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ARTICLE

Interfacial Microstructure and Shear Strength of Cu/Al Bimetal Fabricated by Diffusion Welding

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Abstract: Cu/Al bimetals were fabricated by diffusion welding (DFW) at welding temperatures of 683~803 K for a welding time of 20~80 min under the welding pressure of 15 MPa. The scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) results of the Cu/Al interface show that the width of interface layer gradually increases with increasing the welding temperature and prolonging the welding time. After welding at 803 K for 80 min, intermetallic compounds (IMCs) of Al_4Cu_9, Al_3Cu_4, AlCu, and Al_2Cu form at the Cu/Al interface from the copper side to the aluminum side. The IMCs appear in the sequence of Al_2Cu, Al_4Cu_9, AlCu, and Al_3Cu_4. Shear test of Cu/Al bimetal shows brittle facture, and the interfacial strength increases with lower amounts of IMCs. The maximum shear strength of 63.8 MPa for the Cu/Al bimetal is obtained after DFW at a welding temperature of 723 K for 20 min.

Key words: Cu/Al bimetal; interfacial microstructure; intermetallic compounds; shear strength

Copper/aluminum bimetals have attracted much attention in theoretical and experimental studies due to their cost reduction, light weight, good conductivity and resistance to corrosion, and have been widely used in the aerospace, electronics, smelting and nuclear industries as a suitable replacement for pure copper[1-3]. Several techniques have been used to fabricate Cu/Al conductive heads, such as rolling welding[4], explosive welding[5] and vacuum hot pressing[6], while diffusion welding (DFW) has received more attention owing to its high efficiency and low cost. In particular, DFW is quite effective to realize large-area welding of dissimilar materials with large performance differences, achieving high welding strength, slight welding deformation, stable and reliable joint quality, and a large welding surface[7,8]. During DFW, plastic deformation and/or liquid phase occur at the interface between two metals under the effect of temperature and pressure, and atomic diffusion and mutual infiltration contribute to metallurgical integration. Therefore, detailed characterization of the interfacial microstructures of DFW composites is important for a better understanding of DFW process and achieving high quality composites.

Currently, Cu/Al composites have been studied by scholars around the world. Lee[8] studied the diffusion welded Cu/Al bimetal at welding temperatures of 623~923 K under a pressure of 11 MPa. The results show that 823 K is the most suitable diffusion welding temperature, and in the diffusion process, three main intermetallic compound layers form, i.e., Al_2Cu, $AlCu+Al_3Cu_4$ and Al_4Cu_9. Chen[9] studied the development and growth dynamics of the interface structure of cold-rolled aluminum/copper bimetallic plates. The results show that the Cu/Al interface has an obvious multilayer interdiffusion structure, and the growth of these intermetallic compounds is achieved by the diffusion process. It was also found that the activation energy of Al_2Cu, $AlCu+Al_3Cu_4$, Al_4Cu_9 and the total intermetallic layer is 97.5, 107.4, 117.5 and 107.8 kJ/mol, respectively. Cheng[10] analyzed interfacial microstructure of Al/Cu bimetal at a pressure of 15 MPa and a welding time of 1 h. Based on the interface thickness of the prepared sample, it was found that the thickness of diffusion layer augments from 3.5 μm to 23.6 μm as the welding temperature increases from 723 K to 893 K. Chen[11] studied the effect of interface structure on the welding strength of Cu/Al composites, and the results show that the generation of intermetallic compounds promotes the propagation of cracks

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and weakens the welding strength of composites. With the thickening of the interface, the fracture mechanism changes from ductile fracture to brittle fracture. Nowadays, there is little systematic research on the preparation of Cu/Al conductive heads by diffusion welding.

In this research, Cu/Al bimetals were fabricated by diffusion welding at different welding temperatures and welding time, and microstructure and mechanical properties of the interface were studied. In particular, the IMCs formation trends and fracture mechanisms of the Cu/Al interface were analyzed. The results generated herein may provide theoretical guidance for the preparation of high-quality Cu/Al conducting heads.

1 Experiment

The raw materials used were pure T2 copper and pure 1060 aluminum. Cylindrical specimens with a diameter of 40.0 mm and a height of 30 mm were prepared from the T2 copper and pure 1060 aluminum bars. Before welding, the surfaces to be bonded were ground with SiC paper (grade 800#). Then, pure aluminum was placed in 5wt% NaOH solution and soaked for approximately 30 s. The pure copper was soaked in 10vol% HNO_3 for 10 min. Fig.1 shows schematic diagram of diffusion welding. The Cu/Al specimens were vertically placed in the chamber after furnace vacuum reached up to 5.0×10^{-3} Pa. The heating rate was 288 K/min, the welding temperatures were 683, 723, 763 and 803 K, the welding time was 20, 40, 60 and 80 min and a pressure of 15 MPa was applied. After the Cu/Al welding was completed, the sample was cooled in the furnace.

The interface microstructure and fracture morphology were observed by a JSM-6700f field emission scanning electron microscope (FESEM) and an Oxford INCA energy dispersive spectrometer. X-ray diffraction (XRD) test was conducted by a 7000S X-ray diffractometer to detect the crystallographic phases in the shear fracture. The parameters during XRD were as follows: the diffraction angle ranged from 20° to 80°, the scanning speed was 8°/min and the step size was 0.02°/s. The XRD results were analyzed by Jade8.0 software. An HT-2402-100 materials test machine was used to carry out the shear test for Cu/Al bimetal. During sample loading, the sample and die shear plane were in the same vertical plane, and the load was applied after preloading and perpendicular to the sample pressure. The stress-strain curve was obtained through a shear test, and different interface welding strengths in the Cu/Al specimen were measured to determine the influence on the mechanical properties of the interface. Fig.2 shows schematic illustration of the shear strength test and size of the shear test specimen with a unit of mm.

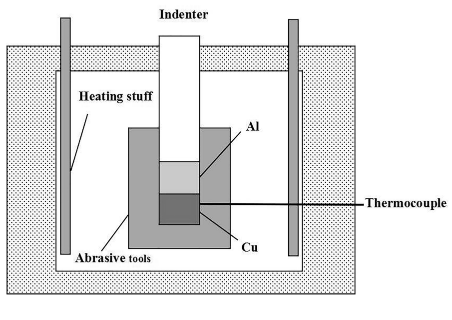

Fig.1 Schematic diagram of diffusion welding

2 Results and Discussion

2.1 Interfacial microstructure evolution

Fig.3 shows typical back-scatter-electron (BSE) images of the Cu/Al interface under different welding parameters. The EDS results of regions marked in Fig.3e and 3f are shown in Fig.4. Fig.3a shows that cellular or island-like structures appear at the interface, and the oxide film is only partially broken at the initial stage of the reaction. Therefore, the newly formed phase is distributed at the interface in isolation. Most Al_2Cu and Al_4Cu_9 phases exist together, but only the Al_2Cu phase exists in some areas. This also confirms that Al_2Cu is formed first, and Fig.4 confirms the result. As shown in Fig.3b, when copper and aluminum are in direct contact, the Cu and Al atoms begin to diffuse into each other. A diffusion solid solution zone is formed on both sides of the interface, and it is easy to form a super-saturated solid solution around the crystal with structural defects. The structure of a super-saturated solid solution is often in an unstable state, and it is easy to generate an IMC crystal core. Since the ultimate solubility of Cu in Al is lower than that of Al in Cu and the diffusion rate of Cu in Al is much higher than that of Al in Cu[12], the super-saturated solid solution region appears on the Al side of the interface first, and then the intermetallic compound Al_2Cu is formed by precipitation. The Al_4Cu_9 nucleates on the Al_2Cu. As shown in Fig.3c, with increasing the reaction time, the newly formed

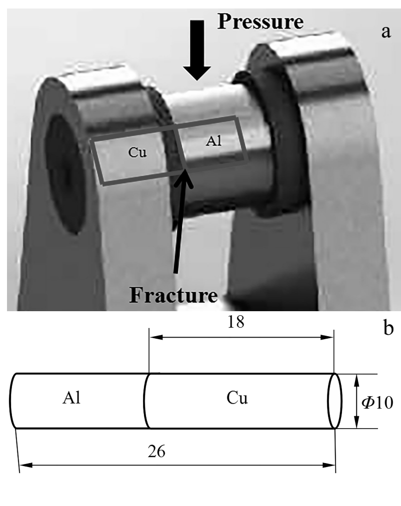

Fig.2 Schematic illustration of the shear strength test (a) and size of the shear test specimen (b)

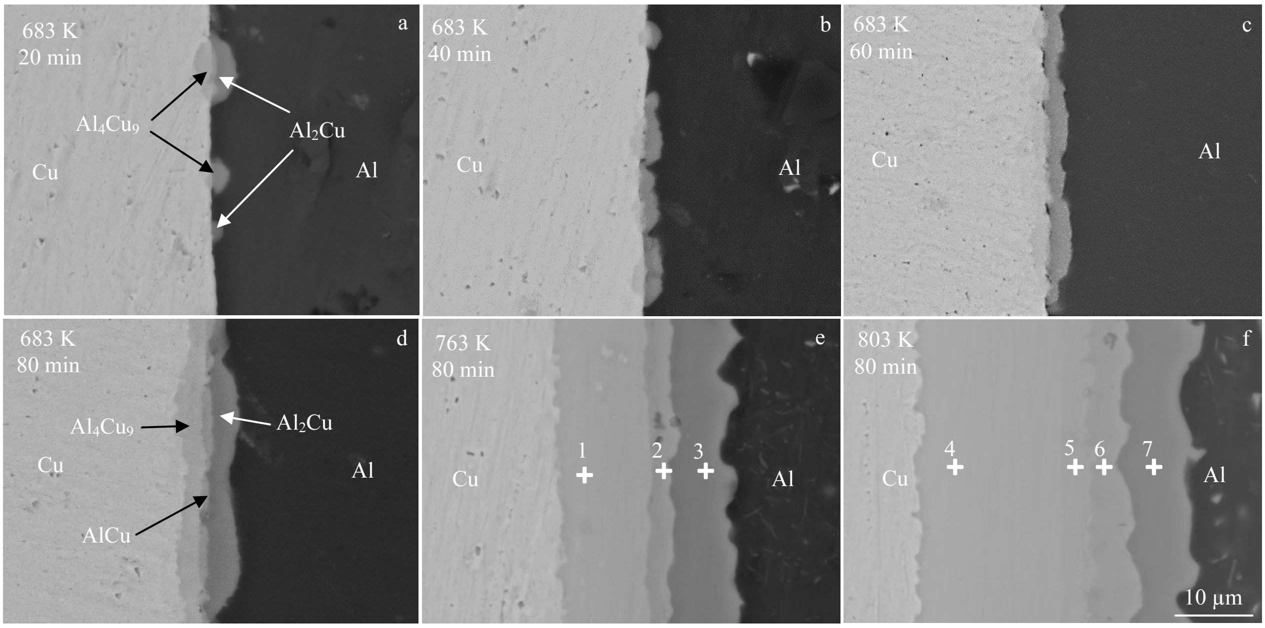

Fig.3 Typical BSE images of Cu/Al interface under different welding parameters: (a) 683 K, 20 min; (b) 683 K, 40 min; (c) 683 K, 60 min; (d) 683 K, 80 min; (e) 763 K, 80 min; (f) 803 K, 80 min

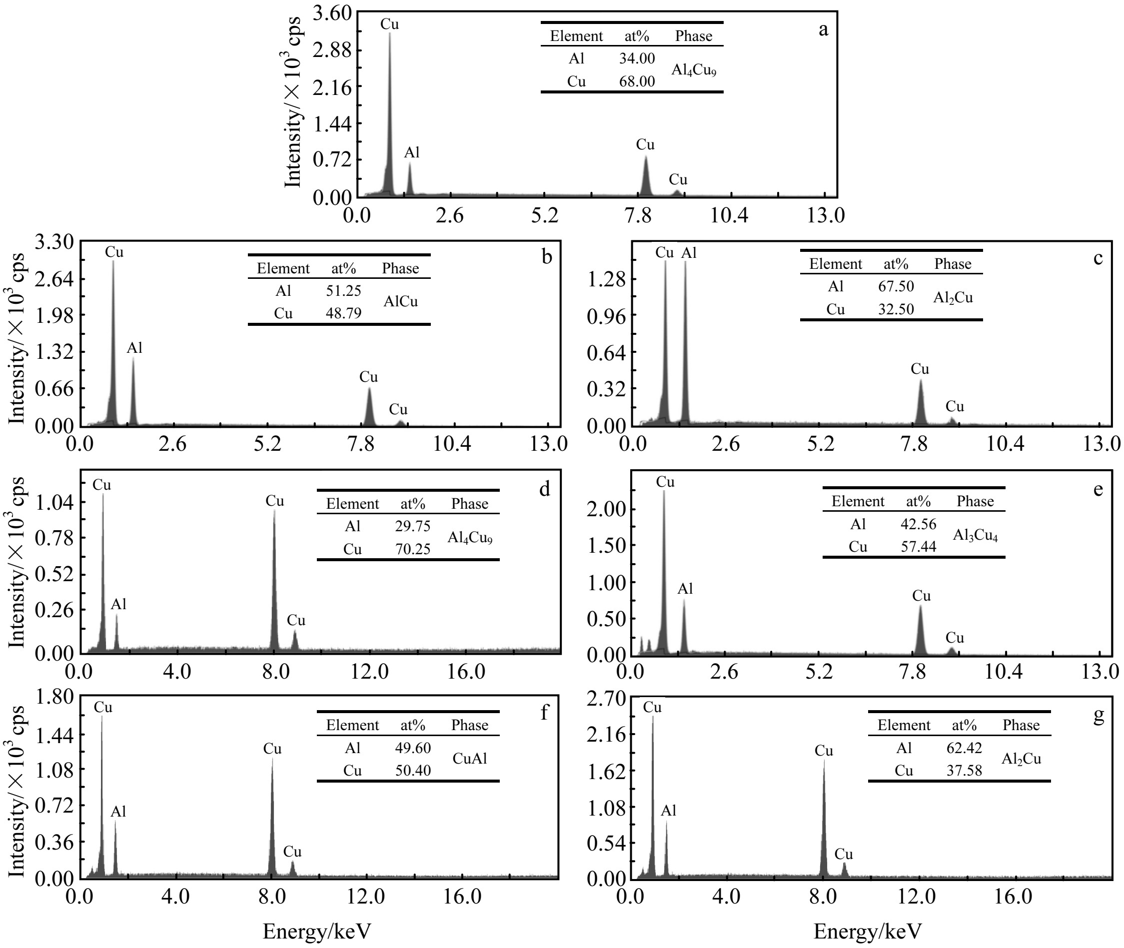

Fig.4 EDS results of typical regions 1~3 marked in Fig.3e (a~c) and regions 4~7 marked in Fig.3f (d~g)

isolated island inter-metallic compounds Al_4Cu_9 and Al_2Cu begin to grow. The growth direction is mainly along the interface, followed by growth along the vertical interface. This is mainly because the activation energy for surface diffusion is lower than that of volume diffusion. So the diffusion of atoms along the interface is faster[13]. As shown in Fig.3d, with the continuous diffusion of Cu and Al atoms to the opposite side, the layers of Al_4Cu_9 and Al_2Cu become thicker gradually, and the Al_4Cu_9 is relatively dense. Therefore, the diffusion of Cu atoms is hindered, and a decreased number of Cu atoms react with Al_2Cu to form the AlCu phase, which is distributed in an island-like shape at the initial stage. As shown in Fig.3e, Al_4Cu_9 and Al_2Cu gradually grows along the direction perpendicular to the interface, which is due to a continuous reaction after formation; the effect of surface diffusion and grain boundary diffusion is gradually declined, volume diffusion begins to play a major role, and the elements in the reaction layer are homogenized. From the energy point of view, this is also consistent with the gradual decrease in the surface energy of the system. As shown in Fig.3f, when the Al_4Cu_9, AlCu and Al_2Cu phases grow to a certain thickness, the fourth phase, namely Al_3Cu_4, appears. Currently, there is almost no exact theoretical basis for the formation of the Al_3Cu_4 phase. Moreover, the nucleation process of the Al_3Cu_4 phase is not observed in the experiment. Due to its long incubation period and fast growth rate, the nucleation process of the Al_3Cu_4 phase is difficult to observe in the experiment. However, according to the nucleation and growth processes of other three phases, the Al_3Cu_4 phase also conforms to this trend: first nucleating between the Al_4Cu_9 and AlCu phases, then growing and welding along the interface, and finally extending longitudinally.

2.2 Kinetics of the interfacial layer formation

In general, the thickness of the interfacial layer is controlled by diffusion dynamics, and the growth of the interfacial layer conforms to the empirical formula[14]:

$$y=Kt^n \tag{1}$$

where y is the thickness of the diffusion layer; K is the growth rate constant, m^2/s; t is the diffusion reaction time, s; n is the time exponent. n=1 indicates that the growth of the intermetallic compounds is controlled by the reaction rate, and the diffusion layer thickness has a linear relationship with time. n=0.5 indicates the diffusion control of the intermetallic compound growth, and the diffusion layer thickness has a parabolic relation with time. Fig.5 shows the linear fitting curve of the interface layer thickness changing with time and temperature under different heat treatment conditions. The thickness of the Al_3Cu_4 phase is calculated along with the AlCu phase. It can be seen that the growth trend of the boundary layer thickness is the same at different temperatures, and the square root of the time and thickness of the interface layer has a strong linear relationship (correlation factor R^2 is greater than 0.96, as shown in Table 1), indicating that the growth of the interface layer of Cu/Al composite material is parabolic, and n is 0.5.

Table 1 shows the values of K^2 and R^2 under different heat treatment conditions. For isothermal reaction conditions, the Arrhenius relationship between diffusion coefficient K and

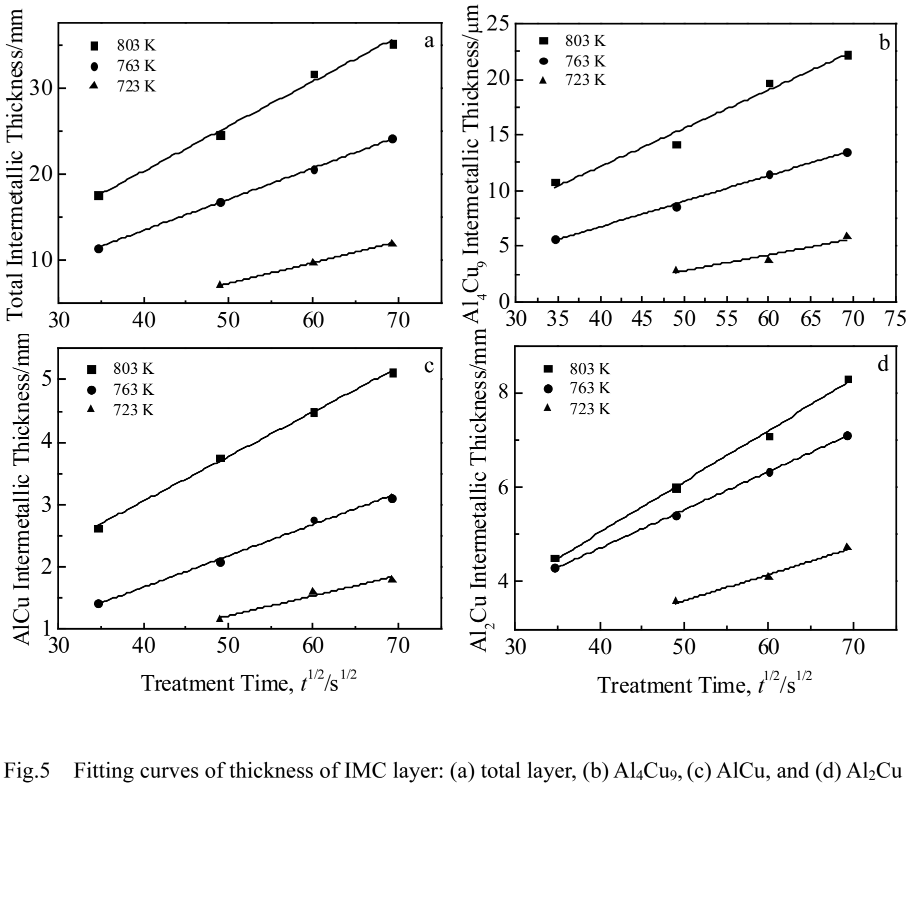

Fig.5 Fitting curves of thickness of IMC layer: (a) total layer, (b) Al_4Cu_9, (c) AlCu, and (d) Al_2Cu

Table 1 Calculated growth rate constants K^2 and the correlation factor R^2 of the fitting curve

Temperature/K	IMC	R^2	$K^2/\times10^{-14}$ m^2·s^{-1}
723	Al_4Cu_9	0.94	2.04
	AlCu	0.997	0.104
	Al_2Cu	0.995	0.31
	Total	0.993	5.855
763	Al_4Cu_9	0.996	5.29
	AlCu	0.991	0.254
	Al_2Cu	0.999	0.66
	Total	0.999	13.13
803	Al_4Cu_9	0.967	11.93
	AlCu	0.943	0.513
	Al_2Cu	0.998	1.17
	Total	0.990	27.21

temperature T is satisfied[15]:

$$K^2 = K_0^{\,2}\exp\left(-\frac{Q}{RT}\right) \quad (2)$$

where K_0 is the frequency factor, m^2/s; Q is the diffusion activation energy, J/mol; R is the gas constant, 8.314 J·mol^{-1}·K^{-1}; T is the thermodynamic temperature, K. Fig.6 shows the linear fitting of T and K^2, and the slope of the curve is $-Q/R$. Therefore, the growth activation energy of the entire interface layer, Al_4Cu_9, AlCu and Al_2Cu can be calculated, and these values are determined to be 92.74, 106.44, 96.03 and 79.81 kJ/mol, respectively.

Braunovic[15] found that the growth rate and activation energy of IMCs are also different in different temperature ranges when studying rolled composites. When the temperature is lower than approximate 623 K, the activation energy Q=66.72 kJ/mol, and when the temperature is higher than 623 K, the activation energy Q=133.42 kJ/mol. The reason for the low activation energy at 623 K is that the crystal defects and dislocations increase. Increased temperatures are considered to reduce crystal defects, and the diffusion mode is mainly controlled by volume diffusion. In this study, the diffusion activation energy of the intermetallic compounds obtained in the temperature range of 723~803 K is similar to that calculated by Braunovic et al[15] at the annealing temperature above 623 K. Upon comparing the properties of rolling annealing and diffusion, it is determined that both the temperature fields and stress fields have similar action modes, and the time of action of the stress fields and temperature fields is different. From the perspective of time, it takes less time to achieve the same diffusion degree and act at the same time. In addition, the diffusion activation energy of Al_2Cu is lower than that of other IMCs because Al_2Cu belongs to the tetragonal crystal system; compared with the properties of other cubic or rhombic crystal system compounds, the tetragonal crystal structure is more prone to dislocations, vacancies and other crystal defects, and atoms diffuse readily through crystal defects. Fig.3d and 3f show that at 683 K, the intermetallic compound width is only 9.57 μm, and as the temperature increases to 803 K, the interface thickness is 31.68 μm. With increasing the temperature, the thickness of the intermetallic compound increases. The higher the thermal diffusion activation energy, the higher the copper and aluminum diffusion speeds as they increase

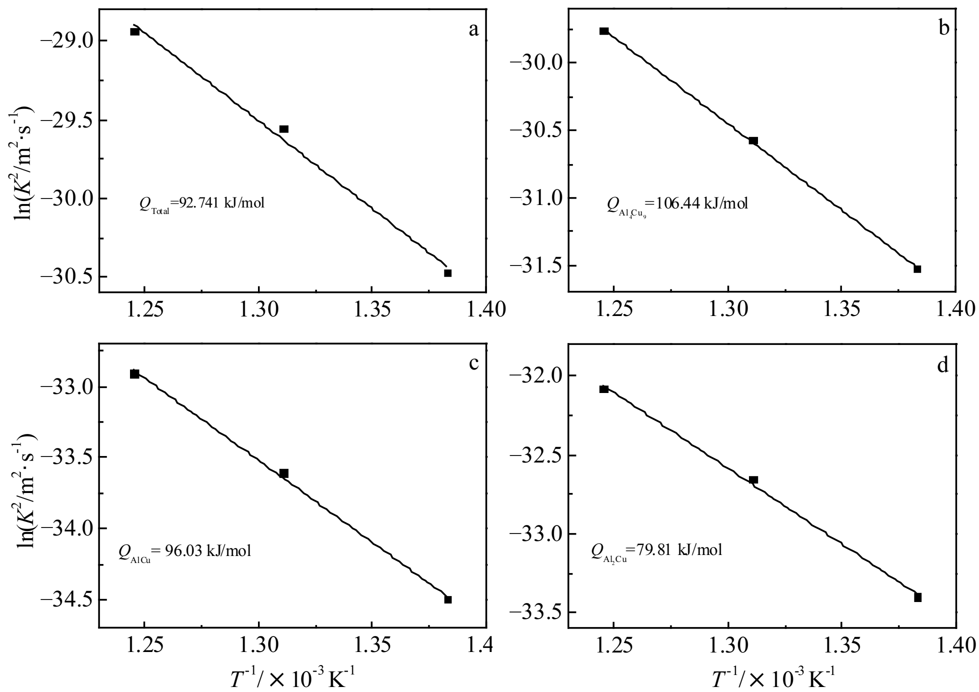

Fig.6 Relation between lnK^2 and T^{-1} for different IMCs: (a) total layer, (b) Al_4Cu_9, (c) AlCu, and (d) Al_2Cu

exponentially. The copper and aluminum atoms constantly move to the front of the interface, and the macroscopic interface width increases. It can be seen from the growth of various intermetallic compounds that the growth order of these three intermetallic compounds is Al_2Cu, AlCu and then Al_4Cu_9. However, a large number of studies[8,9] have shown that on the composite interface, the Al_2Cu phase is generated first, followed by Al_4Cu_9 and AlCu. The kinetics cannot explain the phenomenon because the formation order of intermetallic compound depends on not only the diffusion coefficient and diffusion activation energy but also ΔG_0, as ΔG_0 decreases. It is known that the ΔG_0 value of the Al_4Cu_9 phase is far less than that of other intermetallic compounds, so the Al_4Cu_9 phase appears as the second phase after Al_2Cu.

In summary, during the early stage of the diffusion welding of the interface, many kinds of defects exist, and the compounds formed by the atomic concentrations are far from enough. Diffusion dynamics gradually eliminate defects, such as holes and lattice distortion. The element concentrations increase at the interface, and thermodynamic driving forces gradually increase to values larger than the dynamic constraints.

2.3 Interfacial welding strength

Fig.7 shows effect of welding temperature on shear strength of Cu/Al bimetal at a welding time of 20 min, while Fig.8 shows effect of welding time on shear strength of Cu/Al bimetal at a welding temperature of 803 K. With increasing the temperature, the shear strength first increases and then decreases. When the welding temperature is 723 K, the maximum shear strength is 63.8 MPa. With increasing the welding time, the shear strength tends to decrease. XRD analysis was performed on the fracture on the Cu side. Fig.9 shows the XRD results of the Cu/Al fracture at different temperatures; there are three intermetallic compounds including Al_4Cu_9, AlCu and Al_2Cu on the fracture surface. However, the peak value of Al_4Cu_9 is very weak. As the temperature increases, the Cu peak obviously decreases, and the diffraction peak of the three intermetallic compounds

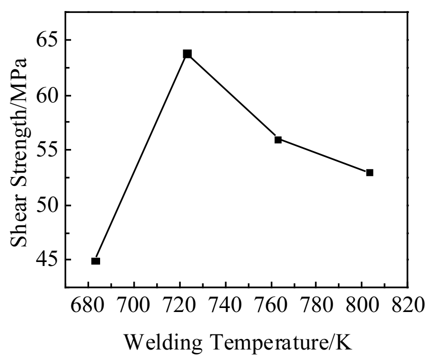

Fig.7 Effect of welding temperature on shear strength of Cu/Al bimetal at a welding time of 20 min

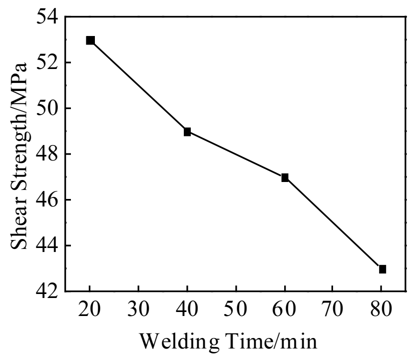

Fig.8 Effect of welding time on shear strength of Cu/Al bimetal at a welding temperature of 803 K

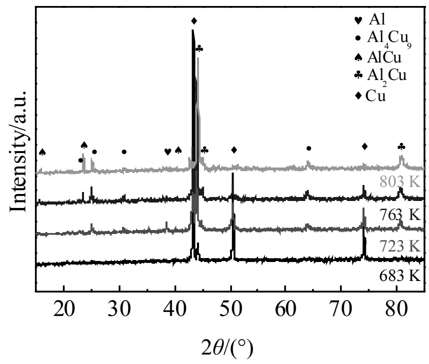

Fig.9 XRD patterns of fracture morphology of Cu side at different welding temperatures

increases gradually until 803 K.

When the Cu peak almost disappears, the peak value of each intermetallic compound reaches the maximum value. The X-ray detection of a certain depth is also reflected from the side that the temperature rises at 763 and 803 K for 60 min of welding, which will lead to the thickening of the intermetallic compound layer, so the Cu peak intensity decreases, and the peak strength of the intermediate layer increases. Fig.10 shows shear fracture surfaces of Cu/Al bimetal under different welding parameters. The EDS results of typical regions in Fig.10 (A, B, C) are shown in Fig.11. Fig.10 shows the fracture morphologies of the Cu side. Fig.10a shows that the fracture is essentially flat at the welding temperature of 683 K. On the black matrix, there are evenly distributed granular compounds and unwelded areas, and the granular compound in region A is the AlCu+oxide phase according to EDS analysis in Fig.11. As the welding temperature increases to 723 K, the grain size in the fracture surface is small, and the intergranular fracture characteristics are not obvious (Fig.10b and 10c). As shown in Fig.11, regions B and C in Fig.10b indicate the AlCu phase and Al_2Cu phase, respectively. Therefore, it can be

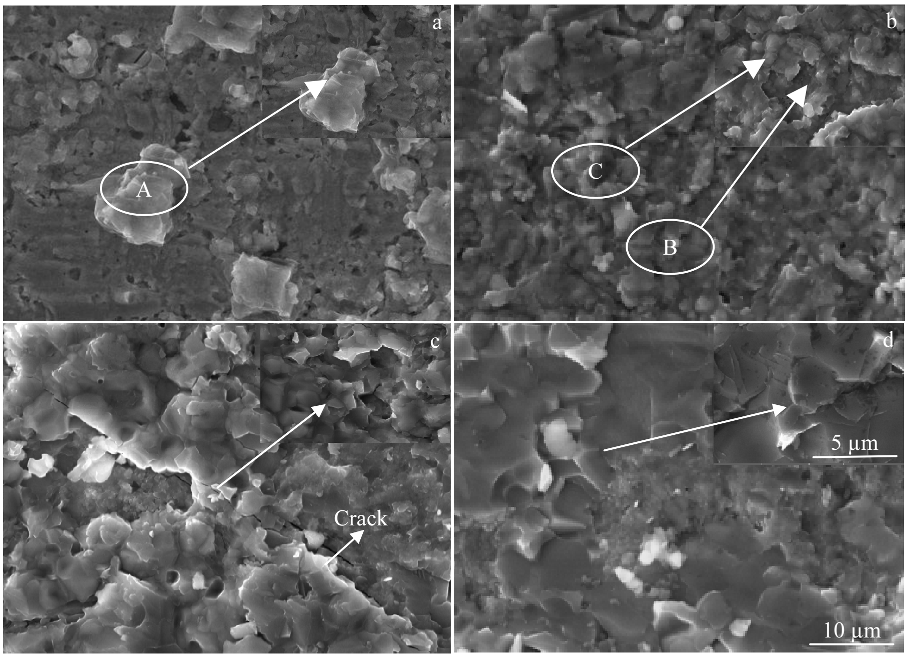

Fig.10 Shear fracture surfaces of Cu/Al bimetal at different welding temperatures for 60 min: (a) 683 K, (b) 723 K, (c) 763 K, and (d) 803 K

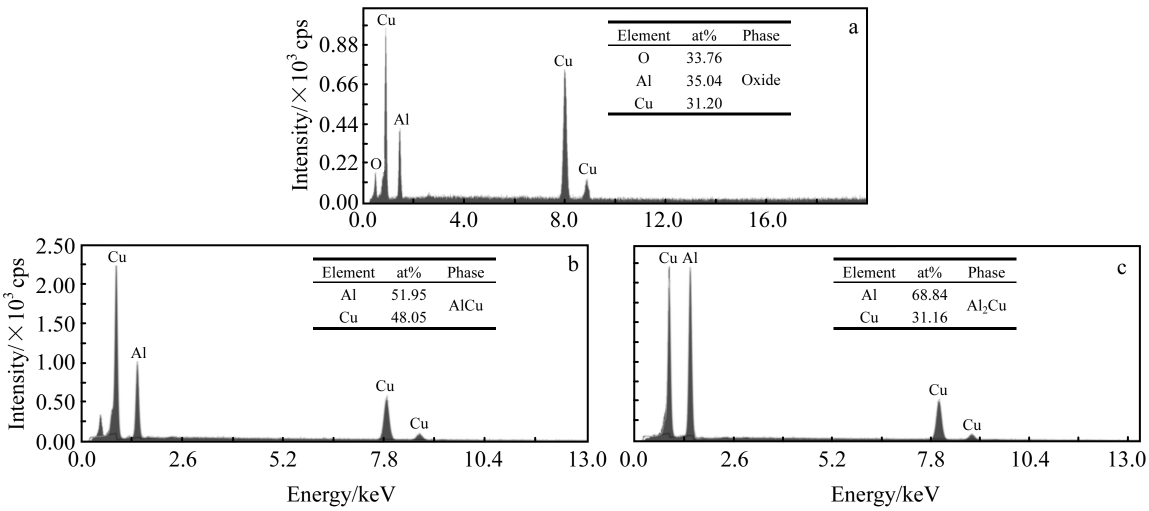

Fig.11 EDS results of typical regions A (a), B (b), and C (c) marked in Fig.10

concluded that the fracture occurs mostly on the Al_2Cu side and Al side, and a small part of the fracture occurs between the Al_2Cu and AlCu because the Al_2Cu layer is relatively narrow. With increasing the welding temperature, it can be seen from Fig.10 that all fracture morphologies contain obviously equiaxed grains, which is also an obvious intergranular fracture feature[16,17]. As shown in Fig.10c, there are cracks on the matrix (AlCu) at a welding temperature of 763 K, which is due to the Kirkendall effect caused by the large difference in the expansion coefficient of the copper and aluminum wires during the hot-press welding process[17]. The crack occurs easily when the atoms in the AlCu phase and the AlCu phase are distorted and have a large thermal stress. As the welding temperature increases to 803 K, the AlCu phase is completely invisible, and the fracture occurs between the Al_2Cu and Al matrix; there are many polygon steps, and each polygon represents the interface of each grain. As shown in Fig.10, the growth pattern of the Al_2Cu grains in the cross section is observed. As the temperature increases from 723 K to 803 K, the grains of the Al_2Cu phase gradually increase. As a consequence, shear strength of Cu/Al bimetal decreases, as shown in Fig.5.

3 Conclusions

1) Cu/Al bimetals are fabricated by diffusion welding. The interface phase is generally divided into three layers: Al_4Cu_9, AlCu and Al_2Cu phases. A new phase of Al_3Cu_4 forms with increasing the welding time and temperature.

2) According to the Arrhenius formula and the growth activation energy of the entire interface layer, Al_4Cu_9, AlCu, and Al_2Cu, $\ln K^2$-T^{-1} relationship curves are fitted, and the diffusion activation energy is 92.74, 106.44, 96.03 and 79.81 kJ/mol, respectively. The formation of interfacial phase is in the sequence of Al_2Cu, Al_4Cu_9, AlCu and Al_3Cu_4 based on phase transition thermodynamics and practical applications.

3) The shear strength of the Cu/Al bimetal increases with increasing the welding temperature from 683 K to 723 K, and then decreases with further increasing the welding temperature. The increase in intermetallic compounds mainly contributes to the decrease of the shear strength. The optimal process parameter is 723 K for 20 min, under which shear strength can reach 63.8 MPa.

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扩散连接制备 Cu/Al 双金属及其界面组织与剪切强度

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摘　要：采用扩散焊（DFW）技术制备了 Cu/Al 双金属，连接温度范围 683~803 K，连接时间范围 20~80 min，连接压力 15 MPa。Cu/Al 双金属界面处的 SEM 实验结果表明，随着焊接温度的升高和保温时间的延长，界面层厚度逐渐增加，在连接温度为 803 K，连接时间 80 min 时，Cu/Al 界面处形成了 Al_4Cu_9，Al_3Cu_4，AlCu 和 Al_2Cu 金属间化合物（从铜侧到铝侧）。根据扩散动力学，金属间化合物（IMCS）的生成顺序为 Al_2Cu、Al_4Cu_9、AlCu、Al_3Cu_4。Cu/Al 双金属的剪切试验显示为脆性断裂，并且界面强度随着 IMC 的减少而增加。在 723 K 的焊接温度下进行 20 min 焊接后，Cu/Al 双金属的抗剪切强度最高为 63.8 MPa。

关键词：铜铝双金属；界面微观结构；金属间化合物；剪切强度

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