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Comparison between two processes using oxygen in the Cu/AlN bonding

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Abstract

The modern electronics industry uses, at the present time, increasingly high intensities of current which produce large quantities of heat which can be dissipated by using a ceramic substrate, having a high thermal conductivity associated with a high electrical resistivity. Aluminium nitride with a good electrical resistivity and thermal conductivity (between 170 and 220 W m^{-1} K^{-1}) closed to copper, can fulfil this role on condition that its interface with the metal, generally copper, allows an acceptable thermal conduction.

On ordinary conditions, it is not possible to get a direct good junction between Cu and AlN. An eutectic phase is necessary to ensure both thermal continuity and good mechanical resistance. This eutectic phase can be seen on the thermodynamic copper-oxygen phase diagram, and is easily formed at 1065 °C. In all cases, oxygen is brought to the interface by copper oxide Cu_2O and by alumina systematically formed by oxidation at the surface of AlN.

Two processes have been investigated:

- the layer of Cu_2O is formed by oxidation of Cu by oxygen before the contact;
- the copper oxide is formed in situ at the interface during contact.

These processes require the control of the contact parameters of copper on aluminium nitride: thickness of Cu_2O formed, partial pressure of oxygen, temperature, contact time, are important parameters of the both processes.

Good connections between copper and ceramic have been obtained by these methods. The analysis of the interfaces by electron microscope, highlight in all cases the role of residual oxygen. Ceramic metal adherence, has been evaluated by mechanical tests and the heat transfer through the interface, has been measured by the flash-laser technique.

The results lead to values of thermal resistance of contact (1.7×10^{-6} m^2 W^{-1} K^{-1}) largely improved compared to commercial assemblies by direct bonding copper (7×10^{-6} m^2 W^{-1} K^{-1}).

Keywords: Aluminium nitride; Thermal conductivity; Substrate; Copper; Joining

1. Introduction

Due to its high thermal conductivity (200 W m^{-1} K^{-1}), AlN is an attractive material, in all applications requiring high currents or high density of electric or electronic components. For such applications, the method of connection through an eutectic phase is the standard technique to carry out a connection between a metal and a ceramic.[1–3] The method was initially developed to join copper to alumina but cannot be applied directly to aluminium nitride. A pre-processing of AlN 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.[3,4] Many studies showed that it was necessary to have a thickness of alumina ranging between 2 and 5 μm to get a good connection. 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 AlN with a thin layer of Al_2O_3. The Cu-O phase diagram indicates that the melting point of copper decreases with the quantity of oxygen of the eutectic (1065 °C). There are two possibilities to form a joining:

- the copper is previously oxidized, to form variable thickness of oxide, then it is put on the oxidized substrate AlN.
- the copper is oxidized in situ by oxygen gas at low pressure to promote a good connection between pre-oxidized AlN and Cu. The copper oxide layer thickness is measured by weight dif-

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ference between the cylinder copper sample and the oxidized sample, considering that the cylinder is perfect. This thickness is controlled by direct measurements and image analysis of SEM photographies. After this oxidation, the excess of copper oxide is removed from the interface by reduction.

2. Starting materials

2.1. Experimental process

2.1.1. Raw materials AlN and copper

Aluminium nitride used was sintered in a traditional way[5] with 3% in yttrium oxide mass, formatted of 25 mm × 25 mm × 0.63 mm parallelepipeds, polished ($Ra = 0.15 \pm 0.3$ μm) and cleaned with acetone. They were oxidized at 1200 °C during 12 h under dynamic oxygen current until obtaining a uniform layer of 4 μm of alumina.

Oxygen Free High Copper (OFHC) copper was machined in the form of cylinders 5 mm in diameter and 6 mm high. They were cleaned by nitric acid, and acetone, then dried.

When the formation of an oxide layer is required, they were heated at 1200 °C to obtain oxide coatings Cu_2O (thickness between 0.2 and 70 μm).

2.1.2. Experimental procedure

The wettability tests were carried out at 1100 °C in a molybdenum resistor furnace according to the sessile drop method.[6] After having obtained a secondary vacuum of 5×10^{-3} Pa, the reactor is filled up of dry argon then maintained at the atmospheric pressure during all the thermal cycle. Partial oxygen pressure is 5×10^{-10} Pa at 1100 °C. The analysis of the images makes it possible to compute the contact angle, the surface tension liquid–vapour and the work of adhesion.

2.1.3. Carrying out of the assemblies

To carry out assemblies, OFHC copper was machined in the form of cylinder 5 mm in diameter and 6 mm of high, and in some experiments in the form of a sheet of 250 μm thick and of the size of the substrate (25 mm × 25 mm).

2.1.4. Measurement of the thermal properties

The "laser flash-light" method is used on a sample of 40 mm thick and 8 mm diameter. The nitride face is lighted by a flash-light of 30 J during 450 ms. The heat flow through the materials is collected on the opposed copper face and detected by a photovoltaic detector HgCdTe which follows the rise at temperature according to the time. Calculations gives "the apparent thermal diffusivity" and the heating flow of the assembly,[7,8] and to go up with the thermal resistance of the interface.

3. Study of wettability

3.1. Copper oxidation before contact with AlN

The stud of the oxidized copper was put on the oxidized AlN substrate and installed in the furnace. The oxygen necessary

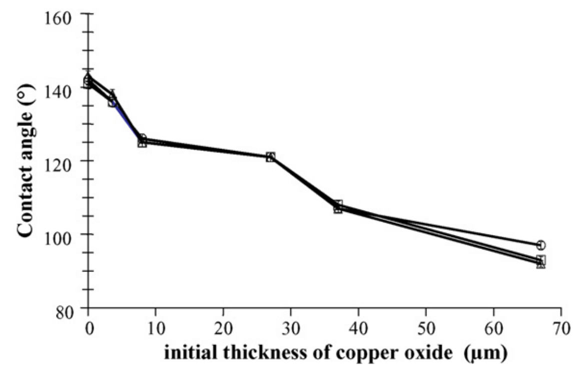

Fig. 1. Evolution of the contact angle with thickness of the copper oxide.

for the connection is provided by the copper oxide formed primary on the surface of the studs during the preliminary oxidation in air. The maximum temperature of the molybdenum resistor furnace is 1100 °C and under our operating conditions, thermodynamics tables indicates the Al_2O_3 stability. Oxygen pressure in the furnace is very low and its control is not possible, during the experiments (10, 20, 40 min at 1100 °C), the quantity of oxygen can be only checked while varying the thickness of the oxide Cu_2O introduced. With a thickness ranging between 0 and 70 μm, the contact angle strongly decreases (Fig. 1). Thus, it passes from 142° for the copper not oxidized to 92° for a thickness of 67 μm of Cu_2O.

This system Cu–Cu_2O/Al_2O_3–AlN passes therefore from one non-wetting state to an almost-wetting state when the oxygen level of the contact area is increased. In the explored interval, between 0 and 70 μm one notes than during the thermal cycle the comportment of the interface depend strongly of the thickness of the Cu_2O layer.

- between 1 and 7 μm, during the thermal treatment a part of Cu_2O is reduced and disappeared. The copper is not linked to the substrate, and the thickness of the Cu_2O layer has been increase.
- between 8 and 40 μm, the results are satisfactory: adherence is good, the layer between copper and AlN is continuous and free from bubbles. To decrease its thickness to the minimum, we chose to work with an 8 μm thickness.
- beyond 40 μm the fusion of the drop is very difficult, and the connection is not established correctly. A thick oxide coating Cu_2O remains at the interface after cooling and some nodules of Cu_2O were formed in the vicinity of the interface.

The microscopic observation of the interfaces shows that oxygen is located in a deep of 8 μm whereas the thickness of the layer of initial alumina deposited on the substrate is 4 μm, and that of copper oxide is 8 μm (Fig. 2).

3.2. Oxidation in situ of copper

The stud of pure copper is put on the oxidized AlN substrate and placed in the furnace. The study has been carried out by the sessile drop method out at 1100 °C in a molybdenum resistor furnace[6] under partial pressures of oxygen ranging 0–22 Pa

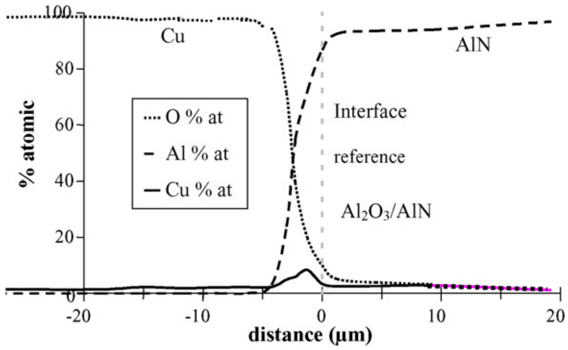

Fig. 2. Composition of the interface between copper and aluminium nitride for an oxidation of 8 μm.

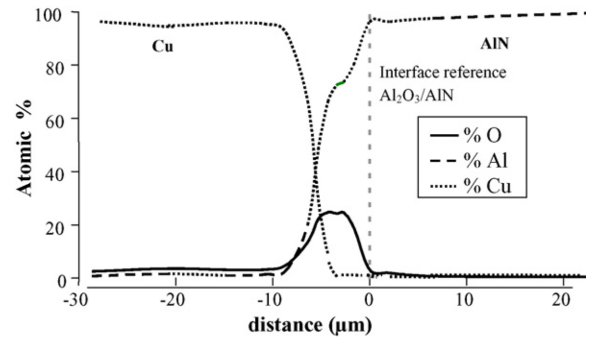

Fig. 4. Repartition of the Cu, Al, O elements at the interface ($P_{O_2} = 2.5$ Pa).

(0–216 ppm) of O_2. 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 50 Pa. For instance, oxygen partial pressure is 5×10^{-10} Pa at 1100 °C. The analysis of the images of the drop during melting makes possible the determination of the contact angle, the liquid vapour surface tension and the work of adhesion.

Copper thus oxidized in situ during the rise in temperature in accordance 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 between the entry and the exit of the furnace[9] 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.

The contact angles measured at 1100 °C versus the pressure partial of oxygen are given at the Fig. 3 and show that:

- 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 7.5 Pa of the oxygen partial pressures, the angles stabilize at 138°, 137° and 135° after 10, 20 and 40 min, respectively.

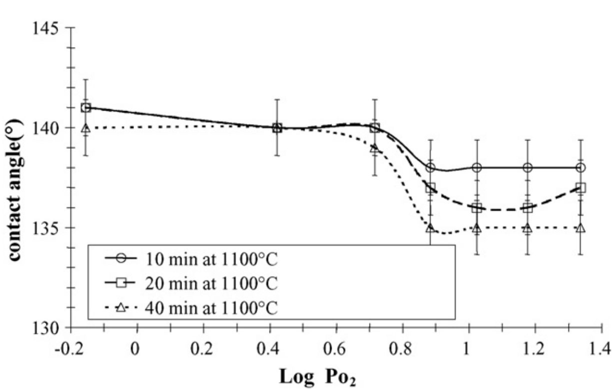

Fig. 3. Contact angle evolution of the system Cu/AlN at 1100 °C in presence of oxygen. Partial pressures between 0.7 and 22 Pa and with different treatment times.

The contact angles measured by different authors[10–14] 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 Al_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.

The microscopic observation of the interfaces shows that oxygen is located in a section of 12 μm thickness whereas the thickness of the layer of initial alumina deposited on the substrate is 4 μm, and that of copper oxide of 8 μm (Fig. 4).

4. Method for realization of the Cu/AlN assemblies

4.1. Process for realization of the Cu/AlN assemblies with copper oxidation before the contact

The assemblies are prepared by the method DBC in which the ceramic substrate is wet by the eutectic phase Cu-O in order to ensure the connection during cooling, oxygen being brought by oxide covering copper and with the participation of a layer of alumina. The connection phase is then the oxidized phase which exhibits a low thermal conductivity. By the way it is necessary to minimize its thickness to reach a minimal thermal resistance. In fact the solution will be a compromise, between a sufficient thickness of the oxide layer to have a good adherence, and a very small thickness to avoid a big thermal resistance.

The first tests were carried out with copper studs oxidized on the surface under the conditions described previously. The stud put on the pre-oxidized aluminium nitride substrate undergoes a thermal cycle with 3 min at the temperature of 1072 °C (between the temperature of formation of the eutectic 1065 °C and the melting point of copper 1085 °C). The speed of cooling is controlled with 5 °C/min until 1000 °C, then with 10 °C/min until the ambient temperature. Thus, for a 8 μm thickness, the stud is completely covered with eutectic liquid (Fig. 5), whereas

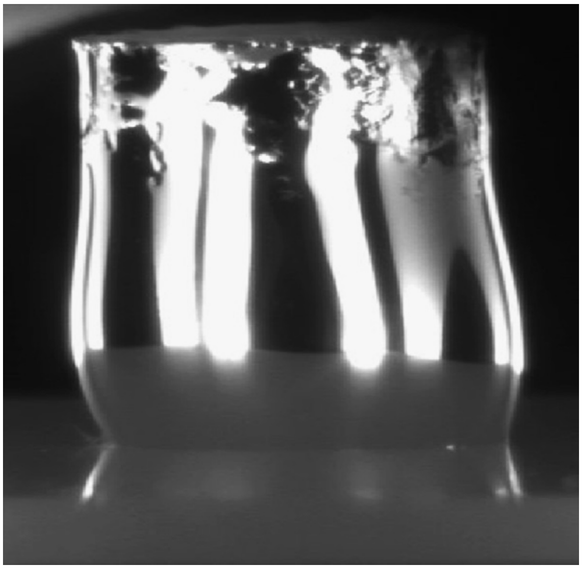

Fig. 5. Surface evolution after 3 min at 1070 °C, Cu_2O thickness of 8 μm.

for lower thickness 4.1 and 7 μm, only some very localised zones are covered with liquid. For the very great thickness of initial oxide, the fusion of the drop is difficult, the connection cannot be done. The stud covered with 8 μm Cu_2O is the only one to adhere to the substrate. The eutectic quantity of phase is then just sufficient to allow the connection.

A second series of tests related to the assembly of an aluminium nitride substrate oxidized with a copper sheet 250 μm thickness. We have determined that the thickness of copper oxide was to be 1.7 μm. Weaker, it does not allow higher adherence, and deforms the copper sheet. The cross section of the assembly then presents a continuous interface without defect. The distribution of elements Al and O observed by EDS at the interface (Fig. 6) shows that oxygen is located in a 8 μm thickness layer. Analyses XRD make it possible to identify $CuAlO_2$ and Cu_2O at this interface oxides. The microstructure of the interface (Fig. 7) shows a layer on the joining area. There are two sorts of grains: the alumina grains, and the thin acicular grains of $CuAlO_2$.

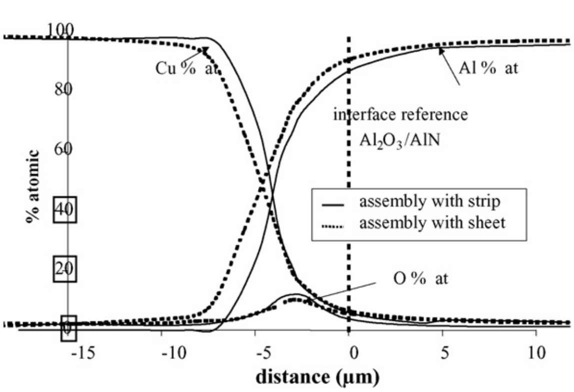

Fig. 6. Repartition of the Cu, Al, O elements at the interface between AlN and Cu for a sample of Cu having an oxidized area thickness of 8 μm.

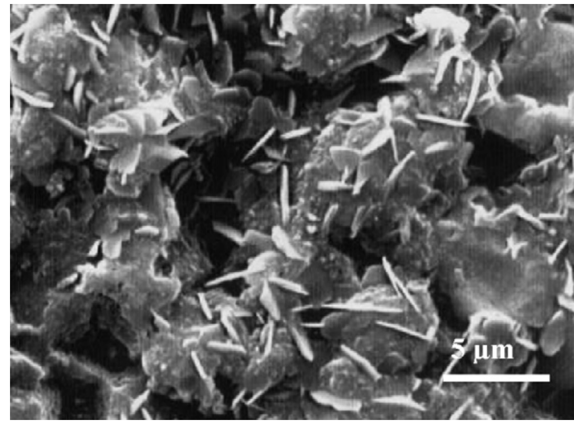

Fig. 7. Microstructure of the interface of the assembly Cu/AlN annealed 10 min at 1072 °C, after breaking the bond, the copper on AlN is dissolved in HNO_3.

4.2. Process for realization of the Cu/AlN assemblies with oxidation in situ of copper

To prepare the assemblies, the ceramic substrate AlN is oxidized (3 μm of alumina) and the 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 temperature. The Fig. 8 shows the aspects of the stud at 1072 °C under 2.5 Pa oxygen pressure.

As it can be seen by classical analysis method (XRD, SEM) the interface is continuous and free from defects. But no interfacial mixed compound is present. The distribution of the oxygen is on around 13 μm thickness, which increases slightly with the partial pressure of oxygen. However taking into account the precision of this type of analysis, it is difficult to bring complementary precise details on the composition of the interface. 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 formation of copper oxide precipitates. These observations justify a short reaction time (3 min) in order to minimize the quantity of oxygen at the interface. At 1072 °C and with a contact time of 3 min it is never

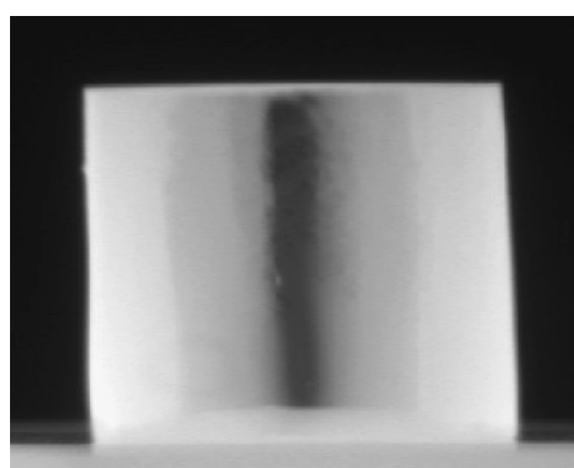

Fig. 8. Surface evolution after 3 min at 1070 °C ($P_{O_2} = 2.5$ Pa).

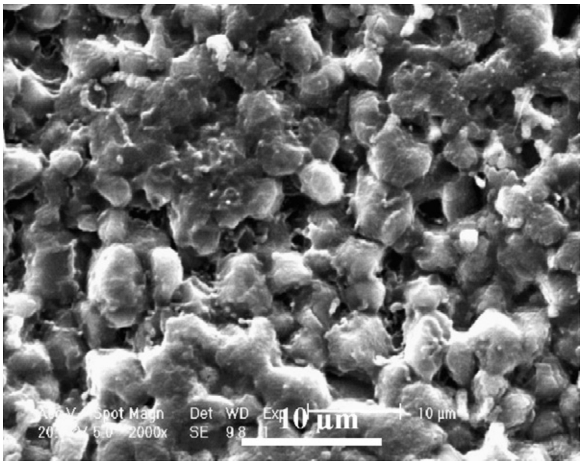

Fig. 9. Microstructure of the interface of the assemblies Cu/AlN after copper dissolution ($P_{O_2} = 2.5$ Pa).

possible to detect any crystallized interfacial compound. But if we increase the contact time to 10 min, XRD analysis shows only the presence of Al_2O_3 and Cu_2O. In a logical way, EDS analysis only reveals the elements Cu, Al and O. The microstructure of the interface shows (Fig. 9), after chemical (HNO_3) copper dissolution, alumina grains on the aluminium nitride surface.

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 by exerting a traction directly on the copper stud. All the assemblies observed by SEM show that the rupture never intervenes in the interfacial Al_2O_3–Cu_2O zone but in the ceramic AlN (Table 1).

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 own resistance of the aluminium nitride.

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

Table 1
Results of the mechanical strength

Mechanical strength (MPa)	Rupture type
Process with atmosphere without oxygen	
27	Cohesive
27	Cohesive
28	Cohesive
Process with controlled oxygen atmosphere	
30	Cohesive
28	Cohesive
33	Cohesive

Table 2
Thermal resistance of contact of the different samples

Tests	Experimental values of thermal resistance of the contact	
	Copper oxidation before contact ($m^2\,W^{-1}\,K^{-1}$)	Oxidation in situ of copper ($m^2\,W^{-1}\,K^{-1}$)
1	$2.0 \pm 0.3 \times 10^{-6}$	$2.0 \pm 0.3 \times 10^{-6}$
2	$2.0 \pm 0.3 \times 10^{-6}$	$2.0 \pm 0.3 \times 10^{-6}$
3	$2.0 \pm 0.3 \times 10^{-6}$	$2.0 \pm 0.3 \times 10^{-6}$
Average	$2.0 \pm 0.3 \times 10^{-6}$	$2.0 \pm 0.3 \times 10^{-6}$

to determine the thermal performance is based on the numerical resolution of the equation which describes the thermal transfer in the assembly.[15,16] 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 (Table 2) is $(1.6 \pm 0.5) \times 10^{-6}\,m^2\,W^{-1}\,K^{-1}$.

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

7. Conclusion

A direct connection of copper with aluminium nitride is possible by developing at the interface an oxide eutectic phase of the Cu–Al–O system. First of all and in all cases it is necessary to form a thin layer (around 4 µm) of Al_2O_3 at the surface of AlN by direct oxidation (1200 °C, 12 h in oxygen).

In the side of copper two ways can be chosen:

- In the first one, a 4 µm layer of Cu_2O is formed by direct oxidation (1100 °C during 1 h in air). To realize the bonding, oxidized copper is put on AlN oxidized and after a thermal treatment of 3 min at 1072 °C successive layers ($AlN/Al_2O_3/Cu_2O/Cu$) give a very good quality bond by formation of a new $CuAlO_2$ phase.
- In the second way the connection is carried out by direct in situ oxidation of Cu. Cu_2O formed at the interface and Al_2O_3 give a sufficient quantity of eutectic phase to ensure a good and strong contact with the formation of a Cu–Cu_2O/Al_2O_3–AlN composite.

The quantity of the eutectic liquid phase formed is proportional to the pressure partial of oxygen in the processing atmosphere and 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 when working on sheets samples during 3 min.

In these conditions, 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 has been observed at the interface by the analysis used and in particular because of the low pressure partial of oxygen used, the mixed phase $CuAlO_2$ is never visible in contrary to the case of the connection carried out by previous oxidation of Cu before the contact.

The Cu/AlN assemblies obtained present a very strong adhesion, the rupture is always observed in the nitride substrate. The interface is thin (<10 μm), poor in oxygen, which is favourable to the thermal transfers between metal and ceramics. That makes it possible to obtain very low thermal contact resistance $1.6 \times 10^{-6}\,m^2\,W^{-1}\,K^{-1}$, better than those of the commercial assemblies.

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