

Improved Stability of Contact Resistance of Low Melting Point Alloy Incorporated Isotropically Conductive Adhesives

Kyoung-Sik Moon, Jiali Wu, and C. P. Wong, *Fellow, IEEE*

Abstract—With the driving force of “green” revolution in the electronics industry, tremendous efforts have been made in pursuing lead-free alternatives. Although lately lead-free alloys have drawn a lot of attention, their technical weaknesses, such as high processing temperature, poor wetting and high surface tension, limit their applications on the thermally sensitive, flexible, nonsolderable substrates and the ultra-fine pitch size flip chip interconnection. Conventional isotropically conductive adhesives (ICAs) have been used widely in surface mount and die-attach technologies for electrical interconnection and heat dissipation. The low temperature processing of ICAs is one of the major advantages over lead-free solders, which brings a low system stress, simple manufacture process and the like. In order to enhance the contact resistance of ICAs, the low melting point alloy (LMA) incorporating technology has been developed by our group. In this paper, LMA fusing methods were studied, since nonfused LMA in ICAs after a curing process can adversely affect the physical property and contact resistance stability. A differential scanning calorimeter (DSC) was used for the basic examination of depleting rate of LMAs in the typical ICAs. The cross-sectional morphology, LMA distribution and intermetallic compound were investigated by a scanning electron microscope (SEM). In addition, contact resistance for the ICA formulation incorporated with LMAs under elevated temperature and humidity was evaluated.

Index Terms—Contact resistance, current density, electrically conductive adhesives, low-melting-alloy, silver flakes.

I. INTRODUCTION

A need for environmental and user-friendly alternatives to Sn/Pb solders is increasing in the electronic industry. Many efforts have been focused on replacing lead-containing solder materials with isotropically conductive adhesives (ICAs) in the electronic industry, which pursues lead-free solder materials as well as low cost interconnection materials. ICAs have been applied to the surface mount technology to establish mechanical and electrical joints between the printed circuit board and the surface mount components. Recently, special efforts have also been dedicated to the ICAs on the flip-chip technology [1], [2].

Besides the environmental issues, ICAs have many advantages over conventional solder, as follows:

- 1) lower processing temperature, less thermomechanical residual stress;

Manuscript received May 1, 2001; revised February 24, 2003. This work was presented in part at the 51st Electronic Components and Technology Conference, Orlando, FL, 2001. This work was recommended for publication by Associate Editor J. Morris upon evaluation of the reviewers' comments.

The authors are with Packaging Research Center, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245 USA.

Digital Object Identifier 10.1109/TCAPT.2003.815101

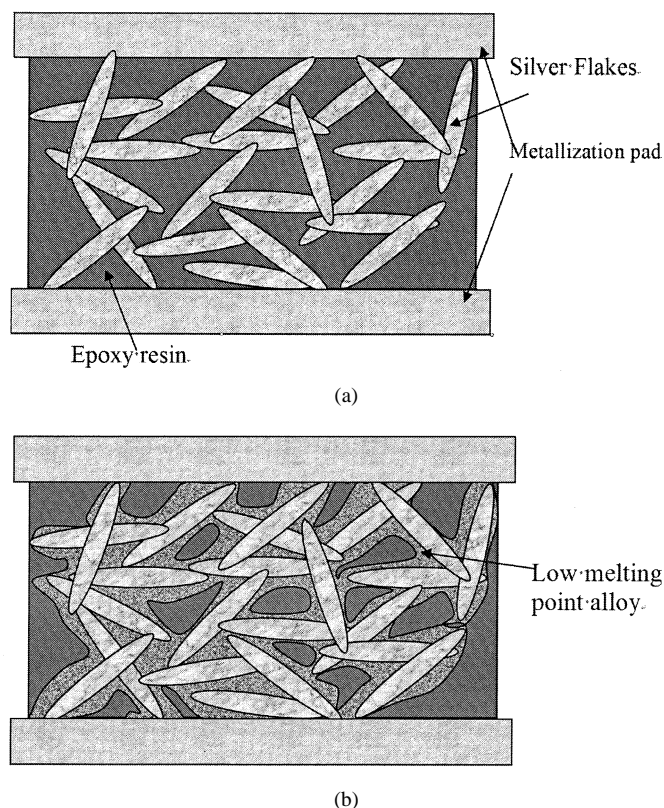


Fig. 1. Illustrations of LMAs filled ICAs: (a) silver flake filled ICAs (physical contact) and (b) LMAs incorporated ICAs (metallurgical contact).

- 2) simpler processing than wave soldering;
- 3) high-resolution capability for fine-pitch interconnection.

One of the drawbacks of ICAs, however, is their lower current density than metal solder materials. Electrical contact resistance of an ICA is composed of the contact resistance between the ICA and the metal pad, bulk resistance of silver flakes in ICAs and contact resistance between silver flakes. To reduce the contact resistances, the incorporation of a low melting point alloy (LMA) was suggested and demonstrated in our group, which is illustrated in Fig. 1 [4], [5]. However, LMAs in the ICA formulation that are not melted after a curing process could be a critical concern to the mechanical and electrical reliability of the ICAs at elevated temperature and humidity. In this study, a new curing process was designed and demonstrated in order to completely fuse LMAs in ICAs. In addition, the stability of contact resistance for samples prepared by the different cure schedules under elevated temperature and humidity was evaluated.

II. EXPERIMENTAL

A. Materials

A low-melting-point alloy (LMA) filler was obtained from Kilobar Company. A bisphenol-F type epoxy resin, Epon 862, was supplied by Shell Chemical Company. Hexahydro-4-Methylphthalic Anhydride (HHMPA) was purchased from Aldrich Chemical Company and used as a curing agent. Tetraphenylphosphonium tetraphenylborate (TPTB) was purchased from TCI American, Inc. and used as a catalyst. Glycerol, maleic acid, adipic acid (from Aldrich Chemicals) were purchased from Aldrich Chemical Company.

Modified ICA formulations were prepared by mixing the LMA with an organic acid first. Then silver flakes (from Ferro Co.) were added according to the weight ratio of LMA to Ag from 1:4 to 1:1. After that, epoxy resin was added in the above metal mixture according to the weight ratio of total metal to epoxy = 4:1.

B. Differential Scanning Calorimetric (DSC) Analysis

Exothermic and endothermic behaviors of ICAs during an initial thermal excursion were monitored by using a DSC (Modulated DSC, model 2920, TA Instruments). Approximately 10 mg of each formulated sample was placed into a DSC pan and it was heated from room temperature to the melting point of LMAs at a 5 °C/min, then it was held at this temperature for 60 min, followed by a continuous thermal ramp to 200 °C. After cooling to room temperature, each sample was heated by the second thermal ramp at a 5 °C/min from room temperature to 200 °C to observe the melt behavior of LMAs in the ICA. Nitrogen was used as a purging gas for the environmental protection of the DSC sample chamber.

C. Microstructure Analysis

A scanning electron microscope (SEM, Hitachi Model S-800) was utilized for the microstructure analysis of ICAs. Samples were formulated and then were cured at the melting point of LMAs for 30 min, followed by curing at 150 °C for an additional 30 min. The cross section of each sample was polished following standard SEM sample preparation steps. A thin layer of Au was deposited on top of each cross-sectional surface of samples for good conductivity when examined by a SEM.

D. Contact Resistance Shift Under Elevated Temperature and Humidity

For the contact resistance test, an ICA paste was dispensed on the gap between metal patterns on the test coupons as shown in Fig. 2 and connected to the metal pad segments. After curing, contact resistance was measured from the two ends of the segments using a multimeter (Keithley Co.). Four specimens were prepared for each sample. The contact resistance was measured periodically during the 85 °C/85% relative humidity (RH) aging test. The average contact resistance of these four specimens is reported.

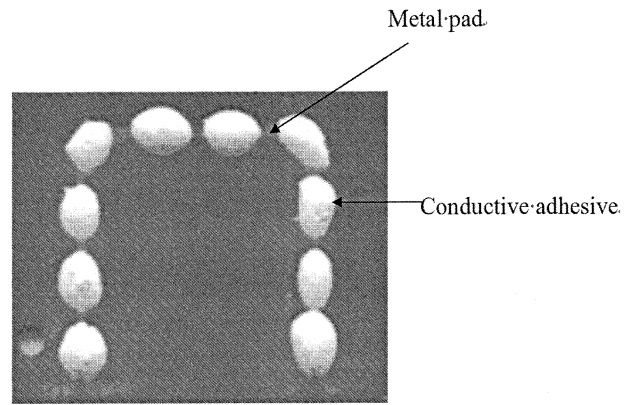


Fig. 2. Test coupon used to evaluate the contact resistance shift during the elevated temperature and humidity test.

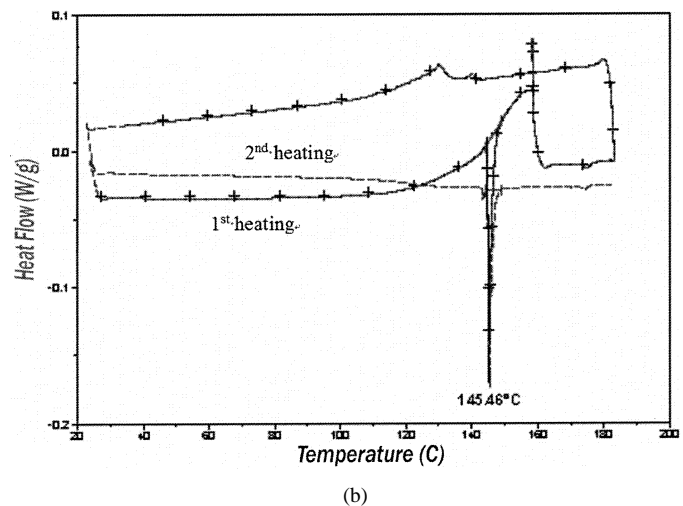
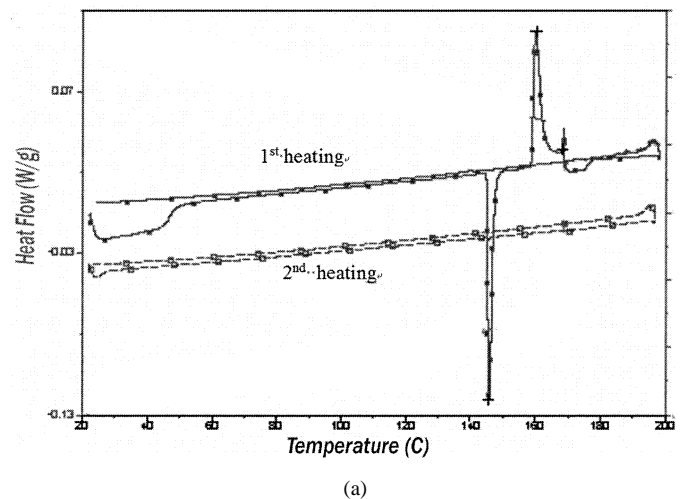


Fig. 3. Thermal profiles of LMA-1 incorporated ICAs: (a) metal 80 wt% + epoxy 20 wt% (LMA-1 1 wt% + Ag 9 wt%) and (b) metal 80 wt% + epoxy 20 wt% (LMA-1 5 wt% + Ag 95 wt%).

III. RESULTS AND DISCUSSION

Fig. 3(a) and (b) show the thermal profiles of the low melting alloy 1 (LMA-1) incorporated ICAs during the heating and cooling cycles in a DSC. The thermal profiles are recorded as per the following procedures: the samples were heated with a ramp rate of 5 °C/min up to 200 °C and cooled down, and

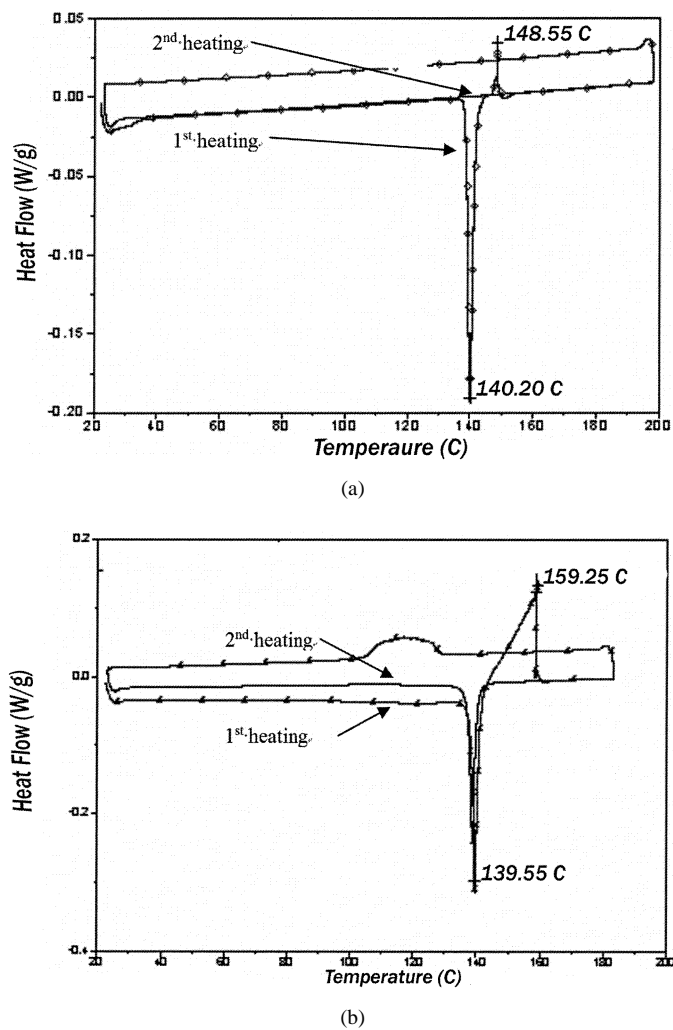


Fig. 4. Thermal profiles of LMA-2 incorporated ICAs: (a) metal 80 wt% + epoxy 20 wt% (LMA-2 1.0 wt% + Ag 99 wt%) and (b) metal 80 wt% + epoxy 20 wt% (LMA-2 5.0 wt% + Ag 95 wt%).

then they were heated up again in the same hermetically sealed pan. The ratio of LMA-1 to silver in (a) is 1:99 by weight and that of (b) is 5:95. The peaks at around 140 °C indicate the melting point of LMA particle in ICA. In Fig. 3(a), the LMA particles show a melting peak during the first heating process, however, during the second heating process a melting peak could not be found. This means that LMAs were fused into the formulation and transformed into another phase during the heating process. In Fig. 3(b), a melting peak of LMAs was also shown during the first heating, but the melting peak still appears during the 2nd heating process. Although a certain portion of LMAs in Fig. 3(b) was fused into the formulation, it is thought that somehow the nonfused portion still remained, which shows a melting peak in the second scan. In addition, epoxy resin curing increases the viscosity of the system due to gelation, and LMAs fusion into the formulation could be hindered. The thermal profiles of LMA-2 filled ICAs were also shown in Fig. 4(a) and (b). Ratios of LMAs to silver in Fig. 4(a) and (b) are the same as in Fig. 3(a) and (b), respectively. LMA-2 shows similar behavior to LMA-1. From Fig. 4(a), it is exhibited that all LMAs of 1 wt% in metal fillers was depleted into the formulation, since the melting peak disappeared after

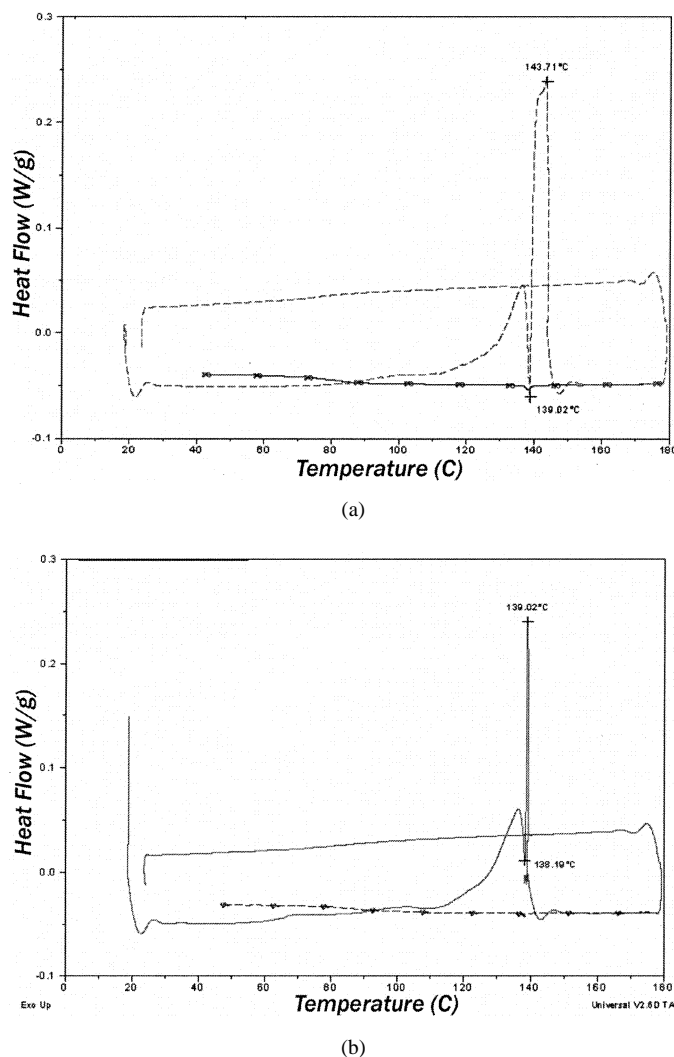


Fig. 5. Thermal profiles for two-step curing processes: (a) metal 80 wt% + epoxy 20 wt% (20 wt% LMA-1 + 80 wt% Ag) and (b) metal 80 wt% + epoxy 20 wt% (20 wt% LMA-2 + 80 wt% Ag).

the first heating process. From Fig. 4(b), it is found that some portions of LMAs of 5 wt% in metal fillers were not completely fused and nonfused particles still exist in the formulation. Consequently, LMA remelting cannot be avoided by only a simple heating process.

To remove the re-melt LMA particles in the formulation, a step-curing process was applied, which includes the two-step curing procedure. The first temperature employed was the melting temperature of each LMA, and this temperature was held for 30 min. and then the temperature was raised to the curing temperature of the epoxy resin to cure the epoxy matrix. Fig. 5(a) and (b) show the thermal profiles of LMA-1 and LMA-2 incorporated ICAs by a two-step curing process, respectively. In this test, the amount of LMAs added was higher than that of Figs. 3 and 4, even though the total metal filler contents were identical. In Fig. 5(a), during the first heating process, a melting peak of LMA-1 appears at around 140 °C and another rising peak appears. The rising peak is attributed to temperature holding and a certain degree of epoxy curing developing. On the second scanning, a re-melt peak was not found. It is thought that all LMAs-1 in metal fillers were

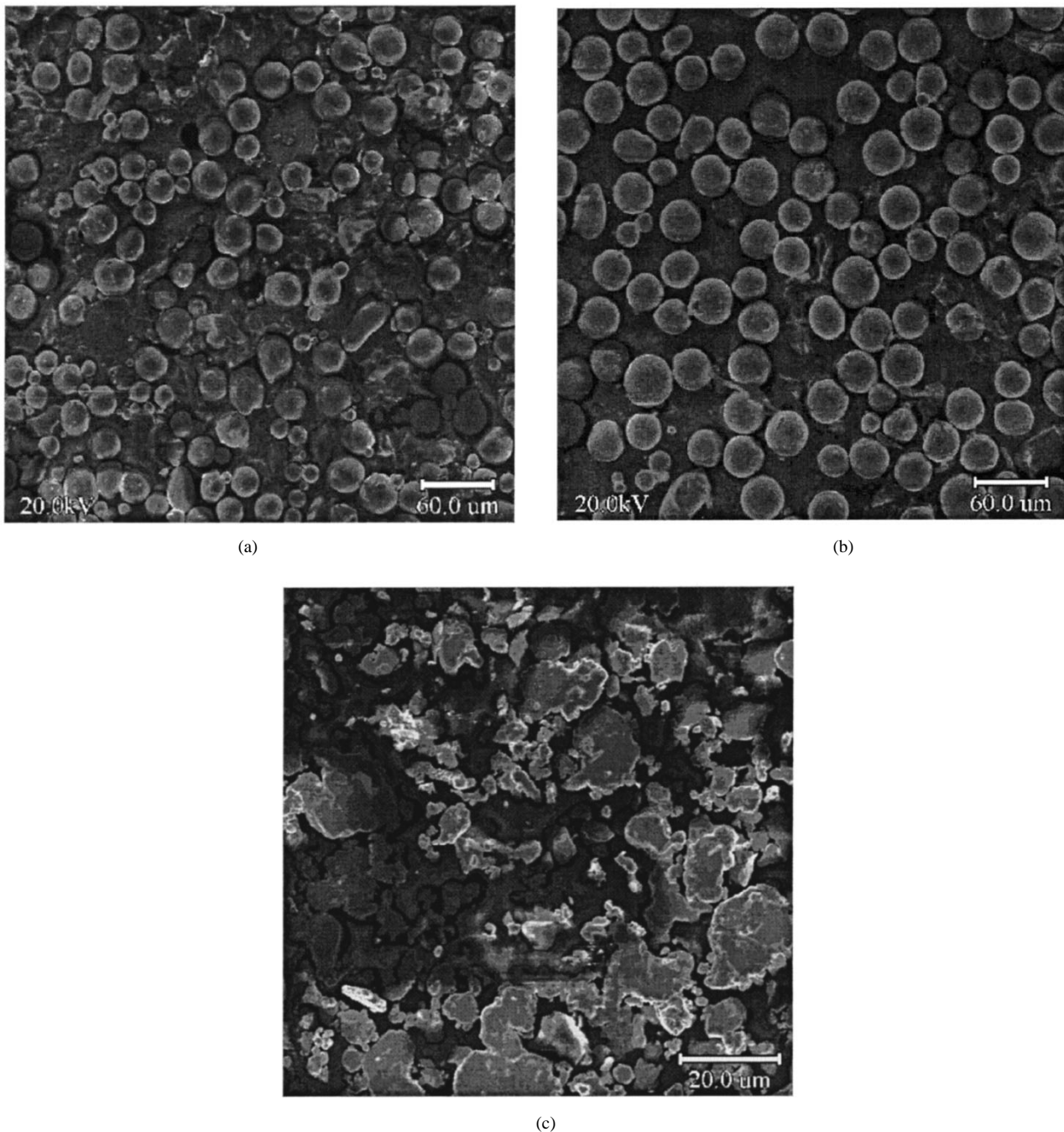
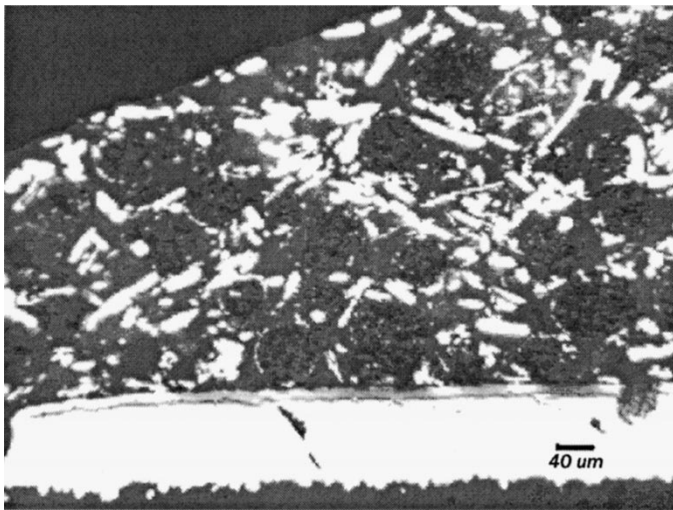


Fig. 6. SEM photos of LMA particles and silver flakes: (a) LMA-1, (b) LMA-2, and (c) silver flakes.

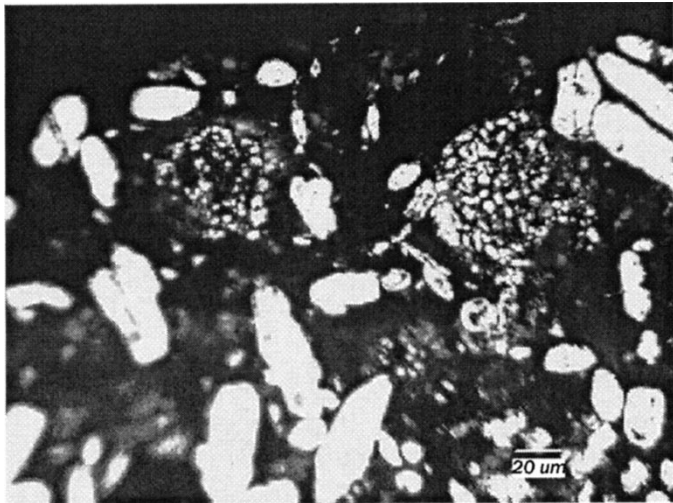
fused into the formulation by a two-step curing process which provides LMAs with enough time to melt. Similar results were also obtained from LMAs-2 incorporated ICAs as shown in Fig. 5(b). Through the two-step curing method, all of LMA-2 were also fused in the formulation and the re-melt LMAs-2 were not found during the 2nd heating process. From these results, it was confirmed that the two-step curing process was effective in fusing LMAs into the formulation.

Fig. 6(a)–(c) show the metal particles used in this study. The particle size of LMA-1 and LMA-2 ranged from 15–25 μm and 30–40 μm , respectively. It is necessary to investigate the morphology of LMA filled ICAs cured by a one-step and two-step

process. Fig. 7(a) and (b) illustrate the morphology of LMA-1 incorporated ICAs by a one-step curing process. The ratio of LMA to silver flakes was 1:3. It is shown that the spherical particles of LMA-1 still remained, not even melting or wetting on the silver flakes. Unlike a one-step cured sample, the different morphology was found in a two-step cured sample as shown in Fig. 8. It is seen that LMAs wet and are fused on the surface of silver flakes. Many segments of fused regions were also shown, which covered the surface of the silver flakes and formed metallurgical connections. Fig. 9(a) and (b) show the morphology of LMA-2 incorporated ICAs prepared by a one-step curing process. It can be seen that the spherical LMA particles are not

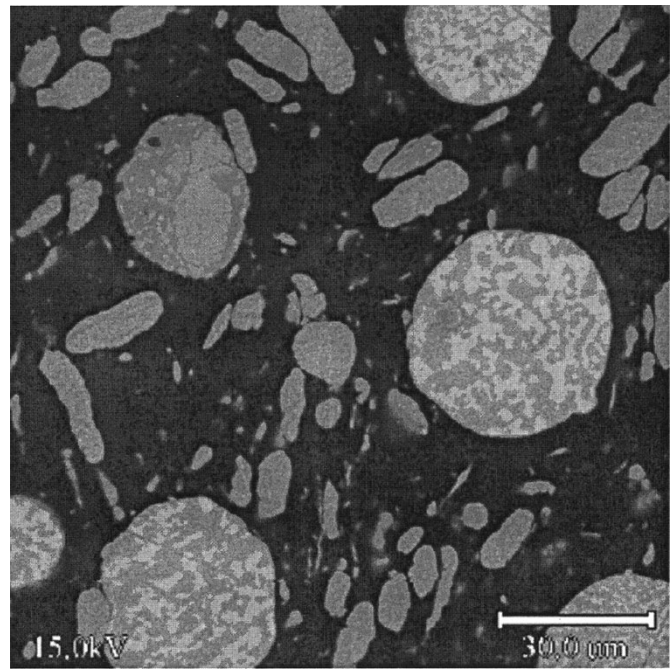


(a)

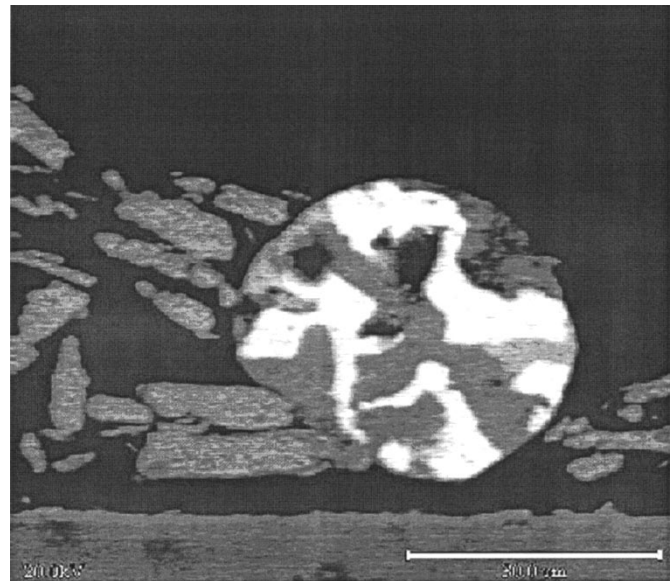


(b)

Fig. 7. Cross section of a one-step cured sample for LMA-1 incorporated ICAs: (b) is a magnified image of (a).



(a)



(b)

Fig. 9. Cross sections of a one-step cured sample for LMA-2 incorporated ICAs.

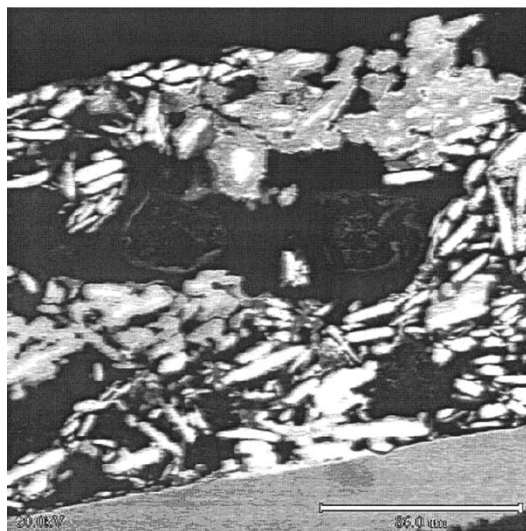
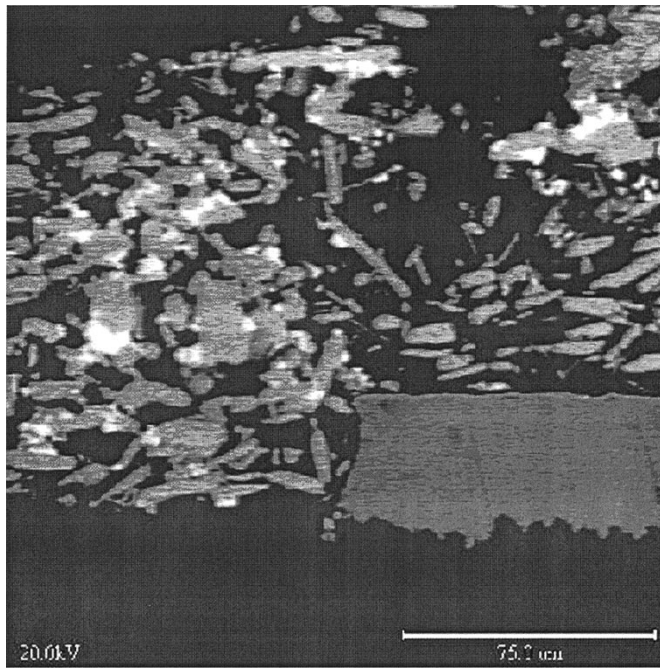
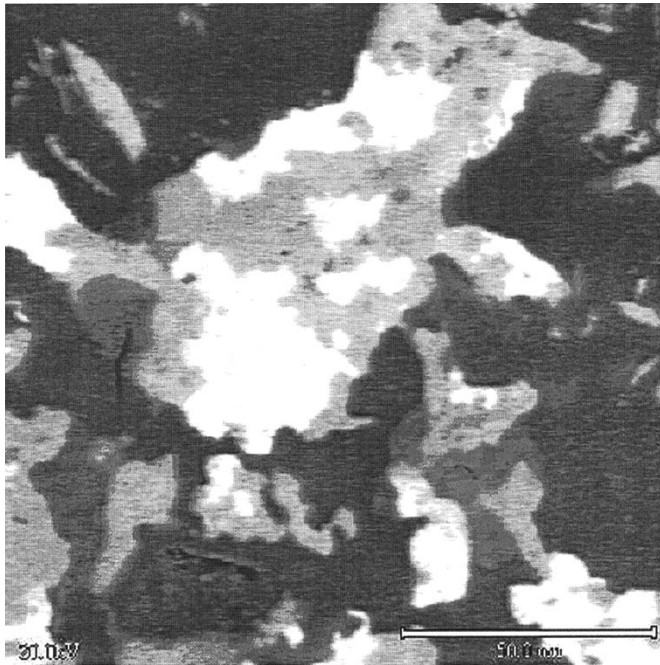


Fig. 8. Cross section of a two-step cured sample for LMA-1 incorporated ICAs.

fused, even though LMAs and silver flakes contact each other. Accordingly, it is thought that the epoxy curing will hinder the melting and wetting of LMA particles and limit the movement of the particles resulting in fixing the shape of the LMA particles. Fig. 10(a) and (b) show the morphology of LMA-2 filled ICAs by a two-step curing process. Similar to Fig. 8, many clods of metal particles are shown, which are from LMAs melting and wetting on the silver surface and are covering the surface of silver flakes. Consequently, it was confirmed by morphological observation that the two-step curing process provides LMA with enough time to wet and cover up the surface of silver flakes forming metallurgical interconnections.



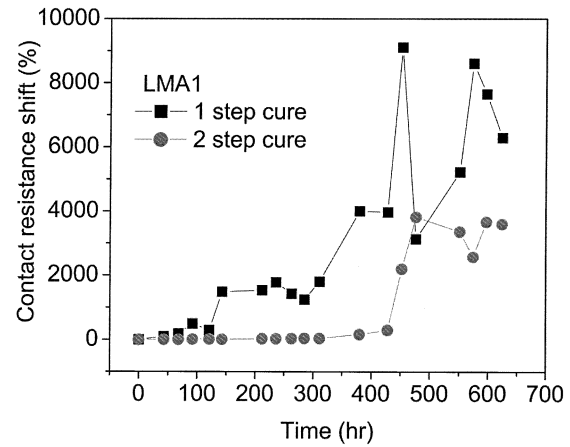
(a)



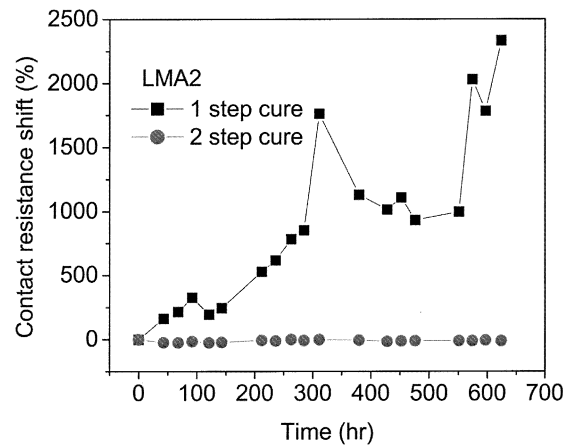
(b)

Fig. 10. Cross sections of a two-step cured sample for LMA-2 incorporated ICAs.

Contact resistance of LMA incorporated ICAs during the harsh environment aging test was evaluated in terms of curing processes. Most silver-filled conductive adhesives exhibit increasing contact resistance on nonnoble metals under harsh environment. This is due to the metal oxide formation resulting from the galvanic corrosion at the interface between ICAs and nonnoble metal [3]. Fig. 11(a) and (b) show the contact resistance shift of one-step and two-step cured ICAs, in which LMAs-1 and LMAs-2 are incorporated, on a Sn surface finish



(a)



(b)

Fig. 11. Contact resistance shift of LMA incorporated ICAs during the 85 °C/85% RH test: (a) LMA-1 and (b) LMA-2.

as a function of aging time under the 85 °C/85% RH condition. In Fig. 11(a), although the contact resistance of a two-step cured formulation increased after 400 h, the one-step cured sample showed a significant increase only after about 100 h. Therefore, a two-step cured sample was more stable in terms of contact resistance than a one-step cured one. For Fig. 11(b), contact resistance of the one-step cured samples started to increase dramatically from the beginning of the aging test and continued increasing. In contrast, a two-step cured sample shows much more stable contact resistance compared with the one-step cured one. Clearly, the ICAs incorporated with LMAs prepared by the two-step curing process showed much more stable contact resistance on Sn than the ICAs prepared by a one-step curing process. Non-fused LMA particles in the ICA formulations remain in the spherical shape and cover up neither silver flakes nor the metal pad. Therefore, nonfused LMAs do not contribute the metallurgical interconnection between either silver and LMAs or LMAs and the metal pad. Consequently, ICAs cured by a two-step curing process showed much more stable contact resistance under the elevated temperature and humidity resulting from the fusion of LMAs into silver flakes and the metallurgical interconnection between silver flakes and LMAs and between LMAs and the metal pad.

IV. CONCLUSION

By a one-step curing process, LMAs in ICAs were not fully fused into the formulation and a melt peak during the second heating scan was found. The two-step curing process provides LMAs in ICAs with enough time to fuse in the formulation and the metallurgical interconnection forms between LMAs and silver and between LMAs and the metal pad. This was confirmed by DSC and SEM observations. The ICA formulation cured by a two-step curing process exhibited much more stable contact resistance under the 85 °C/85% RH condition than that by a one-step curing process.

ACKNOWLEDGMENT

The authors would like to thank C. Rockette, School of Materials Science and Engineering, Georgia Institute of Technology, for assisting this work.

REFERENCES

- [1] J. Liu, Z. Lai, H. Kristiansen, and C. Khoo, "Overview of conductive adhesive joining technology in electronics packaging applications," in *Proc. 3rd Int. Conf. Adhesive Joining Coating Technol. Electron. Manufact.*, Binghamton, NY, 1998, pp. 1–17.
- [2] D. Lu and C. P. Wong, "Novel conductive adhesives for surface mount applications," *J. Appl. Polym. Sci.*, vol. 74, pp. 399–406, 1999.
- [3] D. Lu, Q. Tong, and C. P. Wong, "A fundamental study on silver flakes for conductive adhesives," in *Proc. 4th Int. Sym. Adv. Packag. Mater.*, 1998, pp. 48–52.
- [4] D. Lu and C. P. Wong, "Development of conductive adhesives filled with low-melting-point alloy fillers," in *Proc. 4th Int. Sym. Adv. Packag. Mater.*, 2000, pp. 158–164.
- [5] —, "Isotropic conductive adhesives filled with low-melting-point-alloy fillers," *IEEE Trans. Electron. Packag. Manufact.*, vol. 23, pp. 185–190, July 2000.
- [6] S. A. Durga and T. Fort Jr., *Liquid Boundary Tensions: Pendant Drop Technique*, 1973, ch. 3.



Kyoung-Sik Moon received the M.S. and Ph.D. degrees in materials science and engineering from Korea University, Seoul, in 1999.

He joined the School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, as a Postdoctoral Fellow after receiving the Ph.D. degree. His experience includes epoxy molding compounds, electromagnetic wave absorbing materials, dielectric films, conductive adhesives, underfill encapsulant materials, and polymer thick film technology for electronic applications.



Jiali Wu received the B.S. degree in chemistry from Zhejiang University, China, and the M.S. and Ph.D. degrees in chemistry from the Shanghai Institute of Metallurgy, Chinese Academy of Science, Shanghai, China.

From 1991 to 1997, her major research work focused on microsensor fabrication and application in electrochemistry and die bonding with Au/In bi-alloy isothermal solidification technique. She was a Postdoctoral Fellow for three years in the School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta. She joined IBM, Fishkill, NY, in 2001.



C. P. Wong (F'92) received the B.S. degree in chemistry from Purdue University, West Lafayette, IN, and the Ph.D. degree in organic/inorganic chemistry from the Pennsylvania State University, University Park.

He is a Professor of the School of Materials Science and Engineering and a Research Director of the NSF Packaging Research Center, Georgia Institute of Technology, Atlanta. After his doctoral study, he was awarded two years as a Postdoctoral Scholar, Stanford University, Stanford, CA. He joined AT&T Bell Laboratories, in 1977 as a Member of Technical Staff.

He has been involved with the research and development of polymeric materials (inorganic and organic) for electronic applications. He was elected an AT&T Bell Laboratories Fellow in 1992. His research interests lie in the fields of polymeric materials, high T_c ceramics, material reaction mechanism, IC encapsulation in particular, hermetic equivalent plastic packaging and electronic manufacturing packaging, and reliability processes. He holds over 40 U.S. patents and numerous international patents, and has published over 190 technical papers and 180 presentations in the related area.

Dr. Wong received the 1999 Georgia Tech Outstanding Faculty Research Program Development Award and the 1999 NSF-PRC Faculty of the Year Award. He was the IEEE Components, Packaging, and Manufacturing Technology (CPMT) Society Technical Vice President in 1990 and 1991 and the CPMT Society President in 1992 and 1993.