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Interfacial phase formation of Al-Cu bimetal by solid-liquid casting method

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Abstract: The solid-liquid method was used to prepare the continuous casting of copper cladding aluminium by liquid aluminum alloy and solid copper, and the interfacial phase formation of Al-Cu bimetal at different pouring temperatures (700, 750, 800 °C) was investigated by means of metallograph, scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) methods. The results showed that the pouring temperature of aluminum melt had an important influence on the element diffusion of Cu from the solid Cu to Al alloy melt and the reactions between Al and Cu, as well as the morphology of the Al-Cu interface. When the pouring temperature was 800 °C, there were abundant Al-Cu intermetallic compounds (IMCs) near the interface. However, a lower pouring temperature (700 °C) resulted in the formation of cavities which was detrimental to the bonding and mechanical properties. Under the conditions in this study, the good metallurgical bonding of Al-Cu was achieved at a pouring temperature of 750 °C.

Key words: Al-Cu clad materials; interface; solid-liquid method; microstructure

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Bimetal clad refers to a new type of material, which is prepared by combination of two different alloys with different physical, chemical, or mechanical properties, in order to achieve better properties in comparison to a single metal material [1-2]. Hence, such materials have a far reaching potential in manufacturing applications. For example, the Al-Cu bimetal wire, i.e. the Cu clad Al (CCA) wire, could offer a 50% reduction in weight and 30%–40% reduction in cost for the equivalent conductivity, compared with monolithic copper alloys [3]. For this reason, the CCA wire is a candidate to replace the conventional Cu alloys in cables, yoke coils, air-cooling fins and bus-bar conductor joints.

Many manufacturing methods, such as explosive welding [4], roll bonding [5-6], diffusion bonding [7], and casting [8-11], were used to produce clad metals. Among those, the casting technique is considered an optimal one due to its high efficiency and low cost [12-16]. In recent years, the casting method has been widely applied to produce different kinds of bimetal composites. In this method, two different metal melt are poured into the mold successively, then the clad ingot is pulled out from the other side, obtaining a good metallurgical bonding during the continuous process. The key point of this fabrication technology is the formation mechanism of the clad materials' interface. In the case of CCA material, the horizontal continuous casting is a widely used method for the preparation of hollow, round and square CCA billets. During the conventional process, the copper is firstly poured into the outer mold and shaped because of its higher melting point, and then the aluminum melt is poured and combined with the solidified clad-copper. Adequate remelting and sufficient element diffusion process lead to a good metallurgical bonding, whereas, the excessive or insufficient combination results in defects near the interface and deterioration of the performance.

We prepared the CCA round billet by the horizontal continuous casting method. It was found that the interfacial reaction and bonding between aluminum and copper could determine the success or failure of the whole experiment. Parameters such as pouring temperature, casting speed, and cooling water consumption, which affect the interface reaction, play important roles in the continuous casting process. The pouring temperature of aluminum is considered significant. In this study, a mold casting with solid copper and liquid aluminum alloy was

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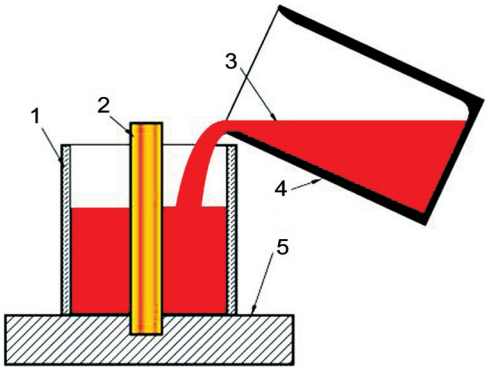
carried out to study the reaction and the interfacial phase formation of Al-Cu bimetal, and to optimize parameters for the continuous process.

1 Experimental method

The materials used in this experiment were Al-7%Si alloy and pure copper. The surface of the copper bar was first ground by fine abrasive paper in order to degrease and remove the oxide film. The schematic diagram of the experimental setup is shown in Fig. 1. The Cu bar (preheated to 250 °C) was installed in the mold and then the aluminum melt was poured in. The pouring temperature was 700 °C, 750 °C and 800 °C, respectively. After obtaining the clad ingot, it was cut transversely, and then ground, polished, and etched by 5% NaOH solution for testing. The microstructure at the interface was observed using optical microscopy, SEM and electron probe X-ray microanalyses. The Vickers hardness profile was measured along the interface layer, and the hardness tests were performed under an indentation load of 100 g for 5 s.



(1) mold; (2) pure Cu; (3) Al-7%Si melt;
(4) graphite crucible; (5) thermal insulating plate

Fig. 1: Schematic diagram of experiment

2 Results

2.1 Macrostructure and microstructure

Figures 2 and 3 show the macro- and microstructures of Al-Cu clad ingots. When the pouring temperature is 800 °C, the shape of the copper bar is distorted significantly due to remelting by the high temperature Al melt (Fig. 2a), and a lot of Al-Cu intermetallic compounds (IMCs) can be seen near the interface (Fig. 3a). When the pouring temperature decreases to 750 °C, a good bonding is obtained (Fig. 2b), and no evidence of Cu overmelting or casting defects near the interface are observed in the macrostructure. In addition, there are scarcely any IMCs in the diffusion zone (Fig. 3b), and the interface between Al-7Si and pure Cu is quite clear. In the case of pouring temperature 700 °C, obvious cracks and cavities due to insufficient reaction are found near the interface (Figs. 2c and 3c), which are detrimental to the bonding of the two alloys. The results also show that the width of the reaction layer of the Al-Cu is narrowed with the decrease of pouring temperature.

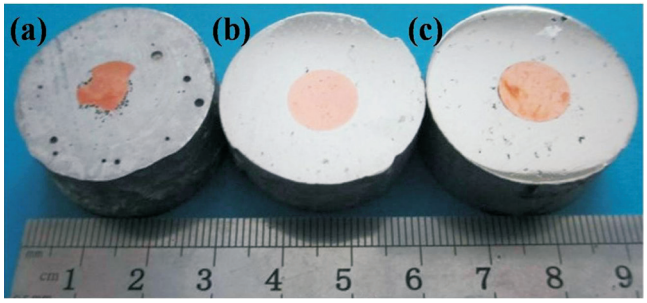


Fig. 2: Macrostructures of clad ingots with different pouring temperatures: (a) 800 °C, (b) 750 °C, (c) 700 °C

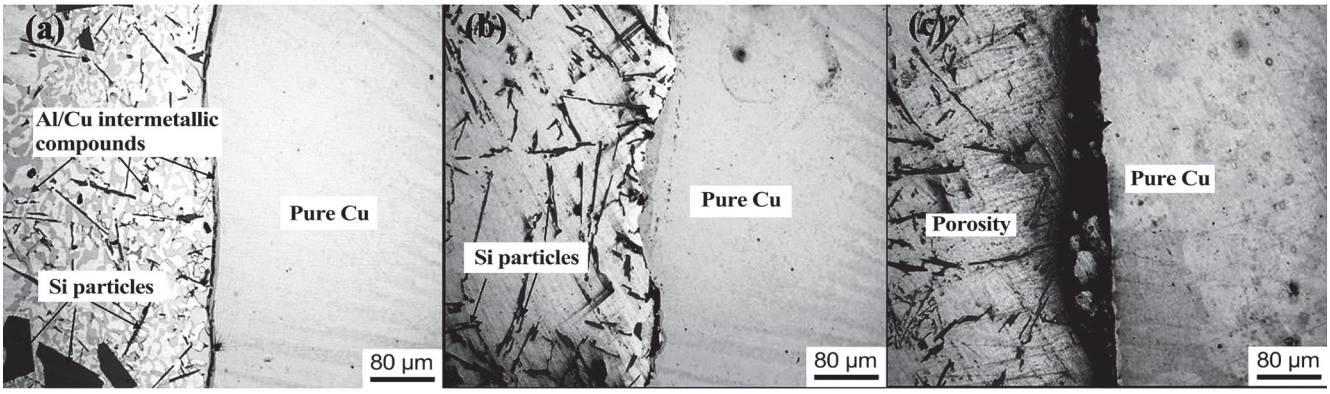


Fig. 3: Microstructures of interface region in clad ingots with different pouring temperatures: (a) 800 °C, (b) 750 °C, (c) 700 °C

In order to study the reaction between liquid aluminum and solid copper, further analysis was carried out by means of SEM and EDS. Figure 4a shows the SEM images taken from the Al-Cu interface with the Al pouring temperature of 800 °C. Several areas of diverse microstructure with different shapes of IMCs can be observed near the interface. Those are marked and magnified in Fig. 4b-d. Figure 4b shows the interfacial region of Al-Cu clad material, which consists of 5 layers: pure Cu, δ phase (Cu_3Al_2), CuAl, $CuAl_2$, and pure Al matrix in turn from the outside to the inside part of the ingot. The results of phase

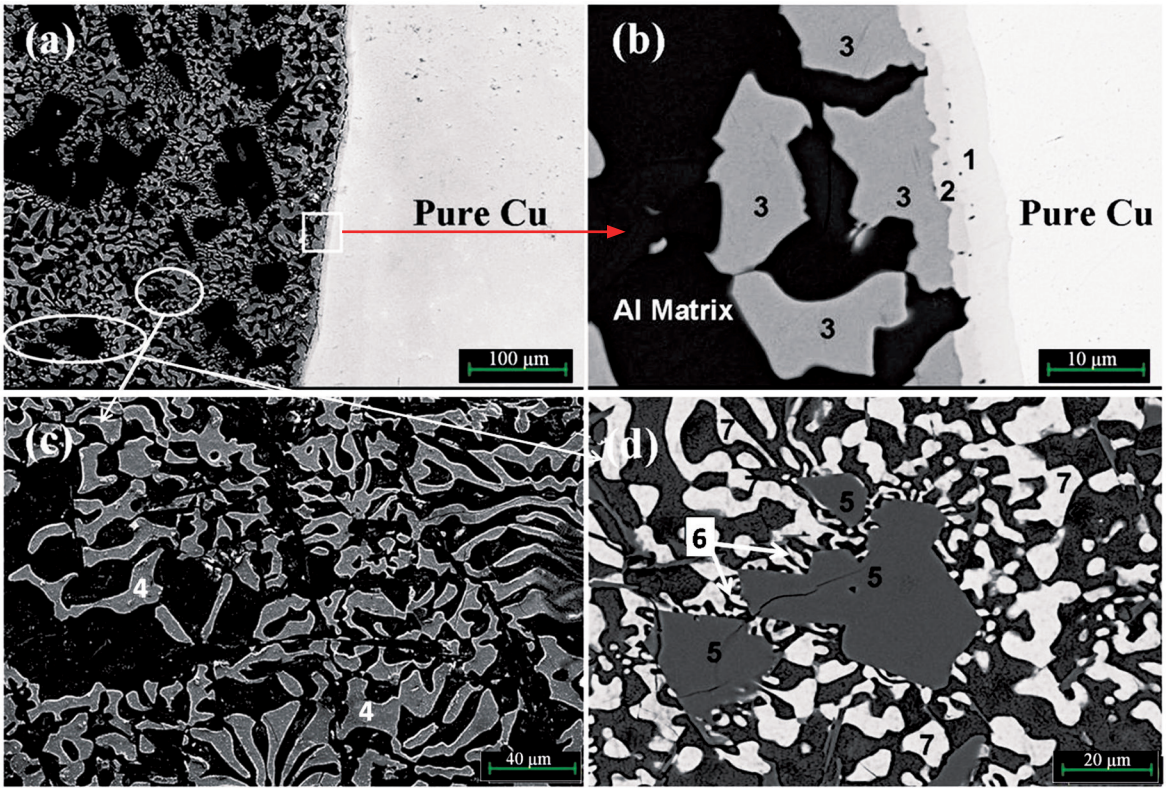


Fig. 4: SEM micrograph of Al-Cu interface when pouring at 800 °C

Table 1: Elemental analysis results of Al-Cu interfaces by EDS

Position	Element (at.%)			Suggested IMCs
	Al	Cu	Si	
1	36.140	63.860	-	δ
2	49.491	50.509	-	CuAl
3	65.769	34.231	-	CuA_{l2}
4	63.68	35.35	0.98	$CuAl_2$
5	-	-	100	Si
6	71.36	27.73	0.92	$CuAl_2$
7	64.66	34.13	1.22	$CuAl_2$

composition are based on the EDS analysis, listed in Table 1. It is noted that the content of Cu is gradually reduced from the Cu side to the Al side. Because of the overreaction of Al-Cu at high pouring temperature, Cu element diffuses deeply through the Al matrix, and a large amount of $CuAl_2$ phase generates in the Al matrix (Fig. 4c). The Al-Cu reaction also has an influence on the Al-Si eutectic reaction: due to the consumption of Al element during the Al-Cu reaction, part of Si precipitates in the form of primary Si (Fig. 4d).

2.2 Vickers hardness

Figure 5 shows the Vickers hardness profile measured perpendicular to the Al-Cu interface. When the pouring

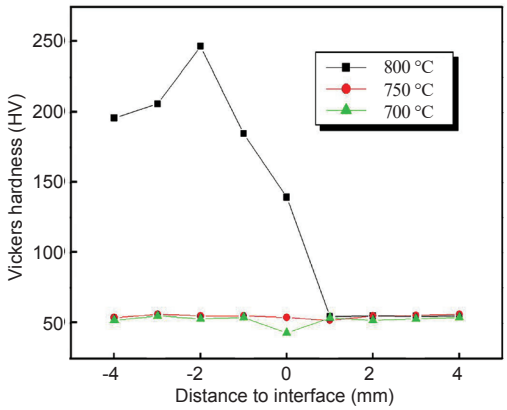


Fig. 5: Vickers hardness across interface of Al-Cu ingots

temperature of aluminum melt is 800 °C, the micro-hardness values are much higher at the Al side and get an obvious decrease at the Cu side. As mentioned above, numerous Al-Cu IMCs are formed in the Al matrix at a higher pouring temperature, and such hard phases make a great contribution to the hardness of the alloy. At 750 and 700 °C pouring temperatures, the variation trend of micro-hardness is fitted reasonably well to a horizontal line, since the Al-Si and Cu have almost equal performance of hardness.

3 Discussion

It is clear that the reasonable pouring temperature of Al-Cu clad ingot by this solid-liquid bonding method is 750 °C, at which a good bonding between Al-Cu is obtained without overreaction or cavities. Hence, 750 °C is considered the optimal pouring temperature of Al melt in this study.

In the case of 800 °C pouring temperature, even though it is much lower than the melting point of pure copper (1,083 °C), the copper bar is still remelted and extremely misshapen. The schematic view of the probable process-formed Al-Cu diffusion zone is shown in Fig. 6. When the Al melt of 800 °C contacts with the solid Cu, the thermal stress on the micro-zone of the copper surface is stronger than its yield strength, resulting in the plastic deformation and creeping of copper. In this case, the Cu surface starts to be melted and reacts with liquid aluminum, forming the Al-Cu IMCs. Since there is a concentration gradient of Cu element from the Cu side to Al side, due to the gradual dissolution of Cu bar, the Al-Cu surface is formed with 5 layers of pure Cu, δ phase (Cu_3Al_2), CuAl, $CuAl_2$, and pure Al matrix in turn. The natural convection in the Al melt may lead to detachment of these IMCs, therefore, a large amount of Al-Cu IMCs (mostly $CuAl_2$ phase) are observed in the Al matrix.

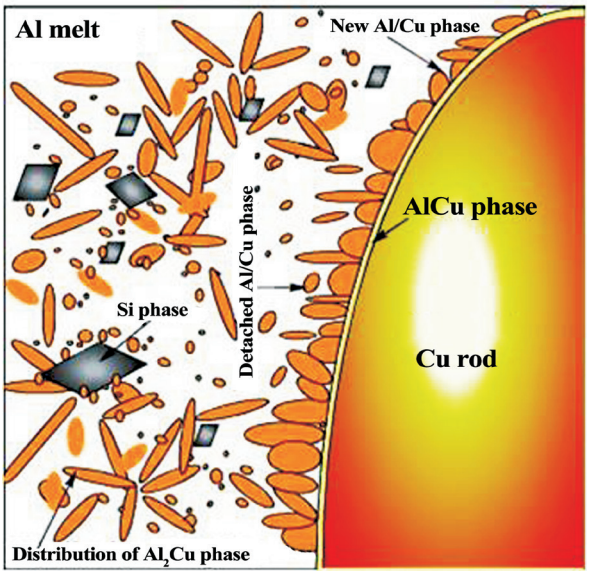


Fig. 6: Schematic drawing of formation mechanism of Cu-Al interface

When the liquid aluminum contacts with solid copper, there will be an inter-diffusion between copper and aluminum. At the initial stage, it needs an incubation period to form IMCs at the interface, which is defined as t_0, and can be expressed as follows:

$$t_0 = k\exp\left[\frac{A+E}{RT}\right] \quad (1)$$

where, k is dissolving constant of reaction phase, A is effective activation energy during this process, E is atomic activation energy of dissolving element, R is gas constant, T is absolute temperature. From this equation, it can be considered that the higher reaction temperature will lead to the shorter incubation time of IMCs formation. The growth of an IMC phase layer may be entirely controlled by diffusion, reaction rate, or the two processes simultaneously.

When the reaction between Al and Cu occurs, $CuAl_2$ phase forms firstly, which is considered as the easiest formation of Al-Cu product, and is detrimental to the interfacial bonding due to its brittleness. However, δ phase (Cu_3Al_2) and CuAl are also observed near the interface in this study, implying that other reactions occur during the solidification, which result in the formation of Cu_3Al_2 and CuAl.

Assuming that Cu_3Al_2 phase is formed by the interaction of Cu atom and $CuAl_2$ via the following reaction:

$$2Cu+CuAl_2 \rightarrow Cu_3Al_2 \quad (2)$$

the standard molar Gibbs free energy is given:

$$\Delta_r G_m{}^0 = \Delta_f G_m{}^0(Cu_3Al_2, s) - \Delta_f G_m{}^0(CuAl_2, s) - 2\Delta_f G_m{}^0(Cu, s) \quad (3)$$

For pure copper, the standard Gibbs free energy of formation $\Delta_f G^0=0$, the standard molar enthalpy of formation $\Delta H^0_{298}=0$, the standard molar entropy $S^0_{298}=33.35$ (J•mol^{-1}•K^{-1}), and isobaric heat capacity $C_p=22.64+6.28\times10^{-3}T$ (J•mol^{-1}•K^{-1}).

The change of standard molar Gibbs energy is given:

$$\Delta G = \Delta H - \Delta(TS) \quad (4)$$

$$\Delta H = \int_{298}^{T} C_p dT = \int_{298}^{T}(22.64+6.28\times10^{-3}T)dT \quad (5)$$
$$= 3.14\times10^{-3}T^2 + 22.64T - 7025.56$$

$$\Delta(TS) = T_2S_2 - T_1S_1 = T\times(S^0_{298} + \int_{298}^{T}\frac{C_p}{T}dT) - 298\times S^0_{298} \quad (6)$$
$$= 6.28\times10^{-3}T^2 + 22.64T\ln\left(\frac{T}{298}\right) + 33.35T - 9938.3$$

Therefore,

$$\Delta_f G^0_m(Cu, s) = -3.14\times10^{-3}T^2 + 22.64T\ln\left(\frac{T}{298}\right) - 10.71T + 2912.74 \quad (7)$$

Under the conditions of standard pressure and temperature, the standard molar Gibbs free energy of the Al-Cu IMCs can be calculated as follows [17]:

$$\Delta G^0_m(Cu_3Al_2, s) = -128440 + 36.9T \quad (8)$$

$$\Delta G^0_m(CuAl_2, s) = -77100 + 22.3T \quad (9)$$

$$\Delta G_m^0(\mathrm{CuAl}, s) = -51380 + 14.8T \quad (10)$$

When T is 1,073 K (800 °C), $\Delta_r G_m{}^0$<0, indicating that the reaction (2) can occur spontaneously. The results suggest that the aluminum melt contacts with the copper bar, forming $CuAl_2$ phase in the Al matrix. Then Cu_3Al_2 phase precipitates by the reaction between Cu and $CuAl_2$. Meanwhile, the reaction $CuAl_2$ + Cu_3Al_2 → 4CuAl also occurs spontaneously (the Gibbs free energy can be calculated in the same way as described above). This explains the presence of δ-Cu_3Al_2 phase and CuAl layer in the transition region between Cu and Al matrix.

Meanwhile, the pouring temperature can also influence the Al-Cu reaction by the element diffusion of Cu atoms. At the 800 °C pouring temperature, the diffusion rate of Cu from the solid to the Al melt is larger than that at lower temperatures (700 and 750 °C), resulting in an increased amount of Cu atoms in the Al melt. This will promote the reaction between Cu and Cu-Al IMCs, as well as the formations of $CuAl_2$, Cu_3Al_2 and CuAl. In this case, abundant Al-Cu IMCs such as $CuAl_2$, Cu_3Al_2 and CuAl can be found near the interface at the condition of 800 °C. In the case of pouring temperature 700 °C, the element diffusion of Cu and the reactions between Al-Cu IMCs are not sufficient for the formation of stable interfacial bonding, with a result of cavities and other casting defects. In contrast, the good bonding was achieved at the reasonable pouring temperature of 750 °C, with a good interface of metallurgical bonding and no defects by appropriate element diffusion of Cu and reaction between Al and Cu.

4 Conclusion

The solid-liquid bonding method was carried out to investigate the phase formation of liquid aluminum alloy and solid copper. The results indicate that the pouring temperature of Al melt has a big influence on the interfacial microstructure and phase formation, by promoting the Cu diffusion from the solid to the Al melt and the reaction between Cu and Al. Under the conditions in this study, the reasonable Al pouring temperature is 750 °C, with a good bonding between Al and Cu. As a contrast, excess Al-Cu IMC phases form near the interface at 800 °C, and cavities as well as other defects can be found at the lower pouring temperature of 700 °C.

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