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Study on Interface Microstructures of Cu-Al Composite Plate Fabricated by Cast Rolling

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The microstructure of Cu-Al composite plate based on the cast-rolling technology is investigated by scanning electron microscope, x-ray diffractometer, energy-dispersive spectroscopy and transmission electron microscopy. The interfacial structure is analyzed by high-resolution transmission electron microscopy. The results show that the copper–aluminum composite plates with oxygen-freed metallurgical bonding interface by cast rolling. The interfacial intermetallic is $CuAl_2$ with a thickness of 0.35 μm. There is a crystallographic orientation relationship between the matrix Al and $CuAl_2$. The (200) crystal plane of $CuAl_2$ parallels to the $(11\bar{1})$ crystal plane of Al with the mismatch of 0.22.

Keywords cast rolling, Cu-Al composite plate, interface, semi-coherent interface

1. Introduction

With the development of science and technology, a single-performance material cannot meet the requirements of modern industry. Bimetallic composite materials can combine the advantages of various components, resulting in a better performance in general (Ref 1, 2). The Cu-Al bimetallic composite plates have the excellent electrical conductivity, thermal conductivity of the copper and lightweight, corrosion resistance and economy of aluminum (Ref 3). Therefore, Cu-Al bimetallic composite plates can be applied not only to the field of signal transmission and power transmission, but also widely to aviation, petroleum, chemical, shipbuilding and other industrial areas (Ref 4-6).

At present, Cu-Al composite materials can be produced through Cu-Al surface welding (Ref 7), explosive composite (Ref 8), rolling composite (Ref 9), core continuous casting (Ref 10), etc. However, cast-rolling method has more advantages, such as low energy consumption, cost-effectiveness and good quality. Without changing the original conductivity of Cu and Al, the cast-rolling composite technology can achieve metallurgical bonding between copper and aluminum interfaces and obtain high interfacial bonding strength. Some intermetallic compounds, such as $CuAl_2$, Cu_9Al_4 and CuAl, would be formed in the composite process of high-temperature aluminum liquid and copper plate. The secondary intermetallic compound formed under extreme conditions significantly deteriorates the interfacial bonding strength of the composite (Ref 11, 12), resulting in a decrease in bonding strength and bending properties of the composite sheet and deterioration in electrical conductivity. Therefore, it is necessary to control the diffusion reaction to obtain the complete interfacial bond, thus extending the applications of Cu-Al clad materials.

Chen et al. (Ref 13) studied the effects of heat treatment on the interfacial structure of Al-Cu prepared by cold rolling and revealed the structural development and growth dynamics of the interface. Lee et al. (Ref 14) fabricated copper–aluminum composite sheets by hot-pressing method, analyzed the mechanical properties of $CuAl_2$, Cu_9Al_4 and CuAl phases by nanometer hardness tester and studied the crystal structure of three phases in detail. RAWERS and PERRY (Ref 15) studied the strengthening and toughening effects on the bridge-crack deformation mechanism using the tensile tests of brittle intermetallic/ductile metallic microlaminates.

Although some scholars have done some research on annealing process, there are few reports about the interfacial microstructure and structure of Cu-Al composite plate produced by cast-rolling technology. This essay aims to analyze the interface phase species and explore the crystallographic orientation relationship between the matrix Al and interfacial layer.

2. Experimental

2.1 Preparation Process

Experiments were carried out using 1050 industrial Al liquid and 1-mm-thick T2 pure Cu. As shown in Fig. 1, the pure Cu plate had a cross-sectional dimension of 1000 mm × 1 mm, and the oil was removed by degreasing. Then, the pure Cu plate was cleaned with 20% HCl solution and dried and then with acetone. The solution cleaned and dried quickly. The cleaned Cu plate was placed in a heating furnace for annealing in order to eliminate inside stress. Al liquid of 800 °C pure was degassed again and held for 15 min. Then, the aluminum liquid was placed in the cast device for storing the aluminum liquid and left until change to semi-molten state to allow the aluminum liquid to flow out from the preheated nozzle. Cu was preheated to 200 °C, and semi-solid Al was poured onto a two-roll microvibratory casting mill to obtain a Cu-Al com-

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posite panel with the width of 8 mm. As shown in Fig. 1, the wire was cut into 10 mm × 10 mm × 8 mm samples and then was ground by sandpaper and polished by mechanical.

2.2 Characterization

The diffusion of the interface region was observed by a scanning electron microscope (SEM) equipped with energy-dispersive spectroscopy (EDS). Bruker D8 x-ray diffraction (XRD) was used to identify the phase of the exfoliated sample interface, with the following parameters: CuK alpha radiation is in the scanning range of 35 kV, 25 mA and 14-92°. The intermetallic compound was analyzed by JEM-2100 transmission electron microscopy (TEM). Atomic micrographs at the interface between Cu and Al and within matrix were characterized by a high-resolution transmission electron microscope (HRTEM).

Table 1 The possible phases at the interface of Cu/Al composite plate

Area	Al, at.%	Cu, at.%	Phase
1	100	0	Al Matrix
2	99.27	0.73	Al Matrix
3	98.87	1.13	Al Matrix
4	66.43	32.57	$CuAl_2$
5	0.06	99.94	Cu Matrix
6	0.02	99.98	Cu Matrix
7	0	100	Cu Matrix

3. Results and Discussion

3.1 Interface Organization and Phase Analysis

Figure 2(a) and (b) shows the SEM images of Cu-Al interfaces. As can be seen from Fig. 2(a), the interface is straight and clean and has no fragmentation. Figure 2(b) is a scan line of the corresponding position in Fig. 2(a). Cu and Al are tightly integrated (Fig. 2a), and the Cu atoms and Al atoms diffuse with each other (Fig. 2b). Therefore, the bonding of interface can be realized through the method of metallurgy bonding. It is also observed that the diffusion of Al atoms has a certain small step at the interface, as shown in A area in Fig. 2(b), indicating that there is a diffusion layer at the interface. The thickness of the diffusion layer is determined by the intermetallic compound and atomic migration at the interface.

The results of EDS analysis are shown in Fig. 2(a), and the interface elements are shown in Table 1. The proportion of Cu and Al atoms of interfacial intermetallic compound is 1:2. Combined with the Cu-Al binary alloy phase diagram (Ref 16), it could be concluded that the intermetallic compound is $CuAl_2$ phase. The formation of $CuAl_2$ phase can be ascribed to high cast-rolling temperature of Al liquid, which provides sufficient

Table 2 The EDS analysis of peeled surface of Cu-Al composite plate

	Cu side						Al side					
	1		2		3		4		5		6	
Element	wt.%	at.%	wt.%	at.%	wt.%	at.%	wt.%	at.%	wt.%	at.%	wt.%	at.%
O K	1.98	7.32	1.70	6.36	1.67	6.22	0.88	1.49	1.54	2.2	1.52	1.24
Cu K	97.02	90.49	97.49	91.85	97.14	91.15	0.34	0.14	38.9	33.0	38.51	32.7
Al K	1.00	2.19	0.81	1.79	1.19	2.63	98.78	98.37	59.56	64.8	59.97	66.06

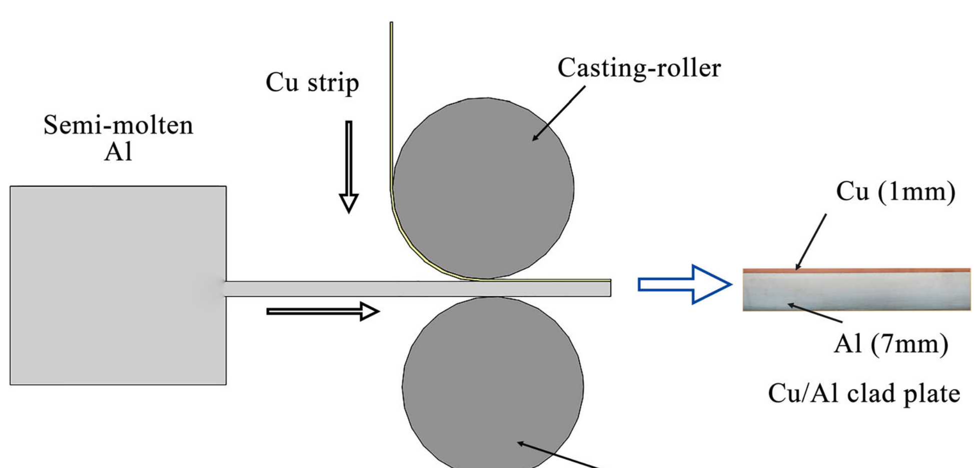

Fig. 1 Diagram of Cu-Al composite plate by cast-rolling process

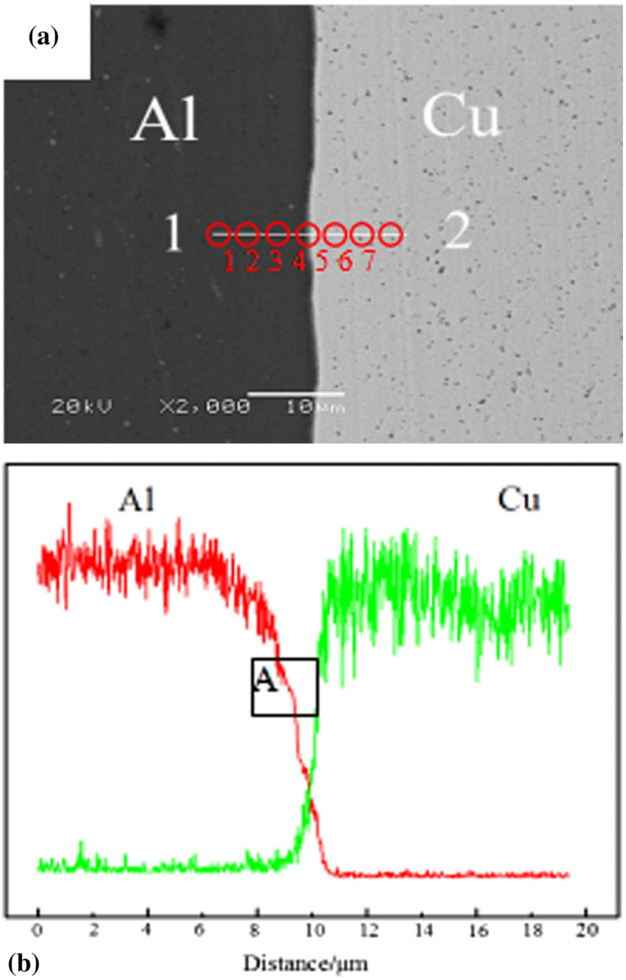

Fig. 2 The SEM image of Cu-Al interfaces

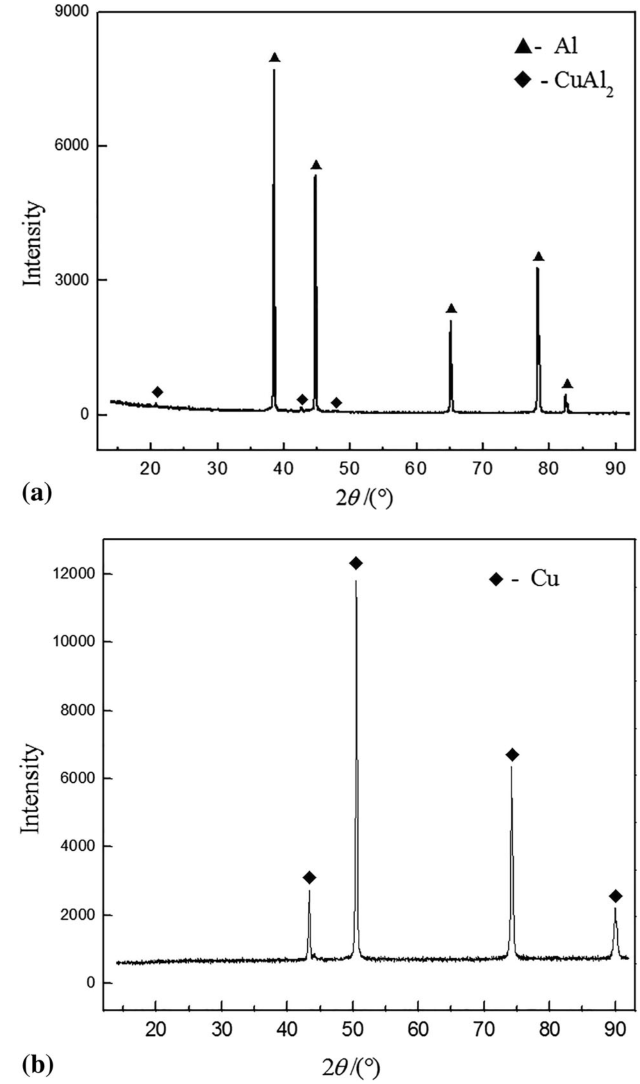

Fig. 3 XRD patterns of Al side (a) and Cu side (b) at the interface of Cu-Al composite plate

thermal energy for Cu and Al atoms, thus exceeding atoms diffusion barrier (Ref 17). During the cast-rolling process, the metallurgical bonding layer is formed at the interface between copper and aluminum, which can improve the bonding quality of the copper–aluminum composite plate. Furthermore, the interface bonding strength is affected by the mechanical property of intermetallic compound and crystallographic orientation relationship between the Al matrix and interfacial intermetallic compound. Therefore, a clear interface structure is crucial for promoting the mechanical property of Cu-Al composite plate.

Diffusion activation energy of Cu atoms in Al matrix is 1.36×10^5 J/mol, and Al atoms in Cu matrix is 1.655×10^5 J/mol (Ref 18). Therefore, Cu atoms are activated firstly during the composite process of Cu-Al composite plate. At the same time, the interatomic gap of copper is smaller than that of aluminum atoms. (Lattice constant α_{Cu}, α_{Al} is 0.3615 nm and 0.4082 nm, respectively.) Therefore, Cu atoms are more likely to diffuse into the lattice position of Al lattice.

The XRD phase analysis is performed on the stripping Al and Cu surface of Cu-Al composite plate, and the results are shown in Fig. 3. There are Al and $CuAl_2$ phases on the Al side, and the $CuAl_2$ phase has a low peak; however, the Cu side only has Cu phase. According to the XRD's results, $CuAl_2$ phase is firstly generated at the interface. It mainly depends on the thermodynamic conditions of the phase, and the diffusion between the atoms of Cu and Al. According to the results of Fig. 2 of line scanning, the diffusion amount of Cu atom is significantly higher than that of Al atom. Therefore, when the thermodynamic conditions are satisfied, Cu begins to diffuse to the Al side to form a solid solution, so the Al content is higher (Ref 19). At the same time, the interface tearing position is between $CuAl_2$ and Cu. It indicates that $CuAl_2$ has a good combination with Al matrix and is firstly generated on the Al side.

Figure 4 shows the surface morphology and EDS spectrum analysis of Cu and Al composite plates. The shape of the Cu strip surface and the pits can be observed. The Al strip has a white coating. It is found that there is a small amount of oxygen element and Al element on the Cu side, while the Al side has more Cu elements. According to Fig. 4(a) 1 point and Fig. 4(b) analysis of EDS elements at 4 points, the measured part is Cu, Al matrix and almost no O element exists. The reason for this phenomenon is that the oxide film on the surface of the Cu substrate would be torn under external mechanical force during the process of rolling. The copper base layer is coated with a

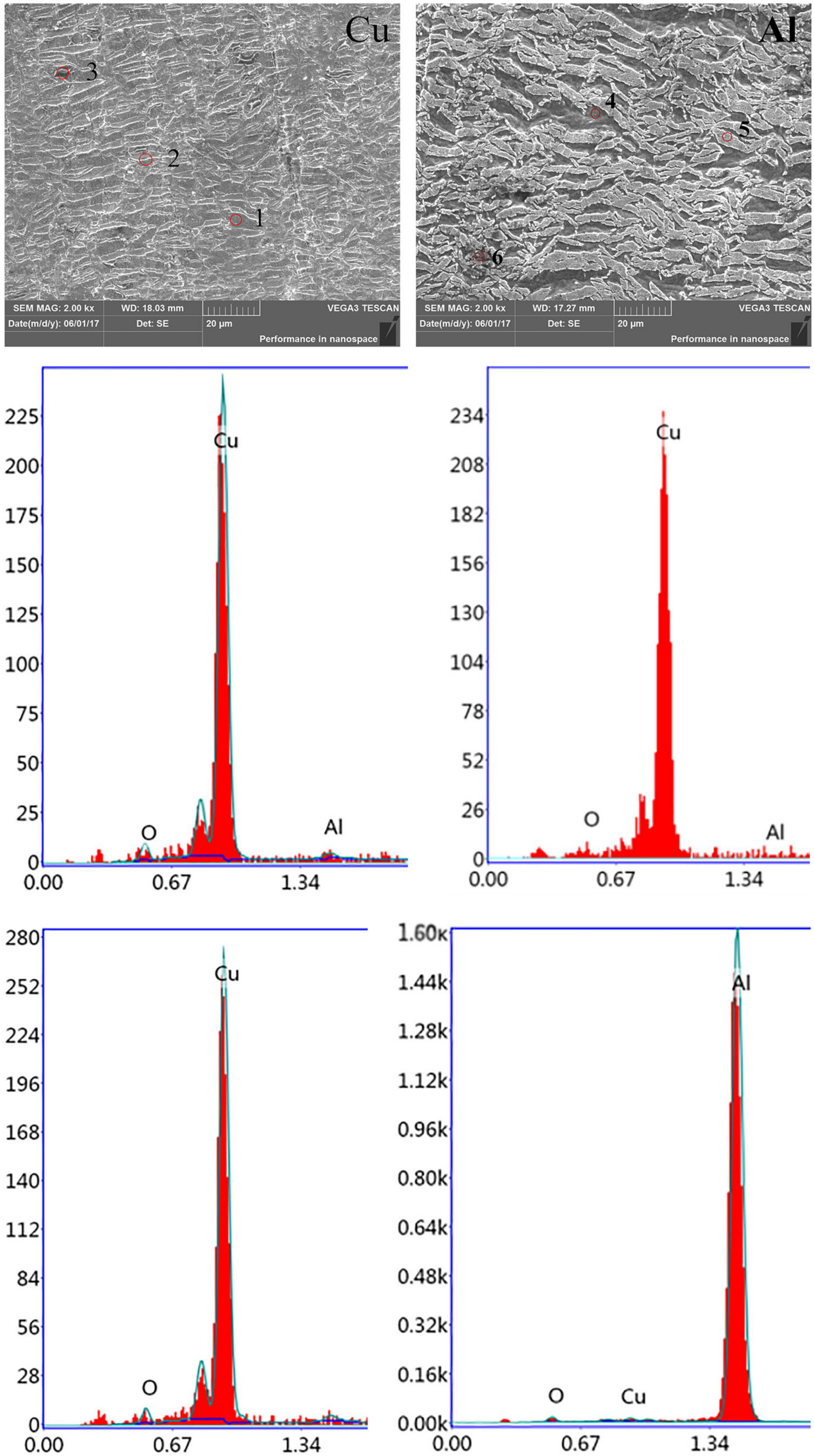

Fig. 4 The morphology and EDS analysis of peeled surface of Cu-Al composite plate

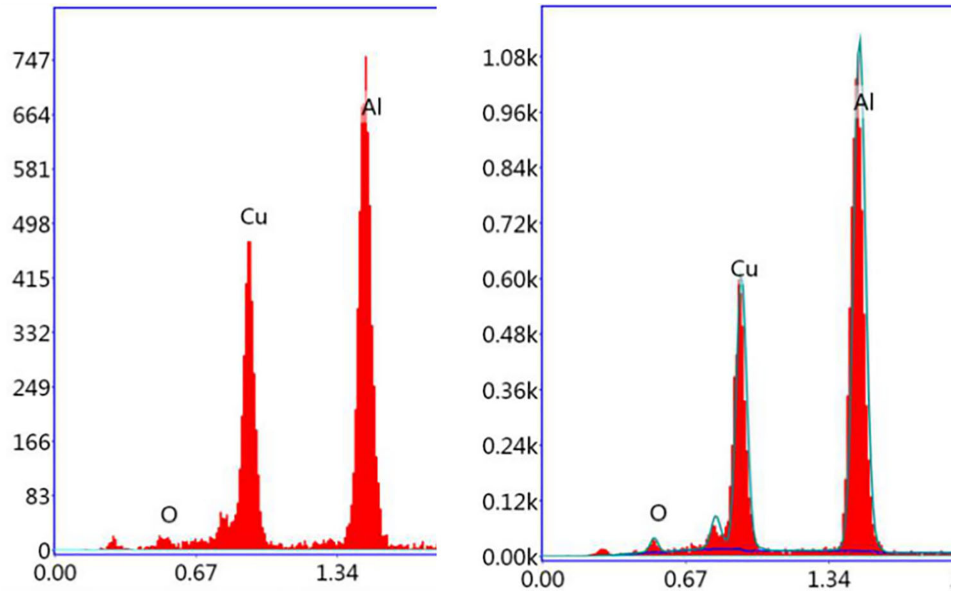

Fig. 4 continued

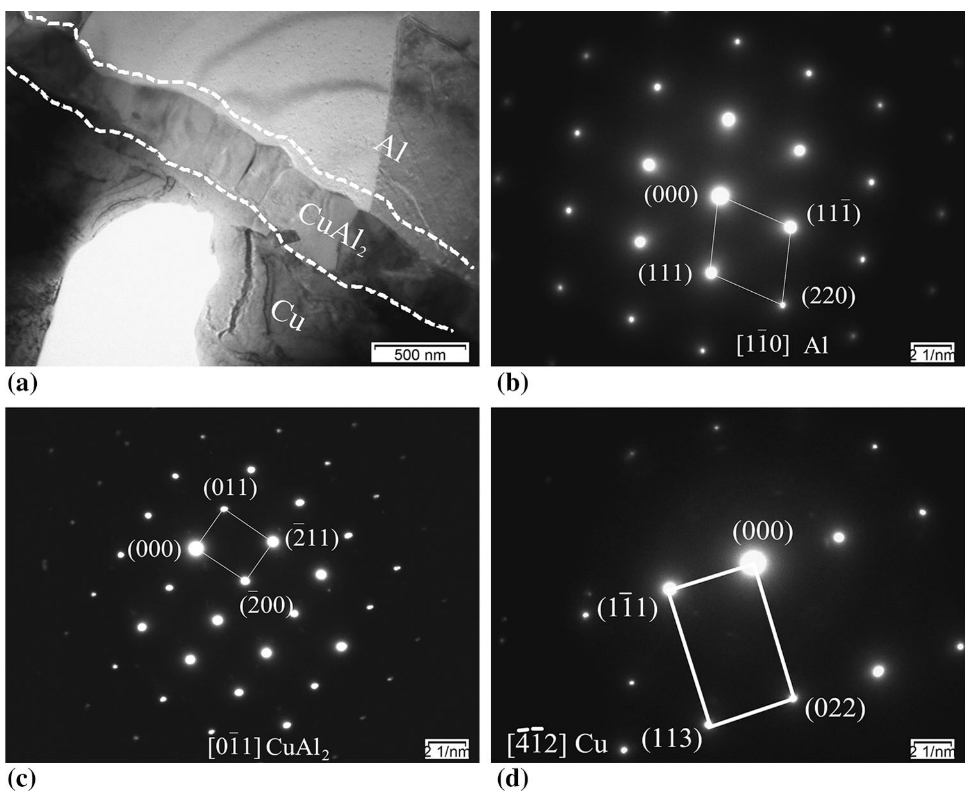

Fig. 5 TEM images and SAED of Cu-Al composite plate: (a) TEM images of interface; (b) ~ (d) SAED of interface

semi-solid aluminum layer, which makes the interface close to the anaerobic environment and reduces the damage of the oxide to the interface. The point 5 area and the point 6 area on the white layer in Fig. 4(b) were analyzed, and the results are shown in Table 2. The copper content is atomic percentage (at.%), the Al atom ratio is close to 1:2 and the overlying intermetallic compound is $CuAl_2$. The measurement results are consistent with the XRD phase analysis of Fig. 3. The flat $CuAl_2$ can be joined to the matrix material to increase the bond strength of the composite plate.

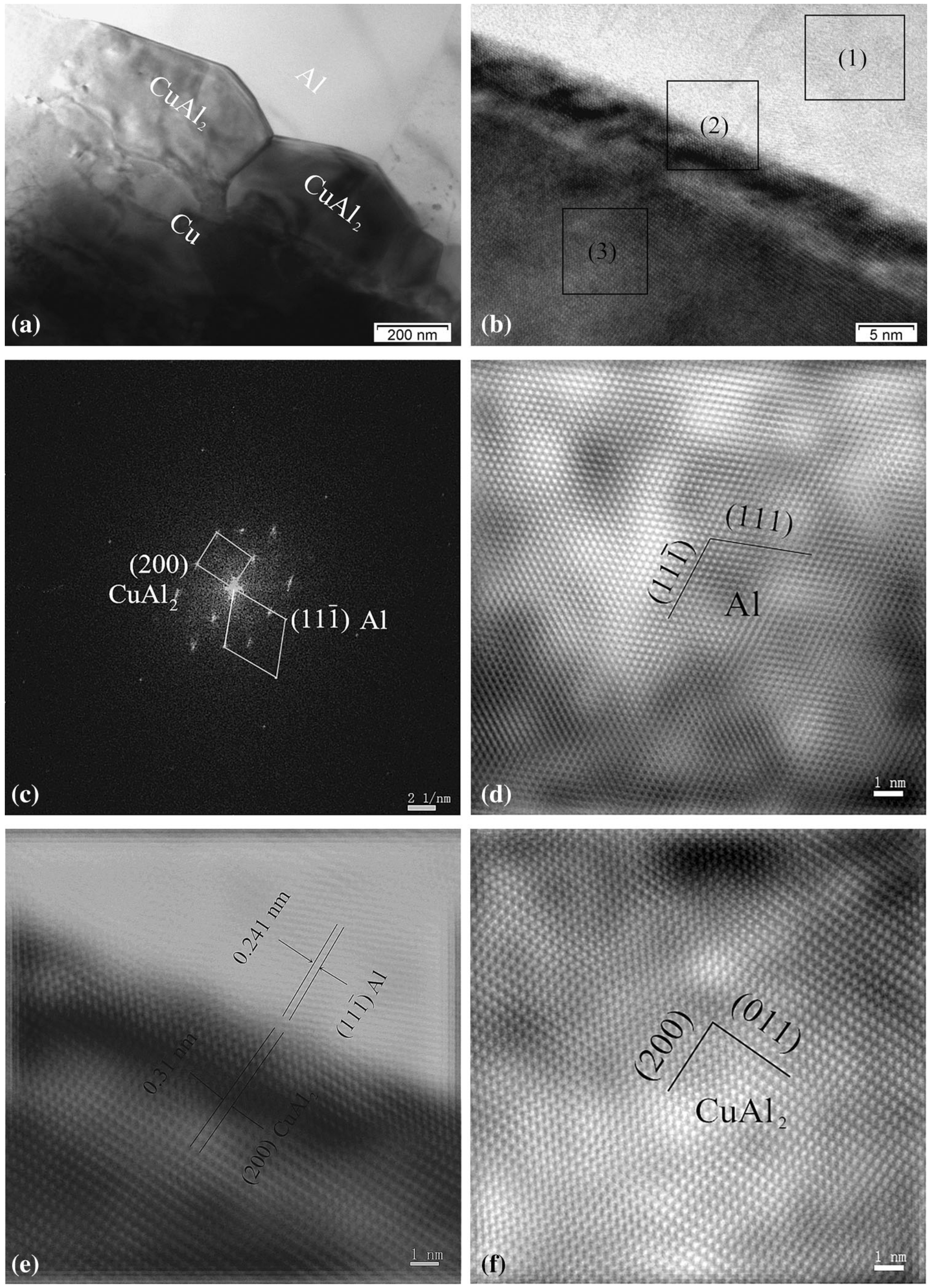

Fig. 6 HRTEM images and SAED of Cu-Al composite plates: (a) TEM images of interface; (b) HREM of interface; (c) SAED of interface; (d-f) IFFT image of area I 1 ~ 3 in (a)

3.2 TEM and HRTEM Image Analysis

The thickness of the diffusion layer is determined by the migration distance between the intermetallic compound and the solid–liquid interface. The TEM and electron diffraction patterns of the Cu-Al composite plate interface are shown in Fig. 5. The interface between the Cu layer and the Al layer has an intermetallic compound-forming layer of about 0.35 μm wide. The upper right picture is the face-centered cubic Al of Fig. 5(a), the left side is Cu, and the interface layer is $CuAl_2$ intermetallic compound. As shown in Fig. 5(c) $CuAl_2$ is a tetrahedral structure, spatial group (140) I4/MCM, lattice constant (a = 0.6065 nm, b = 0.6065 nm, c = 0.4873 nm). Figure 5(b) and (d) shows Al and Cu matrix diffraction patterns.

HRTEM analysis is performed on the region I in Fig. 6(a) to obtain Fig. 6(b), and regions 1, 2, and 3 in Fig. 6(b) are, respectively, subjected to Fourier transform to obtain Fig. 6(d), (e) and (f). Figure 6(c) is a diffraction pattern diagram at a region 2 of Fig. 6b, and Fig. 6b is an interface diagram between Al and $CuAl_2$. From the above, it can be concluded that the (200) crystal plane of $CuAl_2$ is parallel to the crystal plane of Al(11 $\bar{1}$). In order to further confirm $CuAl_2$/Al phase relationships, the interplanar spacing of $CuAl_2$ in the (200) direction is

0.310 nm and the interplanar spacing of Al in the (11 $\bar{1}$) direction is 0.241 nm through measurement and calculation. Their mismatch is merely 0.22.

4. Conclusion

(1) Cu-Al composite plates could be produced successfully utilizing the cast-rolling method, which can realize the metallurgical combination of semi-solid Al and Cu matrix, The anaerobic environment was formed during the bonding process, and the oxide generation was reduced, thereby obtaining composite with a better strength.
(2) Cu atoms diffuse into the Al matrix, and an intermetallic compound $CuAl_2$ having a thickness of 0.35 μm is formed at the interface of the Cu-Al composite plate.
(3) The crystal surface of $CuAl_2$ (200) is parallel to the crystal surface of the matrix Al(11 $\bar{1}$) with the mismatch of 0.22.

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References

1. D.S. Bae, S.K. Kim, S.L. Lee, T. Shibayama, and D.H. Bae, Interface Properties of Cu/Al/Stainless Steel Clad Materials, *Key Eng. Mater.*, 2007, **345**, p 1497–1500
2. T.T. Sasaki, R.A. Morris, G.B. Thompson et al., Formation of Ultrafine Copper Grains in Copper-Clad Aluminum Wire, *Scripta Mater.*, 2010, **63**(5), p 488–491
3. I.K. Kim and I.H. Sun, Effect of Heat Treatment on the Bending Behavior of Tri-layered Cu/Al/Cu Composite Plates, *Mater Design*, 2013, **47**, p 590–598
4. H.C. Tseng, C. Hung, and C.C. Huang, An Analysis of the Formability of Al/Cu Clad Metals with Different Thicknesses by the Finite Element Method and Experiment, *Int. J. Adv. Manuf. Tech*, 2010, **49**, p 1029–1036
5. X. Li, G. Zu, M. Ding, Y. Mu, and P. Wang, Interfacial Microstructure and Mechanical Properties of Cu/Al Clad Sheet Fabricated by Asymmetrical Roll Bonding and Annealing, *Mater. Sci. Eng., A*, 2011, **529**, p 485–491
6. D.G. Li, Q. Wang, T. Liu, G.J. Li, and J.C. He, Growth of Diffusion Layers at Liquid Al-Solid Cu Interface under Uniform and Gradient High Magnetic Field Conditions, *Mater. Chem. Phy*, 2009, **117**, p 504–510
7. S. Lee, I.S. Son, J.K. Lee et al., Effect of Aging Treatment on Bonding Interface Properties of Hot-pressed Cu/Al Clad Material, *Inter. J. Precis. Eng. Man*, 2015, **16**, p 525–530
8. Y.J. Su, X.H. Liu, H.Y. Huang et al., Interfacial Microstructure and Bonding Strength of Cu Cladding Al Rods Fabricated by Horizontal Core-Filling Continuous Casting, *Metall. Mater. Trans. A*, 2011, **42**, p 4088–4099
9. Ken Koyama, Kenji Shinozaki, Kenji Ikeda, Keiji Miki, and Hide-nori Kuroki, Evaluation of Brazing Properties using Al-Si-Mg-Bi Brazing Alloy, *J. Jap. I. Met. Weld. Cons*, 2000, **40**, p 403–410
10. X.J. Sun, J. Tao, and X.Z. Guo, Bonding Properties of Interface in Fe/Al Clad Tube Prepared by Explosive Welding, *T. Nonferr. Metal. So. C*, 2011, **21**, p 2175–2180
11. D.H. Bae, S.J. Jung, Y.R. Cho, W.S. Jung, H.S. Jung et al., Effect of Pre-Heat Treatment on Bonding Properties in Ti/Al/STS Clad Materials, *J. Korean Inst. Met. Ma*, 2009, **47**, p 573–579
12. Y. Guo, G. Qiao, W. Jian et al., Microstructure and Tensile Behavior of Cu–Al Multi-layered Composites Prepared by Plasma Activated Sintering, *Mater. Sci. Eng., A*, 2010, **527**(20), p 5234–5240
13. C.Y. Chen and W.S. Hwang, Effect of Annealing on the Interfacial Structure of Al-Cu Joints, *Mater. Trans.*, 2007, **7**, p 1938–1947
14. KwangSeok Lee, Sangmok Lee, Jong-Sup Lee, Yong-Bae Kim, Geun-An Lee, Sang-Pill Lee, and Dong-Su Bae, Evaluation of Intermediate Phases Formed on the Bonding Interface of Hot Pressed Cu/Al Clad Materials, *Met. Mater. Int.*, 2016, **5**, p 849–855
15. J. Rawers and K. Perry, Crack Initiation in Laminated Metal-Intermetallic Composites, *J. Mater. Sci.*, 1996, **13**, p 3501–3506
16. T. Massalski, The Al-Cu (Al-Cu) system, *J. Phase Equilib.*, 1980, **1**, p 27–33
17. H.T. Gao, X.H. Liu, J.L. Qi et al., Microstructure and Mechanical Properties of Cu/Al/Cu Clad Strip Processed by the Powder-in-Tube Method, *J Mater Proc Tech*, 2018, **251**, p 1–11
18. H. Xu, C. Liu, V.V. Silberschmidt, S.S. Pramana, T.J. White, Z. Chen, and V.L. Acoff, Behavior of Al Oxide, Intermetallics and Voids in Cu–Al Wire Bonds, *Acta Mater.*, 2011, **59**, p 5661–5673
19. Y. Guo, H. Jin, Z. Shi, and G. Qiao, Intermetallic Phase Formation in Diffusion-Bonded Cu/Al Laminates, *J. Mate. Sci*, 2011, **46**, p 2467–2473