MATERIALS FORUM VOLUME 30 - 2006
Edited by R. Wuhrer and M. Cortie

X-RAY MAPPING OF METALLIC ELEMENTS IN ROLL BONDED METAL LAMINATES

R. Wuhrer [1], M. Lee [2], K. Moran [3] and W. Y. Yeung [2]

[1] Microstructural Analysis Unit, University of Technology, Sydney, P.O. Box 123, Broadway, NSW 2007, Australia.
[2] Department of Chemistry, Materials and Forensic Sciences, University of Technology, Sydney, P.O. Box 123, Broadway, NSW 2007, Australia
[3] Moran Scientific Pty. Ltd., 4850 Oallen Ford Road, Bungonia NSW 2580, Australia.

ABSTRACT

Advanced metal laminates have experienced rapid development in functional engineering applications. In this study, copper/aluminium metal laminates were produced by the roll bonding technique at 430°C with a critical 40% rolling reduction and sintering treatment was applied at 450°C. Interface development of the samples was examined using scanning electron microscopy and the distribution of the metallic elements and the subsequent chemical phase formation in the interfacial region was investigated by x-ray mapping. It was found that movement of the copper atoms occurred at a faster diffusion rate into the aluminium region and resulted in a shift of the interface boundary. Growth rate of the interface was determined and its relationship with sintering time was formulated. Development of the metallic phases in the interfacial area of the metal laminates was observed and determined.

1. INTRODUCTION

Metal laminates have experienced rapid development in functional and high performance engineering applications [1,2]. These laminated materials generally possess enhanced mechanical properties, leading to improved service performance. Roll bonding is recognised as an effective method in manufacture of metal laminates. In the roll bonding process, the metals are first bonded under appropriate rolling conditions. Sintering heat treatments are then applied to the bonded metals to enhance their bond strength [3].

Analyses of the solid state bonding of metals [4-7] suggests that under the combined action of pressure and heat over short periods, a three-stage process which involves (i) development of physical contact between the metals (ii) activation of the surfaces in contact and (iii) interaction between the joined materials may occur. A mechanical bond usually forms between the metals during the rolling stage and a strong metallurgical bond eventually develops in the sintering process.

Recent studies by the authors [8-10] suggested that both the rolling and the sintering conditions might affect the interface development and thence the resulting bond strength. The studies also indicated that while the rolling conditions determined the initial physical contacts of the metals, the sintering conditions might control the diffusion behaviour of the metallic elements across those physical contacts of the interfacial area and building up a strong interface, and an optimum strength could be developed.

The present study is a continuation of the previous work. This paper is to report results obtained from an examination of atomic movement of the metallic elements across the interfacial areas via compositional profile and x-ray mapping analyses. The distribution of the metallic elements and the development of the various metallic phases in the interfacial areas were identified and located, and their effects on the property development of the metal laminates were studied.

2. EXPERIMENTAL

Metal laminates of copper and aluminium were produced by roll bonding at 430°C with a 40% rolling reduction in a single pass, Figure 1. These rolling conditions were selected to provide an optimum bond strength development as reported in the previous studies [8]. Post-rolling heat treatments at 450°C were then applied to the bonded samples for various periods up to 3 hours. Location of the examined area was marked such that the interfacial development of the same area could be traced after each sintering heat treatment. Fine polishing was applied to the sample after each heat treatment to remove all contaminants on the surface before examination.

Development of the interface area of the bonded metals was examined by scanning electron microscopy (SEM) and x-ray diffractometry (XRD). X-ray maps and composition profiles were collected at 20kV accelerating voltage using a Moran Scientific energy dispersive x-ray mapping system attached to a Jeol 35CF SEM. The thickness of the interface was determined as the separation between the 99%Al and 99%Cu composition boundaries in the sample. Distribution of the metallic

elements and phases in the interfacial area was studied by the x-ray mapping (XRM). X-ray diffraction (XRD) analysis was performed on a Siemens D5000 diffractometer using copper K_α radiation.

2.1 X-Ray Mapping (XRM)

XRM is the collection of characteristic x-rays as a function of the position of the scanning electron beam on the specimen. X-Ray Mapping (XRM) and more importantly quantitative x-ray mapping (QXRM) are powerful characterization techniques aiding in the understanding of the spatial distribution of elements in materials as well as determining chemical phases within a sample. Quantitative x-ray mapping (QXRM) involves converting the background and overlaping corrected maps by some correction technique, such as ZAF (atomic number, absorption and fluorescence correction).

Once an x-ray map (XRM) has been collected a number of analytical softwares (such as Chemical Imaging) can be used to process the data and create scatter diagrams that can be used to determine further information about the phases and the related characteristics of the material. Through the use of two dimensional scatter diagrams, the x-ray images can be presented as singular or combinations of elements [11-13], where phases can be displayed singularly or superimposed over backscattered or secondary electron information. The scatter diagrams show the pixel frequency with element concentration profiles plotted against each other in two dimensions for selected elements within the sample [14,15]. The clusters observed in the scatter diagrams correspond to different phases and boundaries within the material. The contributing pixels to each cluster can be used to reconstruct the spatial distribution of its associated phase or boundary in a chemical image of the specimen. This is often referred to as chemical phase mapping (CPM) [14,15].

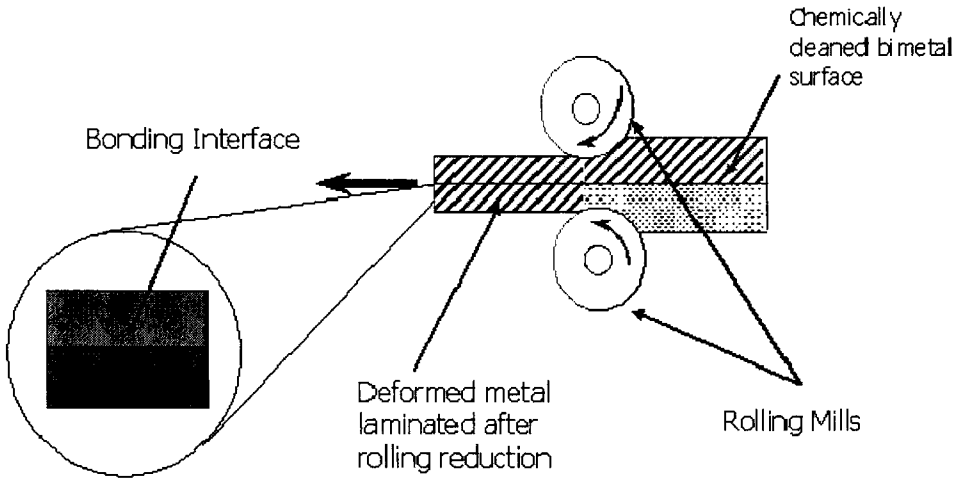


Figure 1. Schematic of the roll bonding process.

3. RESULTS

3.1 Microstructural Characterisation and Interface development

The interfacial development of the bonded metals is shown in Figure 2. A defined interface boundary appeared in the as-rolled sample, Figure 2a. As the sintering time increased, a multi-layer interface area developed, Figure 2b. A string of voids became evident along the copper side of the bonded area after sintering for 2 hours (Figure 2c) and void formation became more serious after sintering for 3 hours (Figure 2d).

The movement of the interfacial fronts was determined after each sintering heat treatment with reference to the marked locations in the sample. The results are shown in Table 1 and Figure 3. It was apparent that the diffusion of copper into aluminium occurs much faster than aluminium into copper, resulting in a shift of the interfacial region into the aluminium metal. The thickness of the interfacial region was also determined. The results are shown in Table 1 and Figure 4. A steady growth in the thickness of the interface area was observed with increasing sintering time. As the sintering time increased, the interfacial thickness continuously increased from 1.0 μm in the as-bonded condition to 25.7 μm after sintering at 450°C for 3 hours.

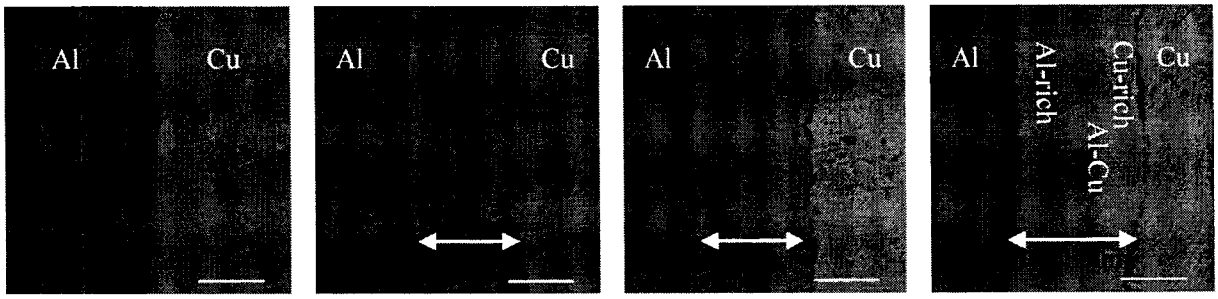
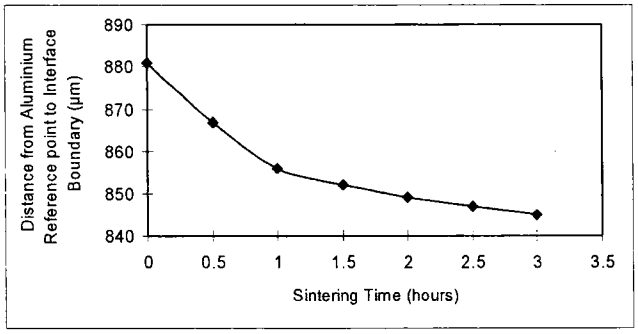


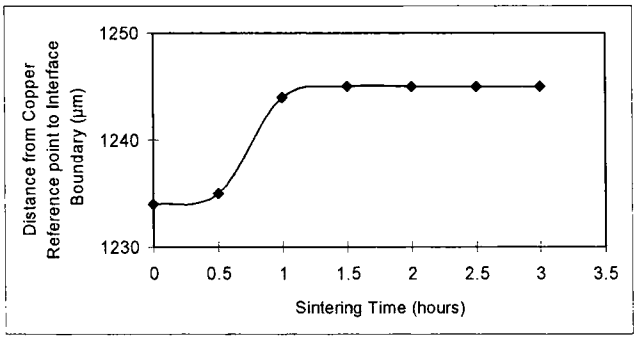
Figure 2. Secondary electron images showing interfacial development of a roll bonded copper/aluminium metal laminate after sintering at 450°C for (a) 0 hour (as-bonded); (b) 1 hour; (c) 2 hours and (d) 3 hours. Width of field (WOF) = 45μm.

Table 1. Interfacial movement in copper/aluminate laminate at 450°C

Sintering Times (hours)	Number of Interfacial Layers	Distance from Aluminium Reference Point to Interface Boundary (μm)	Distance from Copper Reference Point to Interface Boundary (μm)	Interfacial Thickness (μm)
0.0	1	881	1234	1.0
0.5	1	867	1235	13.8
1.0	2	856	1244	16.4
1.5	2	852	1245	18.6
2.0	3	849	1245	20.9
2.5	3	847	1245	23.8
3.0	3	845	1245	25.7



a.



b.

Figure 3. Movement of interfacial fronts in copper/aluminium laminate sintered at 450°C.

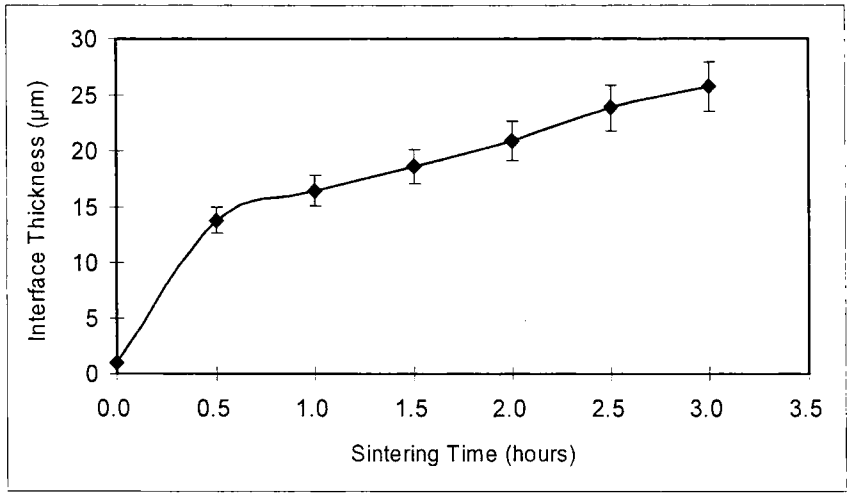


Figure 4. Growth of interfacial thickness versus sintering time at 450°C.

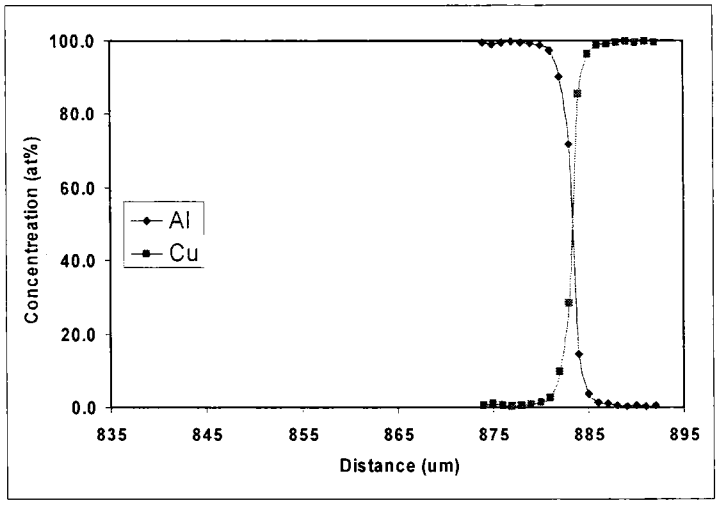
3.2 Interfacial composition profiles

The interfacial composition profiles of the sintered sample determined by energy dispersive x-ray spectroscopy (EDS) are shown in Figure 5. The interfacial composition profiles of the metallic elements across the interfacial area changed substantially with increasing sintering time and reflected the complexity of the interfacial development in roll bonded metal laminates. In the as-rolled material, a sharp compositional change was observed across the interface, Figure 5a. As the sintering process was applied, the composition profile across the interface area changed. With increasing sintering time, several transitional changes in the compositional profile developed, Figures 5b and c, showing the development of a multi-layer interface comprised of different compositions.

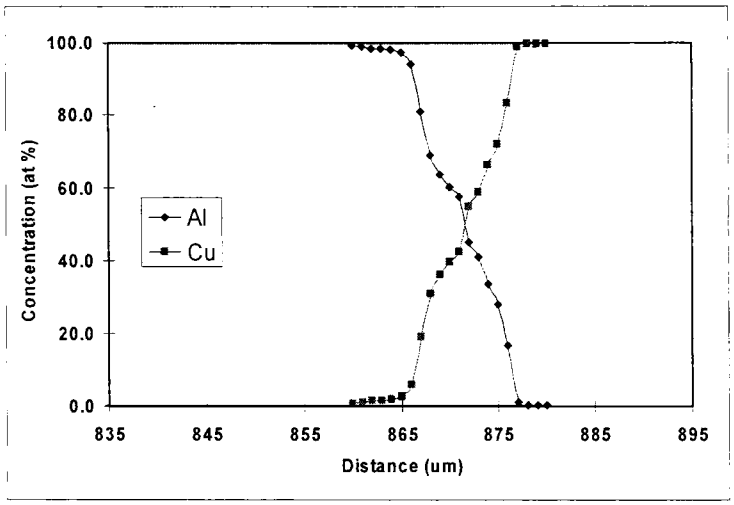
3.3 X-ray mapping (XRM) and chemical phase mapping (CPM)

A thorough analysis was performed through use of x-ray mapping to determine i) the phases present

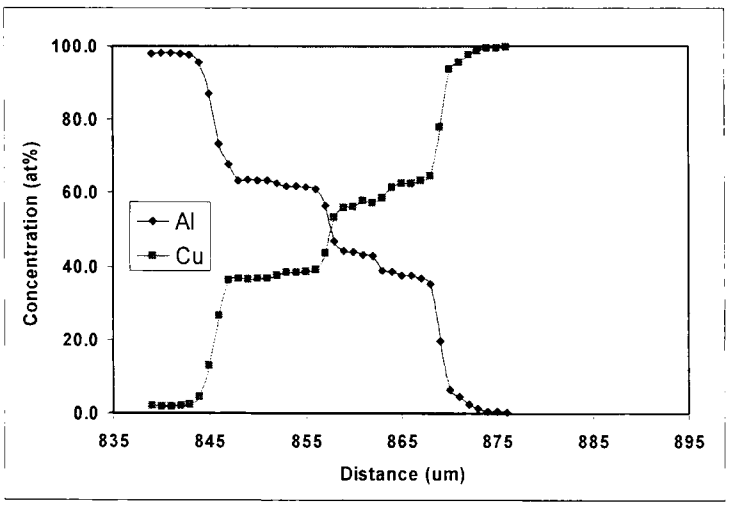
(through CPM), ii) the composition of the phases and iii) the location of these phases in the interfacial area of the metal laminate. Figures 6a-d show the secondary electron image and quantitative x-ray maps for the copper-aluminium rolled bonded material after sintering for 3 hours. Figures 6e-g show the corresponding averaged scatter diagrams for the three respective elements present.



a.



b.



c.

Figure 5. Interfacial composition profiles showing composition changes across the interface of the roll-bonded metals after sintering at 450°C for a) as-rolled b) 0.5 hour and c) 3 hours.

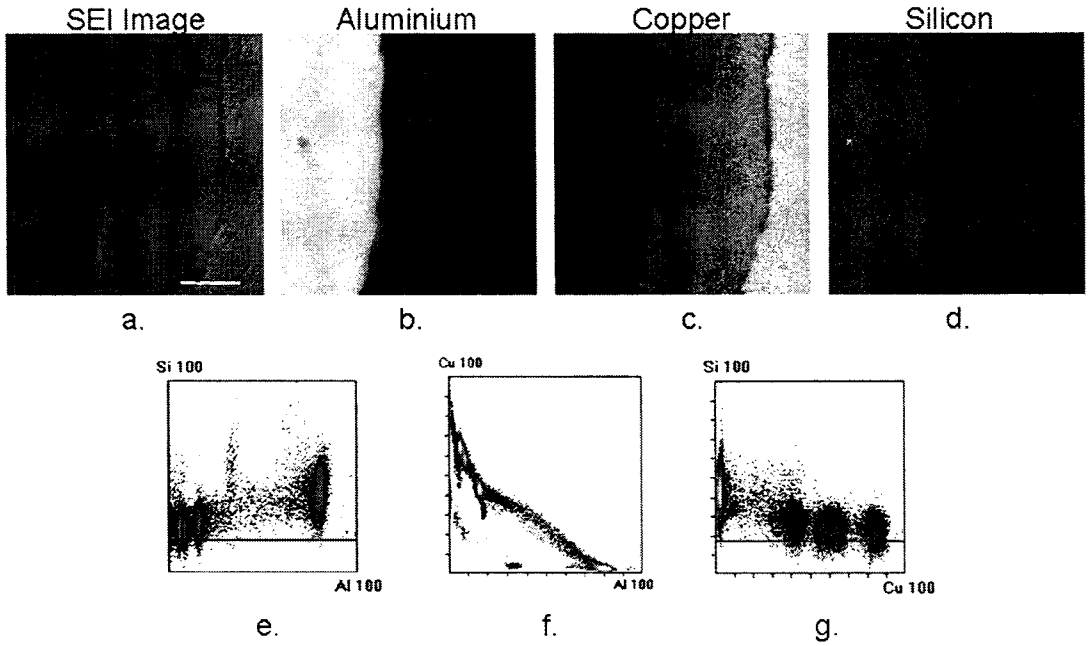


Figure 6. Copper – aluminium roll bonded metal laminate after sintering at 450^{0}C for 3 hours. a) SE image of the interface between the two metals and elemental x-ray maps of b) aluminium, c) copper and d) silicon, and the scatter diagrams showing different clusters in the bond interface region: e) silicon versus aluminium f) copper versus aluminium g) silicon versus copper. Maps collected at 20keV, 512x512 pixel, 100msec/pixel and 7kcps. Width of field (WOF) = 45 μm.

As shown in Figure 7, the selection of a particular cluster can give detail where a phase exists on the image. Consequently, the chemical composition of the phase can be quantified by summation of the pixels spectra from the cluster. This involves adding the spectra collected from each pixel, where the pixel is determined by the cluster. The phases determined by XRM quantification as well as the corresponding XRD analysis results are shown in Table 2. Development of the phases was found to be dependent upon the sintering conditions. With a short sintering time, a $CuAl_2$ phase was observed to form, followed by the Cu_9Al_4 phase. For sintering with a longer period, CuAl and Cu_3Al_2 phases were also found to develop.

4. DISCUSSION

The present study has investigated the distribution of the metallic elements and the development of the multi-phases in the interfacial area of the metal laminate through the sintering process. From an earlier work carried out by Peng et al [8], it has been identified that the maximum bond strength of this roll bonded coper/aluminium metal laminate occurred with sintering times between 1 and 2 hours at 430^{0}C. For longer sintering periods, voids and cracking were observed in the interfacial structure. According to the results of x-ray mapping analysis performed in this investigation, it appears that the development of the peak bond strength for this metal laminate is associated with the evolution of $CuAl_2$ and Cu_9Al_4 phases in the interfacial area. Existence of these interfacial phases has also been confirmed by measurements via conventional x-ray diffractometry conducted at small glancing angles. While the x-ray diffractometry provide the general information in identification of the interfacial phases, x-ray mapping shows its advantages and, with the help of scatter diagrams, locates the exact positions of the individual phases in the interfacial area. The x-ray mapping and chemical phase mapping therefore provide a platform in analysing the properties of individual phases and their contributions to the bond strength of the metal laminates, which are currently being studied in a separate project.

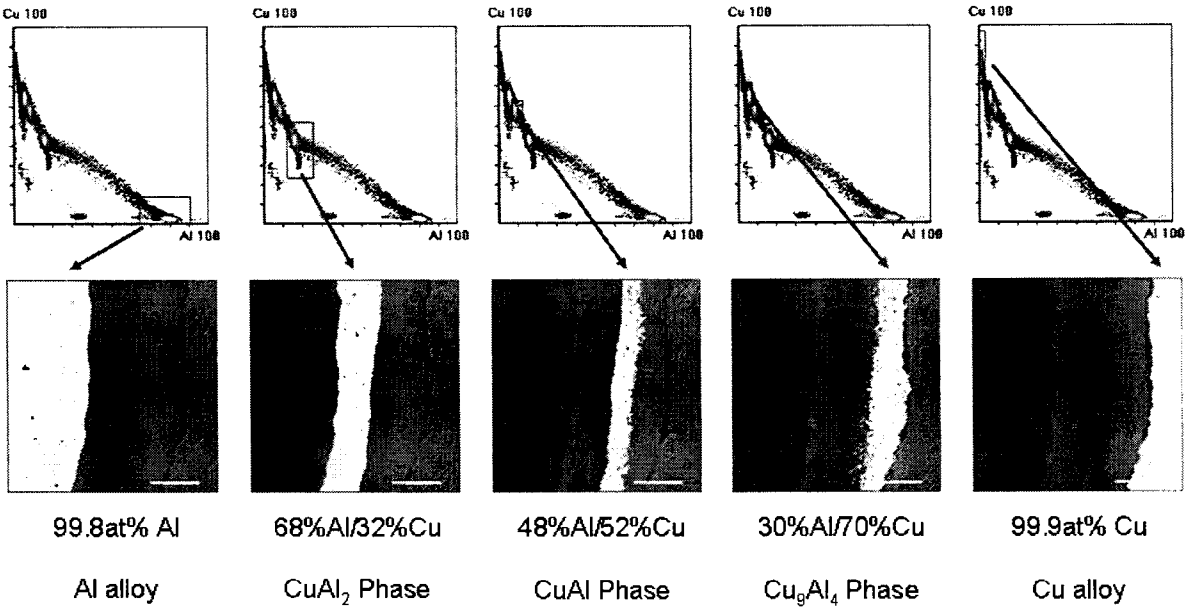


Figure 7. Copper-aluminium scatter diagrams showing many different clusters for the copper – aluminium roll bonded metal laminate after sintering at 450^{0}C for 3 hours. The images below the scatter diagrams are secondary electron images with information from the different clusters of the scatter diagram superimposed over the image. The different yellow regions represent different phases.

Table 2. Phases determined from CPM and XRD analysis.

Sintering Times (hours)	Interface Thickness (μm)	Possible Phases Present (Layers)	Chemical Composition from CPM (at%)	Phases determined from CPM	XRD Analysis of Phases
0.0	1.0	Al Cu	99.8% Al 99.9% Cu	Al Cu	Al Cu
1.0	16.4	Al $CuAl_2$ Cu_9Al_4 Cu	99.8% Al 68%Al/32%Cu 30%Al/70%Cu 99.9% Cu	Al $CuAl_2$ Cu_9Al_4 Cu	Al $CuAl_2$ Cu_9Al_4 Cu
2.0	20.8	Al $CuAl_2$ CuAl or Cu_3Al_2 Cu_9Al_4 Cu	99.8% Al 68%Al/32%Cu 48%Al/52%Cu 30%Al/70%Al 99.9% Cu	Al $CuAl_2$ CuAl Cu_9Al_4 Cu	Al $CuAl_2$ CuAl Cu_9Al_4 Cu
3.0	25.7	Al $CuAl_2$ CuAl or Cu_3Al_2 Cu_9Al_4 Cu	99.8% Al 68%Al/32%Cu 48%Al/52%Cu 30%Al/70%Al 99.9% Cu	Al $CuAl_2$ CuAl Cu_9Al_4 Cu	Al $CuAl_2$ CuAl Cu_9Al_4 Cu

5. CONCLUSIONS

Through the use of x-ray mapping and chemical imaging techniques, a better understanding of the distribution of the metallic elements and the phase development in the interfacial area has been achieved for the roll bonded copper-aluminium. A multiphase development was identified and located in the interfacial area. Development of the $CuAl_2$ and Cu_9Al_4 phases in the interfacial area is believed to enhance the bond strength of the laminated sintered at 450°C.

Acknowledgements
The authors would like to thank the assistance provided from technical staff in the Department of Chemistry, Materials and Forensic Sciences as well as the Microstructural Analysis Unit of the University of Technology, Sydney.

References

1. C. Horvath and G. Haynes, Automotive Engineering 99 (1991) 35-37.
2. J. Bittrich and D. Fluegge, Aluminium 21 (1984) 379-383.
3. R. Baboian and G. Haynes, ASM Metals Handbook 6 (1993) 887-890.
4. Y.L. Krasulin and M.K.H. Shorshorov, Physics and Chemistry of Materials Processing 1 (1967) 1252-1254.
5. M.K.H. Shorshorov and Y.L. Krasulin, Welding Production 14 (1967) 24-29.
6. M.K.H. Shorshorov and E.S. Karalosov, Proceedings Conference on Advances in Welding Processes, Moscow, USSR, April 14-16 1970, 208-213.
7. R.F. Tylecote, The Solid Phase Welding of Metals, St. Marins Press, New York, 1968, 18-77.
8. X.K. Peng, G. Heness and W.Y. Yeung, Journal of Materials Science 34 (1999) 277-281.
9. X.K. Peng, R.Wuhrer, G. Heness and W.Y. Yeung, Journal of Materials Science 34 (1999) 2029-2038.
10. X.K. Peng, R. Wuhrer, G. Heness and W.Y. Yeung, Journal of Materials Science 35 (2000) 4357-4363.
11. D.S. Bright and D.E. Newbury, Analytical Chemistry, Vol. 63 (1991) 243.
12. R. Wuhrer and K. Moran, AMAS VIII-The 8th Biennial Symposium, University of Melbourne (2005) 109.
13. P.G. Kenny, I.R. Barkshire and M. Prutton, Ultramicroscopy, 56 (1994) 289-301.
14. K. Moran and R. Wuhrer, Mikrochimica Acta (2005), in print.
15. R. Wuhrer, K. Moran, M.R. Phillips and P. Davey, Microsc. Microanal. 11 (2005) 466.

MATERIALS FORUM

Materials and Testing

Volume 30, 2006 Edition

The Institute of Materials Engineering Australasia Ltd
(Trading as Materials Australia)
A Technical Society of Engineers Australia
Suite 205, 21 Bedford St, North Melbourne, Victoria, 3051, Australia
email: imea@mateng.asn.au
website: www.mateng.asn.au

ABN 40 004 249 183

ISSN: 1447-6738
ISBN: 1 876855 258