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Interfacial Bonding Mechanism and Annealing Effect on Cu-Al Joint Produced by Solid-Liquid Compound Casting

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Abstract: Copper-aluminum (Cu-Al) based lamellar composites were prepared using a solid-liquid compound casting (SLCC) technology. Characterization results showed that the Cu-Al composites were fully-sintered at 700 °C under an argon atmosphere using the SLCC technology. Cu-Al interfacial bonding was uniform with a well-defined transitional and inter-diffusion region. Intermetallic compounds and solid solutions of CuAl_2 , CuAl , Cu_9Al_4 , CuAl_3 and Cu_3Al_2 were detected at the interfacial region. With the increase of annealing temperature, the width of the Cu-Al interfacial region was increased, and the interfacial bonding strength was also increased, whereas the types of the intermediate phases were changed. With the increase of dwelling time at a given annealing temperature, the width of Cu-Al interfacial region was increased, the interfacial bonding strength was decreased and the mesophases were changed. The bonding strength of the as-prepared composite was 30 MPa, whereas those of specimens annealed at 200 °C for 2 hours, 300 °C for 2

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hours, 400 °C for 2 hours, 300 °C for 30 min and 300 °C for 1 hours were 59, 39, 74, 56, and 49 MPa, respectively. The Cu-Al interfacial bonding mechanisms were identified to be rapid inter-diffusion of copper and aluminum and formation of interfacial and graded microstructures. The formation of copper-aluminum interface is a combined result of inter-atomic diffusion and interfacial chemical reactions, the latter of which is more dominant in the diffusion process.

Key words: Cu-Al composites, annealing treatment, interface, inter-diffusion, interaction

1. Introduction

Cu-Al composites have been widely used in automobile, electronics, machinery, daily appliances and metallurgy fields due to their good corrosion resistance, light weight, high conductivity and low contact resistance, which have been reported by many researchers including Berski et al. (2006) and Wang et al. (1997) Sun et al. (2001) and Dubourg et al. (2002) reported that Cu-Al composite can be obtained metallurgically through interfacial diffusion from single copper and aluminum layer using various technologies. At present, various techniques have been applied to fabricate Cu-Al composites, including solid-solid compound casting technology (SSCCT, e.g. clad-process welding, CPW), liquid-liquid compound casting technology (LLCCT, e.g. core filling continuous casting, CFC, which was reported by Zhang et al. (2014)), and solid-liquid compound casting technology (SLCCT, e.g. horizontal continuous casting, HCC, which was reported by Hu et al. (2016)). Among these methods, Zare et al. (2013) reported that Cu-Al composites prepared by the

SLCCT (i.e., through the interaction between liquid metal and solid metal in the contact interface to achieve a metallurgical bonding) have advantages of non-restriction in sample shape and size, good interfacial bonding strength, high economic efficiency and simple process. However, defects such as cracks and pores are commonly existed inside the obtained composites due to the large differences in the physical properties of Cu and Al (as listed in Table 1). Moreover, various intermetallic compounds of Cu and Al can be easily formed during processes and they are generally hard and brittle. Hug et al. (2011) and Lee et al. (2005) reported that these intermetallic phases have significant influences on manufacturability, mechanical properties, and reliability of the Cu-Al composites. Therefore, it is critical to study the interfacial structures of composite materials prepared using the SLCCT, control their interfacial reactions and understand their influencing factors. For example, Li et al. (2009) investigated the cold rolled Cu-Al composite plate, and found that the Cu-Al diffusion was controlled by the bulk diffusion with a parabolic-law growth of intermetallic compounds. Du et al. (2013) investigated copper clad aluminum composite filament prepared using a combined solid-liquid pouring and drawing method, and concluded that a low temperature annealing stabilized the interfaces and the optimum annealing temperature was 400 °C. Lee and Kwon (2013) investigated Cu-Al composites prepared using a vacuum hot pressing method, and results showed that various compounds of CuAl_2 , CuAl , Cu_4Al_3 and Cu_9Al_4 were formed at the interface. Divandari et al. (2009) reported that various compounds such as CuAl_2 , CuAl and Cu_3Al_2 were formed at the interfaces of casted

Cu-Al composites. Tanaka et al. (2007), Li et al. (2001) and Zhang et al. (2011) also reported that the annealing processes promoted the diffusion of the atoms among the Cu-Al constituents, and the width of bonding regions was widened due to the formation of diffusion layer on both sides of the bonding interface, thus achieving a metallurgical bonding with an improved bonding strength.

Although there is significant progress in this research field, many issues are to be investigated, for example, the diffusion mechanisms and chemical reactions between Cu and Al; the controlling factors determining the sintering process of Cu-Al compounds; the formation process of compound or bonding interface; and the mechanisms of strength enhancement etc. In this paper, Cu-Al composites prepared using the SLCCT were annealed at different temperatures and various dwelling durations to induce inter-diffusion and intermetallic phase formation at the Cu-Al interfaces. The interfacial morphology, formation mechanisms and the growth kinetics of the intermetallic layers were investigated.

2. Experimental

Pure copper (T2) and pure aluminum (1060) were used as raw materials in this study. Two types of sample structures, i.e., the sleeve one and laminated one, were designed and fabricated for testing their different properties. The main components and their basic properties are listed in Tables 1 and 2.

Table 1. Physical properties of pure aluminum and copper.

| Density (g•cm ³) | Melting point (°C) | Atomic radiu s(A) | Resistivity (20 °C× 10 ⁶ Ω•cm) | Linear expansion coefficient | Tensile Strength (MPa) | Brinell hardness (MPa) |
|---------------------------------|--------------------------|-------------------------|---|------------------------------------|------------------------------|------------------------------|
|---------------------------------|--------------------------|-------------------------|---|------------------------------------|------------------------------|------------------------------|

| | | | | | $^{\circ}\text{C}^{-1}\times 10^6$ | | | | |
|----|------|------|-------|--------|------------------------------------|---------|-----|--|--|
| | | | | | $\Omega\cdot\text{cm}$ | | | | |
| Al | 2.7 | 660 | 1.431 | 2.6548 | 24.3 | 68.6~98 | 196 | | |
| Cu | 8.96 | 1083 | 1.278 | 1.673 | 16.8 | 235.2 | 343 | | |

Table 2. Chemical composition of copper and pure aluminum (mass fraction,%).

| | Cu | Al | P | Si | Fe | S | Mg | Ag | Zn | Bal. |
|----|-------|-------|--------|--------|--------|--------|------|--------|------|--------|
| Cu | 99.95 | - | 0.0008 | 0.0006 | 0.0008 | 0.0009 | - | 0.0010 | - | 0.0004 |
| Al | 0.01 | 99.70 | - | 0.08 | 0.15 | - | 0.02 | - | 0.02 | 0.02 |

In order to achieve a good performance of Cu-Al composite, the sintered samples were heated for a short time above the melting point of Al, as reported by Chen et al. (2006). This is because a shorter holding time can reduce the diffusion of copper and avoid excessive formation of intermetallic compounds. The influences of annealing temperature and time on interfacial bonding were then discussed. The detailed processes are listed as follows.

(1) First of all, the raw materials were mechanically polished using 150 to 600 abrasive papers to obtain clean and smooth surfaces. Subsequently, they were ultrasonically cleaned in an acetone bath to remove adhered contaminants. Afterwards, native oxide layers on the sample surfaces were removed by dipping the samples in a solution of 10 vol. % H_2SO_4 solution for 30 seconds at room temperature. The specimens were rinsed with distilled water and dried in air after each chemical cleaning process.

(2) They were then put inside a graphite mould, in which the samples were filled with quartz sands to promote the ease of demolding process by avoiding the interaction between graphite and aluminum alloy.

(3) The graphite mould was put inside a GSL1700X vacuum tube furnace. After

the chamber was pumped down to a base vacuum less than 0.1 Pa, the samples were heated to a temperature 700 °C for 1 min with argon gas protection, in order to prevent the oxidation of materials.

(4) The samples were then cooled down to room temperature in a GSL1700X tube furnace. Annealing was performed at 200 °C, 300 °C and 400 °C, respectively, for 2 hours at atmospheric conditions. Annealing was also performed at 300 °C for 30 min and 1 hour at atmospheric conditions using the furnace.

The polished cross-section surfaces of the Cu-Al composite samples were etched with an etchant (a mixture of 95% distilled water, 2.5% HF, 1.25% HCl and 1.25% HNO₃), and the interfacial structures were characterized using an inverted metallographic microscope. Microhardness of the interfaces was measured using a TUKON2100 Vickers micro-hardness tester with a load of 20 g and a dwell time of 10 seconds. Microstructures of Cu-Al interfaces and fracture morphology were characterized using a scanning electron microscope (SEM, JEM-6700F), and distribution of chemical elements at the Cu-Al interface was obtained through elemental line scans using an energy-dispersive X-ray spectroscopy (EDS) attached with the SEM. Crystalline structures of the Cu-Al samples were investigated using X-ray diffraction (XRD-7000) with a Cu K_α radiation in a 2θ range of 20°-80°. For composite samples of the sleeve type, shear strength (τ) of the Cu-Al composite was measured using an HT-2402 computer-controlled tensile testing machine, and the readings were obtained using the following formula:

$$\tau = P/A \quad (1)$$

where P is the fracture load (N), A is the actual area (mm) of the fracture surface.

3. Results and discussion

Fig. 1 shows optical micrographs of Cu-Al composites after different annealing processes. All the pictures show that the interfacial regions are relatively uniform without apparent cracks and voids. There is insignificant copper diffusion into the aluminum as shown in Fig. 1(a). It can be clearly noticed that intermetallic compounds or solid solutions are formed in the Al-side as shown in Fig. 1(b) after the sample was annealed at 200 °C for 2 hours. In Fig. 1(c), the diffused layer becomes much wider compared with that shown in Figure 1(b). At a higher annealing temperature, the diffusion of copper elements becomes faster, thus more compounds or solid solutions could be easily formed. In Fig. 1(d), the inter-diffusion layer is clearly observed. Owing to the increase of annealing temperature, Cu and Al elements become inter-diffused, and part of the copper is dispersed in the aluminum, thus forming a uniformly dispersed region.

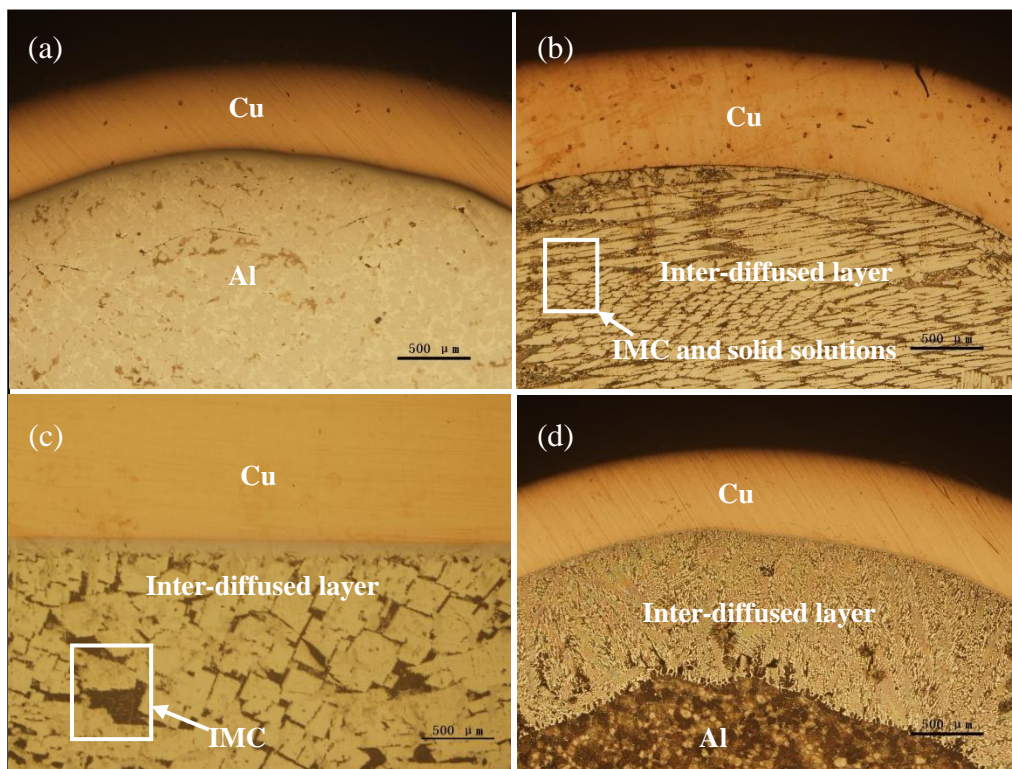


Fig.1 Metallographic photographs of the Cu-Al composite at different annealing

temperatures at the same dwelling time (in which IMC means intermetallic compounds) (a) unannealed, (b) annealed at 200 °C for 2 hrs, (c) annealed at 300 °C for 2 hrs, (d) annealed at 400 °C for 2hrs

Fig. 2 shows optical micrographs of the Cu-Al composites with different dwell durations at the same annealing temperature of 300°C. The gray strip zone is a solid solution formed on the copper side. It can be seen that at the same annealing temperature, the diffusion layer becomes widened as the annealing duration is increased. When the annealing duration is 2 hrs, intermetallic compounds can be clearly seen in the diffusion layer (as shown in Fig.1(c)).

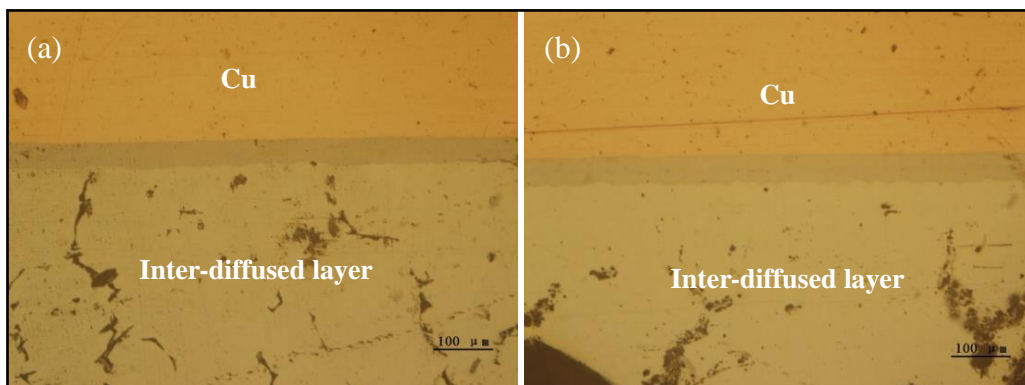
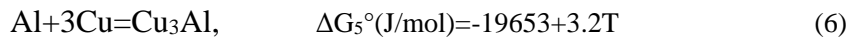
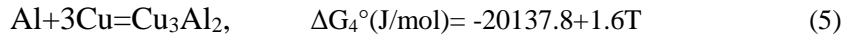
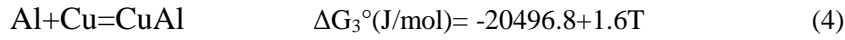
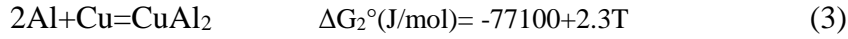
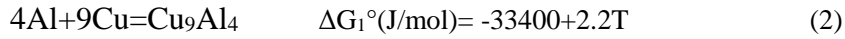


Fig.2 Metallographic photographs of the Cu-Al composite under the different annealing durations at the same annealing temperature

(a) annealed at 300 °C for 30 min, (b) annealed at 300 °C for 1hr

According to Cu-Al binary phase diagram, the solubility of liquid copper and aluminum is infinite, whereas that of the solid copper and aluminum is limited. In the temperature range of 473K~873 K, the possible reactions at the Cu-Al interfaces are listed in Eqs. (2) ~ (6), where ΔG_1° , ΔG_2° , ΔG_3° , ΔG_4° , ΔG_5° are the standard Gibbs free energy values for the formation of intermetallic compounds, respectively,

reported by Zhao et al. (2011). T is the reaction temperature.



As can be seen from the Eqs. (2) ~ (6), several types of intermetallic compounds can be formed. The standard Gibbs free energy values of these intermetallic compounds can be arranged from small to large values, with a sequence of CuAl_2 , Cu_9Al_4 , CuAl , Cu_3Al_2 and Cu_3Al . Clearly, CuAl_2 will be formed firstly at the interface, followed by Cu_9Al_4 , CuAl , Cu_3Al_2 and Cu_3Al . As reported by Chen et al. (2004), AlCu_3 , AlCu , Al_2Cu are unstable, and new phases can be easily generated as the elements continue to diffuse. Compared with Figs. 1(b), 1(c) and 1(d), the morphologies of the transitional layers exhibit completely different patterns, which might indicate that different compounds or solid solutions are formed at the interfaces between Cu and Al.

Fig. 3 shows XRD patterns of the Cu-Al composites annealed at different conditions. As shown in Fig. 3, various intermetallic compounds or solid solutions are formed in the Cu-Al interface. CuAl_2 , Cu_9Al_4 , and CuAl co-exist in the Cu-Al joints annealed at 300°C for 30 min and 1 hr, whereas CuAl , Cu_9Al_4 and Cu_3Al_2 co-exist in the Cu-Al joints annealed at 300°C for 2 hrs. Clearly, the longer the holding time, the intermetallic compounds at the interface of the composite will react each other,

leading to phase transformation. There are four types of mesophases, i.e., CuAl, AlCu₃, Al₂Cu₃ and Cu₉Al₄ can form at the Cu-Al interface in the sample annealed at 400°C for 2 hrs. However, only CuAl, Al₂Cu₃ and Cu₉Al₄ can be observed for the sample annealed at 200°C for 2 hrs. Compared with the annealed samples, the as-sintered/un-annealed samples show five mesophases, including CuAl₂, CuAl, Cu₉Al₄, CuAl₃ and Al₂Cu₃.

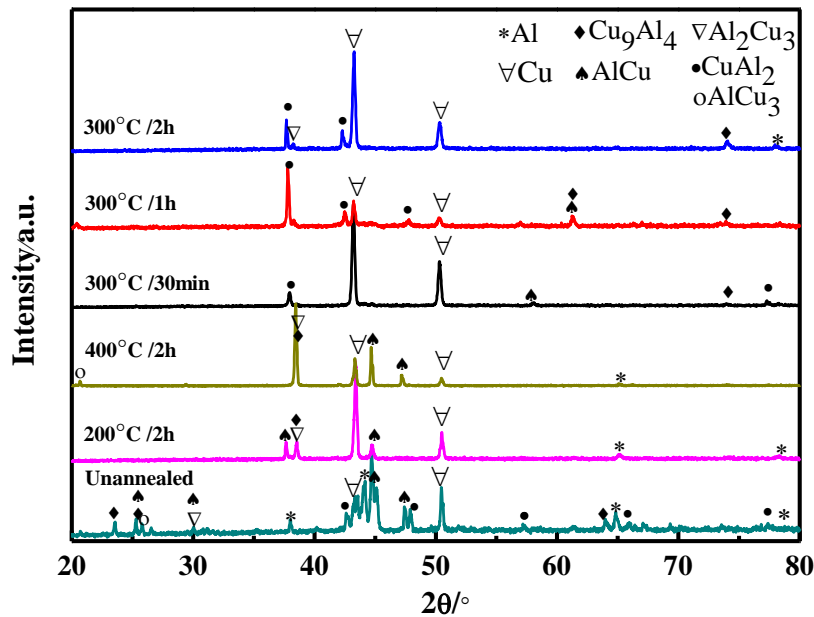


Fig.3 XRD patterns of Cu-Al joints of transition zone under different heat treatment conditions

According to Cu-Al binary phase diagram, there are five intermetallic compounds which are co-existed at room temperature, namely Cu₉Al₄ (γ_2), Al₂Cu₃ (δ), Al₃Cu₄ (ζ_2), CuAl (η_2) and Al₂Cu (θ). The saturated solid solutions of Al(Cu) and Cu(Al) can form on both sides of the interface due to mutual diffusion. It is noted that the solubility limit of Cu in Al is almost two orders of magnitude less than that of Al in Cu. At the early stage of diffusion, Cu firstly diffuses into Al-side and thus creates a solid solution. When the concentration of Cu atoms reaches a certain value, CuAl₂

phase is firstly formed near the Al interface. The Al atoms diffuse into the Cu substrate thus forming a Cu_9Al_4 (γ_2) phase. Phase formation of these intermetallic compounds at the interface has been experimentally observed in literature, for example, by Dong et al. (2016). As the annealing temperature or holding time is increased, Cu and Al atoms are continuously inter-diffused, thus forming new types of intermetallic compounds. Therefore, the diffusion concentration of metal elements can be controlled by adjusting the annealing process, thereby avoiding or reducing the formation of interfacial intermetallic compounds.

SEM morphology and EDS elemental line scans at the Cu-Al interfaces are presented in Fig. 4. As exhibited in Fig. 4(a), the as-sintered/un-annealed interface is clear and the diffusion does not occur. After the sample was annealed at 200°C for 2 hours, the inter-diffusion layer is obvious and a layered structure can be observed. Whereas after the sample was annealed at 400 °C for 2 hours, the transitional zone becomes widened and the interfacial structure becomes homogeneous. This is because at elevated temperatures, the copper and aluminum elements rapidly diffuse and dissolve with each other, thus resulting in the formation of new compounds. After the sample was annealed at 400°C, the layered structure in the diffusion layer of the composite disappears and the transition layer is nearly twice as wide as that annealed at the temperature of 200 °C. Clearly annealing temperature has a significant effect on the thickness of the Cu-Al diffusion layer at the same holding time. Zhang et al. (2011) also reported that inter-diffusion of atoms through the interface were enhanced with a higher temperature annealing and a much thicker Cu-Al diffusion layer was obtained.

In contrast to Figs. 4 (b), 4 (d) and 4 (f), there is sharp distribution of EDS elemental lines in Fig. 4 (b), indicating that un-annealed interface has no obvious transition layers. After the sample was annealed at 200 °C, Cu elements began to diffuse into Al due to its large diffusion coefficient, and a transition layer has been formed at the interface, indicating that the Al and Cu are metallurgically bonded under the diffusion reaction. As the annealing temperature was increased to 400 °C, the Cu-Al inter-diffused region becomes much wider from EDS analysis as clearly shown in Fig. 4 (f).

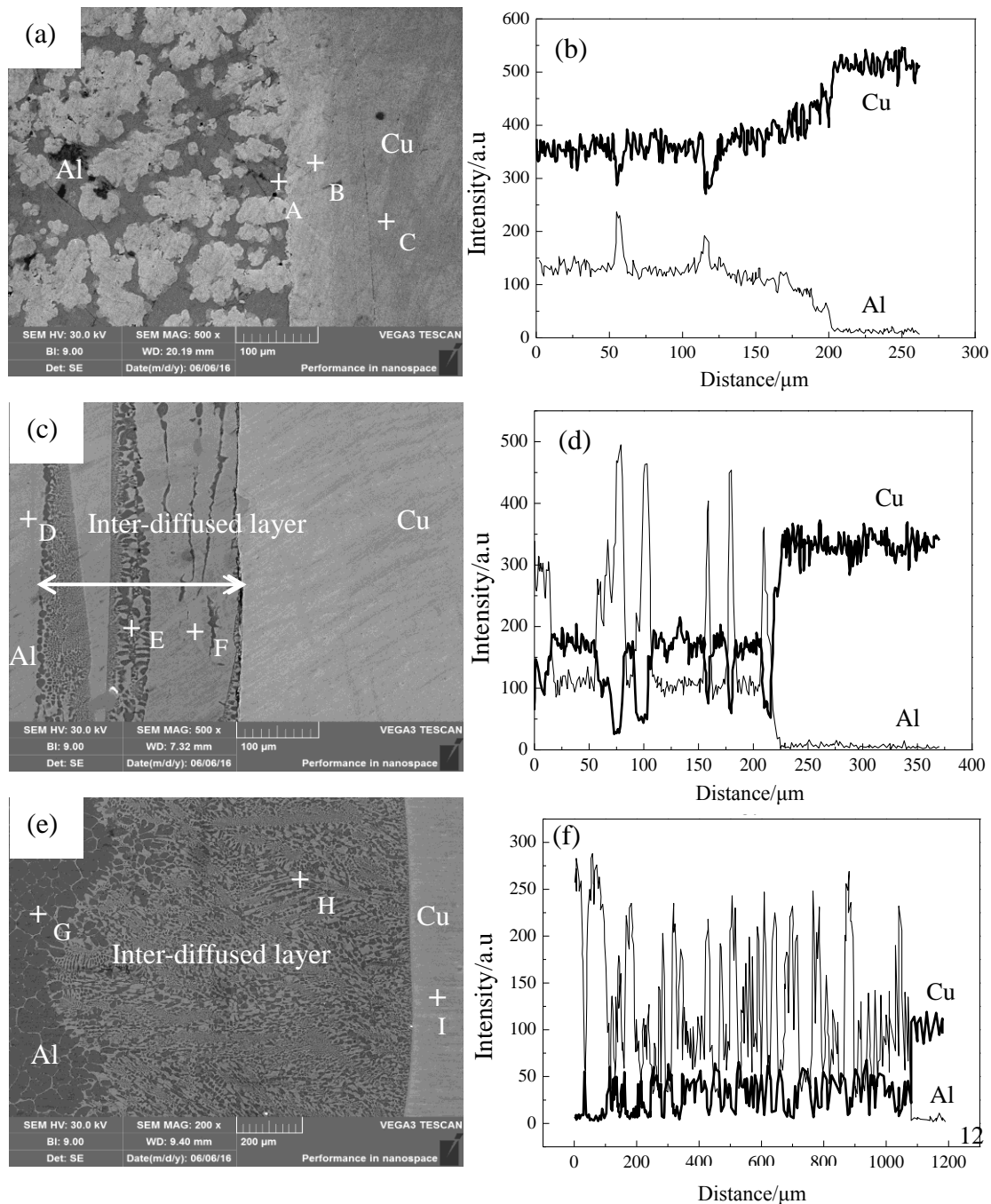


Fig.4 SEM morphology and EDS elemental line scan for Cu-Al interface under the different heating temperature at the same dwelling time

(a) and (b) un-annealed interface, (c) and (d) annealed at 200 °C for 2 hrs, (e) and (f) annealed at 400 °C for 2 hrs.

We can quantitatively describe the increase of interfacial transition layers for the copper and aluminum composites with the increase of temperature. The diffusion layer thickness values y can be calculated using the following formula (7) based on the report from Wang et al. (2014):

$$y^2 = K_0 \exp\left(\frac{-Q}{RT}\right)t \quad (7)$$

where K_0 is the diffusion coefficient (m^2/s) and t the holding time (s), Q and K_0 are the activation energy and pre-exponential factor, T is the absolute temperature (k), and gas constant R has a value of $8.314 J/(mol \times K)$.

If Cu-Al interfacial bonding is governed by the inter-diffusion between the atoms according to Eq. (7), the diffusion layer thickness values y can be calculated as we know that the values of Q and K_0 are $1.2 \times 10^5 J/mol$ and $2.3 \times 10^{-4} m^2/s$ (reported by Wang et al. (2015):

$$y = \sqrt{2.3 \times 10^8 \exp\left(-\frac{1.2 \times 10^5}{8.314 \times 473}\right) \times 7200} = 0.3 \quad (\mu m) \quad (8)$$

$$y = \sqrt{2.3 \times 10^8 \exp\left(-\frac{1.2 \times 10^5}{8.314 \times 673}\right) \times 7200} = 28.3 \quad (\mu m) \quad (9)$$

The calculated widths of the transition layer y are 0.3 μm and 28.3 μm at annealing temperatures of 473 K and 673 K, respectively, which are totally different with the experimental results of 250 μm and 780 μm . Therefore, we need to consider the other diffusion mechanisms occurring in the annealing processes.

As we know, the Cu-Al bonding is mainly controlled by the chemical reactions between atoms, therefore, the value of activation energy Q is related to the standard Gibbs free energy of each intermetallic compound produced by the chemical reaction, i.e., Q is the sum of ΔG^0 . When the annealing temperature is 200°C or 473 k, for reactions (2), (4) and (5), the values of Gibbs free energy and diffusion layer thickness y can be expressed using:

$$\Delta G_1^o + \Delta G_3^o + \Delta G_4^o = -33400 + 2.2 \times 473 - 20496.8 + 1.6 \times 473 - 20137.8 + 1.6 \times 473 = -71480.4$$

$$y = \sqrt{2.3 \times 10^8 \exp\left(\frac{-71480.4}{8.314 \times 473}\right) \times 7200} = 160 \quad (\mu\text{m}) \quad (10)$$

When the annealing temperature is 400°C or 673K, based on the reactions (2) ,(4), (5) and (6), we can obtain:

$$\Delta G_1^o + \Delta G_3^o + \Delta G_4^o + \Delta G_5^o$$

$$= -33400 + 2.2 \times 673 - 20496.8 + 1.6 \times 673 - 20137 + 1.6 \times 673 - 19653 + 3.2 \times 673$$

$$= -79899$$

$$y = \sqrt{2.3 \times 10^8 \exp\left(\frac{-79634.4}{8.314 \times 673}\right) \times 7200} = 1125 \quad (\mu\text{m}) \quad (11)$$

From above equations, the widths of the transition layer were calculated to be 251 μm and 812 μm at 473 K and 673 K, respectively, which are now very close to the experimental results (i.e., 250 μm and 780 μm , respectively). Therefore, the formation of copper-aluminum interface is the result of a combination of diffusion and interfacial chemical reactions, but the dominant process is the interfacial chemical

reaction.

Fig. 5 shows the SEM morphology and EDS elemental line scan at the Cu-Al interfaces under the different holding durations. It can be seen from Figs. 5(a), 5(c) and 5(e), inter-diffusion layer appears after the sample was annealed at 300°C for 30 min. After annealed at 300°C for 1 hr and 300°C for 2 hrs, the inter-diffusion layers are further increased, and the interfacial structures are well established. The thicknesses of the transition layers between Al and Cu are gradually widened as the holding duration is increased, because a longer annealing duration will lead to the increased chemical reactions and diffusion, thus resulting in formation of new mesophases.

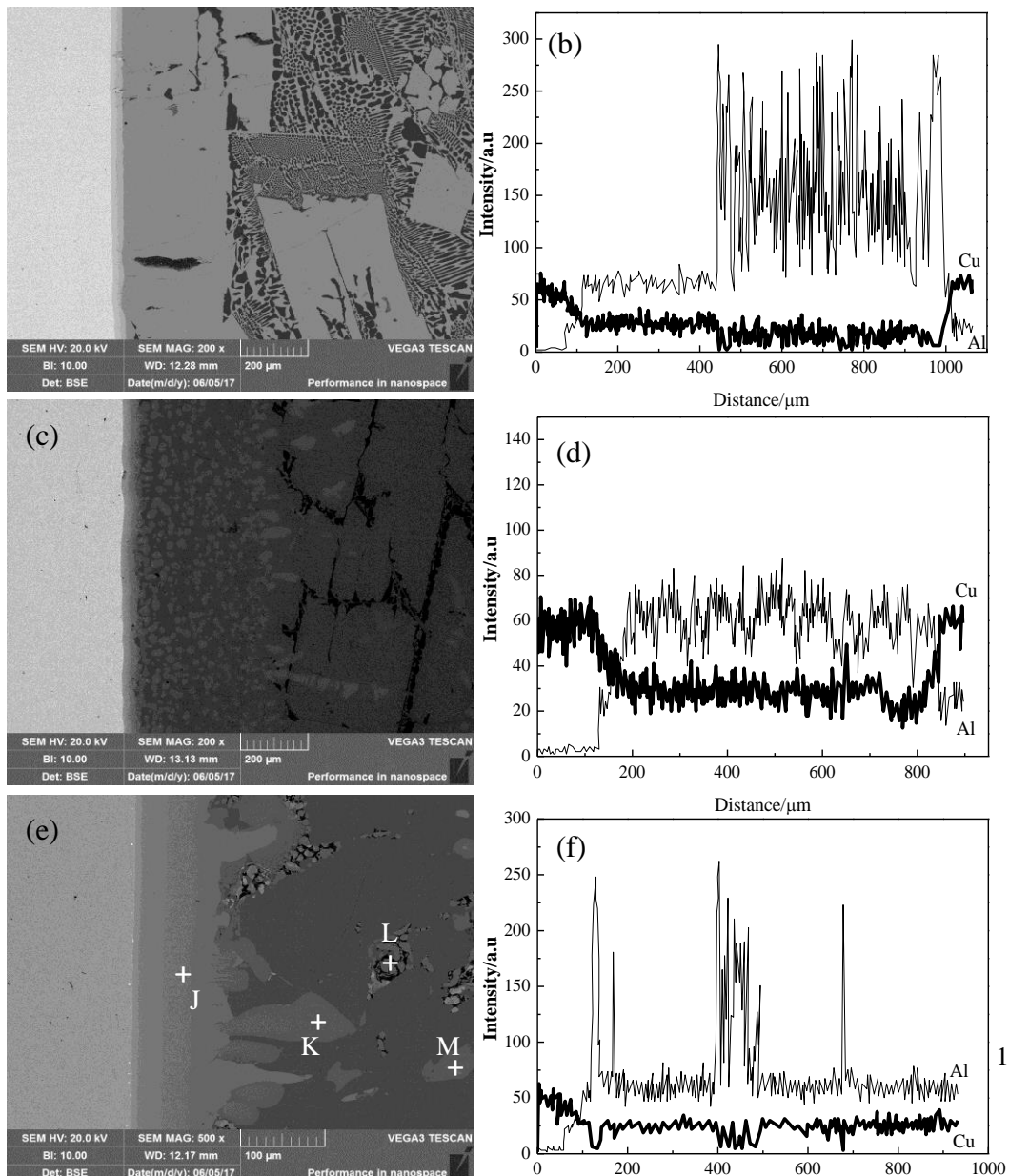


Fig.5 SEM morphology and EDS elemental line scan for Cu-Al interface under the different holding durations at the same heating temperature

(a) and (b) annealed at 300 °C for 30 min, (c) and (d) annealed at 300 °C for 1 hr, (e) and (f) annealed at 300 °C for 2 hrs.

The generation of the new phases makes inter-diffused layer much wider. Under the same annealing temperature, the different holding durations have obvious influences on the thickness of inter-diffused layer. Compared with Figs. 5(b), 5(d) and 5(f), it can be seen that Cu diffuses to Al-side after annealing at 300°C for 30 min, thus forming a transition layer with a thickness of about 400 μm. After annealing at 300°C for 1 hr, the thickness of diffusion layer becomes about 700 μm. The thickness of the inter-diffused layer is the maximum after annealing at 300°C for 2 hrs, which can be supported by the microstructural micrographs.

From Eq. (7) and reactions (2)~(6), the widths of the transition layers were calculated to be 456 μm, 562 μm and 736 μm at 573 K for 30 min, 1 hr and 2 hrs, respectively. This is consistent with the experimental results. It also indicates that the formation of Cu-Al liquid-solid aluminum composite is mainly dominated by the chemical reactions.

Fig. 6 shows the micro-hardness results of the Cu-Al bonding interface after annealed at 400 °C for 2 hours. It can be seen that the hardness of the aluminum

substrate is ~40 HV, whereas that of the copper substrate is ~80 HV. At the interfacial region, the hardness values are much higher, with the highest reading of 252 HV. This is mainly because at a higher temperature, Cu and Al will react to form intermetallic compounds, and these intermetallic compounds have much higher hardness, thus resulting in a significant increase in the hardness at the Cu-Al interfaces. At the same time, Cu and Al form a substitutional solid solution, thus resulting in lattice distortions, which can increase the resistance of dislocation movement. Therefore, the plastic deformation becomes difficult, eventually leading to a significant increase in the hardness of the bonding interface.

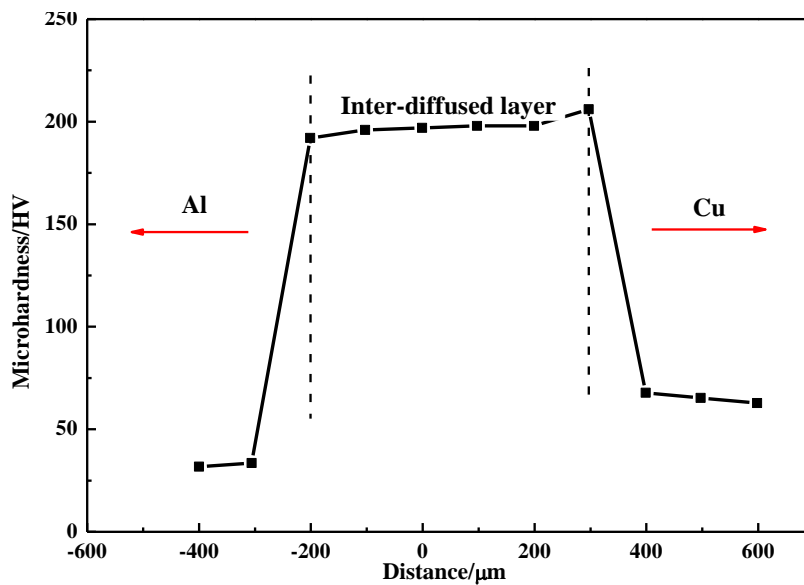


Fig.6 Micro-hardness distribution curve of Cu-Al bonding interface annealing at 400°C for 2h.

Fig. 7 shows the load-displacement curve of Cu-Al composites from the shear test under different annealing conditions. It can be seen that at different annealing temperatures, the annealed specimen shows an obvious elastic deformation initially. The shear force increases linearly with the displacement increment, and decreases abruptly after reaching a maximum load, without showing apparent plastic

deformation. The maximum strength values obtained from the samples annealed at 200 °C for 2 hrs and 400 °C for 2 hrs show little differences. When the sample was annealed at 300 °C for 2 hrs, the maximum strength values are quite low but the samples show a good ductility. With the increase of the load, the elastic deformation is insignificant for the as-sintered/un-annealed specimen. When annealed at 300 °C, the specimen with a holding time of 30 min experiences a period of elastic deformation, followed by a short period of plastic deformation and then fracture. Whereas the loading curves of the specimen with the holding time of 1 hr and 2 hrs show obvious elastic deformation, followed by fracture, without apparent plastic deformation before reaching to the maximum shear stress. The shear strength values of Cu-Al composites of unannealed, annealed at 200 °C for 2 hrs, 300 °C for 2 hrs, 400 °C for 2 hrs, 300 °C for 30 min, 300 °C for 1 hr are 30, 59, 39, 74, 56 and 49 MPa, respectively. As can be seen from the diagram, the increase of the annealing temperature leads to an increase of shear stress, while the increase of the holding time results in a decrease of the maximum shear stress. However, the shear strength of Cu-Al composites annealed at 200 °C for 2 hrs is higher than that of annealed at 300 °C for 2 hrs. This is because different intermetallic compounds are formed at the interface, and the appearance of Al₂Cu will reduce the bonding strength of the interface based on the report from Ling et al (2017). Another possible reason is that the width of the transition layer is different. Results also showed that the formation of intermetallic compounds can enhance the bonding strength of the interface up to a certain content, however, formation of large amount of compounds will deteriorate the interfacial bond strength.

According to Fig. 3, the contents of intermetallic compounds are relatively less at 300 °C, and the diffusion reaction is much faster to complete than that at 200 °C, so the plasticity of the material at 300 °C is better.

In order to further confirm the samples' fracture mechanisms, Fig. 8 shows the corresponding SEM morphology for Cu-Al shear fracture under the different annealing conditions. It can be seen that there is a ductile fracture for the unannealed sample, but for the samples annealed at different temperatures, there are obvious cleavage phenomena observed, which is the typical characteristics of brittle fracture. When the samples was annealed at 300 °C for different holding durations, some tearing morphologies can be observed on the fracture morphology, indicating a quasi-cleavage fracture. Obviously, the analysis results in Fig. 7 can be verified by the fracture photograph shown in Fig. 8.

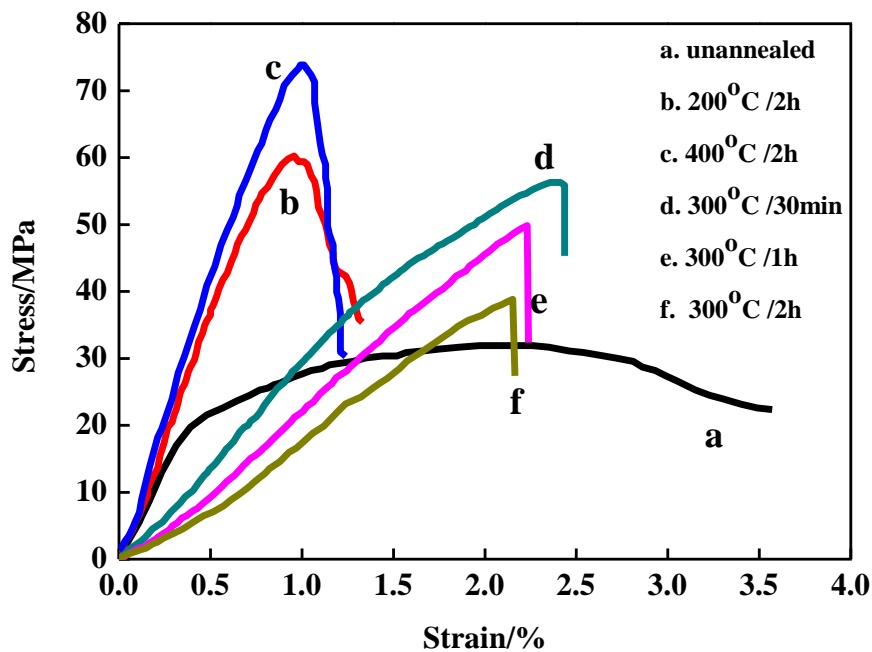


Fig.7 The shear test load-displacement curve of Cu-Al under different heat treatment conditions

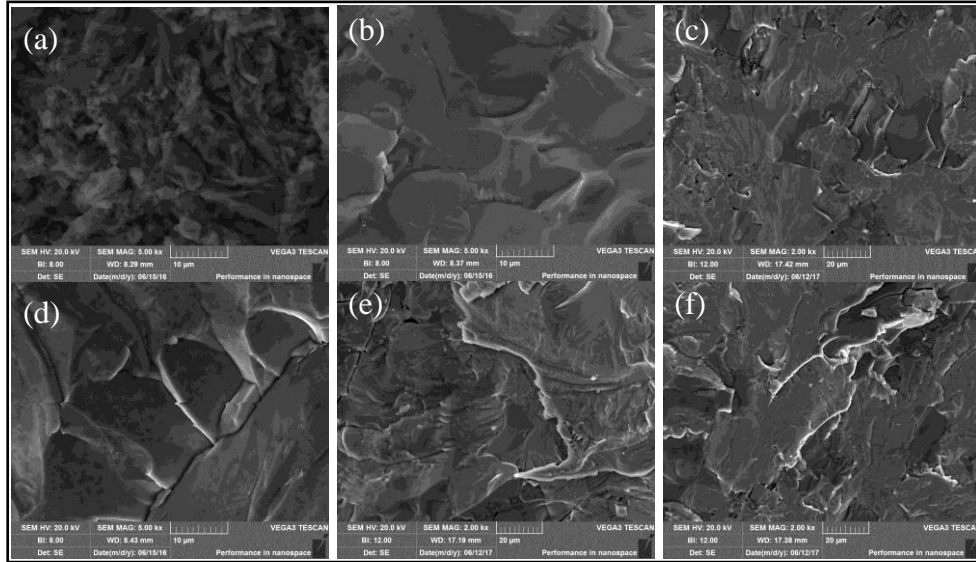
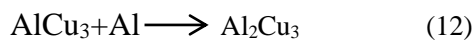


Fig.8 SEM morphology for Cu-Al shear fracture under the different annealing conditions

(a) unannealed (b) annealed at 200 °C for 2 hrs, (c) annealed at 300 °C for 2 hrs, (d) annealed at 400 °C for 2 hrs, (e) annealed at 300 °C for 30 min, (f) annealed at 300 °C for 1 hrs.

Based on the above analysis, it can be concluded that the Cu-Al interfacial layer with a strong metallurgical bonding is formed by the atomic diffusion and interfacial chemical reaction. Annealing at high temperatures, the bonds of Cu atoms (or Al ones) under the high heat activation energy will break and these atoms are inter-diffused with each other. When the liquid phases are co-existed at the high temperature of 700 °C, the inter-diffusion rate becomes much faster. Because of the same crystalline structures of copper and aluminum, they are inter-dissolved and reacted during the bonding process, thus resulting in the formation of compounds of substitutional solid solutions, which results in the significant increase of bonding strength of Cu-Al interface. In order to provide a more intuitive interpretation of the interfacial bonding

process, Fig. 9 illustrates the formation processes of Cu-Al composite interfaces. The Cu-Al binary phase diagram and the elemental energy spectra of the different regions of the Cu-Al interface diffusion layer are shown in Figs. 4 and 5 (as well as listed in Table 3). In the Cu-Al solid-liquid composite, when the temperature reaches the melting point of aluminum, aluminum melts and inter-diffusion occurs between copper and aluminum. Moreover, the diffusion rate of copper is much higher than that of aluminum. The liquid phase diffusion layer at the aluminum-side firstly generate precipitates of χ (Al) solid solution, and the liquid phase diffusion layer is then formed. At the same time, the α phase (Cu) solid solution is formed on the copper side. When the Cu content is in the range of 3 at% to 33 at%, the eutectic reaction occurs, thus the θ phase (CuAl_2) is precipitated and γ phase (Cu_9Al_4) is also formed on the copper-side. In the temperature range of 550 ~ 630 °C, the peritectoid reaction occurs and both η phase (CuAl) and ξ phase (Cu_4Al_3) are formed. With the copper content is further increased due to the inter-diffusion, δ phases (Cu_3Al_2) are subsequently formed in the sample as shown in Fig. 9. Cu and Al atoms are continuously diffused in the opposite direction when annealing treatment, and the metastable phase AlCu_3 reacts with the diffused aluminum atoms to form Al_2Cu_3 , as listed in Eq (12). With the increase of the heat treatment temperature, reactions (13) and (14) also occur, which leads to the generation of different intermetallic compounds at different annealing temperatures. These are consistent with those reported by Chen et al. (2004), i.e:



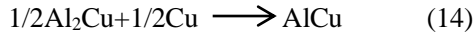


Table 3. The element contents of the energy spectrum of diffusion layer obtained from Fig. 4

(mass fraction,%).

| | A | B | C | D | E | F | G | H | I | J | K | L | M |
|----|-------|-------|-------|-------|-------|-------|------|-------|-------|-------|-------|-------|-------|
| Cu | 72.92 | 86.54 | 96.49 | 64.20 | 26.92 | 97.22 | 3.5 | 24.73 | 95.83 | 68.23 | 46.15 | 29.68 | 23.36 |
| Al | 27.08 | 13.46 | 3.51 | 35.08 | 73.08 | 2.78 | 96.5 | 75.27 | 4.17 | 31.76 | 53.85 | 70.32 | 76.64 |

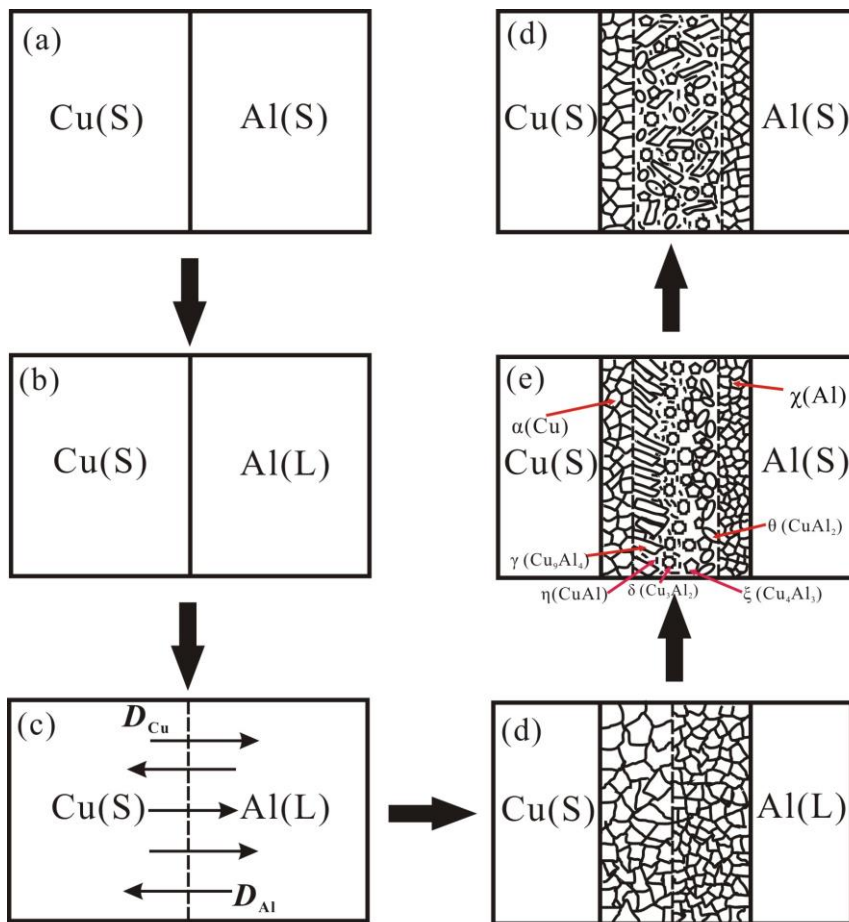


Fig. 9 Diagrams illustrating the proposed microstructure evolution of Cu-Al bonding interface

(a) physical contact, (b) instantaneous melting, (c) diffusion reaction, (d) forming solid solution, (e)

forming intermetallic compounds, (f) metallurgical combination

4. Conclusions

- 1) Cu-Al composite can be well sintered using the solid-liquid compound casting technology at 700°C under the argon atmosphere. The Cu-Al interface is smooth and a certain width of the transitional zone and elemental inter-diffusion layer can be observed. –Intermetallic compounds or solid solutions of CuAl_2 , CuAl , Cu_9Al_4 , Cu_3Al_2 , Cu_3Al are formed at the interface.
- 2) At the same holding duration, the increase of annealing temperature results in the increase of the width of the interfacial transition zone at a certain temperature. The increase of the holding duration decreases the bonding strength at the interfaces. The microhardness values of the interface are significantly higher than those of the two substrates. The shear strength values of Cu-Al composites of unannealed, annealed at 200 °C for 2 hrs, 300 °C for 2 hrs, 400 °C for 2 hrs, 300 °C for 30 min, 300 °C for 1 hr are 30, 59, 39, 74, 56 and 49 MPa, respectively.
- 3) The diffusion mechanisms of Cu-Al solid-liquid bonding are mainly (a) bulk elemental diffusion; and (b) reaction diffusion, with the latter has a more significant effect. Solid solutions and phases of η (CuAl), θ (CuAl_2), ξ (Cu_4Al_3), δ (Cu_3Al_2) and γ (Cu_9Al_4) are formed at the interface.

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