy with Ti additions (wt%)

In Figs. 15–18, the interfacial product layer thickness of the samples heated at 900, 950, 1,000, and 1,050 °C, respectively containing 2%, 5%, and 8%Ti by weight has been plotted as a function of square root of time ($t^{1/2}$) in order to determine if the data follows a parabolic thickening behavior. When the interface is continuous and has a low porosity, the reaction rate is hypothesized to decrease progressively because of the gradual thickening of the product layer [5]. Reaction between the liquid metal and the solid interface is no longer feasible and diffusion through the interface becomes the dominant mechanism. The system then becomes solid-state diffusion controlled kinetics mechanism. A parabolic fit has been assumed since the data is no longer linear and a solid-state diffusion controlled mechanism would typically follow an interface-controlled mechanism.

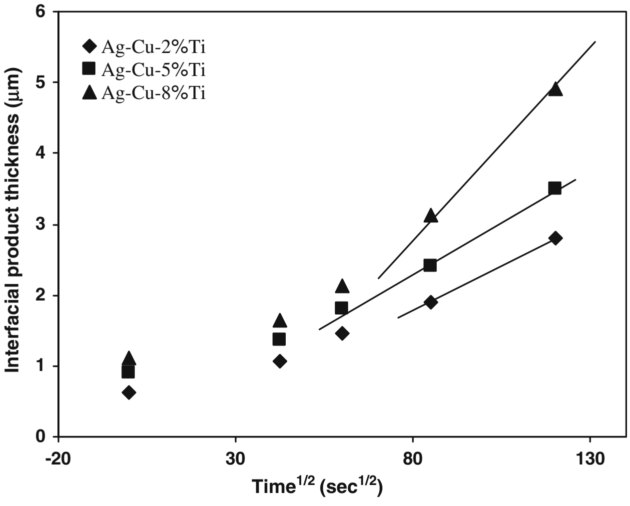

Fig. 16 Interfacial product layer thickness as a function of square root of holding time at 950 °C for AlN in contact with 72Ag–28Cu eutectic liquid alloy with Ti additions (wt%)

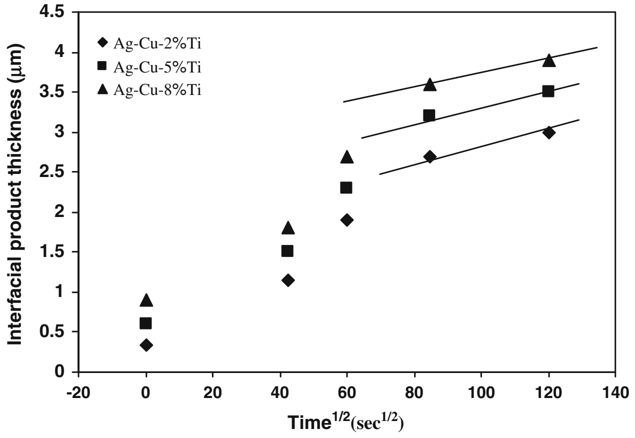

Fig. 17 Interfacial product layer thickness as a function of square root of holding time at 1,000 °C for AlN in contact with 72Ag–28Cu eutectic liquid alloy with Ti additions (wt %)

Thus, the interfacial thickening kinetics is observed to follow a linear rate law at the shorter holding times where as the data at the longer holding times exhibit a non-linear thickening behavior, possibly a mixed reaction kinetics or a parabolic rate law type behavior. However, for most Ti compositions conditions, only two data points are available in the non-linear range. Therefore, there are insufficient data to prove or disprove a parabolic fit. Hence, the second mechanism might be another non-linear mechanism or mixed reaction kinetics as well. However, based upon the

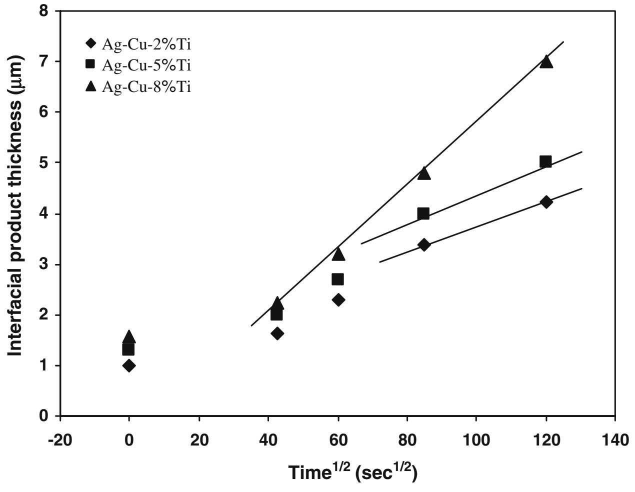

Fig. 18 Interfacial product layer thickness as a function of square root of holding time at 1,050 °C for AlN in contact with 72Ag–28Cu eutectic liquid alloy with Ti additions (wt %)

results of the previous studies on similar systems, the second mechanism has been approximated as parabolic [6, 12, 13]. At longer hold times, the proposed rate-determining step is the solid-state diffusion of the reacting species (Al, Ti and N) through the interfacial product layer. Thus, the general hypothesis is that at relatively short hold times, the kinetics follows a linear rate law while at longer times the kinetics are consistent with a parabolic rate law.

A similar change from a linear to a parabolic thickening mechanism has been observed for the Al/SiC system by J.C. Viala and a possible theoretical explanation for the observed change in mechanism has been proposed [14]. In this project, a similar explanation for the formation of reaction product and a change in the reaction mechanism from linear to parabolic thickening mechanism is proposed for the liquid metal and aluminum nitride reaction couples.

In the early stage of the reaction process, TiN crystals begin to nucleate and grow at the AlN/Ti interface, probably at the AlN surface flaws. As a result of the nucleation and growth process, the nitrogen concentration decreases at the vicinity of the TiN and hence a concentration gradient is established that provides a driving force for the further migration of nitrogen to regions where TiN product precipitates grow. Aluminum diffuses in the copper rich phase in the metal. During this stage of the reaction, the TiN crystals extend linearly, protecting larger and larger areas of AlN surface. This results in the development of AlN crystal with pyramidal shapes separated by dissolution valleys that become deeper and deeper beneath the TiN crystals. The dissolution and precipitation process continues until a continuous layer of the TiN covers the whole surface of the AlN substrate. Once this stage is reached, the growth of the interface continues only by the solid-state diffusion of atoms through the TiN reaction product. The stages of the growth of the interface are graphically explained by a schematic representation in Fig. 19.

The simplest reaction that is consistent with the above analysis is:

$$\mathrm{Ti} + \mathrm{AlN} = \mathrm{TiN} + \mathrm{Al} \tag{3}$$

Loehman reports the above reaction as thermodynamically favorable at 1,200 K with ΔG_{R} = –37 kJ (–8.8 kcal) [9]. The titanium nitride precipitates at the interface. The aluminum metal formed were not observed as a separate product layer or an intermetalic layer (e.g. Ag_3Al) but was observed to be dissolved in solution in the copper-rich phase in the metallic region of the microstructure. This is consistent with the gradual decrease in the activity of the Al and N, and a gradual increase in the Ti activity moving from the AlN across interface and into the braze alloy.

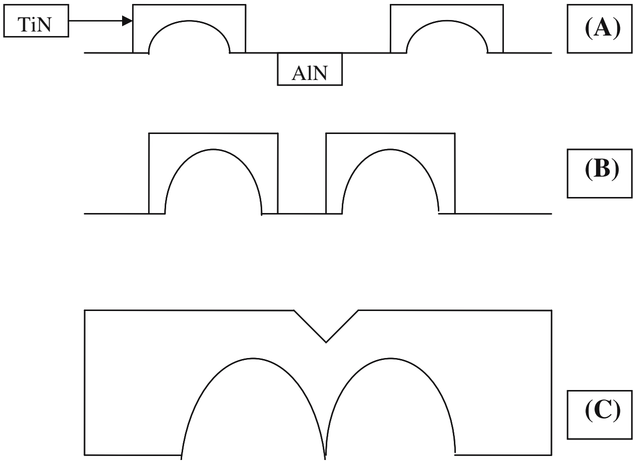

Fig. 19 Schematic description of the three successive stages of growth of TiN at the AlN/72Ag–28Cu–Ti interface

The above result is consistent with the findings of Kuzumaki et al. [6]. The results of their study showed that when Ag–26.6Cu–5Ti (wt%) was brazed to AlN at 850–950 °C for various times (90–1,800 s), the reaction product was identified as TiN and no aluminum was observed as a separate product layer [6].

Loehman and Tomsia have observed that $TiN_{0.7}$ formed at the interface when brazing AlN using 8.6Ti–55.1Ag–36.3Cu (at%) and 1.9Ti–59.1Ag–39.4Cu (at%) alloys at 1,000 °C and 1,100 °C for 30 min in an argon atmosphere [10]. The thickness of the reaction product ($TiN_{0.7}$) under the given test condition has been reported as 25 μm. They observed that in the braze alloy away from the ceramic/metal interface, the alloy exhibits the Ag–Cu eutectic structure with no Ti; essentially all the Ti has segregated to the interface. TEM studies have proved the presence of a η-nitride phase i.e. $(Ti, Al, Cu)_6$ N between the Ag–Cu eutectic and the $TiN_{0.7}$ product layer. However, the layer was very thin and was below the spatial resolution of the SEM used for this study and therefore was not observed in this study [10].

Based on the current analysis and the literature review, the interface is expected to be a titanium rich product, probably TiN. As the reaction progresses, with the increase in hold time and temperature, the interface becomes continuous. After the interface is continuous, the thickening of the interface continues through the diffusion of the reaction elements. It is expected that Al diffuses out of AlN through the interface (TiN) and is present in the copper rich phase of the melt. The dark phase which is rich in copper and the bright phase which is rich in silver are rather uniformly distributed through out the microstructure. This result is in agreement with the findings of Kuzumaki et al. [6]. The direction of diffusion of Ti and N depends on the direction of growth of the interface. If the growth of the interface occurs towards the AlN substrate, diffusion of Ti is the dominant mechanism for the interface growth. However, if the interface grows in the direction of the liquid metal, diffusion of nitrogen dominates the growth of the interface. The interface can actually grow in either directions or in both the directions simultaneously. In the present study the direction of growth of the interface has not been ascertained. However, based on the information gathered from the literature, Loehman proposes that AlN is actually consumed by reaction with Ti that diffuses through the TiN product layer [9]. Hence, it is assumed that after the interface becomes continuous, growth of the interface occurs more towards the aluminum nitride substrate surface, dominated by the diffusion of the reducing species (Ti) through the TiN interface and consuming more AlN with increasing time. A solid state, non-linear diffusion controlled thickening behavior has also been observed by Kuzumaki et al. for an Ag–26.6Cu–5Ti/AlN heated at 850, 900, and 950 °C [6]. When indium or cobalt were added to the braze alloy containing silver–copper and titanium, the system exhibited the same non-linear thickening behavior.

Chemical and phase analysis

The microstructure of eutectic silver–copper Ti/AlN diffusion couple containing 8 wt% Ti heated at 1,050 °C for 7,200 s is presented in Fig. 20. The different phases present in the sample have been resolved using a semi-quantitative analysis by SEM/EDS for each part of the different phases present in order to quantify the possible reactions that occurred between the aluminum nitride substrate and the eutectic silver–copper–titanium diffusion couple at this brazing temperature and hold time. Table 5 summarizes the results of the semi-quantitative and EDS analysis performed at the different phases present in the microstructure.

No cracking was observed within any of the phases including the reaction product phase and the AlN. There was also no cracking between any of the interfaces including the AlN/reaction product interface. The lack of cracking indicates that the ductility of the residual alloy on cooling is sufficient to accommodate the thermal expansion mismatch stresses developed between the ceramic, the interfacial reaction products, and the metal, during cooling. This suggests that excellent adherence of the metallized layer to AlN has been obtained.

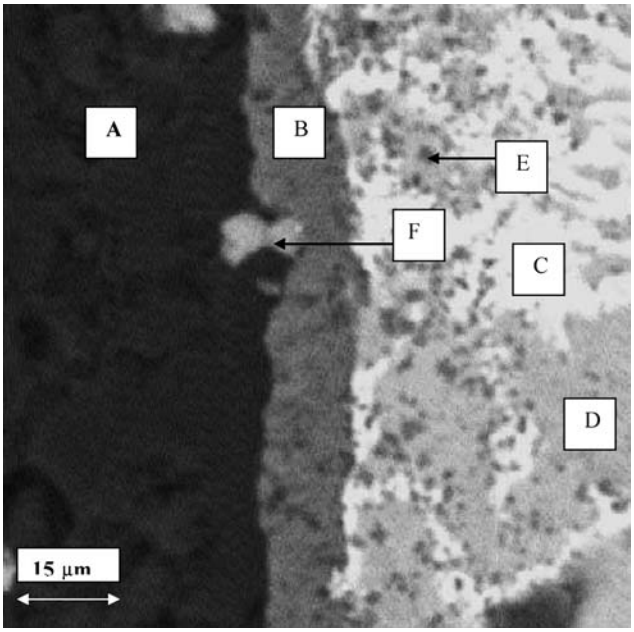

Fig. 20 Microstructure of the 72Ag–28Cu filler alloy containing 8 wt% Ti and AlN reaction couple heated at 1,050 °C for a hold time of 7,200 s. The interface is thick, continuous and uniform (~1,000×). **A**–**F** represent regions where point scans were performed. Semi-quantitative analysis was also performed in regions **B**–**D**

Mechanical properties of AlN/Ag–Cu–Ti brazed joints

In the present study, the mechanical strength of AlN/AlN brazed joint using eutectic Ag–Cu braze alloy with 2 and 5 wt% Ti added, has been analyzed using the four-point bend test in an universal testing machine

Table 5 Chemical identification in the microstructure of the sample presented in Fig. 20

Semi-quantitative analysis					EDS point scans
Phase	Cu (wt%)	Ag (wt%)	Ti (wt%)	Al (wt%)	Comments
A					Al rich phase
B	4	5	90	0.5	Ti rich phase
C	8	91	0.06	0.5	Rich in Ag (also contains Cu)
D	94	1	0.00	4	Cu rich
E					Ti rich
F					Y, Ca and Mg

A, B, C, D, E, F are the various phases identified in Fig. 20

(Instron 8482). Table 6 reports the monolithic strength of AlN materials A and C procured from ART and Vactronics, respectively [7].

In Fig. 21, the effect of hold time on the bond strength of aluminum nitride bonded at 1,000 °C using eutectic silver–copper filler alloy containing 2 and 5 wt% Ti are plotted together for comparison. The AlN joint prepared using 2 wt% Ti, heated at 1,000 °C for a hold time of 2,700 s has the highest bond strength of 196 MPa. As the hold time increases, the bond strength decreases. The mechanical properties of the bonded zone generally decrease by the thickening of the reaction layer. The reaction layer is brittle and as the thickness of the reaction layer increases, it becomes more difficult to accommodate thermal stresses generated by CTE mismatch.

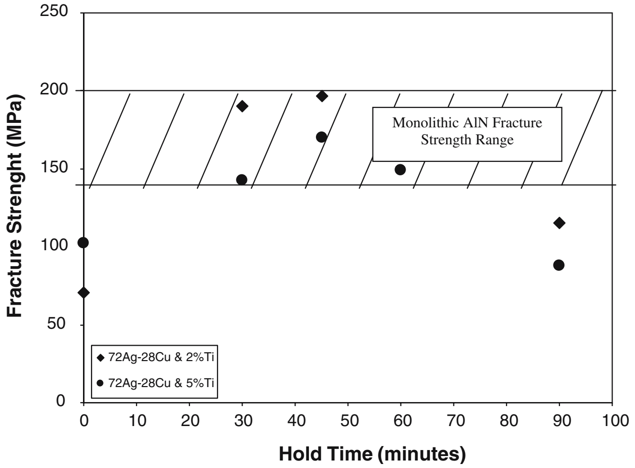

Fig. 21 The effect of hold time on the bond strength of aluminum nitride using 72Ag–28Cu alloy with 2 wt% Ti additions and 72Ag–28Cu–5 wt% Ti, respectively, as a filler alloy at 1,000 °C. Each data point is the average value for two samples

The results obtained are in agreement with the results reported by Huh et al. for the AlN/Cu system using an indium based filler metal [10]. Their results indicated that the highest strength interfacial can be obtained without forming a continuous reaction layer at the joint interface [15].

However, it has been reported by El-Sayed et al. that the strength of the interface increases continuously with the increase in the interface thickness for AlN/V system. A maximum bond strength of approximately 105 MPa was obtained at a interfacial product layer thickness of 12 μm [16].

Imanka et al. reported that when Ag–Cu–Ti braze alloy was used to bond AlN, a maximum bonding strength of 19 kg/mm^2 (186 MPa) was obtained by bonding at 880 °C for 360 s. TiN was detected at the interface between AlN and the braze alloy via XRD. After performing an SEM analysis of the interface, it was concluded that the high bonding strength was due to the anchor mechanism i.e. the mechanical bonding between TiN and the braze alloy was the dominant joining mechanism [12]. A similar explanation has been cited by Carim and Loehman [17] regarding the AlN/V system.

Based on the results obtained in the present study, the AlN/eutectic silver–copper containing 2 wt% titanium reaction couples processed at 1,000 °C for a hold time of 2,700 s (45 min) had the highest bond strength (196 MPa). At these processing conditions, the reaction product formation follows a linear thickening kinetics. It should be noted that the sample exhibits the highest bond strength while the interface is discontinuous. The bond strength decreases as the interface becomes continuous because of the thickening of the interfacial reaction product. The gain in strength due to the formation of a continuous product layer is offset by a greater loss in strength due to thickening of the product layer.

Table 6 Fracture strength for monolithic AlN samples tested in a four-point bend test configuration (from Colpetzer et al. [7])

Material	Fracture strength (MPa)
ART (Material A)	230 ± 59
Vactronics (C)	186 ± 37

Conclusions

The microstructure, reaction kinetics, and mechanical properties were evaluated for AlN/Ag–Cu–Ti interfaces. The processing ranges studied were 0–14 ks, 900–1,050 °C and a Ag–Cu eutectic alloys with 2–8 wt% Ti additions. For the AlN/Ag–Cu–Ti reaction couples:

1. Only a single product layer was observed (Ti-rich phase).
2. Aluminum nitride/Ag–Cu–Ti reaction couples followed a two-step reaction product thickening mechanism in the temperature range of 900–1,050 °C varying the titanium addition from 2 wt% to 8 wt%.
3. For shorter times (typically time < 3,600 s), the thickening kinetics follow a linear rate law. At longer times a shift from the linear mechanism is evident. The second mechanism may be a mixed reaction kinetics or a parabolic rate law.
4. A transition from a discontinuous to a continuous reaction product layer is observed in the transition times where the linear to non-linear thickening

kinetics mechanism transition was observed. This supports the proposed two-step mechanism.

5. The maximum bond strength of the AlN/Ag–Cu–Ti joint was 196 MPa for a 2 wt% Ti addition joined at 1,000 °C for 2.7 ks (45 min). The maximum bond strength was obtained when the interface was still discontinuous and hence the reaction product formation was still in the linear thickening kinetics regime.

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