

Performance, Reliability, and Approaches Using a Low Melt Alloy as a Thermal Interface Material

Chris G. Macris, Thomas R. Sanderson, Robert G. Ebel, Christopher B. Leyerle
Enerdyne Solutions
125 West North Bend Way
North Bend, WA 98045
(425) 888-1880
info@enerdynesolutions.com

Abstract

The use of an all-metal interfacial thermal path is highly desirable because its relatively low thermal resistance allows the use of less aggressive and generally cheaper thermal management components. Low Melt Alloys (LMAs), unlike eutectic solders, are well-suited as a thermal interface between materials of dissimilar Coefficients of Thermal Expansion (CTEs); however, reliability problems in production implementations, resulting in catastrophic failure, have retarded their adoption. Mechanical problems include shake-out due to mechanical shock and drip-out due to low viscosity, especially with vertically-oriented interfaces. Thermal problems include dry-out caused by thermal cycling, leading to the creation of voids in the interface and catastrophic failure; the growth of thermally resistive intermetallic compounds through interfacial contact, and oxidation/corrosion in non-hermetically-sealed applications, both leading to a steady decrease in performance and eventual thermal failure.

The current work looks at the influence of typical environmental testing conditions on thermal performance and mechanical/chemical robustness of typical LMA thermal interface materials and presents approaches to mitigating the major failure mechanisms.

Keywords

Thermal interface material, Low melt alloy, Metallic thermal interface, Liquid metal

Nomenclature

LMA – Low Melt Alloy
TIM – Thermal Interface material
CTE – Coefficient of Thermal Expansion
MEMS – Micro Electro-Mechanical System

Introduction

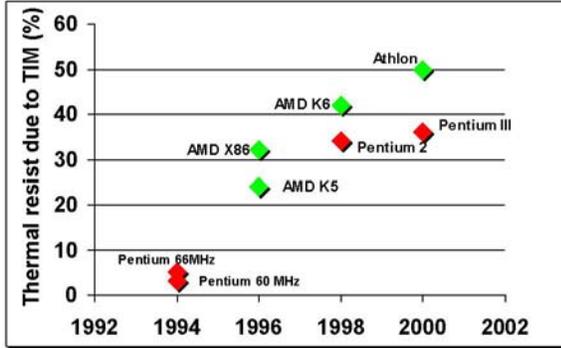
Today's electronic components generate significant amounts of heat which must be removed to maintain the component's junction temperature within safe operating limits. Failure to effectively conduct away heat leaves these devices at high operating temperatures,

ultimately resulting in decreased performance and reliability.

The heat removal process involves heat conduction between the electronic component and heat exchanger, or heat sink, via a thermal interface material. Small irregularities on both the component and heat sink surfaces prevent intimate contact and create air gaps that increase the resistance to the flow of heat. With many of today's microprocessors, a significant amount of the overall thermal budget is consumed by the thermal interface [1]. The thermal resistance of the interface between these two surfaces can be reduced by providing a thermally conductive interface material which fills the air gaps and voids in the surfaces.

Liquids have low interfacial resistance because they wet a surface forming a continuous contact with a large area. Most liquids do not, however, have very high conductivity. Solids, and in particular metals, have very high conductivity but high interfacial resistance.

Figure 1



Most common heat transfer materials combine highly conductive particles with a liquid or plastic in order to exploit both characteristics. Examples of the former are greases and gels while the latter include filled epoxies, silicones and acrylics.

Liquid metals, such as alloys of bismuth, gallium and indium, potentially offer both low interfacial resistance and high conductivity. Several alloys of gallium with very low melting points have also been identified as potential liquid metal interface materials. Thermal performance of such an interface would be more than one order of magnitude greater than many adhesives typically in use.

Although LMAs offer both low interfacial resistance and high conductivity, they have historically suffered from various reliability issues including: corrosion/oxidation, intermetallic formation, drip-out, dewetting, and migration. Unless mitigated, these mechanisms will continue to degrade the interface, resulting in a thermally related catastrophic failure of the actual electronic component.

LMA Material Options

Many alloy combinations can be classified as a LMA for TIM applications. Alloys which possess a liquidus point below the operating temperature of the electronic component are needed to allow the LMA to adequately flow into all surface asperities of the interface. In general, alloys comprised of the fewest number of constituents possess the highest thermal conductivities.

Common LMA candidates include bismuth-based or gallium-based alloys as depicted in Table 1 [2, 3]. However, due to the toxicity and environmental issues associated with cadmium and lead, alloys 117, 136 and 21 may not be viable LMA candidates.

Table 1

LMA Alloys with Melting Temperatures Between 10°C and 81°C

Alloy	Liquidus (°C)	Solidus (°C)	Composition (%)
51	10.7E	10.7	62.5 Ga, 21.5 In, 16 Sn
60	15.7E	15.7	75.5 Ga, 24.5 In
6077	25	15.7	95 Ga, 5 In
85.6	29.8E	29.8	100 Ga
117	47.2E	47.2	44.7 Bi, 19.1 In, 6.3 Sn, 22.6 Pb, 5.3 Cd
136	58E	58	49 Bi, 21 In, 12 Sn, 18Pb
19	60E	60	32.5 Bi, 51 In, 16.5 Sn
21	69	58	49 Bi, 18 In, 5 Sn, 18 Pb
162	72E	72	33.7 Bi, 66.3 In
174	79E	79	57 Bi, 26 In, 17 Sn
27	81E	81	54.02 Bi, 29.68 In, 16.3 Sn

Performance

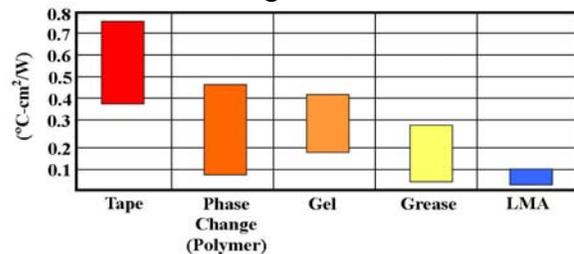
Table 2 [4, 5, 6] illustrates several published LMA products and their respective thermal performance values. It can also be seen that the melting points of these LMAs are approx. 20 °C below the maximum operating temperatures of typical microprocessors.

Table 2

LMA	Liquidus (°C)	Thermal Res. (°C-cm ² /W)
Alloy 19	60	0.058
Supplier A (a)	60	0.060-0.013
Supplier A (b)	72	0.060-0.013
Supplier B (a)	62	0.030
Supplier B (b)	67	0.030
Supplier B (c)	71	0.030

Figure 2 [7] shows the evolution of common TIM materials and the potential for LMAs to satisfy the continuously shrinking thermal budgets of the next generation of electronics components.

Figure 2



Reliability

Corrosion, considered to be the main failure mechanism in LMA materials, is driven primarily by moisture, oxygen and heat. The liquid phase of these alloys at operating temperatures facilitates rapid diffusion, accelerating the corrosion process.

The impact of corrosion on a LMA is apparent in Figures 3a through 3c. Figure 3a illustrates a typical LMA alloy supported by a nickel plated copper foil sheet before clamping to a silicon die and exposure to an environment consisting of 85 °C and 85% humidity (85/85). Within Figure 3b, the sample, subjected to 24 hrs in the 85/85 test environment, can be seen with the die removed and significant corrosion around the reflowed perimeter of the sample. Figure 3c, an enlarged image of Figure 3b, shows a black corrosion band around the perimeter of die footprint. Additionally, discontinuous corrosion products can be seen as discolored regions directly under the die.



Figure 3a



Figure 3b



Figure 3c

LMA alloys can also induce the growth of intermetallic layers with poor thermal and mechanical properties. Webb, et al. [8] performed thermal cycling tests with alloy 117 tinned on a nickel plated (5 micron) 50 micron copper strip. After cycling to a maximum of 80 °C, the LMA sample was inspected using Back Scatter Electron (BSE) imaging and was found to have formed intermetallic compounds with micro-cracks. It is believed that these intermetallic layers are of low thermal conductivity and therefore would result in unacceptable thermal performance on a long-term basis.

During testing of a commercially supplied LMA product by Lee, et al. [9], depicted in Table 3, degraded thermal performance was observed after temperature cycling and ageing with and without elevated humidity. These results corroborate the susceptibility of at least some LMA systems to temperature and moisture induced failure mechanisms.

Table 3

STRESS CONDITION	RELIABILITY DATA (R _p)
End of Line	0.27 (°C/W) T = 0
T/C (-45 °C to +125 °C)	0.82 (°C/W) After 50 cycles
Bake (125 °C)	0.35 (°C/W) After 144 hours
HAST (130 °C / 85% RH)	0.68 (°C/W) After 50 cycles

Therefore, reliability requirements for TIM materials in microprocessor applications are presented in Table 4 [10]. For LMA systems to withstand the stress conditions equivalent to a ten year device life, failure mechanisms must be identified and mitigated with appropriate design.

Table 4

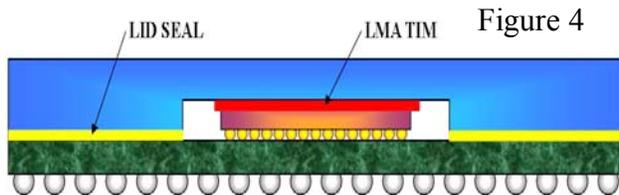
RELIABILITY REQUIREMENTS	
ENVIRONMENTAL STRESS	7 - 10 years Equivalent Duration & Condition
Thermal Mechanical	T/C "B" (-45 °C to +125 °C) T/C "T" (0 °C to +125 °C) T/C "R" (-25 °C to +125 °C) P/C (RT to TJ)
Physic - Chemical	Bake at 150 °C Bake at 125 °C Bake at 100 °C
Mechanical Shock	Trapezoidal 50g, 11msec pulse, Velocity change 170 in/sec, 3 drops in each of six directions
Vibration	5-20 Hz 0.01g/Hz sloping up to 0.02 g/Hz, 20-500 Hz 0.02g/Hz, 3.13 GRMS random, 10 minutes / axis

Approaches to Mitigating Failure Mechanisms

Oxidation / Corrosion

Corrosion of a LMA is primarily an electrochemical process in which surface atoms of the alloy react with a substance in contact with the exposed surface. Electricity passes from a negative region to a positive region (both on the LMA) through an electrolyte or corroding medium. In the typical electronics environment, the corroding medium is liquid or vapor phase moisture. Moisture films on a LMA may contain dissolved substances which affect corrosion: Oxygen, various oxides/dioxides, sulfates, chlorides and metal ions.

Corrosion may also be accelerated by Galvanic effects which operate by a difference in potential between dissimilar metals. As most LMA combinations lie near the anodic end of the galvanic series, the LMA will preferentially corrode when electrically in contact with a metal of higher cathodic potential and an electrolyte.



Many current flip chip packages of the type depicted in Figure 4 do not contain a lid seal, but instead use a partial bead of adhesive to allow venting of the package cavity. The die underfill provides all the moisture protection needed. To provide adequate LMA moisture protection, the package cavity must be of a closed configuration. Longest package lifetimes will be obtained with epoxies, or alternatively sealants being developed for near hermetic MEMS packaging.

Table 5

PUBLISHED PERMEABILITY DATA	
Type	Vapor Transmission Rate $\text{g}\cdot\text{mm}/\text{m}^2\cdot\text{day}$
Acrylic	Not Listed
Epoxy	0.7 - 0.94
Polyurethane	0.94 - 3.43
Silicon Rubber	1.73 - 3.11

Published data [11] regarding the vapor transmission rates of the sealant classes is shown in Table 5. Epoxies, as a rule, have lower transmission rates than polyurethanes and silicones. Therefore, by providing a near-hermetic seal between the package lid and package laminate (Figure 4), corrosion due to moisture films can be significantly reduced.

Mechanical Stability

Liquid metals flow quite well. This characteristic alone poses some special challenges to overcome if they are to be used successfully as a TIM. Booth et al. [12] has proposed incorporating a wire mesh in the thermal interface to control excess LMA, and making a paste of the LMA by incorporating various materials in particulate form to increase viscosity and reduce migration.

The solid structures or phases proposed for incorporation within the thermal interface address the basic problem of getting an LMA to stay put when in service. These structures increase the surface contact area with the LMA in the thermal interface. As long as the total solid-liquid interface energy is less than the interface energy of the liquid-gas and solid-gas interfaces it replaces, the LMA will minimize its surface energy by wetting the surfaces within the interface.

The LMA may still wet the surface adjacent to the thermal interface if it is the same wettable surface used under the die, particularly when acted upon by an additional force. Additional forces will arise from shock, vibration, and CTE mismatches between the LMA and other components. Once the LMA has wet the surface adjacent to, but outside the thermal interface, it is doubtful surface tension alone will retain it within the interface when acted upon by external forces. Others have proposed to address this difficulty with gaskets to contain the LMA and fillers or non-eutectic (slushy) compositions to increase its viscosity.

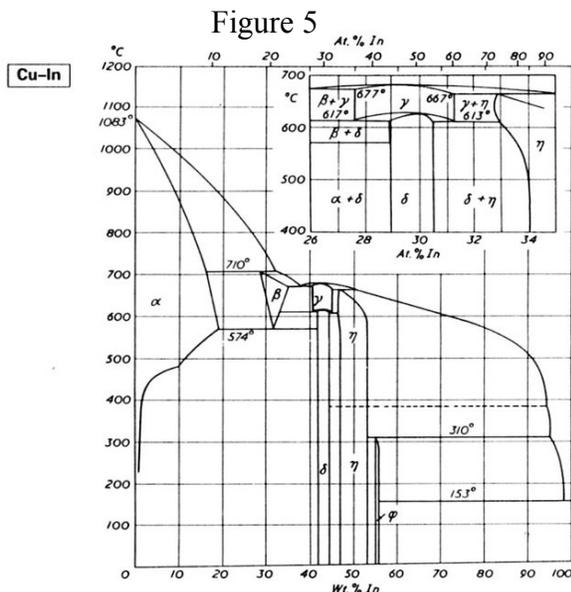
We have found that simply modifying the surface around the thermal interface so that the LMA will not wet it is sufficient to contain the LMA within the interface during shock, vibration, and temp cycling. It is conceivable that if excess LMA were incorporated during assembly, this excess could end up airborne from shock or vibration. Therefore, LMA TIM should be deployed in closed cavities where no opportunities for shorts or adverse reactions with other metals exist.

Chemical Stability

Designing an LMA thermal interface system has similarities to designing a solder joint system. As with a solder joint system, no deleterious intermetallics must form at the liquid-solid interfaces of the LMA system. For the LMA system, deleterious intermetallics will be any having poor thermal conductivity that grow thick enough to decrease performance during the life of the component.

The possibility of intermetallic formation for a given metals system can be determined from the binary equilibrium phase diagrams for the various metals present, but finding thermal conductivities for most intermetallics in the literature will be unlikely, and finding parameters necessary to calculate growth rates for them is even less likely. Consequently, for a system where intermetallics are likely to form as indicated by the phase diagram, systems will need to be aged at elevated temperature, thermal performance will need to be tested periodically, and if a decrease in thermal performance is observed, cross sections will need to be prepared to identify the offending intermetallic so it may be eliminated.

An example of such a system would be an LMA containing indium, and a heat sink with a copper base. The phase diagram of Figure 5 [13] indicates that at equilibrium, three different intermetallics will exist at temperatures below 310 °C. If any of these grows readily and has poor thermal conductivity, this metals system will be unacceptable as a LMA TIM.



Systems containing gallium pose additional challenges. Gallium metal is quite corrosive to other metals (including aluminum and copper) because of the rapidity with which it diffuses into the crystal lattices of metals. The few metals that tend to resist attack are molybdenum, niobium, tantalum, and tungsten [14].

To prevent amalgamation with another metal, a non-reactive coating such as Teflon, siloxane, hydrogenated carbon or thin ceramic layers may be applied to the interfaces [15]. Additionally, refractory metals possessing good thermal performance and chemical inertness may be deposited. Anodized/oxide or conversion coatings can also provide the necessary chemical stability for various LMA compositions.

Conclusions

LMA alloys as a thermal interface material offer superior thermal performance due to their high thermal conductivities and low contact resistance, resulting from excellent surface wetting. Reworkability, ease of handling, and a lack of cure make this attractive in a high volume setting.

The various failure mechanisms which have plagued the past and present LMA products will be mitigated by applying a multidisciplinary approach to the challenge. A LMA system in qualification trials at Enerdyne promises to deliver LMA performance while providing a stable and robust product to satisfy the environmental and testing demands of the microelectronics industry.

Acknowledgements

The authors would like to thank David L. Saums of DS&A for his support and insights through the various stages of this effort.

References

- [1] N. Dean, "Materials for Thermal Management, Properties and Processes", *Advanced Packaging Magazine*, Vol. 12, No. 3, pp. 15-20, March, 2003.
- [2] R. Webb, J. Gwinn, "Low Melting Point Thermal Interface Material", 2002 Inter Society Conference on Thermal Phenomena, pp. 671-676, 2002.

[3] Arconium Alloy Product List, Arconium Specialty Alloys, Providence, RI, 1994.

[4] R. Webb, J. Gwinn.

[5] Thermagon T-Ima 105 Properties Datasheet, Thermagon, Cleveland, Ohio.

[6] TherMax HiFlux Datasheet, TherMax Korea Corp., Seoul, Korea.

[7] S. Lee, P. Chen, "Development of High Performance Thermal Interface Material", Intel Technology Symposium, Seattle, Washington, September 27-28, 2001.

[8] R. Webb, J. Gwinn.

[9] S. Lee, P. Chen.

[10] Ibid.

[11] "Permeability and other Film Properties of Plastics and Elastomers", Plastics Design Library, 1996.

[12] Booth, et al., "Liquid Metal Matrix Thermal Paste", U.S. Patent No. 5,198,189, March 30, 1993.

[13] C.J. Smithells, "Smithells Metals Reference Book, 1992.

[14] D. Considine, "Van Nostrand's Scientific Encyclopedia", Van Nostrand Reinhold Company, fifth edition, New York, pg. 1130. 1976.

[15] Booth, et al.