The formation and growth of intermetallic compounds during interdiffusion of Al/Cu bimetals

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Abstract

The diffusion couple technology was used to study the formation and growth of intermetallic compounds (IMCs) of Al/Cu bimetals at the temperature range of 480–540 °C for 5–20 h. The interfacial microstructure formed during interdiffusion and the growth kinetics of IMCs are determined. The results show that four different kinds of IMCs (Al₂Cu, Al₄Cu₉, AlCu and Al₂Cu₃) were formed at the Al/Cu interface, which is related to the interfacial diffusion reaction and the migration of phase interfaces. The growth of IMCs is mainly controlled by volume diffusion, and follows a parabolic growth kinetics, i.e. \( L = kt^{1/2} \). Based on the effective heat of formation model and Gibbs free energy change calculation, the Al₂Cu is predicted to form first and the formation sequence of the four IMCs is Al₂Cu, Al₄Cu₉, AlCu and Al₂Cu₃.

1. Introduction

Al/Cu bimetals are potential materials for industrial applications due to their excellent properties combining lightweight, corrosion resistance of aluminum, with good electrical and thermal conductivity of copper [1, 2]. However, the formation and growth of intermetallic compounds (IMCs) at the interface have a detrimental influence on both mechanical and electrical properties of the Al/Cu bimetal materials [3–5]. Therefore, to obtain a better understanding of the growth behavior of IMCs at the interface is technically and scientifically important for the production of Al/Cu bimetal materials, such as copper-clad-aluminium (CCA) wire [6], Al/Cu laminated composite [7, 8] and Al/Cu wire bonds [9].

Previous studies have shown that different IMCs may form at Al/Cu interface under different methods and technological parameters used in the experiments. The work report by Y. Funamizu and K. Watanabe [10] focus on the interdiffusion in Al/Cu diffusion couples at the temperature range of 400–535 °C for up to 80 h, where all of the five intermediate phases (Al₂Cu, Al₄Cu₉, Al₃Cu₁₄, Al₂Cu₃ and Al₆Cu₁₉) existing in the phase diagram were formed in the diffusion zone. Ke Liu et al. [11] studied the kinetics of reaction diffusion in Al-Cu binary systems recently by means of diffusion couple technology, where four kinds of IMCs (Al₂Cu, Al₄Cu₉, Al₃Cu₁₄ and Al₆Cu₁₉) were formed at 400 and 540 °C for 360 and 48 h, respectively. Chien-Pan Liu et al. [12] studied the interfacial formation and kinetic growth behavior of IMCs during high thermal storage reliability test. It was found that Al₂Cu, Al₄Cu₉ and Al₆Cu₁₉ were formed at the interface after 2000 h of annealing at 150 °C. The same IMCs were also detected by F. Moisy et al. [13] in the early stage of the reactive interdiffusion of CCA wires annealed at 300–350 °C using in-situ TEM. Only two IMCs (Al₃Cu and Al₆Cu₁₉) were found in Al/Cu clad material fabricated by differential speed rolling followed by a post heat treatment at 400 °C for 60 min [14]. Therefore, the types and amounts of IMCs at the Al/Cu interface are closely related to the preparation technology and the corresponding heat treatment. Meanwhile, understanding the growth characteristics and the formation sequence of the IMCs is conducive to optimize the interfacial bonding for Al/Cu bimetals. However, there is still some differences on the types and the formation sequence of IMCs about the reactive diffusion between Al and Cu that need to be clarified.
In this study, the diffusion couple technique was employed, which can establish a correlation between the morphology developed in the diffusion zone of the couple and a certain type of phase relations in the system [15]. The formation and growth of IMCs at Al/Cu interface during isothermal diffusion at different temperatures for different diffusion times were mainly studied. The interfacial microstructure formed during diffusion bonding are examined. The growth kinetic and the activation energies of the IMCs are determined simultaneously. Besides, the sequence of IMCs formation and the related mechanism are discussed. This work paves an avenue for regulating interface IMCs and optimizing interfacial bonding of Al/Cu bimetallic materials.

2. Experimental procedure

Pure Al (99.99 wt%) and pure Cu (99.97 wt%) cylindrical samples with a diameter of 15 mm and a length of 10 mm were used to prepare Al/Cu diffusion couples. Firstly, the cross-sections of the Al and Cu samples were carefully ground, fine polished and ultrasonically cleaned in acetone to remove the oxide layer and modify the initial interface contact. Secondly, the surface-treated Al and Cu samples were preliminary mechanical bonded under an applied axial pressure generated by a tablet press (axial pressure 100 MPa and dwell time 15 min), then further clamped and fixed with stainless steel clamp. Finally, the assembled Al/Cu samples were placed in a vacuum tube furnace, and the diffusion heat treatment experiments were conducted at various temperatures of 480, 500, 520 and 540 °C for different diffusion times of 5, 10, 15 and 20 h, respectively. After the heat treatment experiments, the Al/Cu diffusion couples were taken out of the furnace and cooled in air. The temperature was measured using a K-type thermocouple just above the diffusion couple. The schematic diagram of the preparation and diffusion heat treatment of Al/Cu diffusion couple is shown in figure 1(a).

Scanning electron microscope (SEM, Zeiss supra 55) was used to characterize the interfacial microstructures in the diffusion zone. Combined with Al-Cu binary phase diagram (figure 1(b)), the distribution of elements and the type of IMCs in the diffusion zone were examined using energy dispersive spectroscopy (EDS) and electron probe microanalysis (EPMA-1600). It can be seen that five IMCs, including Al2Cu (θ), AlCu (η2), Al3Cu4 (ξ2), Al3Cu5 (δ) and Al4Cu9 (γ1), may formed at the diffusion temperature \( T = 480–540 \, ^\circ C \) investigated in this study. The samples were cut perpendicular to the diffusion contact surface and then the longitudinal section of the diffusion couples were ground, polished and ultrasonic cleaned using conventional metallographic techniques. To understand the performance of IMCs, nanoindentation test was conducted at room temperature across the interfacial region.

3. Results and discussion

3.1. Intermetallic compounds and nanoindentation hardness

A typical back-scattered electron (BSE) image of the Al/Cu diffusion couple annealed at 540 °C for 20 h is shown in figure 2(a). The brightest region on the right side is the Cu sample and the darkest region on the left side is the Al sample. As can be seen, various continuous layers of IMCs with different contrasts are observed around the interface of Al/Cu diffusion couple. The concentration distribution of Cu at the interfacial region (along red horizontal line 1) of Al/Cu diffusion couple was obtained from the EDS line scanning, as shown by blue curve in figure 2(a). In order to identify each layer, quantitative composition analysis was done along the direction
The EDS analysis results obtained from the layers A-D marked in figure 2(a) are shown in figure 2(b). Combined with Al-Cu phase diagram and EDS analysis results, the IMCs layers from the Al side to the Cu side are Al$_2$Cu, AlCu, Al$_2$Cu$_3$ and Al$_4$Cu$_9$, respectively. The total thickness of the IMCs reaches approximately 128 μm. The formation of different types of IMCs is closely related to the diffusion temperature and holding time. In this study, only the Al$_2$Cu$_3$ is not formed due to the lower diffusion temperature and shorter diffusion time under the conditions of 480 °C and 500 °C for 5h.

Figure 3 shows the typical force-displacement curves of various IMCs formed in Al/Cu interfacial region. The nanoindentation hardness of Al$_2$Cu, AlCu, Al$_2$Cu$_3$ and Al$_4$Cu$_9$ are 7.38 GPa, 9.99 GPa, 10.7 GPa and 9.68 GPa, respectively, which are much greater than the matrix of Cu (1.85 GPa) and Al (1.42 GPa). The fracture toughness of the IMCs is lower than that of the matrix, which indicates that the formation and overgrowth of brittle IMCs at the Al/Cu interface will reduce the interfacial bonding strength [17]. Therefore, the formation and growth of IMCs should be reasonably controlled through optimizing the technological parameters to improve the interfacial bonding strength.

3.2. Growth kinetics of the intermetallic compounds
The growth kinetics of the IMCs in the Al/Cu diffusion couples is analyzed by measuring the thickness of the diffusion layers under different diffusion parameters. As well known, the shape of the interfacial IMCs layers is irregular, the average thickness $L_i$ of compound $i$ is determined by the following equation:

$$L_i = \frac{S_i}{W}$$

where, $S_i$ is the cross-sectional area of compound $i$ corresponding to the linear length ($W$). The length is equivalent for all the IMCs layers.

Figure 4 shows the relationship between the thickness of IMCs layers and diffusion time for Al/Cu diffusion couple at the same diffusion temperature. The morphologies of interfacial diffusion layer in Al/Cu diffusion
couples after annealing at 540 °C for 1, 5, 10 and 20 h (one set of experiments) are also provided, as shown in figure 5. The results show that the thickness of all different kinds of IMCs layers increases with increasing of diffusion time. It is also found that the thickness of Al₄Cu₉ layer is much thicker than that of the other three IMCs layers, and the AlCu layer is the thinnest layer at all temperatures examined, which is attributed to the different growth rates of different IMCs under each temperature condition.

Figure 4. Relationship between the thickness of IMCs layers and diffusion time. (a) 480 °C, (b) 500 °C, (c) 520 °C, (d) 540 °C.

Figure 5. Morphologies of interfacial diffusion layer in Al/Cu diffusion couples after annealing at 540 °C for different time: (a) 1 h, (b) 5 h, (c) 10 h, (d) 20 h.
Figure 6 shows the relationship between the thickness of IMCs layers and diffusion temperature for Al/Cu diffusion couple at the same diffusion time. The morphologies of interfacial diffusion layer in Al/Cu diffusion couples after annealing at 480 °C, 500 °C, 520 °C and 540 °C for 20 h (one set of experiments) are also provided, as shown in figure 7. It can be seen that the thickness of all IMCs layers increases with increasing of the diffusion temperature. In addition, the thickness of Al2Cu3 and Al4Cu9 layers changes with temperature more than that of Al2Cu and Al4Cu layers. Therefore, the growth of Al2Cu3 and Al4Cu9 are more sensitive to temperature.

Figure 6. Relationship between the thickness of IMCs layers and diffusion temperature: (a) 5 h, (b) 10 h, (c) 15 h, (d) 20 h.

Figure 7. Morphologies of interfacial diffusion layer in Al/Cu diffusion couples after annealing at different temperatures for 20 h: (a) 480 °C, (b) 500 °C, (c) 520 °C, (d) 540 °C.
In the solid-solid diffusion process, the relationship between the thickness of IMCs layer and the time at a given temperature can be generally expressed by the following equation [18]:

\[ L = kt^n \]  

where, \( L \) is the thickness of the IMCs layer, \( t \) is the diffusion time, \( k \) and \( n \) are the growth rate constant and time exponent, respectively. In general, the solid-state growth mechanism of IMCs can be estimated by the value of \( n \) [19]. When \( n = 0.25 \), the growth is mainly controlled by the grain boundary diffusion. When \( n = 0.5 \), the growth is mainly controlled by volume diffusion, and the thickness follows a linear relationship with the square root of diffusion time, i.e. \( L = kt^{1/2} \). When \( n = 1 \), the growth is mainly controlled by the interfacial reaction, and the thickness has a linear relationship with diffusion time, i.e. \( L = kt \).

Taking the logarithm on both sides of equation (2):

\[ \ln L = \ln k + n \ln t \]  

The slope \( n \) values (0.45–0.55) are obtained by plotting the logarithm of IMCs layer thickness (\( \ln L \)) and the logarithm of diffusion time (\( \ln t \)), which are all close to 0.5. Based on this \( (n = 0.5) \), the thickness of IMCs layer \( (L) \) versus the square root of the diffusion time \( (t^{1/2}) \) are shown in figure 8.

Through linear regression processing, the thickness still follows a linear relationship with the square root of diffusion time (linear correlation coefficients \( R^2 \) are all greater than 0.98). The results show that the growth of each IMC is mainly controlled by volume diffusion, i.e. the solid-state growth of IMCs follow a parabolic growth kinetics, and the slopes of the lines are the growth rate constants.

In isothermal diffusion process, an Arrhenius-type relationship is used to determine the activation energy for the growth of IMCs:

\[ k^2 = k_0^2 \exp \left( \frac{-E_a}{RT} \right) \]  

where, \( k_0^2 \) is the frequency factor, \( E_a \) is the activation energy, \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), and \( T \) is the absolute temperature. Equation (4) can also be written in the following form:

\[ \ln k^2 = \ln k_0^2 - \frac{E_a}{RT} \]  

Figure 9 shows the relationship between the logarithm of growth rate constants of IMCs layers and inverse temperature. The activation energy of IMCs can be calculated from the slope of the linear fit, and the frequency factor is determined from the intercept of the line on the vertical coordinate. Finally, the activation energy
calculated for the growth of total IMC, Al$_2$Cu, AlCu, Al$_2$Cu$_3$ and Al$_4$Cu$_9$ are 157.39 kJ mol$^{-1}$, 120.73 kJ mol$^{-1}$, 79.74 kJ mol$^{-1}$, 285.01 kJ mol$^{-1}$ and 149.78 kJ mol$^{-1}$, respectively.

Table 1 summarizes the activation energy data of IMCs at different temperature range. It is found that there are some differences in the activation energy of each IMC under different conditions. It can be explained from the following two aspects. First, the preparation method of Al/Cu samples is different. Second, the heat treatment parameters (diffusion temperature, diffusion time, pressure, etc) are different. However, the order of the activation energy of different IMC available from the literatures is generally consistent, i.e. $E_a$(Al$_2$Cu$_3$) $>$ $E_a$(Al$_4$Cu$_9$) $>$ $E_a$(Al$_2$Cu) $>$ $E_a$(AlCu), the same experimental result is obtained in this work.

### 3.3. Prediction of phase formation sequence

The experimental results show that only the Al$_2$Cu$_3$ is not formed at 480 and 500°C for 5 h, and we can preliminary conclude that the formation of Al$_2$Cu, AlCu and Al$_2$Cu$_3$ are all earlier than that of Al$_4$Cu$_9$. However, we could not determine which phase of Al$_2$Cu, AlCu and Al$_2$Cu$_3$ is formed first and the formation sequence of the other two phases.

In the study of predicting the first phase formation in a binary solid-state diffusion reaction system, the effective heat of formation (EHF) model proposed by Pretorius et al [23, 24] has been widely used. From the perspective of thermodynamics and kinetics, the EHF model combines the heat of formation of the phase in the system with the effective concentration of the reaction element at the growth interface, and successfully predicts the first phase formation in many metal-metal binary systems [25].

According to the EHF model, the effective heat of formation for IMCs can be expressed as:

$$\Delta H^\prime = \Delta H^0 \times \frac{C_e}{C_0}$$

where, $\Delta H^0$ is the heat of formation for IMCs, $C_e$ is the effective concentration of limiting element at the growth interface, $C_0$ is the concentration of the limiting element in the IMCs to be formed. For Al-Cu binary system, the elements concentration corresponding to the lowest eutectic point temperature are 82.9 at.% Al and 17.1 at.% Cu.
In this case, the Cu element will be consumed and Al is in excess when formed Al\(_2\)Cu, Al\(_{1.2}\)Cu, Al\(_{1.3}\)Cu\(_4\), Al\(_{1.4}\)Cu\(_3\), or Al\(_{1.5}\)Cu\(_9\). Thus, Cu is the limiting element and the corresponding concentration is 17.1 at.%. According to equation (6), the effective heat of formation for IMCs was calculated and listed in Table 2. Meanwhile, the effective heat of formation diagram for IMCs formation with the Al–Cu binary phase diagram is obtained, as shown in Figure 10. It is found that the effective heat of formation for Al\(_2\)Cu is the lowest. Therefore, the Al\(_2\)Cu will be formed first at the Al/Cu interface according to the EHF model.

Based on the above analysis, it can be known that the Al\(_2\)Cu is formed first, and the Al\(_{1.3}\)Cu\(_4\) is formed last. The formation sequence of the other two phases (Al\(_{1.2}\)Cu\(_2\) and Al\(_{1.4}\)Cu\(_3\)) can be judged by calculating the Gibbs free energy. The Gibbs free energy change of the IMCs in the binary A–B system can be expressed as:

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (7)
where, $\Delta H$ is the enthalpy change, and $\Delta S$ is the enthalpy change. The enthalpy change of IMCs is very small due to its long-range ordered structure and can be ignored. The enthalpy change can be calculated by Miedema semi-empirical theory \cite{27, 28}, which is calculated according to the basic physical parameters of the elements, and can be expressed as:

$$D = D_{\text{chem}} + D_{\text{el}} + D_{\text{struct}}$$

where, $D_{\text{chem}}$ is the chemical term (electron distribution difference), $D_{\text{el}}$ is the elastic term (size difference), and $D_{\text{struct}}$ is the structural term (structure difference) of enthalpy change, respectively.

When calculating the enthalpy change of IMC, due to the long-range ordered arrangement of the atoms, the lattice distortion caused by the difference in atomic size is negligible, i.e. the elastic term can be negligible. In addition, there is no contribution to the structural term for IMCs. Finally, the Gibbs free energy change of IMCs in the Al-Cu binary system can be expressed by the chemical term of its enthalpy change, i.e. $\Delta G = \Delta H^c$. In a binary system composed of a non-transition metal (Al) and a transition metal (Cu), the chemical term of the enthalpy change for IMCs can be expressed as:

$$\Delta H^c = \frac{2x_A f_{A}^B P V_{A}^{2/3}}{(n_{\text{elec}}^A)^{1/3} + (n_{\text{elec}}^B)^{1/3}} \left[ -(\Delta \phi)^2 + \frac{Q P}{P} (\Delta n_{\text{elec}}^{1/3})^2 - \frac{R}{P} \right]$$

where, $x_A$ and $x_B$ are the atomic fractions of elements A and B, $n_{\text{elec}}$ is the electron density, $\Delta \phi$ is the electronegativity difference of elements, and $V^{2/3}$ is the atomic volume. For the Al-Cu binary system, $P = 12.3$, $Q/P = 9.4$ and $R/P = 0.57$ \cite{29}. $f_{A}^B$ represents the extent to which atom A is surrounded by atom B, which is related to the relative content and the atomic size, and can be expressed as:

$$f_{A}^B = C_B^S [1 + \gamma (C_A^S C_B^S)^2]$$

where, $\gamma$ represents the order degree of alloy. For the IMCs, $\gamma = 8$. $C_A^S$ and $C_B^S$ are the surface concentrations of A and B atoms, respectively, and can be calculated by the following equation:

$$C_A^S = \frac{x_A V_{A}^{2/3}}{x_A V_{A}^{2/3} + x_B V_{B}^{2/3}}$$

$$C_B^S = \frac{x_B V_{B}^{2/3}}{x_A V_{A}^{2/3} + x_B V_{B}^{2/3}}$$

where, $V^{2/3}$ is the volume of pure metal element in the binary system.

Based on the relevant parameters in Table 3, the Gibbs free energy change of IMCs can be calculated according to equations (7)–(12), i.e. $\Delta G(\text{AlCu}) = -15.39 \text{ kJ mol}^{-1}$ and $\Delta G(\text{Al}_{4}\text{Cu}_{9}) = -13.2 \text{ kJ mol}^{-1}$.
Table 4. Interfacial diffusion reactions on both sides of the IMCs layers at different diffusion stages

| Interface               | Different diffusion growth stages |
|-------------------------|-----------------------------------|
|                         | (c) \( \text{Al}_2\text{Cu} \)   | (d) \( \text{Al}_2\text{Cu} + \text{Al}_4\text{Cu}_9 \) | (e) \( \text{Al}_2\text{Cu} + \text{AlCu} + \text{Al}_4\text{Cu}_9 \) | (f) \( \text{Al}_2\text{Cu} + \text{AlCu} + \text{Al}_4\text{Cu}_9 + \text{Al}_4\text{Cu}_9 \) |
| I (\( \text{Al}/\text{Al}_2\text{Cu} \)) | \( 2\text{Al} + \text{Cu} \rightarrow \text{Al}_2\text{Cu} \) | \( 2\text{Al} + \text{Cu} \rightarrow \text{Al}_2\text{Cu} \) | \( 2\text{Al} + \text{Cu} \rightarrow \text{Al}_2\text{Cu} \) | \( 2\text{Al} + \text{Cu} \rightarrow \text{Al}_2\text{Cu} \) |
| II (\( \text{Al}_2\text{Cu}/\text{Cu} \))  | \( 9\text{Cu} + 4\text{Al} \rightarrow \text{Al}_2\text{Cu}_9 \) | — | — | — |
| III (\( \text{Al}_4\text{Cu}_9/\text{Cu} \)) | — | \( 9\text{Cu} + 4\text{Al} \rightarrow \text{Al}_2\text{Cu}_9 \) | \( 9\text{Cu} + 4\text{Al} \rightarrow \text{Al}_2\text{Cu}_9 \) | — |
| IV (\( \text{Al}_2\text{Cu}/\text{Al}_4\text{Cu}_9 \)) | — | \( 2\text{Al}_2\text{Cu} + 7\text{Cu} \rightarrow \text{Al}_4\text{Cu}_9\text{Al}_4\text{Cu}_9 + 14\text{Al} \rightarrow 9\text{Al}_2\text{Cu} \) | — | — |
| V (\( \text{Al}_2\text{Cu}/\text{AlCu} \)) | — | — | \( \text{Al}_2\text{Cu} + \text{Cu} \rightarrow 2\text{AlCu} \text{AlCu} + \text{Al} \rightarrow \text{Al}_2\text{Cu} \) | \( \text{Al}_2\text{Cu} + \text{Cu} \rightarrow 2\text{AlCu} \text{AlCu} + \text{Al} \rightarrow \text{Al}_2\text{Cu} \) |
| VI (\( \text{AlCu}/\text{Al}_4\text{Cu}_9 \)) | — | — | \( 4\text{AlCu} + 5\text{Cu} \rightarrow \text{Al}_4\text{Cu}_9\text{Al}_4\text{Cu}_9 + 5\text{Al} \rightarrow 9\text{AlCu} \) | — |
| VII (\( \text{AlCu}/\text{Al}_2\text{Cu}_3 \)) | — | — | — | — |
| VIII (\( \text{Al}_2\text{Cu}_3/\text{Al}_4\text{Cu}_9 \)) | — | — | — | — |
Therefore, the Gibbs free energy change of Al₄Cu₉ is greater than that of Al₁Cu, indicating that the Al₄Cu₉ is formed earlier than Al₁Cu.

In summary, the formation sequence of the four IMCs in Al/Cu diffusion couples is: Al₂Cu, Al₄Cu₉, AlCu and Al₁₂Cu₃.

3.4.3.4 The formation mechanism of IMCs

Figure 11 shows a schematic of the growth process for IMCs at the Al/Cu interface. In the initial stage of diffusion, Al and Cu elements diffuse at the initial interface, and form Cu (Al) and Al (Cu) solid solutions, as shown in Figure 11(b). The solid solubility of Cu in Al (2.48 at%) is much smaller than that of Al in Cu (19.7 at%) in the temperature range studied in this paper, but the diffusion rate of Cu in Al (6.5 × 10⁻⁵ m² s⁻¹) is much greater than that of Al in Cu (4.5 × 10⁻⁵ m² s⁻¹) [31], which cause the Al (Cu) solid solution to reach saturation first and form Al₁Cu on the A1 side, as shown in Figure 11(c). When the Al₁₂Cu₃ layer is formed, its subsequent growth requires Cu to diffuse through the Al₂Cu layer and then react with Al at the Al/Al₁₂Cu₃ interface (Interface I), i.e. the continuous migration of the interface I to the A1 side. Meanwhile, Al diffuse through the Al₂Cu layer to the Cu side, which cause the Cu (Al) solid solution also to reach saturation and form Al₄Cu₉ on the Cu side. Besides, the Al₁₂Cu₃ can also form at the Al₁₂Cu/Al₄Cu₉ interface (Interface IV) through the 2Al₁₂Cu + 7Cu → Al₄Cu₉ reaction, as shown in Figure 11(d). After that, the growth of Al₄Cu₉ layer is realized through the continuous migration of the interface IV and interface III. With the diffusion time increases, the AlCu begins to form at the A₁₄Cu₉/Al₄Cu₉ interface through the 5Al₁₄Cu + Al₄Cu₉ → 14A1Cu reaction, and the Al₁₂Cu + Cu → 2AlCu and Al₁₄Cu₉ + 5Al → 9AlCu reactions can also contribute to the formation and growth of AlCu, i.e. the growth of AlCu layer is controlled by the migration of the interface V and interface VI, as shown in Figure 11(e). Similarly, the Al₄Cu₉ forms at the AlCu/Al₄Cu₉ interface through the 6Al₁₁Cu + Al₄Cu₉ → 5Al₁₄Cu₉, 2AlCu + Cu → Al₄Cu₉ and Al₁₄Cu₉ + 2Al → Al₄Cu₉ reactions with the diffusion time further increases, and the subsequent growth of Al₁₄Cu₉ layer is also controlled by the migration of the interface VII and interface VIII, as shown in Figure 11(f).

Throughout the diffusion process, it is found that the left interface of Al₂Cu and the right interface of Al₄Cu₉ will always migrate to the A1 side and the Cu side through the 2Al + Cu → Al₂Cu and 9Cu + 4Al → Al₄Cu₉ reactions, respectively. However, the right interface of Al₁₂Cu₃, the left interface of Al₄Cu₉, and the both sides of interface of AlCu and Al₁₄Cu₉ may have multiple interface diffusion reactions at different stages. The interfacial diffusion reactions that may occur at the formed IMCs interfaces are listed in Table 4. For clearness, the example is given to illustrate that the interfacial diffusion reactions may occur on both sides of the Al₄Cu₉ at different diffusion stages.

(1) Stage (c)-(f): 9Cu + 4Al → Al₄Cu₉ (Al₄Cu₉ growth)
(2) Stage (d): 2Al₂Cu + 7Cu → Al₄Cu₉ (Al₄Cu₉ growth)
(3) Stage (d): Al₁₂Cu₃ + 14Al → Al₁₄Cu₉ (Al₁₄Cu₉ consumption)
(4) Stage (e): 4AlCu + 5Cu → Al₁₂Cu₃ (Al₁₂Cu₃ growth)
(5) Stage (e): Al₁₂Cu₃ + 5Al → 9AlCu (Al₁₂Cu₃ consumption)
(6) Stage (f): 2Al₂Cu + 3Cu → Al₄Cu₉ (Al₄Cu₉ growth)
(7) Stage (f): Al₁₂Cu₃ + 2Al → Al₂Cu (Al₁₂Cu₃ consumption)

In the evolution of Al₁₂Cu₃ is related with the interfacial diffusion reactions ①–⑦. The interfacial reactions ③④⑤ can promote the growth of Al₄Cu₉, while the interfacial reactions ③④⑤ consumes the already formed Al₄Cu₉. Finally, the growth of Al₁₂Cu₃ is determined by the combined effect of these 7 reactions at the interfaces. Based on the above analysis, the formation and growth of IMCs in Al/Cu diffusion couple are essentially realized through the interfacial diffusion reaction and the migration of phase interfaces.

4. Conclusions

The formation and growth of IMCs in Al/Cu diffusion couple during isothermal diffusion at various temperatures for different diffusion times was studied. Four different kinds of continuous layered IMCs (Al₁₄Cu₉, Al₁₂Cu₃, Al₄Cu₉ and Al₄Cu₉) are formed at the Al/Cu interface except for Al (Cu) and Cu (Al) solid solution. The thickness of all IMCs layers increases with increasing diffusion time and temperature, and controlled by the interfacial diffusion reaction and the migration of phase interfaces. The growth kinetics of IMCs conforms to the parabolic law, i.e. $L = kt^{1/2}$, indicating that the growth of IMCs is controlled by volume diffusion. According to
Arrhenius relationship, the activation energy calculated for the growth of $\text{Al}_2\text{Cu}$, $\text{AlCu}$, $\text{Al}_2\text{Cu}_3$ and $\text{Al}_4\text{Cu}_9$ are 120.73 \text{kJ mol}^{-1}, 79.74 \text{kJ mol}^{-1}, 285.01 \text{kJ mol}^{-1}$ and 149.78 \text{kJ mol}^{-1}, respectively. Besides, the $\text{Al}_2\text{Cu}$ is predicted to form first and the formation sequence of the four IMCs is $\text{Al}_2\text{Cu}$, $\text{Al}_2\text{Cu}_3$, $\text{AlCu}$ and $\text{Al}_4\text{Cu}_9$ based on the EHF model and Gibbs free energy change.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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