Alumina-Copper Eutectic Bond Strength: Contribution of Preoxidation, Cuprous Oxides Particles and Pores

H. Ghasemi[1,*], M.A. Faghihi Sani[1], A.H. Kokabi[1] and Z. Riazi[2]

Abstract. *The influences of cupric oxide layer thickness, cuprous oxide particles and pores on the mechanical properties and microstructure of an alumina-copper eutectic bond have been investigated. The furnace atmosphere in the first stage was argon gas with 2×10^{-6} atm oxygen partial pressure. In the second stage, the furnace atmosphere was the same as the first stage except that the cooling interval was between 900-1000°C and the hydrogen gas was injected into the furnace atmosphere. Finally, in the last stage, a vacuum furnace with 5×10^{-8} atm pressure was chosen for the bonding procedure. The peel strength of first stage specimens shows that a cupric oxide layer with 320 ± 25 nm thickness generates maximum peel strength (13.1 ± 0.3 kg/cm) in the joint interface. In the second stage, by using hydrogen gas, a joint interface free from any cuprous oxide particles was formed. In this case, the joint strength has increased to 17.1 ± 0.2 kg/cm. Finally, the bonding process in the vacuum furnace indicates that the furnace gas does not have a considerable effect on joint interface pores. Furthermore, the bonding process in the vacuum furnace reduces the peel strength of the joint due to the formation of more pores. A thorough study of pore formation is presented.*

Keywords: *Alumina-copper; Bonding; Peel strength.*

INTRODUCTION

One of the methods for joining copper and alumina is gas-metal eutectic bonding. The bonding of copper to alumina is carried out at $1075 \pm 2°C$ in a properly controlled oxygen-containing atmosphere [1]. The role of oxygen is to improve the wetting process of alumina by liquid copper in order to achieve a homogeneous, liquid copper film spreading along the bonding interface [2]. So far, the mechanical properties of eutectic bonding and corresponding interactions within the bonding area have been studied extensively by several authors [2-8]. Yoshino [2] observed that the peel strength of an alumina-copper bond is predominantly affected by dissolved-oxygen concentration. He reported that the cuprous oxides and voids also contribute to the true bond strength. Oxygen seems to affect the peel

strength of the alumina/copper bond, principally in two ways: Through a change in cohesive bond energy and through the formation of cuprous oxide. The measured bond strength is the combination of these effects. Yoshino predicted that by removing the oxide particles from the interface the peel strength of the joint can be increased to 15 kg/cm. Moreover, Trumble et al. [7] have reported that Cu_2O particle concentration can be reduced after bonding without any loss in bond strength. Ning [8] showed that a threshold thickness of the cupric oxide layer generates the highest bonding strength. This threshold thickness is a function of the alumina substrate profile. On the source of pore formation and pore effects on the peel strength of the eutectic bond, Yoshino [2] reported that the pores within the bonding interface can be formed due to the release of oxygen gas in the liquid copper. Therefore, increasing the thickness of the cupric oxide layer will result in larger pore size. However, Seager et al. [6] found that smaller pores (1-3 μm) may be pullouts of the Cu_2O particles observed on the alumina fracture surface, while the large pores observed by Yoshino are due to argon entrapment in liquid copper during processing. Concerning the influence of pores on the

mechanical strength of eutectic bond, Reimanis [9] have observed that crack-front perturbation occurs when the crack tip is in contact with a pore; the crack front is drawn into the pore which causes the debonding of the regions immediately surrounding the pore. Despite several investigations, the accurate contribution of preoxidation, cuprous oxide particles and pores on the peel strength of this bond is unclear. The goal of the current research is to shed more light on the effects of cupric oxide layer thickness, cuprous oxides and pore density, size and distribution on the peel strength of an alumina-copper eutectic bond. Besides, the sources of pore formation have been investigated thoroughly.

EXPERIMENTAL SETUP AND METHODOLOGY

Experiments were carried out in three stages. In the first stage, the effect of preoxidation on peel strength of alumina-copper bond has been examined. In the second stage, the influence of cuprous oxide particles on the peel strength of an alumina-copper bond has been investigated. Finally, in order to decrease the interface pores, the bonding process was performed in a vacuum furnace. All of the alumina-copper bonds began with 99.99% Cu strips and 97% Al_2O_3. Copper strips and alumina specimens were 350 and 200 mm in length, 25 mm in width and 0.8 and 1.5 mm thick, respectively. Copper strips were prepared in three steps. Firstly, the strips were degreased by scrubbing the joint surfaces in a solution of liquid detergent, washed with clean hot water and dried thoroughly in a steam of hot air. Secondly, the strips were immersed in 25% nitric acid for 30s. Thirdly, the strips were dipped in ethyl alcohol washed by clean cold water and dried by hot air. On the other hand, alumina specimens were polished by diamond paste with an average particle size of 0.5 μm, cleaned by ultrasonic treatment in ethyl alcohol for 15 min and rinsed in distilled water. At the final step, alumina specimens were annealed in air at 1000°C to eliminate any hydroxyl groups.

Copper strips were preoxidized at various temperatures and several times to obtain a range of cupric oxide (CuO) thickness. On account of the phase stability diagram of copper oxidation, the formed oxide phase below 400°C under atmospheric pressure will be CuO [10]. The thickness of the cupric oxide layer was calculated from the weight difference before and after preoxidation. In the first stage, the bonding process was carried out in a tube furnace under an argon atmosphere (< 2 ppm O_2). The gas flows for heating and cooling procedures were respectively, 150 and 200 L/hr. The samples were heated at a rate of 10°C/min to 1000°C, followed by a rate of 2°C/min to 1075°C, where they were held for 1 hr. During the holding time, an alumina-copper bond was formed.

After 1 hr, the temperature was decreased slowly (5°C/min) to 700°C and then 10°C/min to 400°C. The temperature was held for 1 hr at 400°C to reduce thermal stresses. Finally, the furnace cooled to room temperature. The furnace temperature curve is shown in Figure 1. In the second stage, the experimental procedure for bond formation was identical to the first stage, except for the cooling interval which was between 900-1000°C in which hydrogen gas was injected into the furnace atmosphere. In the last stage, the bonding process was carried out in a vacuum furnace. A vacuum tube with a mechanical pump and an oil diffusion pump can achieve a vacuum atmosphere of 5×10^{-8} atm. The oxygen partial pressure was measured by a CaO-stabilized ZrO_2 oxygen sensor. The peel strength of the bonded specimens was measured by an Instron Machine Model 1115. Fracture surfaces were analyzed by optical microscopy and scanning electron microscopy.

RESULTS AND DISCUSSION

Cupric Oxide Layer Thikness

The thickness of the cupric oxide layer, formed under different conditions of temperature and oxidation time, is shown in Figure 2. It shows that the thickness variation of the cupric oxide layer is gradual and uniform within the range of 0 to 600 nm above which the thickness increase is abrupt and discontinuous. Samples having an oxide layer thickness greater than 600 nm present a discontinuous and cracked oxide layer surface. Furthermore, the cohesion between the cupric oxide layer and the copper strips has decreased notably. These discontinuities on the cupric oxide layer surface are due to the thickness of the CuO layer. The more the oxide layer thickness, the more the sensitivity to a thermal expansion coefficient mismatch. Since the thermal expansion coefficients of Cu (20×10^{-6} °C^{-1}) and CuO (4.3×10^{-6} °C^{-1}) have a great difference, the stresses formed in cooling are high. The thermal stress
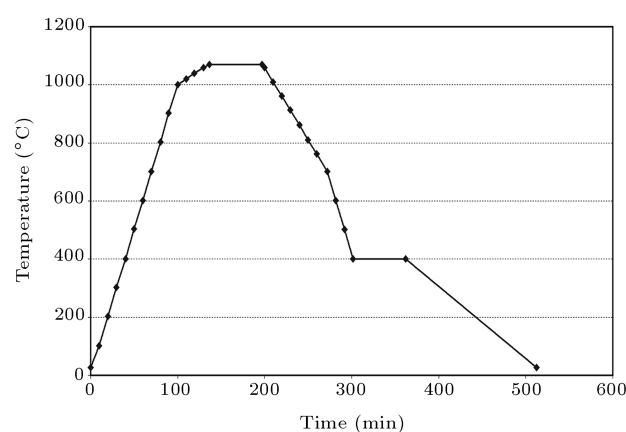

Figure 1. The furnace curve in bonding process.

field generates discontinuities and cracks within the cupric oxide layer, which in turn results in an increase of the copper oxidation rate, due to a greater copper exposure. Hence, the preoxidation conditions, which do create more than, approximately, a 500-600 nm oxide layer, result in unsuitable strips for the bonding process.

Peel Strength Measurments

The peel strengths of first stage specimens are shown in Figure 3. As shown in Figure 3a, an optimum oxide layer thickness results in the highest peel strength $(13.1 \pm 0.3 \text{ kg/cm})$ under a 2×10^{-6} atm oxygen partial pressure. This optimum thickness is a result of the interaction between the wetting of the alumina surface and the percentage of oxide particles at the interface. Thicker Cupric oxide layers introduce more oxygen into the interface and, subsequently, the wetting angle will be decreased [11] and more cuprous oxide particles (Cu_2O) will remain in the interface after bonding. Similarly, Figure 3b shows an optimum point. By comparing the optimum layer thickness in Figures 3a and 3b, a difference of approximately 25 nm is observed. This difference can be resulted from errors in the peel strength and oxide layer thickness measurement. Thus, it can be said that 320 ± 25 nm is the optimum oxide layer thickness for alumina-copper bonding under 2×10^{-6} atm oxygen partial pressure. The peel strength difference in these two states is low; it shows that oxidation at different temperatures, to obtain a certain oxide layer thickness, does not affect the peel strength. Both Figures 3a and 3b reveal that, before reaching the optimum point, the peel strength of both specimens has raised steadily. It can be concluded that improved wetting, due to an increase in the oxygen content of the liquid copper, has heightened the peel strength. After an optimum point, the effect of the Cu_2O content predominates, decreasing the bond strength. Figure 3c

shows the peel strength of specimens oxidized at $400°C$. In contrast to Figures 3a and 3b, in the preoxidation time span of this temperature, the peel strength of specimens has decreased slowly. It means that one of the factors affecting peel strength is predominant. Obviously, in this time span, the Cu_2O content of the interface layer is the predominant parameter to the wetting of the alumina by liquid copper. The important point in Figures 3a and 3b is the rising and falling rate of the peel strength versus the oxide layer thickness. It shows that the effect of wetting on peel strength is more significant than the effect of the Cu_2O content of the interface. This state is clear in the Ning investigations [8].
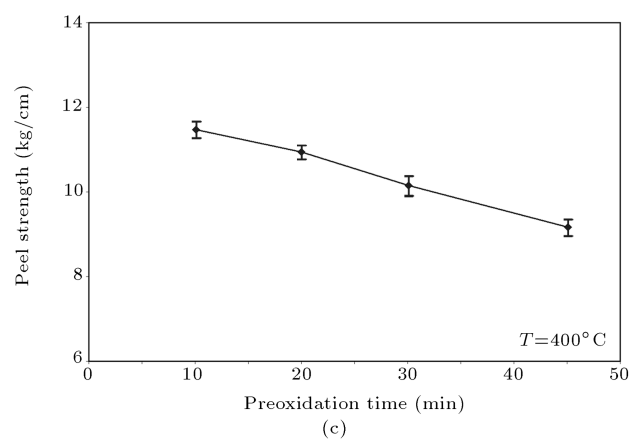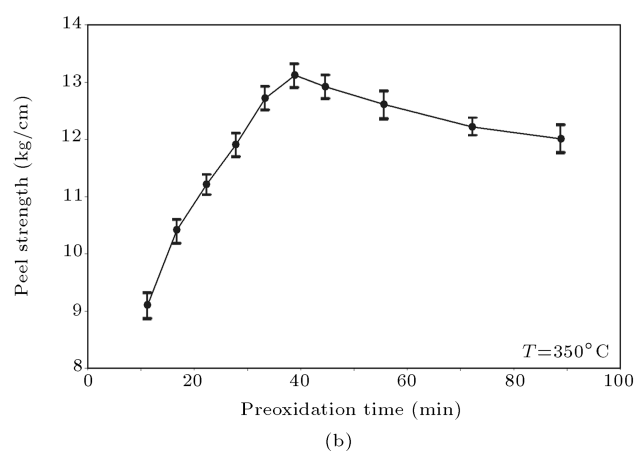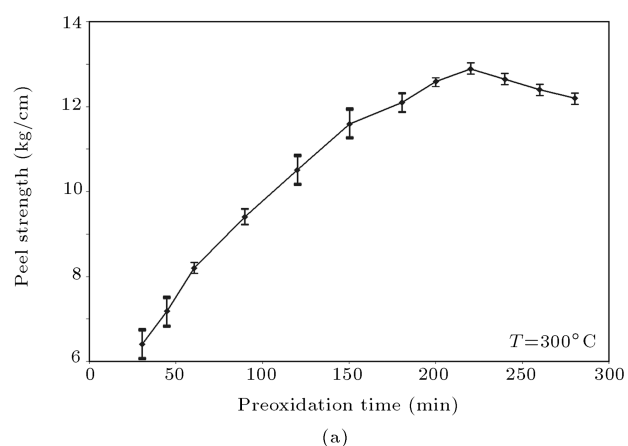
To achieve more strength in the alumina-copper bond, it is desirable to remove cuprous oxides from the interface. This fact is due to the higher strength of the Cu/Al_2O_3 bond compared with Cu/Cu_2O and Cu_2O/Al_2O_3 [2,4,7]. Hence, during the cooling interval of $900\text{-}1000°C$ within the second stage, the hydrogen gas was injected into the furnace atmosphere in order to remove Cu_2O particles from the eutectic zone of the interface. Figure 4 shows the cross section of the alumina-copper joint at the second stage. It surprisingly shows no trace of the interface layer; the joint is directly established between alumina and copper. In addition to copper and alumina, no sign of any other phase is detectable at the fracture surfaces. The peel strength measurements of the joint at this stage are shown in Figure 5.

In addition, Figure 6 depicts the force versus distance curve of the maximum peel strength at the first and second stages. As shown in Figure 5, in contrast to first stage specimens, the peel strength of the joint has raised considerably, regardless of the oxide layer thicknesses. Moreover, the maximum peel strength of specimens increased to 17.1 ± 0.2 kg/cm corresponding to a new optimum value of the cupric oxide layer thickness. The increasing peel strength of the eutectically bonded interface is attributed to the removal of Cu_2O particles from the interface. After the solidification of the interfacial liquid, there is a distribution of Cu_2O particles in the interface. If a reducing atmosphere exists, the Cu_2O particles will reduce to Cu. The removal of Cu_2O particles from the interface results in the substitution of Cu_2O/Al_2O_3 and Cu_2O/Cu interfaces by a Cu/Al_2O_3 interface. According to Chiang et al. and Sun and Driscoll investigations [4,12], the strength of the Cu/Al_2O_3 interface is greater than that of the Cu_2O/Cu interface. Therefore, an improved alumina-copper contact surface and a decreasing stress concentration, owing to the absence of Cu_2O particles, resulted in the increase of the peel strength.

Three main factors determine the peel strength of the joint: Wetting properties of the copper-oxygen
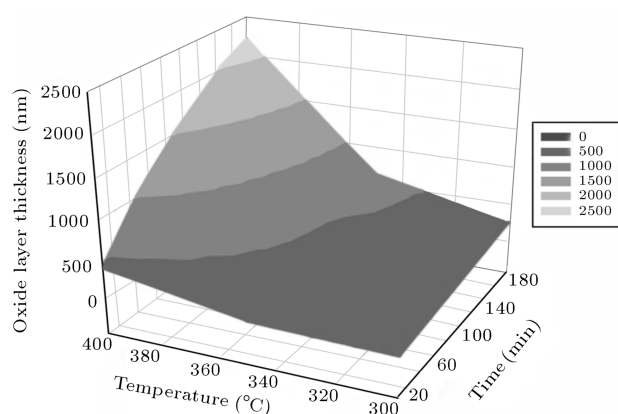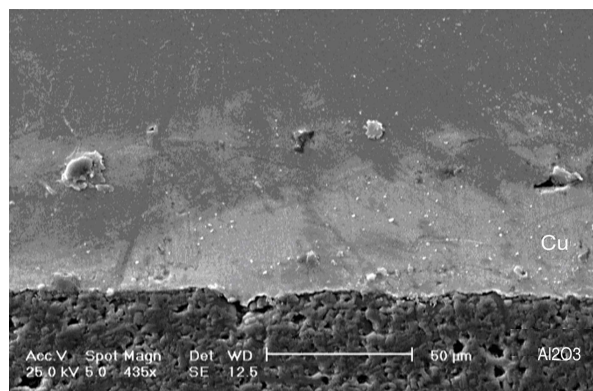

Figure 2. The variation of oxide layer thickness in different preoxidation conditions.
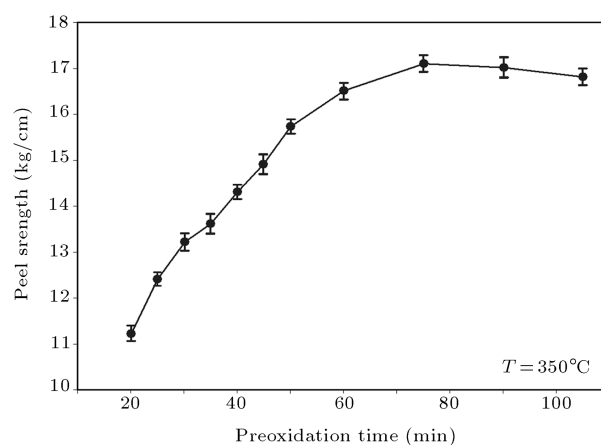
Figure 4. The cross section of alumina-copper joint after removing the Cu_2O particles.

Figure 5. The peel strength of the second stage specimens.

Figure 3. The peel strength of specimens preoxidized in different conditions.

Figure 6. The maximum peel strength in the first and second stages.

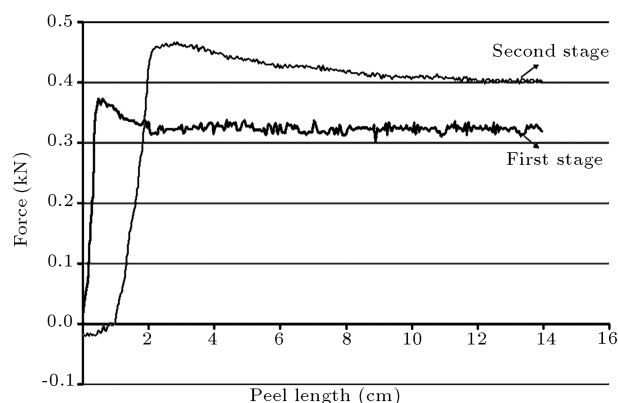liquid on the alumina surface, Cu_2O particle density and distribution, and pores. Yoshino reported that the pores detrimental effect on the peel strength is low compared to the wetting effect [2]. Since, at the second stage, Cu_2O particles have been removed, the wetting parameter remains the dominant parameter on peel strength. It has been proved [11,13] that by reaching a threshold value for the oxygen content within the copper-oxygen liquid phase, the wetting angle does not change considerably. The observed decrease of peel

strength for high thicknesses of cupric oxide layers after reaching optimum peel strength, as shown in Figure 5, is due to an increase in pore density on the bonding interface.

The change of the CuO optimum layer thickness at this stage was predicted. Due to a reduction in Cu_2O particles, the effect of wetting is more significant

than that of an increase in pore concentration and distribution for the increasing oxygen content of the liquid copper, resulting in a shift of the optimum peel strength to the values corresponding to a thicker CuO layer. By reducing one mole of Cu_2O, two mole of Cu will appear. The volume ratio of one mole of Cu_2O to two mole copper is calculated in the following equation:

$$\frac{V(1 \text{ mol } Cu_2O)}{V(2 \text{ mol } Cu)} = 1.459. \tag{1}$$

Since the volume ratio is more than one, the pullout of Cu_2O particles results in an increase of the pore density on the interface. Copper side fracture surfaces, corresponding to different stages, are shown in Figure 7. In contrast to the first stage, the pores sizes are diminished in the second stage. On account of the smaller pores in the interface, the tolerance in peel strength has diminished, which is clear in Figure 6. Paying close attention, it can be found that smaller spherical pores are the same at the two stages. However, larger pores at the first stage, which have an irregular shape, are contracted to smaller irregular pores at the second stage.

According to Sun & Driscoll investigations [12], the Cu_2O content of the interface layer, after solidification, is more than the Cu_2O content of the eutectic point (the Cu_2O content of the eutectic point is 4.3% vol.). Moreover, this fact is clear in pictures that other researchers have taken from the alumina-copper bond [5,6,8]. So, there are some Cu_2O particles in liquid copper in the bonding temperature. These Cu_2O particles can be reduced at the bonding temperature in a 2×10^{-6} atm oxygen partial pressure. The reduction of Cu_2O particles forms O_2 (gas) molecules. These molecules can form spherical pores at the interface. But, this reduction reaction is not completed during the bonding process. The Cu_2O particles in the interface after solidification are evidence of this conclusion. Thus, until now there are two sources of pore formation. The first is the O_2 molecules that are formed due to the reduction of Cu_2O particles in the liquid copper. The pullout of Cu_2O particles from the copper fracture side is the second. Comparing the Cu_2O particles on the alumina fracture surface with irregular pore sizes, it is clear that Cu_2O particles are smaller than irregular pores on the copper fracture side. So, maybe the irregular pores on the fracture surface of copper are formed due to several sources.

In view of the fact that furnace atmosphere gas was predicted as being one of the sources of pore formation [6], in the hope of removing some pores, the final stage of bonding was carried out in a vacuum furnace. The vacuum atmosphere was 5×10^{-8} atm. The maximum peel strength of this stage is illustrated in Figure 8. As depicted in Figure 8, the peel strength has decreased and its tolerances are more,

(First stage)

(Second stage)

(Third stage)
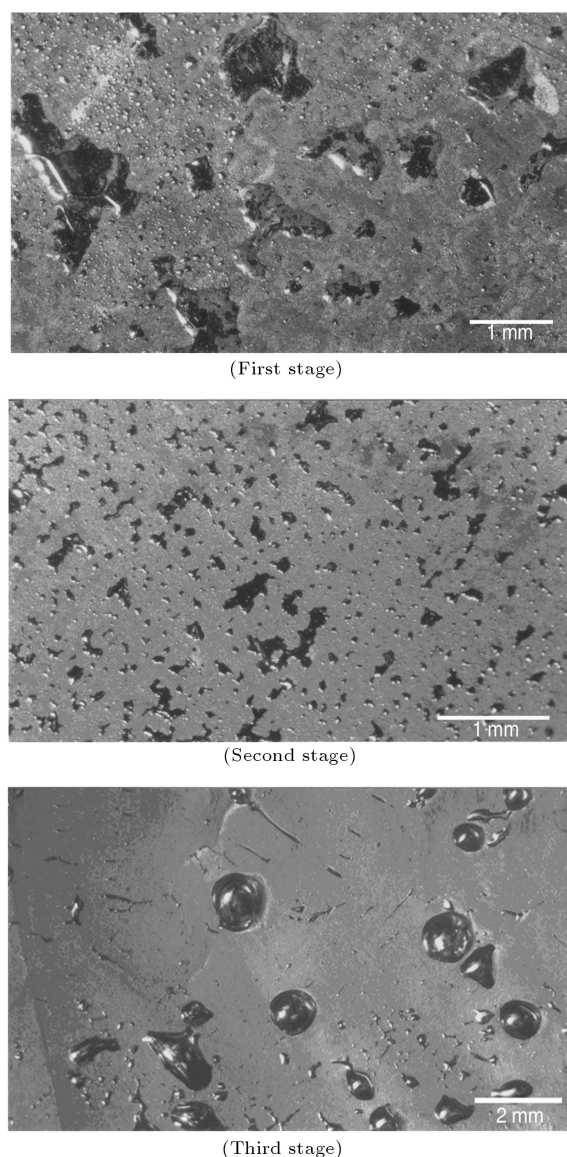
Figure 7. The copper side fracture surfaces of three stages.

in comparison with the second stage. At this stage, as at the second stage, the interface is free of Cu_2O particles, as predicted, due to a suitable environment for Cu_2O particle reduction. The outstanding point at the third stage is the formation of larger pores on the interface (Figure 7). Furthermore, the shape of them has changed. The drop in peel strength is related to the formation of larger pores, and these pores are the cause of more tolerances in peel strength.

The formation of larger pores can be attributed to the furnace atmosphere. There are two reactions responsible for larger pores: The reduction of Cu_2O particles in liquid copper and the presence of a vacuum condition. As mentioned before, there are some Cu_2O particles in liquid copper in the bonding temperature. Since the furnace oxygen partial pressure is 10^{-8} atm, these oxide particles reduce more than at the two
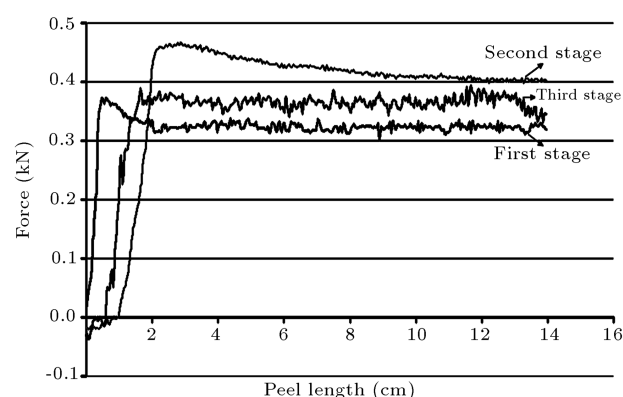
Figure 8. The comparison between maximum peel strength in three stages.

previous stages and liberate more O_2 gas. Also, due to bonding in the vacuum furnace environment, the pressure difference between the furnace environment and the released O_2 (gas) is high; O_2 molecules can extend to larger dimensions. Therefore, it can be said that the furnace environment gas does not have a significant effect on pore formation.

In conclusion, the pores on the alumina-copper eutectic bond can be formed due to two reasons: O_2 gas release, and the pullout of Cu_2O particles. However, in some pores both conditions were prepared. In these pores, a portion of the pore is formed due to gas release and, at the perimeter of these pores, Cu_2O particles are present. These Cu_2O particles are responsible for the irregular shape of these kinds of pore.

CONCLUSION

1. Creating more than 500-600 nm cuprous oxide layer thickness by preoxidation makes the strips improper for eutectic bonding due to the forming of cracks in the oxide layer and a loss of adhesion.

2. The optimum cuprous oxide layer thickness for providing the highest peel strength in an alumina-copper eutectic joint, in 2×10^{-6} oxygen partial pressure, is 320 ± 25 nm, which results to 13.1 ± 0.3 kg/cm peel strength.

3. By removing all of the Cu_2O particles from the alumina-copper interface, the peel strength has risen to 17.1 ± 0.2 kg/cm.

4. Furnace gases do not have a significant effect on pore formation in an alumina-copper interface.

5. Performing the alumina-copper eutectic bond in a vacuum furnace decreases the peel strength and causes more fluctuations in joint strength due to the formation of larger pores.

6. The pores at the alumina-copper interface are formed due to two reasons: O_2 gas release, and the pullout of Cu_2O particles.

REFERENCES

1. Burgess, J.F. and Neugebauer, C.A. "Direct bonding of metals with a metal-gas eutectic", U.S.Pat., 3854892 (1974).

2. Yoshino, Y. "Role of oxygen in bonding copper to alumina", *J. Am. Ceram. Soc.*, **72**(8), pp. 1322-1327 (1989).

3. Yoshino, Y. and Ohtsu, H. "Interface structure and bond strength of copper-bonded alumina substrates", *J. Am. Ceram. Soc.*, **74**, pp. 2184-2188 (1991).

4. Chiang, W.L., Greenhut, V.A., Shanefield, D.J., Johnson, L.A. and Moore, R.L. "Gas-metal eutectic bonded Cu to Al_2O_3 substrate-mechanism and substrate additives effect study", *Ceram. Eng. Sci. Proc.*, **14**(9-10), pp. 802-812 (1993).

5. Kim, S.T. and Kim, C.H. "Interfacial reaction product and its effect on the strength of copper to alumina eutectic bonding", *J. Materials Science*, **27**, pp. 2061-2066 (1992).

6. Seager, C.W., Kokini, K., Trumble, K. and Krane, M.J.M. "The influence of $CuAlO_2$ on the strength of eutectically bonded Cu/Al_2O_3 interfaces", *Scripta Materialia*, **46**, pp. 395-400 (2002).

7. Trumble, K.P. "Thermodynamic analysis of aluminate formation at Fe/Al_2O_3 and Cu/Al_2O_3", *Acta Metall. Mater.*, **40**, pp. S105-S110 (1992).

8. Ning, H., Ma, J., Huang, F. and Wang, Y. "Preoxidation of the Cu layer in direct bonding technology", *Applied Surface Science*, **211**, pp. 250-258 (2003).

9. Reimanis, I.E., Trumble, K.P., Rogers, K.A. and Dalgleish, B.J. "Influence of the Cu_2O and $CuAlO_2$ interphases on crack propagation at Cu/α-Al_2O_3 interfaces", *J. Am. Ceram. Soc.*, **80**(2), pp. 424-432 (1997).

10. Kubaschewski, O and Hopkins, B.E. "Oxidation of metals and alloys", *Butterworths Publications* (1967).

11. Diemer, M., Neubrand, A., Trumble, K.P. and Rodel, J. "Influence of oxygen partial pressure and oxygen content on the wettability in the copper-oxygen-alumina system", *J. Am. Ceram. Soc.*, **82**(10), pp. 2825-2832 (1999).

12. Sun, Y.S. and Driscoll, J.C. "A new hybrid power technique utilizing a direct copper to ceramic bond", *IEEE Trans. Electron Devices*, **ED-23**(8), pp. 961-967 (1976).

13. Lewinsohn, Ch.A., Singh, M. and Loehman, R. "Advances in joining of ceramics", *J. American Ceramic Society*, **90**, pp. 77 (2003).