Effect of Annealing on the Interfacial Structure of Aluminum-Copper Joints

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The aim of this study is to investigate the structure development and growth kinetics of the interfacial structure of cold roll bonded Al/Cu bimetal sheet. An interfacial structure is developed during the annealing process. The characteristics of the constituent phases at the interface of Al/Cu bimetal are studied by means of scanning electron microscope (SEM), X-ray diffraction (XRD) and transmission electron microscope (TEM). The results indicate that an obvious multi-layers interdiffusion structure is developed at the Al/Cu interface. The diffusion layer is consisted of four intermetallic compounds; AlCu, AlCu, AlCu and AlCu. The growth of these intermetallics during annealing can be achieved by the diffusion process. The activation energies of AlCu, AlCu + AlCu, AlCu and the total intermetallic layer are found to be 97.504, 107.46, 117.52 and 107.85 kJ/mol, respectively. These intermetallics generally possess higher hardness values than those of the corresponding base metals. AlCu and AlCu exhibit much higher hardness than that of AlCu and AlCu, which implies lower fracture toughness. The observation of crack propagation paths shows that fracture mainly occurs in the intermetallic compound layers of AlCu and AlCu, which are located between AlCu and AlCu.

1. Introduction

In recent years bimetallic joints, particularly aluminum-copper have been increasingly used in a variety of electrical applications such as conductive strips used in high frequency AC (alternative current) equipment. Such bimetal (or trimetal) joints, made by pressure welding, diffusion, roll bonding, flash welding and explosion welding, are characterized by a relatively stable bond interface. Dissimilar clad metal sheets produced by roll bonding have been widely used because of their higher comprehensive properties. The effects of intermetallic phases on the mechanical and electrical properties of an Al/Cu bimetal sheet are of great importance to its applications. The mechanical and electrical properties of Al/Cu bimetallic bonds, prepared by roll bonding are dramatically affected by the formation and growth of intermetallics at the bond interface.1–4) Some studies show that the interfacial reactions occurred during the annealing process dominate the variation of bond strength. However, if the annealing time and/or temperature exceed a certain value, the development of interfacial structure leads to the formation of weak layers in the interfacial region and damage the bonds.5–8) Al/Cu joint rapidly loses its mechanical integrity when the total width of intermetallic phases exceeds 1 um. However, some questions require further studies and the interfacial structure for misfit materials needs to be investigated in depth. Some studies have focused on atomic structure of metallic interfaces in solid-state joints to understand the basic behaviour of heterophase interface.9–14) These studies have built various models to depict the interfaces morphology at as-bonded and annealed conditions. The development of interface, which has great influence on the fracture mechanism, is interpreted as the result of inter-diffusion between Al and Cu atoms.15,16)

In this study, Al/Cu bimetal sheets are made using cold roll bonding. The identification of interfacial structure and growth mechanism under various annealing conditions is performed. The objectives of the present study are to investigate the development of the intermetallic structure and the growth kinetics of intermetallic compounds formed under various annealing conditions. The results of the analysis can improve the predictability and reliability of joint properties.

2. Experimental Procedures

2.1 Fabrication of Al/Cu bimetal sheet

The bimetallic sheets used in this study are produced using cold roll bonding of pure copper (C11000) with the primary dimensions of 300 × 65 × 0.8 mm and aluminum (AA1050) of 300 × 65 × 2 mm. The specifications of aluminum and copper sheets are shown in Table 1.

A schematic presentation of the cold roll bonding process is shown in Fig. 1. The manufacturing of Al/Cu bimetal is carried out using a laboratory rolling mill with a roll load capacity of 200 tons. The roll diameter is 400 mm and the roll speed is about 10 m min⁻¹. Before rolling, the aluminum and copper sheets are degreased by swabbing with acetone and dried in the air. Then, the surfaces of aluminum and copper

<table>
<thead>
<tr>
<th>Grade</th>
<th>Chemical composition, mass%</th>
<th>Yielding (MPa)</th>
<th>Before bonding</th>
<th>As-bonded (1.2 mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA1050</td>
<td>99.5Al, Si = 0.03, Fe = 0.34, Cu = 0.034, other &lt; 0.05</td>
<td>103</td>
<td>2</td>
<td>0.84</td>
</tr>
<tr>
<td>C11000</td>
<td>Cu &gt; 99.9, O₂ &lt; 0.04</td>
<td>249</td>
<td>0.8</td>
<td>0.36</td>
</tr>
</tbody>
</table>

![Fig. 1 A schematic presentation of cold roll bonding.](Image)
sheets are wire brushed using a brush roller to obtain a clean and suitable rough surface. The brush roller is a hollow cylinder which is 200 mm in diameter and made of carbon steel. Stainless steel wires with a diameter of 0.3 mm are attached to the roller. The brush roller is rotating in a speed of 1200 rpm. The aluminum and copper sheets are brought in contact with the brush with a contact force of 1 kgf. They take one second for the sheet with 300 mm in length to pass through the brush roller. The surface morphology and roughness of the aluminum and copper sheets after wire brushing are shown in Fig. 2. The surface roughness \( R_y \) of the brushed aluminum sheet is 23.78 \( \mu \)m and that of the brushed copper sheet is 13.27 \( \mu \)m as shown in Fig. 2(b).

The aluminum and copper sheets are packed and roll bonded in one pass at room temperature. During the roll bonding process, aluminum and copper sheets are drawn into roll gap and extruded out. The high roll pressure promotes joints built between aluminum and copper. The original thickness for aluminum and copper sheets before bonding is 2 mm and 0.8 mm, respectively. The thickness after bonding is 0.84 mm and 0.36 mm, respectively for aluminum and copper sheet. A total reduction of 57% is performed for the roll bonding process.

2.2 Material analysis

The Al/Cu bimetal samples are annealed under various temperatures of 200, 250, 300, 400, 500, and 540 °C for different holding times. The temperature deviation of the annealing furnace is ±2 °C. The development of interfacial structures is identified using Wavelength-Dispersive Spectrometer (WDS). The bimetal sheet is then undergone a peel test to break off the sample. The X-ray diffraction technique (GIS, Rigaku D/MAX2500) is then conducted to identify the phases on the fracture surfaces of the Cu-side and Al-side at a scanning speed of 3° min\(^{-1}\). Field Emission Scanning Electron Microscope (FESEM, Hitachi S-4100) is then used to observe the surface morphology and path of crack propagation.
The growth rate of the intermetallic phases is determined by measuring the thicknesses of the interdiffusion layers from their Backscattered Electrons Images (BEI), which are taken from the samples at selected time intervals under various annealing temperatures. TEM samples are prepared from slices of 250 μm in thickness, cut from the specimen perpendicular to the interface. These slices are ground to a thickness of 40 μm by diamond slurry and finally polished by an ion-milling device carefully. The samples are examined by a FEI Tecnai G² electron microscope operated at 400 KV. Hardness of the intermetallics is performed using a Shimazu micro-hardness tester equipped with a Vickers indenter using a load of 0.1 N (10 grams).

3. Results and Discussion

3.1 Interface structure of Al/Cu bimetal sheet

Micrographs of the Al/Cu bimetal sheet for different stages during the roll bonding process, ranging from the instant when the sheet is drawn into the roll gap up to the instant when the sheet is extruded out, are shown in Fig. 3.

Figure 4 shows the equilibrium phase diagram of the Al/Cu system. It can be seen that several Al/Cu intermetallic phases, which include Al₂Cu (θ), AlCu (η₂), Al₃Cu₄ (ζ₂), Al₄Cu₉ (ζ₃), may develop at the annealing temperatures investigated in this study. Figure 5 shows the development of interfacial structure of Al/Cu bimetal sheet under various annealing conditions. It is understood that both Al and Cu atoms are thermally activated and some intermetallic compounds are developed through diffusion during the annealing process. For the as-bonded sheet, no obvious interface development can be observed as shown in Fig. 5(a). For the annealing process, the bimetal sheet is treated for 30 minutes under various annealing temperatures. For annealing temperature of 300°C, an interfacial layer with a thickness of about 1.4 μm is developed as shown in Fig. 5(b). As the annealing temperature increases to 400°C, the interfacial layer continues to thicken to a thickness of 5.6 μm and a visible multi-layers structure can be observed as shown in Fig. 5(c). When the annealing temperature reaches 500°C, the interface continues to grow to a thickness of 18 μm with a 4-layers structure.

WDS is applied to identify the 4-layers interdiffusion layers developed at the Al/Cu interface which are sufficiently large to allow positioning of WDS beam. Figure 6 shows the WDS study of intermetallic compounds development of Al/Cu bimetal sheet for the annealing condition of 500°C–180 min. The lower figure reveals the chemical compositions of Al and Cu across the interfacial region. The dash lines correspond to the interfaces of the various phases. According to the equilibrium phase diagram of Al-Cu system, it can be seen that several Al-Cu phases are stable in the studied temperature intervals of 300°–500°C. The Al-Cu phases corresponding to the measured atomic percents are categorized as Al₂Cu (θ), AlCu (η₂), Al₃Cu₄ (ζ₂), Al₄Cu₉ (ζ₃). The formation of the interfacial phases is affected by their formation energies. According to a previous study, the formation energies of Al₄Cu₉ and Al₂Cu are 0.83 eV and
0.78 eV. And the diffusivity of Cu in Al is greater than that of Al in Cu. Thus Al$_2$Cu is presumed to form first and then the next reaction phase is Al$_4$Cu$_9$. AlCu and Al$_3$Cu$_4$ are exhibited to form after the formation of the previous two phases. Stages in formation of interface structure during diffusion joint of Al/Cu bimetal sheets under the annealing temperature of 300°C for (a) 5 minutes, (b) 10 minutes, (c) 30 minutes, (d) 120 minutes are shown in Fig. 7.

Figure 8 shows hardness value (HV) of different intermetallics for Al/Cu bimetal sheet annealed at 500°C for 180 min. Those intermetallics generally possess higher hardness values than those of corresponding base metals of aluminum and copper. AlCu and Al$_3$Cu$_4$ show higher hardness than the other phases, which implies lower fracture toughness. Laminate brittle intermetallic compounds developed at the Al/Cu interface weaken the bonding. From the observation of fracture morphology of the specimen with fully developed interface (500°C–60 min), most cracks propagate through the zone of the AlCu and Al$_3$Cu$_4$ layers and the remaining cracks attack some local parts of the Al$_2$Cu$_9$ and Al$_3$Cu layers as shown in Fig. 9. This phenomenon becomes more obvious while the interfacial zone (especially for AlCu and Al$_3$Cu$_4$) continues to thicken.

The fracture morphology on the surfaces of Al/Cu peel tested samples can be observed from Fig. 10. For the as-rolled condition, areas of ductile fracture dimples, which are separated by unbonded regions of original scratch-brushed surface, can be observed. For the annealing conditions of 400°C–30 min. and 500°C–30 min., brittle cleavage can be seen to cover almost the entire fracture surfaces.

X-ray diffraction is applied to investigate chemical composition on the fracture surfaces of both Cu-side and Al-side specimens prepared by peel test. Figure 11 shows the X-ray diffractographs of both Cu- and Al-side fracture surface specimens for different annealing conditions. At the annealing temperature of 300°C for 30 min, only aluminum is detected on Al-side fracture specimen and only copper is detected on Cu-side fracture specimen. This can be attributed to the fact that the thickness of interdiffusion layer is too thin to be detected. As the annealing temperature increases to 400°C and above, the intermetallic compounds of Al$_2$Cu and Al$_4$Cu$_9$ thicken and can be detected on the fracture surfaces. Al$_2$Cu phase is detected mainly on the Al-side sample and Al$_4$Cu$_9$ is shown on the Al-side sample. AlCu and Al$_3$Cu$_4$ are still not detected because of these two phase are still too thin and part of them fall off during crack propagation as shown in
Fig. 9. Diffraction peaks of aluminum and copper then become gradually weaken.

3.2 TEM analysis in the interfacial transition zone

The micrograph for the vicinity of Al/Cu interface for as-bonded condition by TEM is shown in Fig. 12. The EDS pattern shows an obvious change of composition near the Al/Cu interface. It is believed that the energy produced by plastic deformation and friction between roller and sheet is dissipated as heat with a corresponding rise in temperature. In this study, surface temperature can rise up to 80°C, which is detected on the Al-side surface of Al/Cu bimetal using a k-type thermocouple after roll bonding. The temperature rise can promote the Cu atoms to diffuse into aluminum. Moreover, the locally severe plastic deformation at the joint surface can cause the Cu atoms to move across the interface and enhance metallurgy bonding.
The bonding between Al and Cu is greatly affected by the interface structure of Al/Cu bimetal. To clarify further the structure of the intermetallics developed at Al/Cu interface, some thinly sliced samples, which were annealed at 500°C for 30 min., were cut from the Al/Cu interfacial region and then prepared by ion mill for TEM and electron diffraction analysis. The TEM micrograph, electron diffraction pattern and schematic index diagram of these intermetallics are shown in Fig. 13. Figure 13(a) shows the TEM bright field image, the electron diffraction pattern and schematic index diagram of Al$_2$Cu phase. The zone axis of Al$_2$Cu is $Z = \frac{1}{2}[011]$ and the diffraction pattern shows a tetragonal structure (lattice constant $a = 0.487$, $b = 0.487$, $c = 0.607$). Further observations are made of the diffusion zone near the Cu-side where the second major phase is Al$_4$Cu$_9$ as shown in Fig. 13(b). The zone axis of Al$_4$Cu$_9$ is $Z = [011]$ and the lattice constant is $a = 1.44$, $b = 0.815$, $c = 0.995$ nm. The diffraction pattern also shows orthorhombic structure as shown in Fig. 13(d).

### 3.3 Growth kinetics of interfacial structure

The growth rate of the intermetallic phases (Al$_2$Cu ($\theta$), Al$_4$Cu$_9$ ($\gamma$), AlCu ($\eta_2$), Al$_3$Cu$_4$ ($\xi_2$)) is determined by measuring the thicknesses of the interdiffusion layers from their Backscattered Electrons Images (BEI), which are taken from the samples at selected time intervals under various annealing temperatures. The annealing times are 120 min., 120 min., 90 min., 60 min., and 90 min. for the annealing temperatures of 300°C, 350°C, 400°C, 500°C, and 540°C respectively. The thickness of AlCu ($\eta_2$) and Al$_3$Cu$_4$ ($\xi_2$) are measured together because of the difficulty in differentiating these two phases from the BEI images. The results of the thickness measurements are shown in Fig. 14. All intermetallic compounds thicken with increasing annealing time. At higher temperature of 540°C for 90 min, the thickness of intermetallic compound reaches approximately 38 μm. The...
increasing thickness of intermetallic compound layer can be expressed as a function of the square root of time for each annealing temperature. The atomic diffusion of Cu and Al across the interface is the main controlling step for the growth of intermetallic compound during annealing. Within the scatter of experimental data, the relationship between the thickness of the developed layer \( d \) and the time \( t \) at a given temperature can be generally expressed by the following parabolic equation:

\[
d = Dt^n
\]

where \( d \) is the thickness of the intermetallic layer, \( D \) is the growth rate constant, \( n \) is the time exponent and \( t \) is the reaction time.

In general, the solid-state growth for the intermetallic compound can follow linear or parabolic growth kinetics. Linear growth implies that growth rate is limited by the reaction rate at the growth site. In contrast, parabolic growth implies that the growth is controlled by volume diffusion. If the growth process is controlled by volume diffusion, the growth of the intermetallic compound layer can be represented by the above equation where \( n \) equal to 0.5.\(^{19}\) It can be seen that the growth of Intermetallics follows a parabolic law as shown in Fig. 14, which implies that a diffusion controlled model is applied to the growth of intermetallics during annealing. The growth rate constant can be calculated form
the linear regression analysis of $d$ versus $t^{1/2}$. A simple Arrhenius relationship is used to determine the activation energy characterizing the rate of formation of intermetallics

$$D^2 = D_0^2 \exp \left( - \frac{Q}{RT} \right)$$

where $D_0^2$ is the frequency factor, $Q$ is the activation energy, $R$ is the gas constant (8.314 J/mol K), and $T$ is the annealing temperature. The activation energy can be calculated from the slope of the Arrhenius plot, which shows a strong linear relationship, as shown in Fig. 15. The apparent activation energies calculated for Al$_2$Cu, Al$_4$Cu$_9$, (AlCu + Al$_3$Cu$_4$) phases, and total intermetallic layer are 97.50, 117.52, 107.46, and 107.85 kJ/mol, respectively. The lower activation energy of Al$_2$Cu is generally considered as the indication of the formation of intermetallics by short-circuit diffusion via structural defects such as grain boundary and/or dislocation commonly found in tetragonal structure. The higher activation energy for other intermetallics is believed to be associated with cubic and orthorhombic structures.

Fig. 13 Bright-field TEM image, diffraction pattern and schematic index diagram of (a) Al$_2$Cu phase, (b) Al$_4$Cu$_9$ phase, and (c) AlCu phase, (d) Al$_3$Cu$_4$ phase for Al$_3$Cu bimetal annealed at 500°C for 30 min.
4. Conclusions

The structure development and growth kinetics of the interfacial structure of cold roll bonded Al/Cu bimetal sheet are investigated in this study. The following conclusions may be drawn from this study:

1. The interfacial layer of Al/Cu bimetal is consisted of the intermetallic compounds of Al$_2$Cu ($\theta$), AlCu ($\eta_2$), Al$_3$Cu$_4$ ($\xi_2$), and Al$_4$Cu$_9$ ($\gamma_1$). The formation of the interfacial phases is affected by their formation energies and the interdiffusion rate of atoms. The first reaction product is found to be Al$_2$Cu and then the next reaction phase is Al$_4$Cu$_9$. AlCu, and Al$_3$Cu$_4$ are shown to form after Al$_2$Cu and Al$_4$Cu$_9$.

2. The crystal structures of the intermetallic compounds are investigated by TEM. Al$_2$Cu has a tetragonal structure and Al$_4$Cu$_9$ has a cubic structure. Both AlCu and Al$_3$Cu$_4$ have orthorhombic structures. AlCu and Al$_3$Cu$_4$ are shown to have higher hardness and more brittle.

3. The growth of intermetallic compounds is controlled by volume diffusion mechanism. The apparent activation energies calculated for Al$_2$Cu, Al$_4$Cu$_9$, (AlCu + Al$_3$Cu$_4$) phases, and total intermetallic layer are 97.50, 117.52, 107.46, and 107.85 kJ/mol, respectively.

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Fig. 14 Intermetallic layer thickness with various times and temperatures: (a) Al$_2$Cu, (b) Al$_4$Cu$_9$, (c) AlCu + Al$_3$Cu$_4$, and (d) total intermetallic layer.
Fig. 15 Arrhenius plot for the growth rate of the intermetallic layer: (a) Al$_2$Cu, (b) Al$_4$Cu$_9$, (c) AlCu + Al$_3$Cu$_4$, and (d) total intermetallic layer.

REFERENCES