Thermal Interface Materials

D.D.L. Chung

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Thermal interface materials for facilitating heat transfer by conduction across two adjacent surfaces are reviewed. They include thermal fluids and pastes, solders, phase change materials (PCMs), and resilient thermal conductors.

Keywords conduction, heat transfer, phase change material, solder, thermal contact, thermal interface, thermal paste

1. Introduction

The transfer of heat by conduction is involved in the use of a heat sink to dissipate heat from an electronic package, the heating of an object on a hot plate, the operation of a heat exchanger, the melting of ice on an airport runway by resistance heating, the heating of a cooking pan on an electric range, and in numerous industrial processes that involve heating or cooling. Effective transfer of heat by conduction requires materials (such as a heat sink material) of high thermal conductivity. In addition, it requires a good thermal contact between the two surfaces (such as the surface of a heat sink and the surface of a printed circuit board) across which heat transfer occurs. Without good thermal contacts, the use of expensive thermally conducting materials for the components is a waste. The attainment of a good thermal contact requires a thermal interface material. Much more research has been conducted on high thermal conductivity materials than on thermal interface materials. An example of a thermal interface material is a thermal grease, which must be thin (small in thickness) between the mating surfaces, must conform to the topography of the mating surface, and preferably should have a high thermal conductivity as well. This paper is a review of thermal interface materials. Due to the critical importance of heat dissipation in electronics, thermal interface materials are commercially important.

Thermal interface materials include thermal fluids, thermal greases (pastes), resilient thermal conductors, solders (applied in the molten state), and phase change materials (PCMs, which change to the liquid state from the solid state while they are in service). A thermal fluid, thermal grease, molten solder, or molten PCM is spread on the mating surfaces. A resilient thermal conductor is sandwiched by the mating surfaces and held in place by pressure. Thermal fluids are most commonly mineral oil. Thermal greases (pastes) are most commonly conducting particle (usually metal or metal oxide) filled silicone. A common disadvantage of using a liquid or semiliquid carrier is that it tends to flow out, regardless of whether it is in service. Thus, a better choice is a carrier, which is in the solid state at room temperature and in the liquid or semiliquid state at a slightly higher temperature, *i.e.*, at the service temperature. Resilient thermal conductors are most commonly conducting particle filled elastomers. Out of these types of thermal interface materials, thermal greases (based on polymers, particularly silicone) and solder are by far most commonly used. Resilient thermal conductors and PCMs are not as well developed as solder, thermal fluids, or greases.

Because the materials to be interfaced are good thermal conductors (such as copper), the effectiveness of a thermal interface material is enhanced by high thermal conductivity and low thickness of the interface material and low thermal contact resistance between the interface material and each mating surface. Because the mating surfaces are not perfectly smooth, the interface material must be able to flow or deform, so as to conform to the topography of the mating surfaces. If the interface material is a fluid, grease, or paste, it should have a high fluidity (workability) so as to conform and to have a small thickness after mating. On the other hand, the thermal conductivity of the grease or paste increases with increasing filler content, and this is accompanied by a decrease in the workability. Without a filler, as in the case of an oil, the thermal conductivity is poor. A thermal interface material in the form of a resilient thermal conductor sheet (*e.g.*, a felt consisting of conducting fibers clung together without a binder, and a resilient polymer-matrix composite containing a thermally conducting filler) usually cannot be as thin or conformable as one in the form of a fluid, grease, or paste, so its effectiveness requires a very high thermal conductivity within it.

2. Solder

Solder is commonly used as a thermal interface material for enhancing the thermal contact between two surfaces. This is because solder can melt at rather low temperatures and the molten solder can flow and spread itself thinly on the adjoining surfaces, thus resulting in high thermal contact conductance at the interface between solder and each of the adjoining surfaces. Furthermore, solder in the metallic solid state is a good thermal conductor. In spite of the high thermal conductivity of solder, the thickness of the solder greatly affects the effectiveness of the solder as a thermal interface material; a small thickness is desirable. Moreover, the tendency for solder to react with copper to form intermetallic compounds[1] reduces the thermal contact conductance of the solder-copper interface.

D.D.L. Chung, Composite Materials Research Laboratory, State University of New York at Buffalo, Buffalo, NY 14260-4400. Contact e-mail: ddlchung@acsu.buffalo.edu.

Table 1 Thermal contact conductance for various thermal interface materials between copper disks at 0.46 Ma contact pressure[6,7]

Thermal Interface Material		Interface material thickness (μm) ($\pm$10)	Thermal contact conductance (10^4 W/m^2·°C)	Viscosity (cps) ($\pm$0.3)
Description	Designation			
PEG	A	<25	11 $\pm$ 0.3	127(a)
PEG + BN (18 vol.%)	B	25	12.3 $\pm$ 0.3	…
PEG + Li salt (1.5 wt.%)	C	<25	12.3 $\pm$ 0.3	143(a)
PEG + Li salt (1.5 wt.%) + BN (18 vol.%)	D	25	13.4 + 0.4	…
PEG + water + DMF	J	<25	12.5 + 0.2	75.6(a)
J + Li salt (0.75 wt.%)	E	<25	11.4 $\pm$ 0.3	79.7(a)
J + Li salt (1.5 wt.%)	F	<25	16 $\pm$ 0.5	85.6(a)
J + Li salt (3 wt.%)	G	<25	11.6 $\pm$ 0.2	99(a)
J + Li salt (4.5 wt.%)	H	<25	9.52 $\pm$ 0.25	117(a)
J + Li salt (6 wt.%)	I	<25	7.98 $\pm$ 0.16	120(a)
F + BN (16 vol.%)	F_1	25	18.5 $\pm$ 0.8	…
F + BN (18 vol.%)	F_2	25	18.9 $\pm$ 0.8	…
F + BN (19.5 vol.%)	F_3	25	15.3 $\pm$ 0.2	…
F + BN (21.5 vol.%)	F_4	25	14 $\pm$ 0.5	…
G + BN (16 vol.%)	G_1	25	17 $\pm$ 0.5	…
G + BN (18 vol.%)	G_2	25	17.3 $\pm$ 0.6	…
G + BN (19.5 vol.%)	G_3	25	14.9 $\pm$ 0.6	…
G + BN (21.5 vol.%)	G_4	25	13.4 $\pm$ 0.4	…
H + BN (18 vol.%)	H_1	25	13.9 $\pm$ 0.4	…
Solder	…	25	20.8 $\pm$ 0.6(b)	…
Sodium silicate + BN (16 vol.%)	…	25	18.2 $\pm$ 0.7	…
Sodium silicate + BN (17.3 vol.%)	…	25	15.5 $\pm$ 0.4	…
Sodium silicate	…	<25	14.1 $\pm$ 0.5	206(c)
Silicone/BN	…	25	10.9 $\pm$ 1.5	…
Silicone	…	<25	3.08 $\pm$ 0.03	8800(d)
None	…	…	0.681 $\pm$ 0.010	…

(a) Measured using the Ubbelohde method
(b) At zero contact pressure (not 0.46 MPa)
(c) Measured using the Ostwald method
(d) Value provided by the manufacturer

3. Thermal Pastes

Thermal pastes are predominantly based on polymers, particularly silicone,[2–5] although thermal pastes based on sodium silicate have been reported to be superior in providing high thermal contact conductance.[6] The superiority of sodium-silicate-based pastes over silicone-based pastes is primarily due to the low viscosity of sodium silicate compared to silicone, and the importance of high fluidity in the paste so that the paste can conform to the topography of the surfaces that it interfaces.

A particularly attractive thermal paste is based on polyethylene glycol (PEG, a polymer) of a low molecular weight (400 amu).[7] These pastes are superior to silicone-based pastes and are as good as sodium-silicate-based pastes due to the low viscosity of PEG and the contribution of lithium ions (a dopant) in the paste to thermal conduction. Compared to the sodium-silicate-based pastes, the PEG-based pastes are advantageous in their long-term compliance, in contrast to the long-term rigidity of sodium silicate. Compliance is attractive for decreasing the thermal stress, which can cause thermal fatigue.

Table 1 gives the thermal contact conductance for different thermal interface materials. Included in the comparison are results obtained with the same testing method on silicone-based paste, sodium-silicate-based pastes, and solder.[6,7] The PEG (*i.e.*, A) gives much higher thermal contact conductance (11×10^4 W/m^2 °C) than silicone (3.08×10^4 W/m^2 °C), due to its relatively low viscosity, but the conductance is lower than that given by sodium silice (14.1×10^4 W/m^2 °C), in spite of its low viscosity, due to the molecular nature of PEG. The addition of the Li salt (1.5 wt.%) to PEG (*i.e.*, to obtain C) raises the conductance from 11×10^4 to 12.3×10^4 W/m^2 °C, even though the viscosity is increased. The further addition of water and DMF (*i.e.*, F) raises the conductance to 16×10^4 W/m^2 °C and decreases the viscosity. Thus, the addition of water and DMF is very influential, as water and DMF help the dissociation of the lithium salt. The still further addition of BN particles (18 vol.%) (*i.e.*, F_2) raises the conductance to 18.9×10^4 W/m^2 °C. The positive effect of BN is also shown by comparing the results of C and D (which are without water or DMF, which is N,N-dimethylformamide, or $HCON(CH_3)_2$) and by comparing the results of A and B (which are without Li^+). In the absence of the lithium salt, water and DMF also help, though not greatly, as shown by comparing A and J. The viscosity increases with the lithium salt content, as shown by comparing J, E, F, G, H, and I. Comparison of E, F, G, H, and I shows that the optimum lithium salt content for the highest conductance is 1.5 wt.%. That an intermediate lithium salt content gives the highest conductance is probably because of

the enhancement of the thermal conductivity by the Li^+ ions and the increase of the viscosity caused by the lithium salt addition. Both high conductivity and low viscosity (good conformability) are desirable for a high contact conductance. Comparison of F_1, F_2, F_3, and F_4 shows that the optimum BN content is 18 vol.%, as also indicated by comparing G_1, G_2, G_3, and G_4. Among all the PEG-based pastes, the highest conductance is given by F_2, as it has the optimum lithium salt content as well as the optimum BN content. An optimum in the BN content also occurs for BN-filled sodium-silicate-based pastes.[6] This optimum BN content is attributed to the increase in both the thermal conductivity and the viscosity of the paste as the BN content increases. The best PEG-based paste (*i.e.*, F_2) is similar to the best sodium-silicate-based paste in the conductance. Both are better that BN-filled silicone, but both are slightly inferior to solder. Although solder gives the highest conductance, it suffers from the need of heating during soldering. In contrast, heating is not needed in the use of PEG-based pastes, silicone-based pastes, or silicate-based pastes.

4. Phase Change Materials

The PCMs, usually meaning solid-liquid PCMs (because the latent heat change for a solid-to-solid transition is usually considerably less than that for a solid-to-liquid transition), have received considerable attention in recent years due to their high heat storage capacity.[8–13] Various forms of PCMs, usually encapsulated, have been utilized as thermal storage media for cooling and heating applications.[14,15,16]

The PCMs can be roughly classified as inorganic compounds (mainly salt hydrates)[13] and organic compounds,[16,17,18] although inorganic ones are much more common. A review of PCMs for use as latent heat materials was given by Lane.[8] Abhat[19] also reviewed a number of materials with low melting temperatures (0 to 120 °C).

Organic PCMs can be classified as paraffins and nonparaffin organics. A detailed discussion of the properties of paraffins can be found in Ref 20. Himran *et al.*[21] reviewed paraffin waxes for use as energy storage materials. The PCMs as a possible thermal management solution for commercial electronic products have received increasing attention in recent years.[22,23,24] The reason to use PCM in such cases relates to the high latent heat. Pal and Joshi[22] studied the thermal control of a heat source by using a paraffin, *n*-triacontane, which was housed in a sealed heat sink and put in close proximity to the heat source. Numerical analysis of a finned surface surrounded by a paraffin (nonadecane) was conducted for the case of high heat flux levels.[23] However, at high heat flux levels, the poor thermal conductivity of PCMs limits their thermal control performance.

Common problems associated with inorganic PCMs are supercooling and thermal instability. Because solidification involves nucleation, numerous nucleating additives have been investigated in order to reduce the supercooling. Although a nucleator with a crystal structure similar to the PCM and with little solubility in the PCM is preferred, many nucleators were found just by intuition and no explanation of their effectiveness was provided. Telks[25] tested several isostructural nucleation additives and found that the best nucleator for $Na_2SO_4 \cdot 10H_2O$ was $Na_2B_4O_7 \cdot 10H_2O$, which reduced the supercooling of $Na_2SO_4 \cdot 10H_2O$ (about 15 °C) to the range of 1.4 to 1.9 °C. The nucleation of $CaCl_2 \cdot 6H_2O$ was studied by numerous workers. In particular, $BaI_2 \cdot 6H_2O$,[26] BaO and $Ba(OH)_2$,[8] copper powder,[27] Al_2O_3,[28] $NiCl_2 \cdot 6H_2O$,[29] and many other additives were found to help the nucleation of $CaCl_2 \cdot 6H_2O$.

The reliability of PCMs can be much better than that of thermal pastes based on liquid and semiliquid carriers. In addition, the performance may be enhanced by mixing the PCM with polymers and with particulate fillers of high thermal conductivity. However, most PCMs with high-energy storage density have an unacceptably low thermal conductivity. Generally speaking, a PCM with melting temperature a little above room temperature, large heat of fusion, low viscosity in the liquid state, small or negative supercooling, good thermal cycling stability, and thermal conductivity is attractive for use as a thermal interface material.

Paraffin wax, with or without α-Al_2O_3 or BN particles, is potentially good thermal interface materials, because of the negative supercooling (down to −7 °C), large heat of fusion (up to 142 J/g), and excellent thermal cycling stability. Microcrystalline wax is not suitable, due to its unclear endothermic and exothermic peaks and wide melting temperature range. The addition of 20 to 60 wt.% α-Al_2O_3 to paraffin wax decreases the melting temperature by 7 °C. Beyond 60 wt.% α-Al_2O_3, the melting temperature of paraffin wax increases toward the value without α-Al_2O_3. The heat of fusion of paraffin wax attains a minimum at 20 wt.% α-Al_2O_3. The addition of BN has little effect on the phase change behavior of paraffin wax.[30]

The inorganic materials $Na_2SO_4 \cdot 10H_2O$ and $CaCl_2 \cdot 6H_2O$, with their melting temperature (about 30 °C) slightly above room temperature, are two typical inorganic PCMs. Telks[8] used $Na_2SO_4 \cdot 10H_2O$ to build the first PCM-heated solar house shortly after the end of the Second World War. $CaCl_2 \cdot 6H_2O$ was investigated for passive applications, as in heat pumps, and in forced air heating systems in the 1970s.[8] $CaCl_2 \cdot 6H_2O$ was mentioned as a thermal energy storage material.[13] However, both $Na_2SO_4 \cdot 10H_2O$ and $CaCl_2 \cdot 6H_2O$, with and without nucleating additives, are not suitable for use as thermal interface materials, due to their incongruent melting and decomposition behavior, large supercooling (8 °C or more), and thermal cycling instability.[30]

The evaluation of the actual performance of PCMs as thermal interface materials still needs to be performed.

5. Conclusions

Thermal interface materials to facilitate heat transfer by conduction across two adjacent surfaces include thermal fluids, thermal pastes, resilient thermal conductors, solders, and PCMs. Thermal pastes involving polyether glycol and sodium silicate matrices exhibit thermal contact conductance approaching that provided by solder. Phase change materials are potentially attractive, though evaluation of the thermal contact conductance is still needed.

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References

1. D. Grivas, D. Frear, L. Quan, and J.W. Morris, Jr.: *J. Electronic Mater.*, 1986, vol. 15 (6), pp. 355-59.
2. S.W. Wilson, A.W. Norris, E.B. Scott, and M.R. Costello: *National Electronic Packaging and Production Conf.*, Proc. Technical Program, Reed Exhibition Companies, Norwalk, CT, 1996, vol. 2, pp. 788-96.
3. A.L. Peterson: *Proc. 40th Electronic Components and Technology Conf.*, IEEE, Piscataway, NJ, 1990, vol. 1, pp. 613-19.
4. X. Lu, G. Xu, P.G. Hofstra, and R.C. Bajcar: *J. Polymer Sci.*, 1998, vol. 36 (13), pp. 2259-65.
5. T. Sasaski, K. Hisano, T. Sakamoto, S. Monma, Y. Fijimori, H. Iwasaki, and M. Ishizuka: *Jpn. IEMT Symp. Proc. IEEE/CPMT Int. Electronic Manufacturing Technology (IEMT) Symp.*, IEEE, Piscataway, NJ, 1995, pp. 236-39.
6. Y. Xu, X. Luo, and D.D.L. Chung: *J. Electronic Packaging*, 2000, vol. 122 (2), pp. 128-31.
7. Y. Xu, X. Luo, and D.D.L. Chung: *J. Heat Transfer*, in press.
8. G.A. Lane: *Solar Heat Storage: Latent Heat Material*, CRC Press, Inc., Boca Raton, FL, 1983, vol. 1.
9. F.J. Whitfield and A.T. Doyel: U.S. Patent 4,466,483, Aug. 21, 1984.
10. I.O. Salyer: U.S. Patent 4,711,813, Dec. 8, 1987.
11. I.O. Salyer: U.S. Patent 4,797,160, Jan. 10, 1989.
12. J.C.H. Chen and J.L. Eichelberger: U.S. Patent 4,504,402, Mar. 12, 1985.
13. G.A. Lane and H.E. Rossow: U.S. Patent 4,637,888, Jan. 20, 1987.
14. A. Kurklu: *Renewable Energy*, 1998, vol. 13, p. 89.
15. M. Marinkovic, R. Nikolic, J. Savovic, S. Gadzuric, and I. Zsigrai: *Solar Energy Mater. Solar Cells*, 1998, vol. 51, p. 401.
16. H. Bo, E.M. Gustafsson, and F. Setterwall: *Energy*, 1999, vol. 24, p. 1015.
17. S.D. Sharma, D. Buddhi, and R.L. Sawhney: *Solar Energy*, 1999, vol. 66, p. 483.
18. J.F. Wang, G.M. Chen, and F. Zheng: *Int. J. Energy Res.*, 1999, vol. 23, p. 277.
19. A. Abhat: *Solar Energy*, 1983, vol. 30, p. 313.
20. G. Egloff: *Physical Constants of Hydrocarbons*, Reinhold Publishing Corporation, New York, NY, 1939, vol. 1.
21. S. Himran, A. Suwon, and G.A. Manosoori: *Energy Sources*, 1994, vol. 16, p. 117.
22. D. Pal and Y.K. Joshi: in *Advances in Electronic Packaging*, D. Agonater, M. Saka, and Y.-C. Lee, eds., ASME, 1999, vol. 2, p. 1625.
23. R. Clarksean, Y. Chen, and M. Marongiu: in *Advances in Electronic Packaging*, D. Agonater, M. Saka, and Y.-C. Lee, eds., ASME, New York, NY, 1999, vol. 2, p. 1611.
24. Randy Clarksean and Yitung Chen: in *Advances in Electronic Packaging*, Dereje Agonater, Masumi Saka, and Yung-Cheng Lee, eds., ASME, New York, NY, 1999, vol. 2, p. 1631.
25. M. Telks: *Ind. Eng. Chem.*, 1952, vol. 44, p. 1308.
26. G.A. Lane and H.E. Rossow: U.S. Patent 4,272,390, 1981.
27. N. Nishizaki, K. Sakagami, H. Okazaki, and A. Mitsuibara: Japanese Patent Kokai 55-82, 182, 1980.
28. K. Narita, H. Kimura, H. Ohama, K. Mutoh, and J. Kai: Japanese Patent Kokai 50-90, 585, 1975.
29. H. Miyoshi and K. Tanaka: Japanese Patent Kokai 53-70, 990, 1978.
30. Z. Liu and D.D.L. Chung: *Thermochim. Acta*, 2001, vol. 366 (2), pp. 135-47.