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On the interface development and fracture behaviour of roll bonded copper/aluminium metal laminates

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Copper/aluminium laminates were prepared by roll bonding at 430 °C with a 60% rolling reduction in a single pass. Sintering treatments at temperatures between 300 and 500 °C were applied to the as-rolled laminates. The interface development and fracture behaviour of the sintered materials were studied. It was found that two major diffusion controlled interface reactions, namely interfacial phase transformations and Kirkendall void formation, occurred in the sintering process. Four different types of phase development were detected in the interface region. As the sintering time and/or temperature increased, the Cu_9Al_4 phase became dominant. Microhardness measurements confirmed that copper-rich phases possessed higher hardness than the aluminium-rich phases, contributing a higher bond strength. On the other hand, as the sintering time and/or temperature increased, Kirkendall void formation was found to became significant with agglomeration of voids, leading to the formation of a weak layer in the interface region. It was found that the resulting bond strengths of the metal laminates generally increased to maximum values under optimum sintering conditions and then decrease substantially after sintering at high temperatures for prolonged periods. *© 1999 Kluwer Academic Publishers*

1. Introduction

Metal laminates have become increasingly popular for engineering applications in recent years [1, 2]. They usually possess enhanced mechanical properties and corrosion resistance, resulting in improved service performance. Roll bonding is one of the major production methods commonly used in the manufacture of metal laminates. After the rolling process, a sintering heat treatment is usually employed to the as-rolled materials to enhance the bond strength of the laminates [3]. The bond strength and mechanical properties of the laminates are generally governed by both the rolling and sintering conditions. Previous studies on the solid state bonding of metals [4–7] suggest that under the combined action of pressure and heat over short periods, the reactions between the metal laminates involve a three-stage process of (i) development of physical contact, (ii) activation of the surfaces in contact and (iii) interaction within the materials being joined. It is believed that a mechanical bond between the metal first forms in the rolling process and then a strong metallurgical bond develops at the interface of the metal laminates in the sintering heat treatment. However, the complex interface development of the metal laminates during the rolling and sintering processes is not yet fully understood.

Recent studies of copper/aluminium laminates [8–10] show that several important process parameters including rolling temperature, rolling reduction, sintering temperature and sintering time significantly affect the bond strength of the laminates. It was found that as the sintering time increased, the bond strength of the laminate generally increased to a maximum and then dropped to much lower values after prolonged sintering. Critical sintering conditions therefore existed to achieve optimum bond strengths [8]. The rolling reduction and temperature applied in the rolling process were also found to greatly affect the mechanical properties of the sintered laminates [9, 10]. As the rolling reduction increased, higher bond strengths for the laminates were achieved in both the as-rolled and sintered conditions [9]. On the other hand, as the rolling temperature increased, the bond strength of the laminates first increased to a maximum at a rolling temperature of 430 °C, and then decreased substantially for roll bonding at 500 °C [10]. The present paper reports the results in relation to the interface development and fracture behaviour of the copper/aluminium laminates under different sintering conditions. The relation between the process conditions and the interface development of the metal laminates is investigated.

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2. Experimental

Metal laminates of copper/aluminium were prepared by roll bonding at 430 °C with a 60% rolling reduction in a single pass. The copper and aluminium strips were of initial thickness of 2.6 mm and 1.0 mm respectively before roll bonding. Post-rolling heat treatments were applied to the rolled samples at 450 °C for various periods. Sintering at other temperatures between 300 and 500 °C were also conducted for comparison purpose. Peel tests were carried out on sintered samples of dimensions in 100 (L) × 10 (W) mm to study the fracture behaviour of the laminates. Interface morphology and fracture characteristics of the laminates were examined using scanning electron microscopy (SEM) at 15 kV. Compositions across the interface of the metal laminates were determined using energy dispersive X-ray spectroscopy (EDS) conducted in a scanning electron microscope. The thickness of the interface was determined as the separation between the 95%Al/5%Cu and 95%Cu/5%Al composition boundaries in all the samples. Formation of intermetallic phases in the interface was analysed by X-ray diffraction technique on the as-peeled samples using a Siemens D5000 diffractometer with CuK_α radiation at small scattering angles of 1–3° and a scan rate of 0.02° s^{-1}. The divergent slit was set at 1° and the receiving slit at 0.1°. Microhardness measurements were conducted across the interface of selected samples at a load of 10 grams.

3. Results

3.1. Interface development

A steady growth in thickness of the interface was observed with increasing sintering times. Interfacial thickness of the samples after sintering at 450 °C is shown in Fig. 1. As the sintering time increased, the interfacial thickness continuously increased from 5.7 μm, in the as-rolled condition to 28.6 μm after sintering at 450 °C for 3 hours. Scanning electron microscopy revealed that the interface consisted of several different microstructural layers. Aluminium-rich and copper-rich layers were clearly distinguished, Fig. 2a and b. Voids and cracks were not significant at the interface in the samples sintered at 450 °C. However, when the sintering temperature was increased to 500 °C, voids and agglomeration of voids were observed to develop in the interface region, Fig. 3a and b. In general, the voids were found to develop in the copper-rich region for short sintering periods and agglomerate near to the boundary between the copper-rich region and the copper base metal after a prolonged sintering.

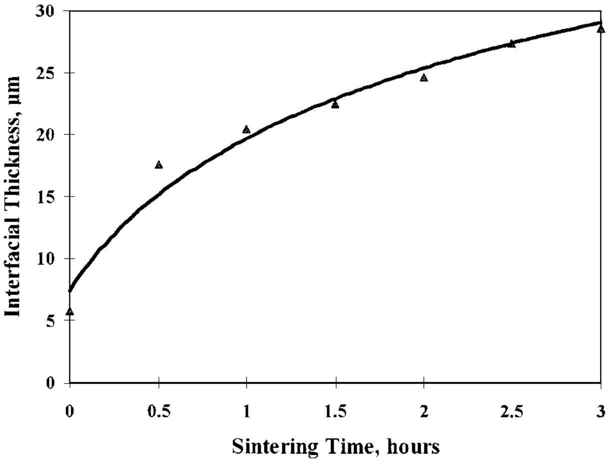
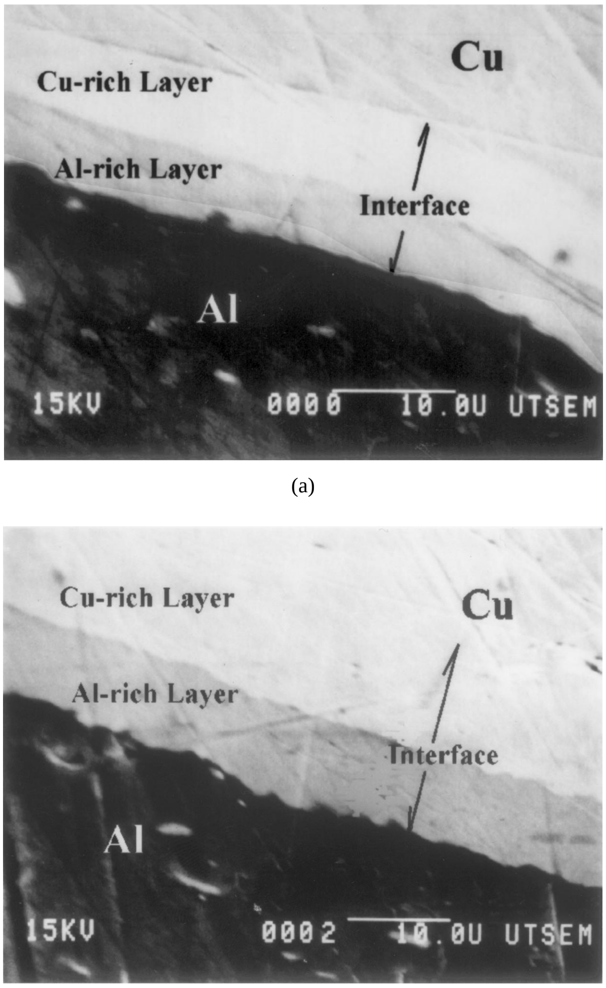


Figure 1 Growth of interfacial thickness at 450 °C for different times.



(a)

(b)

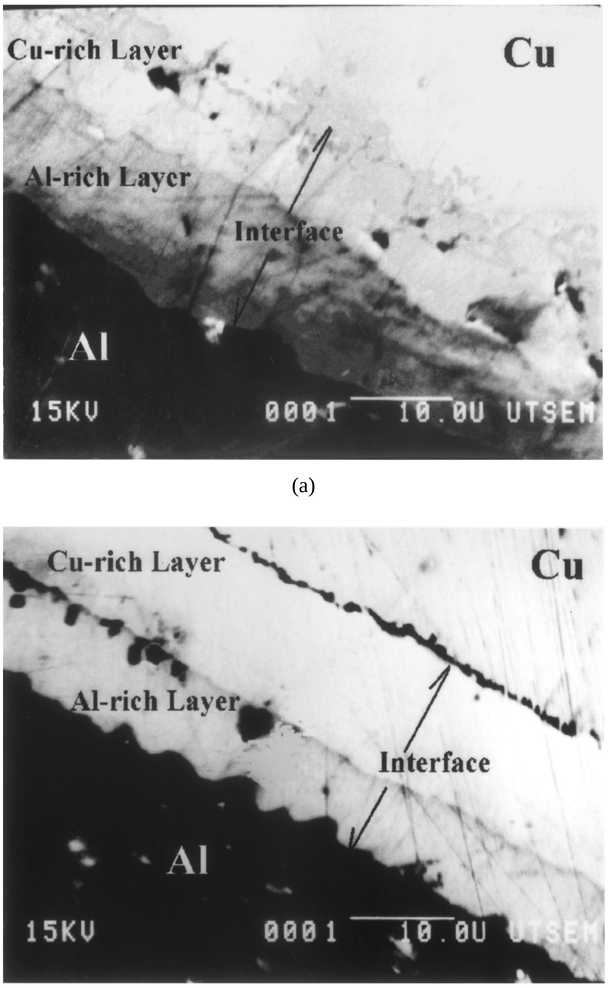
Figure 2 Scanning electron micrographs showing interface development of copper/aluminium laminates after sintering at 450 °C for (a) 1 hour and (b) 3 hours.

3.2. Microhardness across the interfacial structures

Microhardness measurements were conducted across the interface of selected samples. Fig. 4 shows the variation of microhardness, in the copper-rich and aluminium-rich layers, with sintering time at 450 °C. The copper-rich region was found to have much higher hardness than the aluminium-rich region. No apparent age hardening was detected in both copper-rich and aluminium-rich regions of the sintered samples.

3.3. Interfacial phase transformations

Distribution of the interfacial phases across the fracture surfaces of the peel test samples was determined using X-ray diffraction. Fig. 5a and b show the X-ray diffractographs for the as-rolled laminates. Aluminium and copper were respectively detected on the aluminium



(a)

(b)

Figure 3 Scanning electron micrographs showing interface development of copper/aluminium laminates after sintering at 500 °C for (a) 0.5 hour and (b) 2 hours.

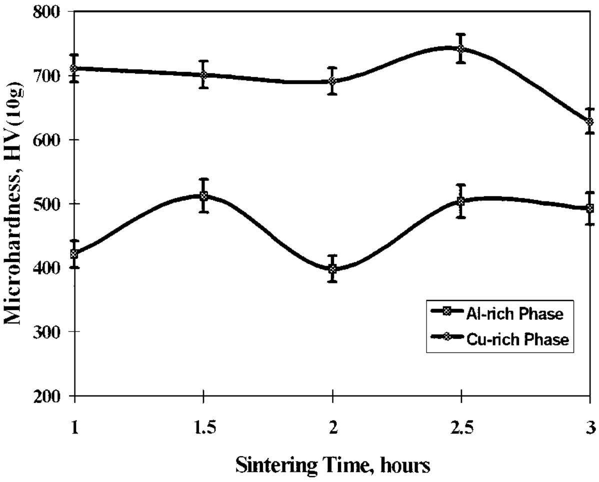


Figure 4 Microhardness variation of copper-rich and aluminium-rich regions in the interface with different sintering times.

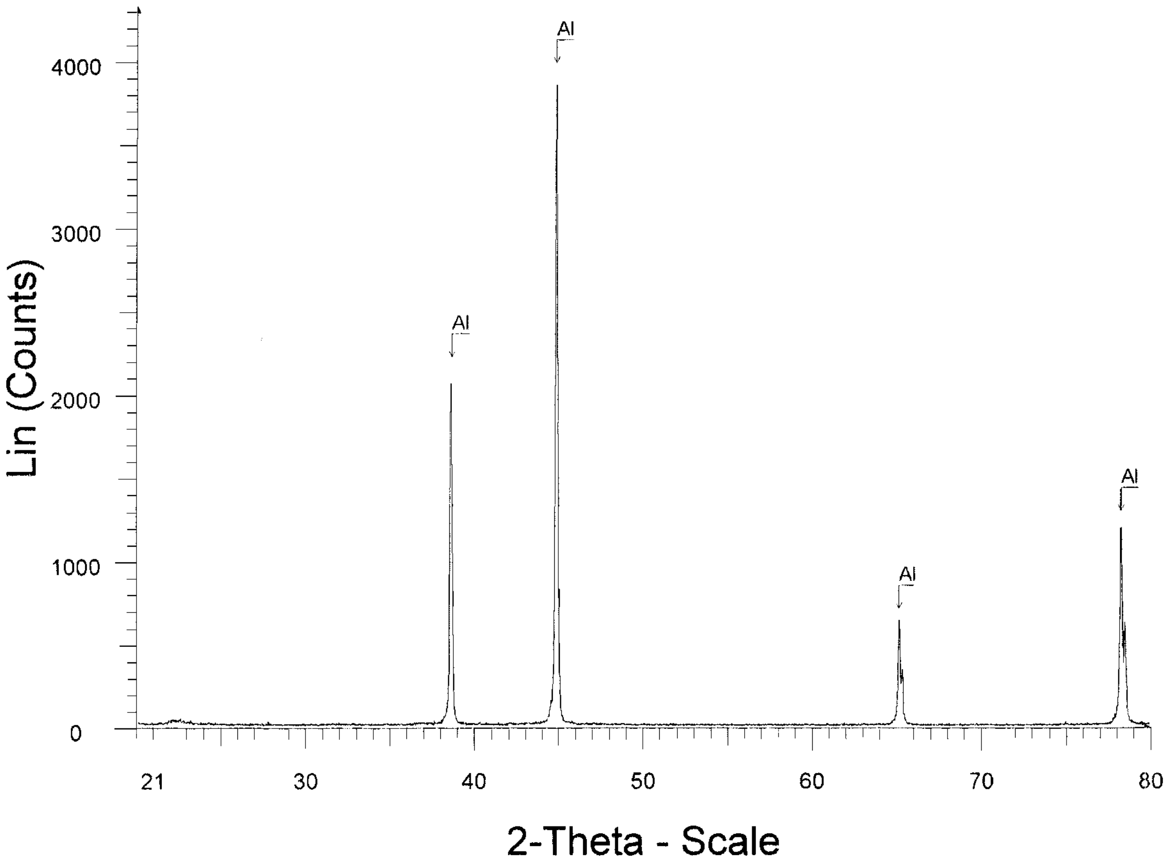
and copper sides of the samples. On sintering different phases were found to develop. $CuAl_2$ and Cu_9Al_4 were the dominant phases detected on the fracture surfaces and trace phases of Cu_3Al and Cu_4Al were occasionally observed in some of the samples. It was found that the development of the phases could be categorised into four main types. Formation of the major phases at 450 °C and other sintering temperatures is summarised in the Table I. At a sintering temperature of 300 °C, trace phase of $CuAl_2$ was found to develop on the aluminium side of the laminates whilst no significant phase development was detected on the copper side of the material, Fig. 6a and b. After short sintering periods at 450 °C, $CuAl_2$ and Cu_9Al_4 phases were found to develop on the aluminium side of the laminates and Cu_9Al_4 on the copper side of the laminates, Fig. 7a and b. As the sintering proceeded for longer periods, $CuAl_2$ and Cu_9Al_4 phases were found on both aluminium and copper sides of the as-peeled samples, Fig. 8a and b. At 500 °C, Cu_9Al_4 became dominant on the aluminium side of the laminates and copper appeared on the copper side of the laminates, Fig. 9a and b.

3.4. Fracture morphology

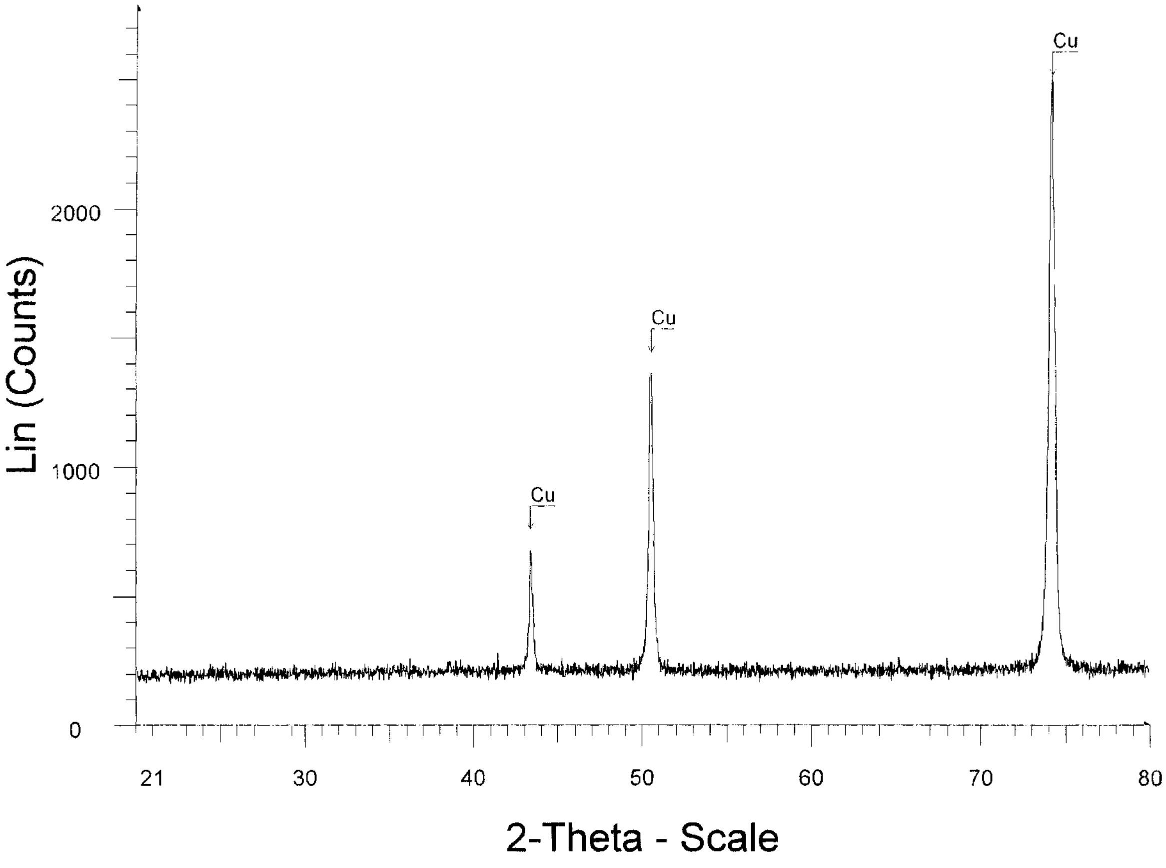
Fracture surfaces of the peel test samples were examined to identify origins of failure. Scanning electron microscopy of the fracture surfaces showed different fracture morphologies in samples sintered under different conditions. Fig. 10a–c show the typical fracture morphologies observed in the samples sintered at 450 °C for 0.5 to 3 hours. In general, a faceted fracture was observed in samples sintered at lower temperatures for short periods. As the sintering temperature and/or time increased, a porous structure became evident on the fracture surfaces.

TABLE I Phase formation detected on the fracture surfaces of the as-peeled samples for different sintering conditions

Type I Al + $CuAl_2$ trace (Al side) Cu (Cu side)		Type II Al + $CuAl_2$ + Cu_9Al_4 (Al side) Cu + Cu_9Al_4 (Cu side)		Type III Al + $CuAl_2$ + Cu_9Al_4 (Al side) Cu + $CuAl_2$ + Cu_9Al_4 (Cu side)		Type IV Al + $CuAl_2$ + Cu_9Al_4 (Al side) Cu (Cu side)	
Sintering temp. (°C)	Sintering duration (h)	Sintering temp. (°C)	Sintering duration (h)	Sintering temp. (°C)	Sintering duration (h)	Sintering temp. (°C)	Sintering duration (h)
300	0.5	350	0.5	400	3	500	0.5
300	3	350	2	450	2	500	2
		400	0.5	450	3		
		400	2				
		450	0.5				
		450	1				



(a)

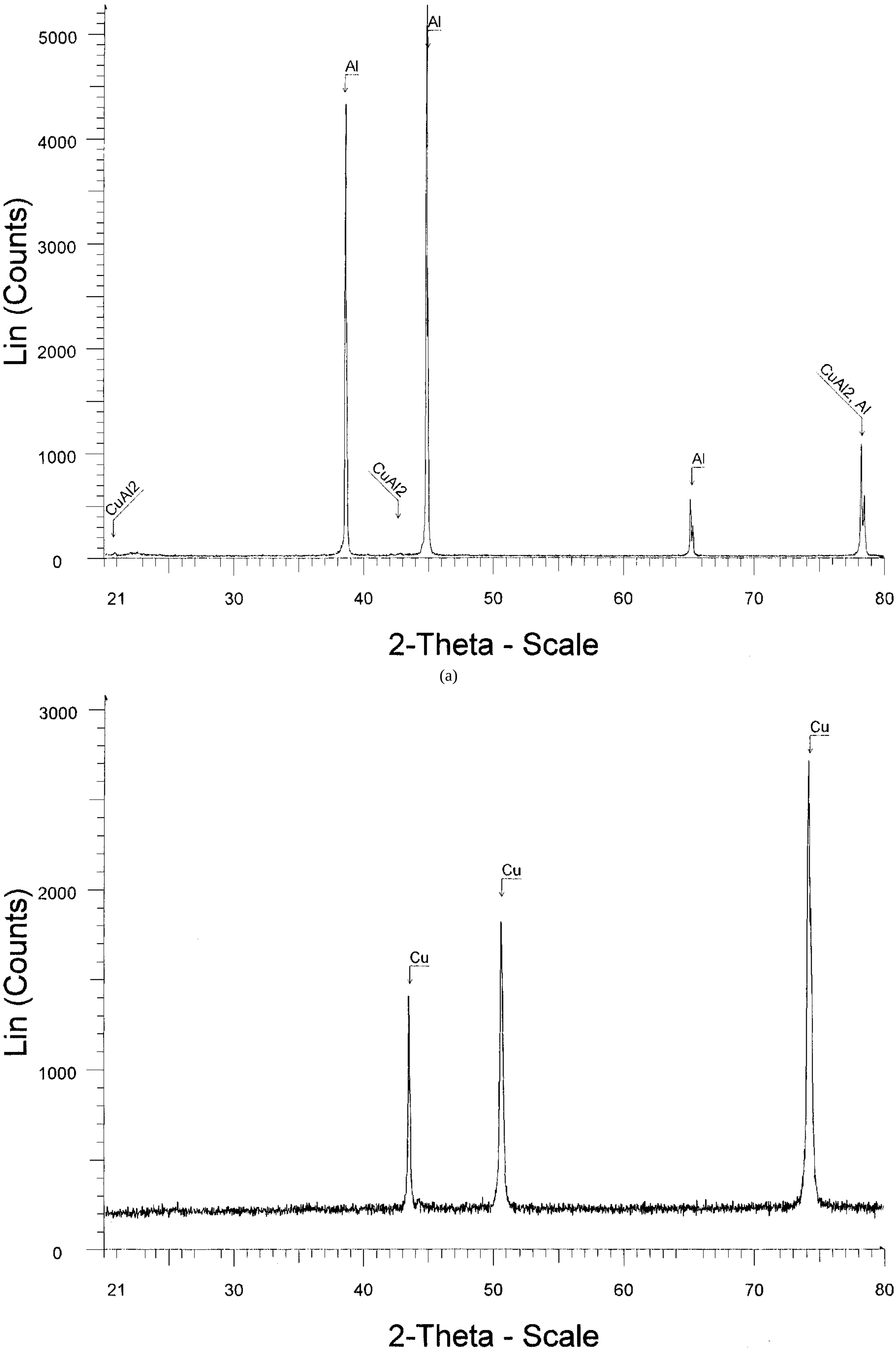


(b)

Figure 5 X-ray diffraction spectra measured on the as-rolled samples: (a) aluminium side and (b) copper side.

4. Discussion

Results from the present study reflect the complexity of the interface reactions which occur during the sintering treatment of the laminates. As the sintering time increased, the interface continued to thicken and different microstructural layers developed across the interface. It is understood that both copper and aluminium atoms will be thermally activated in the



(a)

(b)

Figure 6 X-ray diffraction spectra measured on the samples sintered at 300 °C for 3 hours: (a) aluminium side and (b) copper side.

sintering treatment process but the diffusivity of copper in aluminium is greater than that of aluminium in copper [11], creating a composition gradient of the metallic elements across the interface and resulting in the formation of different phases. According to the phase equilibrium diagram of the copper-aluminium system [12], eight types of intermetallic phases may possibly develop in the present materials. X-ray diffraction

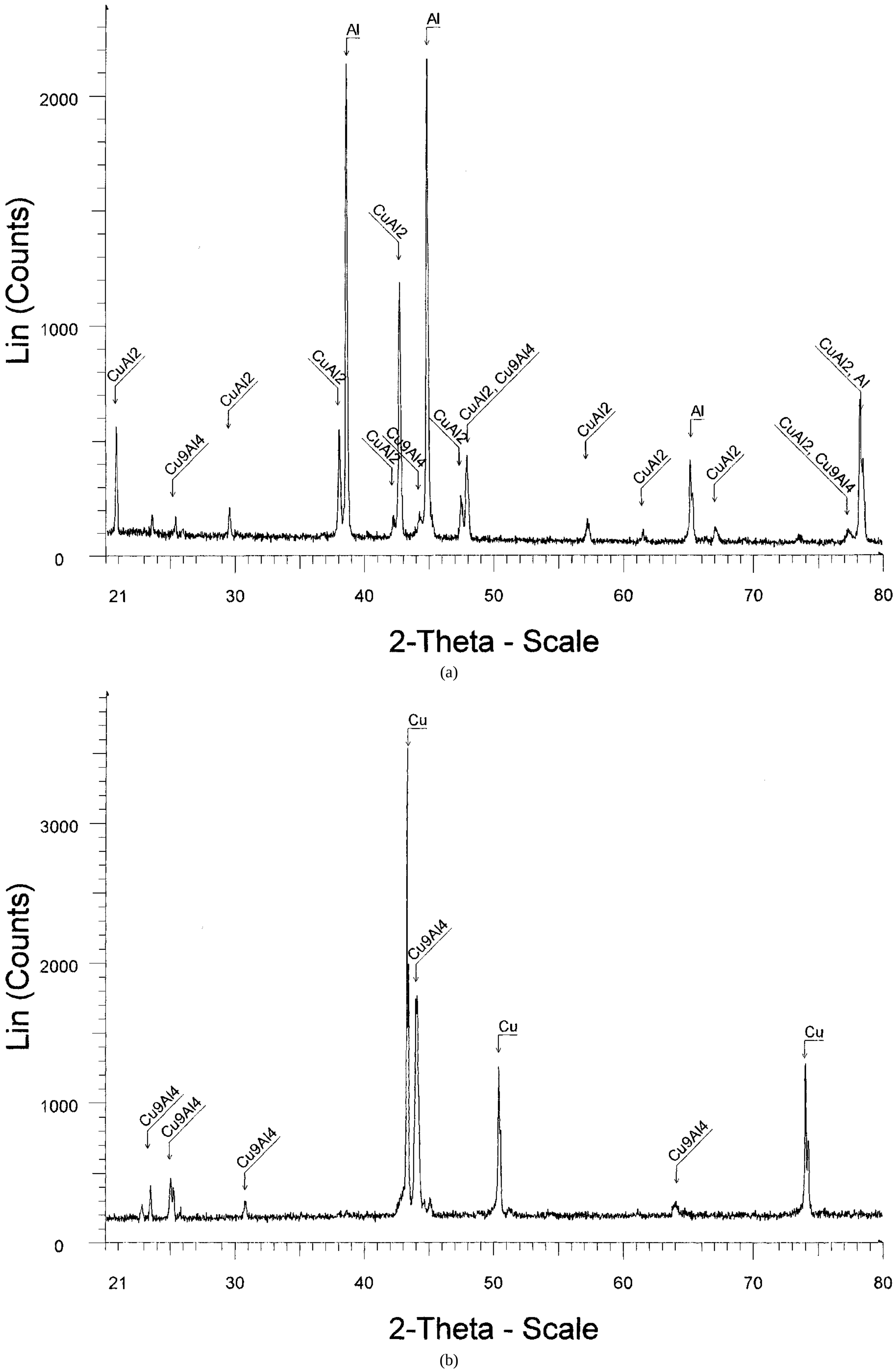
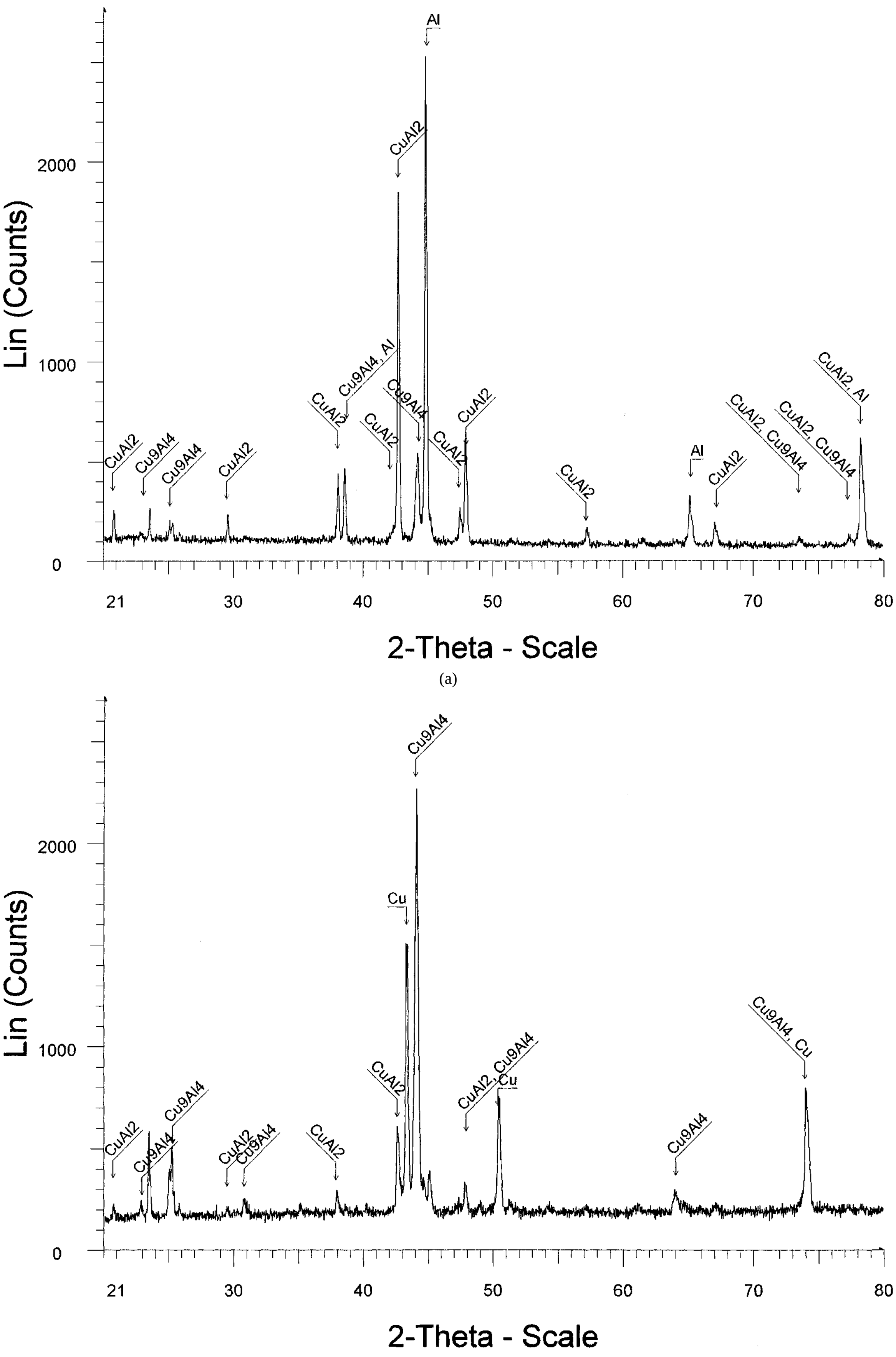


Figure 7 X-ray diffraction spectra measured on the samples sintered at 450 °C for 1 hour: (a) aluminium side and (b) copper side.

measurements detected on the fracture surfaces of the as-peeled samples confirm that $CuAl_2$ and Cu_9Al_4 generally form in the interface and four types of phase development occur under different sintering conditions. Because of the higher diffusivity of copper in aluminium, increased sintering time allows for the volume of copper-rich structure to increase, resulting in the formation of the dominant Cu_9Al_4 phase. Development of



(a)

(b)

Figure 8 X-ray diffraction spectra measured on the samples sintered at 450 °C for 3 hours: (a) aluminium side and (b) copper side.

the interfacial phases is also affected by their energies of formation. In a study of phase development in the copper-aluminium system, Jiang *et al.* [13] reported that the formation energies of Cu_9Al_4 and $CuAl_2$ are 0.83 eV and 0.78 eV respectively. With a higher sintering temperature, the activation energy provided in the heating process is substantially increased, thus the formation of Cu_9Al_4 becomes more viable at higher

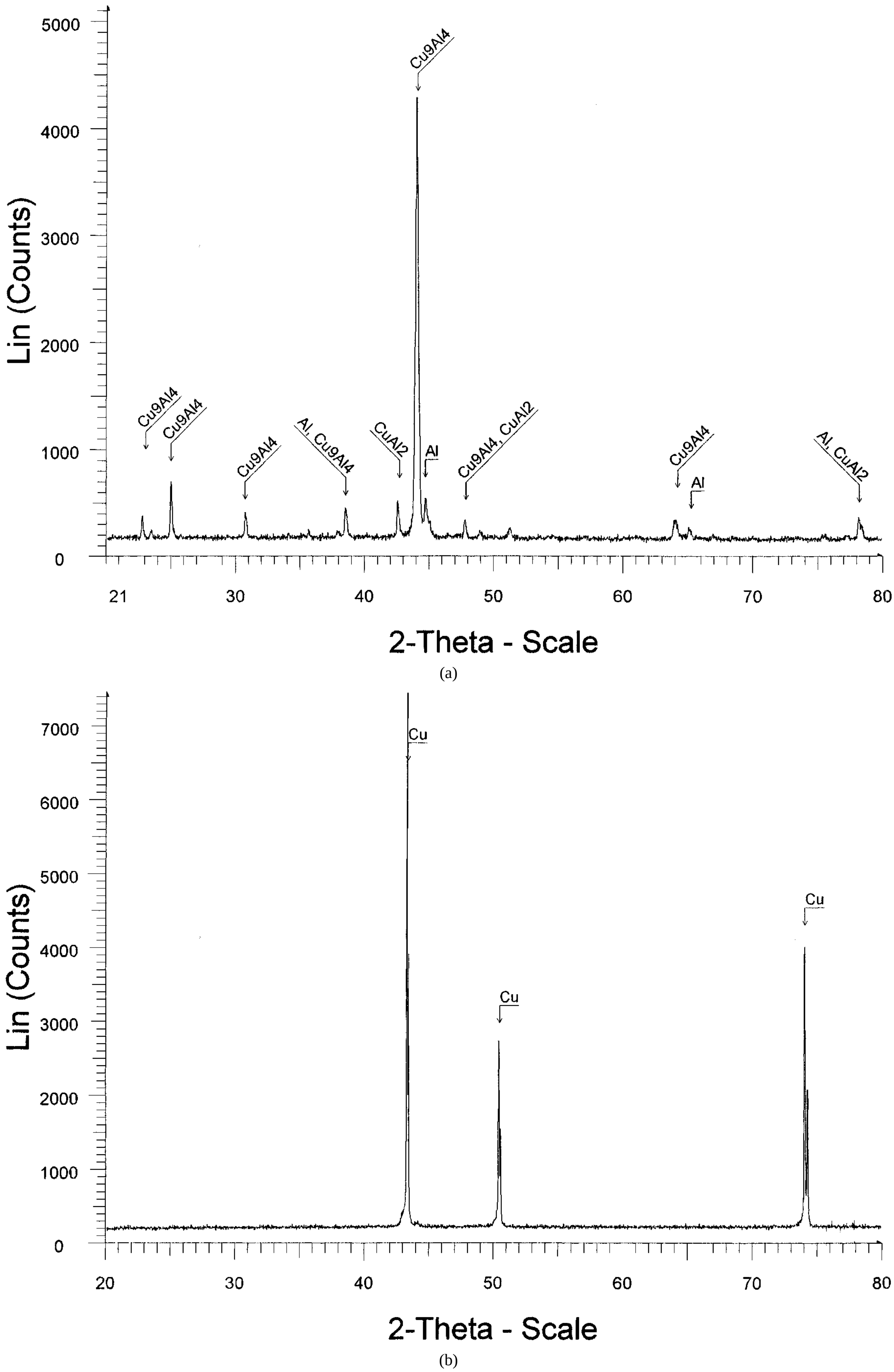
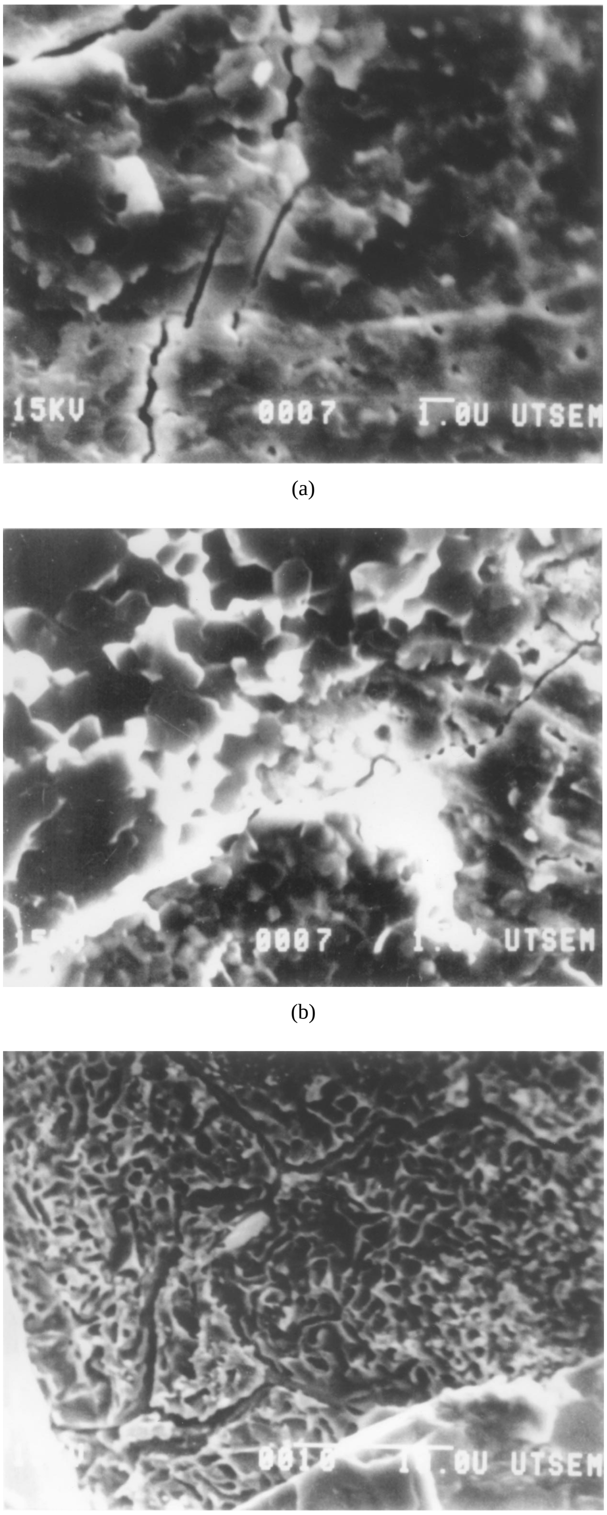


Figure 9 X-ray diffraction spectra measured on the samples sintered at 500 °C for 0.5 hour: (a) aluminium side and (b) copper side.

sintering temperatures, as observed in the present study.

The development of different interfacial phases will affect the bond strength and fracture behaviour of the metal laminates. Microhardness measurements across the interface of the copper/aluminium laminates show that the copper-rich structures of Cu_9Al_4 phase generally possess a much higher hardness than the



(a)

(b)

(c)

Figure 10 Scanning electron micrographs showing fracture morphology of the laminates after sintering at 450 °C for (a) 0.5 hour, (b) 1 hour and (c) 3 hours.

aluminium-rich layers. As the volume of the copper-rich phases increases, it is expected that the interfacial bond strength of the laminates will increase as well. Studies on the bond strength of the copper/aluminium laminates [8–10] however show that the peel strengths of the laminates generally increase to maximum values and then decrease substantially after prolonged sintering at high temperatures, suggesting that other mechanisms may be involved in the sintering process.

Results of the present study show that the Kirkendall effect of void formation is another important mechanism occurring during the sintering process, affecting the properties of the copper/aluminium laminates. Because of the higher diffusion rate for copper in aluminium, copper atoms penetrate into aluminium at a faster rate. As a consequence, the interface migrates and a net flow of vacancies develop in the opposite direction to the movement of the copper atoms. The vacancies that move towards the copper side of the metal laminates in the diffusion zone reach high concentrations and agglomerate into pores in the sintering process. For short sintering times, the Kirkendall voids were observed to distribute in the copper-rich phase regions, as shown in Fig. 3a. After prolonged sintering at high temperatures the Kirkendall voids were found to gather at the boundaries between the copper-rich layers and the copper base metal, forming a weak layer of defects shown in Fig. 3b. Laminates fractured along these weak layers in the peel tests. The results are further confirmed by the fractographic examination of the peeled samples. A porous fracture structure was generally evident in the samples sintered at high temperatures and/or for prolonged times as shown in Fig. 10c whilst a faceted structure with much less porosity was observed on the fracture surfaces of the samples sintered at low temperatures for short periods, Fig. 10a.

The interfacial phase development and Kirkendall void formation occur simultaneously in the sintering process. According to the results obtained in the recent research [8–10] and the present study, it is believed that the two interfacial reactions oppose each other in the bond strength development of the laminates. Despite the difficulty in quantitatively predicting the complex interface reactions involved in the sintering process, the general effects of the phase development and void formation on the bond strength of the metal laminates under different sintering conditions are depicted in Fig. 11.

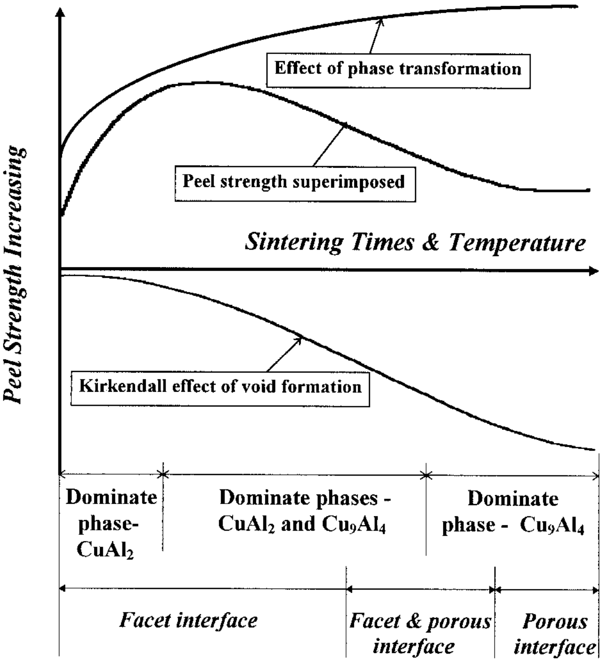


Figure 11 The combined effects of interface reactions on the peel strength of the copper/aluminium laminates.

As the sintering temperature and/or sintering time increase, the Kirkendall effect will promote the formation of voids and defects, reducing the bond strength of the metal laminates via the formation of a porous region. On the other hand, with increased sintering time, the formation of Cu_9Al_4 becomes dominant, resulting in a high interfacial bond strength. An increase of the sintering temperature will accelerate the processes of phase development and void formation. Under the combined effects of the above interface reactions, the resulting bond strengths of the metal laminates generally increase to maximum values under optimum process conditions and then decrease to substantially low values after sintering at high temperatures for prolonged periods.

5. Conclusions

Copper/aluminium laminates were prepared by roll bonding at 430 °C with a 60% rolling reduction in a single pass. Sintering treatments at temperatures between 300 and 500 °C were employed to the as-rolled materials to enhance the bond strength of the laminates. The interface development and fracture behaviour of the sintered materials were studied. It was found that two major diffusion controlled interface reactions, namely interfacial phase transformations and Kirkendall void formation, occurred during the sintering process and affected the fracture behaviour and bond strength of the laminates. Four different types of phase development were detected on the fracture surfaces of the sintered samples. At lower sintering temperatures, $CuAl_2$ was found to first develop in the interface. As the sintering time and/or temperature increased, the volume of Cu_9Al_4 phase increased. Microhardness measurements confirmed that the copper-rich phases generally possessed higher hardness than the aluminium-rich phases, thus contributing a higher bond strength to the metal laminates. On the other hand, further increases in sintering time and/or temperature resulted in Kirkendall void formation which became the significant mechanism and agglomeration of voids occurred, thus weakening the bond strength of the laminates and creating a porous fracture structure. The opposing effects of the two interface reactions were examined in the present study.

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