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Influence of oxygen on the joining between copper and aluminium nitride

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Abstract

Aluminium nitride has been developed for electronic ceramic packaging applications because of its high thermal conductivity and high electrical resistivity. To improve the heat dissipation at the metal/ceramic interface, a high quality bonding between the substrate and the copper conductor is needed. This process requires a previous step of AlN pre-oxidation of the substrates by oxygen gas at 1200 °C, in order to form a thin layer of Al_2O_3 at the surface of AlN. The junction between Cu and the substrate is carried out at 1075 °C in controlled oxygen atmosphere which promote the oxidation of the copper and the formation of an eutectic phase which can form a strong junction with AlN via the layer of Al_2O_3. The goal of the current work is to study the influence of oxygen supplied by gaseous phase to form the exact amount of the eutectic phase needed to get a strong junction. First, in order to fix conditions for joining, the wetting behaviour of copper has been studied using the sessile drop method. The influence of oxygen brought by surrounding gas is given in terms of wettability of the liquid, interfacial tension and chemical reactions. According to previous results, copper foils and copper cylinders have been directly joined to AIN substrates. Interfacial reactions, mechanical and thermal properties have been investigated.

Keywords: Joining; Thermal conductivity; AlN; Substrate; Copper; Cu

1. Introduction

Due to its high thermal conductivity (200 W m^{-1} K^{-1}), AlN is an attractive material, in all applications requiring strong currents or strong density of electric or electronic components. For such applications, the formation of an eutectic phase at the interface is the standard technology to carry out a connection between a metal and a ceramic.[1–5] The method was initially developed to bind copper to alumina but cannot be applied directly to aluminium nitride and a pre-processing of AIN surface is necessary for an effective connection. Currently, this one is carried out by surface oxidation of the substrate AlN to form a thin layer of Al_2O_3. In that condition, the contact with copper is then related to the oxidized surface.[3–5] Many studies showed that it was necessary to have a thickness of alumina ranging between 2 and 5 μm to ensure a good connection. In the side of copper the principle of our method is to form a liquid film around copper by using the eutectic Cu–O to ensure a good wettability of the copper on the substrate. The Cu–O phase diagram indicates that the melting point of copper decreases with the quantity of oxygen of the eutectic (1065 °C). The in situ oxidation of copper by oxygen gas at low pressure promotes a good connection between pre-oxidised AlN and Cu. After this oxidation, we have tried to remove by reduction the excess of copper oxide at the interface.

2. Materials

2.1. Raw materials AlN and copper

Aluminium nitride used was sintered in a traditional way[6] with 3% mass in yttrium oxide, formatted of 2.5 mm × 2.5 mm × 0.63 mm parallelepipeds, polished (Ra = 0.15 ± 0.03 μm) and cleaned with ultra-sonic assistance by acetone. They were oxidised with 1200 °C during 12 h under dynamic oxygen current until obtaining a uniform layer of 4 μm of alumina. OFHC copper was machined in the form of cylinder (5 mm in diameter and 6 mm high) cleaned in the nitric acid, acetone then dried.

2.1.1. Experimental procedure

The wettability tests are carried out at 1100 °C in a molybdenum resistor furnace according to the sessile drop method.[7]

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After having obtained a secondary vacuum of 10^{-3} Pa, the reactor is filled up of a mixture of argon and oxygen.

2.1.2. Carrying out of the assemblies

To carry out assemblies, we used OFHC copper, samples have the same size than the substrate and are 250 μm thick.

2.1.3. Measurement of the thermal properties

The "laser flash-light" method was used on a sample of 4 mm thick and with a diameter of 8 mm. The nitride face is lighted by a 450 ms flash-light of 30 J. The heat flow is collected on the opposed copper face using a photovoltaic detector HgCdTe which follow the rise at temperature as a function of the time. The thermal transfer of the assembly and the thermal resistance of the interface is then computed.

3. Study of the wettability

3.1. Experimental conditions

The study has been carried out by the sessile drop method out at 1100 °C in a molybdenum resistor furnace[7] under partial pressures of oxygen ranging 0–22 Pa (0–216 ppm) of O_2. The stud of copper introduced in the furnace is put on the AlN substrate.

On-line liquid drop image acquisition was carried out by a camera CCD i2SC c 800 attached to a computer, a software developed at laboratory permitted to measure the drop contour, its contact angle with the substrate and its surface tension. This measurement system presents a high precision with an experimental error less than ±0.5° on contact angle and less than 2% on the value of σ_{LV} on work of adhesion.The mixture of gas ($Ar + O_2$) is introduced into the furnace at the ambient temperature after having carried out a secondary vacuum (10^{-3} Pa) during 15 min. The oxygen partial pressure is varied between 0 and 22 Pa. For instance, under vacuum oxygen partial pressure is 5×10^{-10} Pa at 1100 °C. Then, the heating rate is controlled with 10 °C/min from ambient to 1000 °C, and 5 °C/min to 1100 °C.

Copper thus oxidise in situ during the rise in temperature in accordance with thermodynamic calculations to form CuO and Cu_2O when the partial pressures of oxygen are higher than 0.8 Pa. The decrease of the partial pressure of oxygen in the flow between the entry and the exit of the furnace[8] indicates a beginning of reaction of oxidation starting from 300 °C. The consumption of oxygen increases until 1100 °C, and the copper oxide formed, controlled by X rays analysis is Cu_2O.

3.2. Contact angle

The contact angles (Fig. 1) are measured at 1100 °C according to the pressure partial of oxygen.

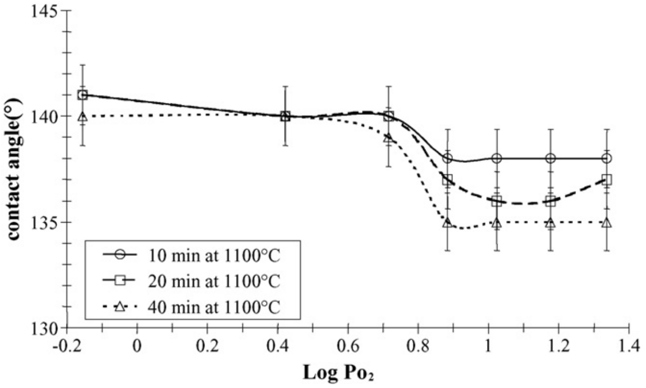

Fig. 1. Contact angle evolution of the system Cu/Al_2O_3-AlN at 1100 °C with oxygen partial pressures between 0.7 and 22 Pa.

- For the partial pressure of oxygen lower than 5 Pa (that is to say log $P_{O_2} = 0.7$), the contact angle remain nearly constant: 140° after 20 min, 139° after 40 min. These values are very close to that of pure copper: 141 ± 2°.
- For partial pressures of oxygen between 5 and 7.5 Pa (that is to say log P_{O_2} between 0.7 and 0.9), the contact angle decreases continuously with the time: 138° after 10 min, 137° after 20 min and of 135° after 40 min.
- For the higher values above 22 Pa of the oxygen partial pressures, the angles stabilize at 138°, 137° and 135° after 10, 20 and 40 min, respectively.

Many authors have studied the influence of oxygen on the wettability of copper on substrates of alumina[8–10] for large fields of oxygen partial pressures values. The contact angles measured by these authors are weaker than those mentioned above due to the fact that we use AlN substrates oxidized in contrary to the authors who use dense sintered $A1_2O_3$ substrates. In spite of this difference, the evolution of the contact angles with the increase of the quantity of oxygen are similar but the comparisons are difficult taking into account the lack of information on the operating conditions reported in these studies.

3.3. Surface tension

The calculation of the liquid–vapour surface tension (σ_{LV}) was carried out in relation with the pressure partial of oxygen (Fig. 2). The value of this parameter is not affected by the

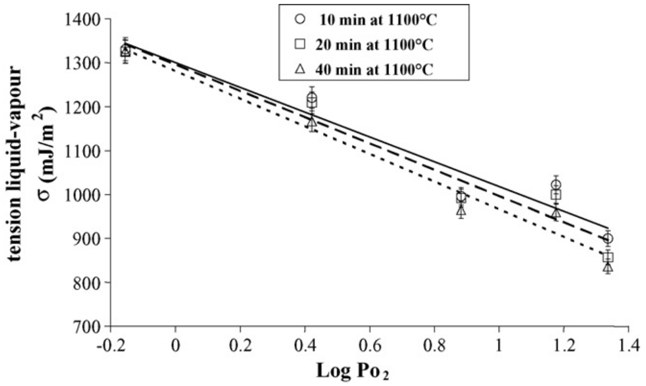

Fig. 2. Liquid–vapour surface tension evolution at 1100 °C for oxygen partial pressures between 0.7 and 22 Pa.

Table 1
Surface tensions of copper on alumina substrates at 1100 °C

Surface tension of copper on AlN oxidized surface (MJ m^{-2})	Values from the literature sintered Al_2O_3 (mJ m^{-2})
1331 ± 27	1290 ± 20, Chatain and coworkers[8] 1290 ± 20, Leroux et al.[7] 1368, Mehrotra and Chaklader[11] 1360, Ownby and Liu[10]

substrate, and for the lowest partial pressure of oxygen are in conformity with other experimental studies (Table 1).

The liquid–vapour surface tension strongly decreases with the pressure partial of oxygen but also with the dwell time at 1100 °C. This behaviour is usually observed in the literature.[8–11]

By using in the Young–Dupre equation $\sigma_{SL} = \sigma_{SV} - \sigma_{LV} \cos\theta$, the value of σ_{SL} given by RHEE[12] and the value of σ_{LV} computed above, we can calculate σ_{SV} as 0.76 N m^{-1} at 1100 °C.

The evolution of the solid–liquid surface tension versus the increasing of the partial pressure of oxygen is linear (Fig. 3). This is similar with the evolution of the liquid–vapour surface tension. Our results are thus in conformity with those of the literature.[7–11]

3.4. Characterisation of the interfaces

We can then determine the relative adsorption of oxygen to the interfaces liquid–vapour and solid–liquid by using the adsorption equation of Gibbs–Langmuir,[12,13] considering that oxygen was the only active specie in the mixture in fusion. Adsorption of oxygen at the liquid–vapour and solid–liquid interfaces is then calculated versus times at 1100 °C (Fig. 4). It constantly increases with the time of maintenance.

Oxygen adsorption at the solid–liquid interface (between 1.5×10^{-5} and 2.2×10^{-5} mol m^{-2}) remains always lower than that with the liquid interface vapour (between 1.8×10^{-5} and 2.4×10^{-5} mol m^{-2}). In Fig. 3, we can follow the evolution of the solid–liquid surface tension at 1100 °C versus oxygen partial pressure between 0.7 and 22 Pa.

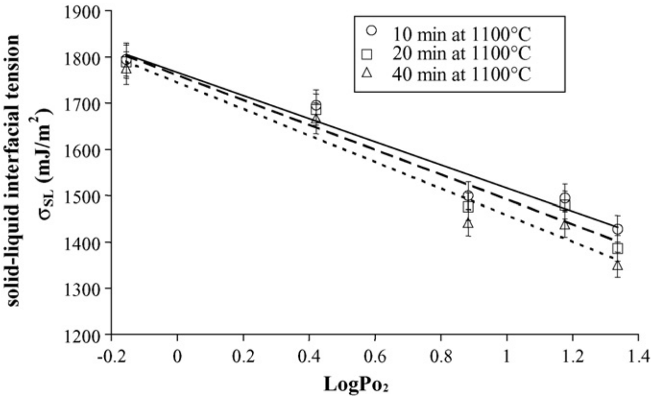

Fig. 3. Solid–liquid surface tension at 1100 °C for oxygen partial pressure between 0.7 and 22 Pa.

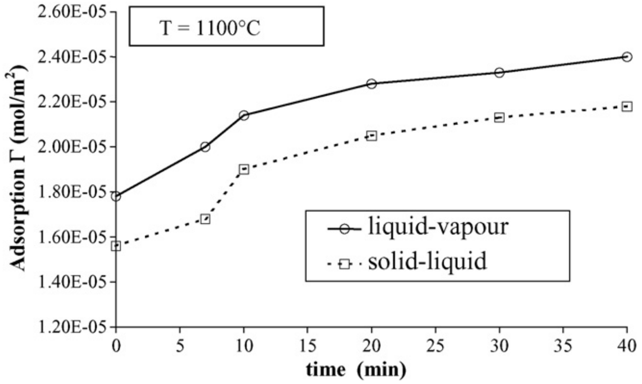

Fig. 4. Adsorption evolution at interfaces liquid–vapour and solid–liquid with the time at 1100 °C.

Diemer et al.[9] and Ownby and Liu[10] found adsorptions interfacial solid–liquid of 3.5×10^{-6} and 7.6×10^{-6} mol m^{-2}, respectively. For adsorption on the liquid–vapour surface, the values are included between 4.8×10^{-6} [12] and 1.4×10^{-5} mol m^{-2} [13].

Compared with the literature, our values are raised, but in our study, the gas containing oxygen is introduced before the beginning of the rise in temperature, which authorizes a surface oxidation of copper during heating and causes a modification of the properties of adsorption. The studies referred in the literature do not provide any indication on the introduction of gas and the experimental parameters, and the comparisons cannot be established in a precise way.

4. Method for realization of the Cu/AlN assemblies

To prepare the assemblies, the ceramic substrate AlN is oxidized (3 μm of alumina) and a Cu stud is put at its surface, the oxygen is given by gas ($Ar + O_2$). The system undergoes a thermal cycle with 3 min at 1072 °C. The speed of cooling is controlled with 5 °C/min until 1000 °C then 10 °C/min until ambient one. Fig. 5 shows the aspects of the stud at 1072 °C under 2.5 Pa oxygen pressure.

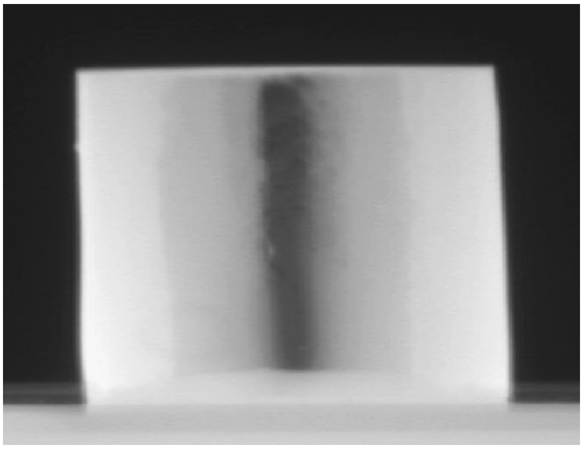

Fig. 5. Surface evolution: aspect of the stud at 1072 °C with $P_{O_2} = 2.5$ Pa.

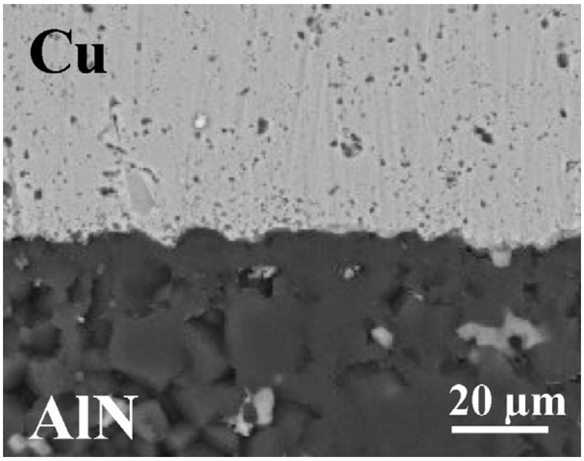

Fig. 6. Microstructure of the interface Cu/AlN after joining (3 min, 1072 °C, $P_{O_2} = 2.5$ Pa).

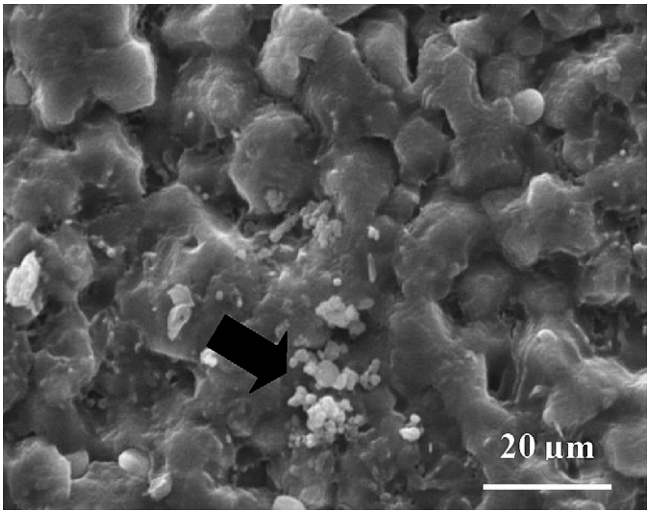

Fig. 8. Microstructure of the surface of AlN after breaking of the bond and attack by HNO_3. the arrow shows the small grains of $CuAlO_2$.

For a partial pressure of oxygen of 2.5 Pa, the interface is continuous and free from defects (Fig. 6). At the interface (Fig. 7) the oxygen can be detected on around 13 µm thickness, which increases slightly when the partial pressure of oxygen increases. The quantity of liquid phase increases with the time and can involve a light deformation besides. The zone rich in oxygen in parallel tends to widen, which results in the appearance of copper oxide precipitates.

These thin crystallizes on the copper/AlN interface after heating are given in Fig. 8 after copper dissolution by HNO_3. EDAX analysis confirms the presence of elements Cu, Al and O, but taking into account the precision of this type of analysis, it is difficult to bring complementary precise details on the composition of the interface.

These observations justify the use of short time of reaction (3 min) to minimize the quantity of oxygen at the interface. At 1072 °C and a time contact of 3 min it was never possible to detect any crystallized compound. In a logical way, EDAX analysis only reveals the elements Cu, Al and O.

The work of Kara-Slimane and Ali,[14] shows that in the following conditions: $P_{O_2} = 0.65$ Pa, $T = 1000$ °C, time = 30 min to 2 h, physical pressure applied = 30 MPA, the $CuAlO_2$ phase can be formed and has been detected at the interface. But our conditions are quiet different: $P_{O_2} = 2.5$ Pa, $T = 1072$ °C, time = 3 min, no physical pressure applied, and we only observe the small crystallizes shown in Fig. 8. We think that this phase could be assimilated at the phase $CuAlO_2$, but we have never proved it, probably due to its too much small quantity.

5. Mechanical properties of the assemblies

The assemblies carried out under the conditions defined above are characterized in mechanical term of behaviour of the connection. The experimental device (Fig. 9) used makes it possible to measure the breaking stress by exerting traction directly on the copper stud. For all the assemblies, the rupture intervenes in ceramics and the observation of the facieses by electronic scan microscopy shows that the zones of fractures are either at interface AlN/$A1_2O_3$ or with the Cu/Cu_2O interface (Fig. 10).

In many cases, a fine layer of aluminium nitride remains adherent at the base of the stud whereas a wrenching is noted in ceramics. This type of fracture suggests a correct connection, higher than 27 MPa. The mechanical resistance of the Cu/AlN assemblies is limited by the self resistance of the aluminium nitride.

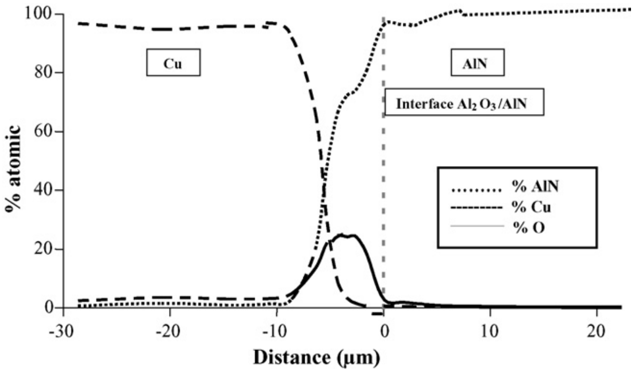

Fig. 7. EDAX analysis of the interface Cu/AlN. Elements repartition at the interface for the assembly at $P_{O_2} = 2.5$ Pa.

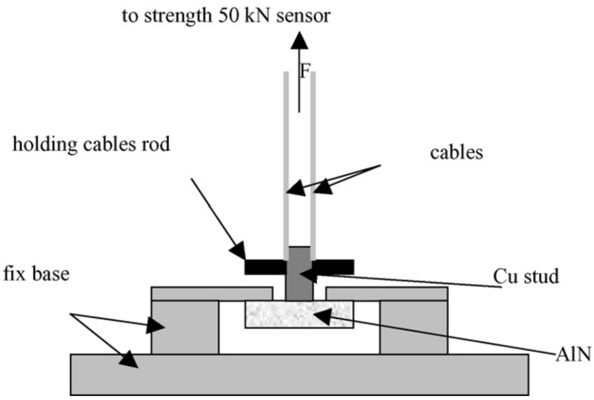

Fig. 9. Experimental device to measure the breaking stress.

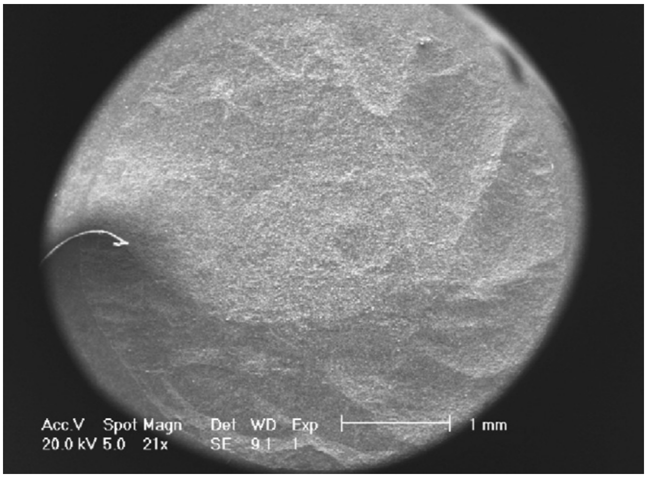

Fig. 10. Cohesive breaking of the joining Cu/AlN in the ceramic, surface of AlN after breaking joined on the copper stud.

6. Thermal properties of the assemblies

The improvement of the thermal transfer at the interface of these assemblies being the first goal of this work. The method to determine their thermal performance is based on the numerical resolution of the equation which describes the thermal transfer in the assembly.[15–17] The comparison between the experimental and calculated answers, shows a variation being explained by the existence of a thermal resistance of contact (TCR) between the two layers. By this method, the value of the TCR is (1.6 ± 0.5) $10^{-6}\,\mathrm{m^2\,W^{-1}\,K^{-1}}$.

Clear improvement in the thermal performances is thus obtained since the TCR commercial DBC assemblies that we measured, lie between 3×10^{-6} and $7 \times 10^{-6}\,\mathrm{m^2\,W^{-1}\,K^{-1}}$.

7. Conclusion

The formation of a direct connection between the copper and aluminium nitride with a thin layer of Al_2O_3 was carried out by forming at the eutectic phase Cu_2O at the interface Cu/Al_2O_3-AlN. This phase is formed by controlled oxidation in situ of copper and AlN at the time of the realization of the contact. The liquid phase formed is proportional to the pressure partial of oxygen in the processing atmosphere must be present in sufficient quantity to ensure a total covering, without being however in excess. This goal is reached perfectly with a pressure partial of oxygen of 2.5 Pa for the copper studs, and must be brought back to 1.6 Pa for sheets. The connection obtained is very strong since the rupture intervenes in ceramics.

Under the conditions thus defined, oxygen is distributed to the interface on a thickness of approximately 13 μm, composed of the layer of initial alumina and layer of copper oxide ensuring the connection. This minimal quantity of oxygen to the interface is a priori favourable to the transfer of heat between copper and ceramics. No interfacial compound is observed with the interface on an analysis scale used and in particular because of the low pressure partial of oxygen used, the mixed phase $CuAlO_2$ is never visible contrary to the case of the connection carried out by oxide contribution.

Under these conditions, the thermal resistance of contact is around $1.6 \times 10^{-6}\,\mathrm{m^2\,W^{-1}\,K^{-1}}$, values largely lower than those obtained with currently available traditional assemblies.

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