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Short communication

Effect of thermal contact heat transfer on solidification of Pb–Sn and Pb-free solders

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Abstract

The effect of thermal contact heat transfer on the solidification of spherical droplets of four solder alloys, namely, Sn–37Pb, Sn–9Zn, Sn–0.7Cu and Sn–3.5Ag, was studied using SOLIDCAST simulation package. A significant drop in the arrest time was observed for increase in heat transfer coefficient from 1000 to 2000 W/m^2 K. Effect of contact conductance and thermal diffusivity of solder alloys on arrest time is quantified by the power relation, $\beta = m(\phi)^n$ where β and ϕ are defined as arrest time and heat transfer parameters, respectively. Experiments were also carried out to investigate the effect of cooling rate on solidification behaviour of the solder alloys used in simulation. The results indicated the significant effect of mould material on interfacial heat flux and metallurgical microstructure.

1. Introduction

Soldering is a well known metallurgical joining method that uses a filler metal known as solder, conventionally a lead–tin eutectic alloy. Solder has a melting point lower than the metals to be joined and is carried out at temperatures generally less than 400 °C. In electronics industry, solder plays a vital role by providing electrical, thermal and mechanical continuity in electronic assemblies [1–3]. Tin–lead eutectic solders have been traditionally used because of their low cost, good workability, ease of handling, adequate mechanical properties, low melting temperature, etc. [4]. However, increased environmental and health concerns regarding the toxicity of lead have stimulated research and development of lead-free solders. A good number of lead-free solders have been developed, but none is suitable for drop-in replacement meeting all standards including material properties, manufacturability and affordable cost [5–9]. For example, Sn–9Zn alloy has melting point close to that of conventional solder but its wetting and oxidation behaviours are inferior.

Tin is generally the basic material in lead-free alloys because of its attractive properties such as low cost, easy availability, excellent physical, electrical and thermal properties. The ability of the tin to wet and spread on a wide range of substrates using mild fluxes, ability to form compounds with many metals and comparably low melting point have made it common and principal component of most solder alloys – both lead based and lead-free. Elements that may be combined with tin in order to make lead-free alloy are silver (Ag), copper (Cu), zinc (Zn), bismuth (Bi), indium (In), etc. Among these, the eutectic combinations of Sn with Ag, Cu and Zn are showing promising results [2,3,10].

The wetting of substrate by the molten solder and its subsequent solidification are important from the solderability and reliability points. Majority of solder alloys exhibit shrinkage upon solidification and cooling. This generally leads to the formation of an air gap between the solidifying solder alloy and substrate metal which in turn reduces the thermal contact heat transfer at the interface. Such a situation strongly affects the joint strength [11]. The thermal contact heat transfer is characterized either by

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an interfacial heat flux (q) or heat transfer coefficient (h) at the interface. The overall heat transfer coefficient at the solder/base metal interface is called thermal contact conductance and it is calculated as, $h = q/\Delta T$, where q is the interfacial heat flux and ΔT is the temperature drop at the interface. A good thermal contact conductance at the interface results in better quality of solder joint [12,13].

The use of solidification simulation technique has made possible the prediction of temperature distribution and shrinkage defects in castings. This methodology can also be extended to solder solidification. However, the success of such a numerical simulation technique mainly depends on a reliable data base on the thermo-physical properties of the solder alloys and also on the heat transfer coefficient specified at the solder droplet/substrate interface [14]. The solidification rate of solder significantly affects the quality of the joint formed. The rate at which solder joint solidifies depends not only on the speed at which the heat is removed away but also on the size of the joint as well as the materials surrounding the joint [12–15].

In the present work, the effect of heat transfer coefficient on solidification of varying size spherical droplets of three lead-free potential solder candidates, Sn–9Zn, Sn–0.7Cu and Sn–3.5Ag, and conventional Sn–Pb eutectic alloy (Sn–37Pb) was investigated by using SOLIDCAST simulation software. Experiments were also carried out to investigate the effect of cooling rate on solidification behaviour of four solder alloys used in the simulation. The aim was to assess the solder/metal interfacial heat transfer and to study its effect on the fineness of the metallurgical microstructure.

2. Experimental

Fig. 1 shows a sketch of the spherical drop model used in the simulation study. TC1 and TC2 represent the virtual thermocouples located at the geometric center of the drop and the exterior surface, respectively. After assigning the material and heat transfer coefficient, the solid model was discretised using a meshing process. A grid size of 0.1 mm was used in these experiments. Thermo-physical properties of the solder alloys used in the simulation are given in Table 1 [3,11–14,16–19]. Simulation experiments were carried out for spherical drops of sizes 0.5, 1 and 2 for heat transfer coefficient values of 1000, 2000, 4000 and 8000 $W/m^2 K$. Four eutectic solder alloys (Sn–37Pb, Sn–9Zn, Sn–0.7Cu and Sn–3.5Ag) were selected for simulation experiments.

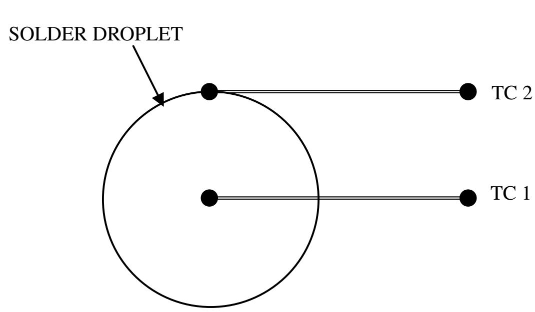

Fig. 1. Schematic sketch of solder droplet instrumented with virtual thermocouples.

Table 1
Thermal properties of solder alloys

Property	Sn–37Pb	Sn–9Zn	Sn–0.7Cu	Sn–3.5Ag
Eutectic temperature (°C)	183	199	227	221
Latent heat of fusion (kJ/kg)	37	43.42	44.375	44
Thermal conductivity (W/m K)	51	56	53	56
Specific heat (J/kg-K)	150	236	223	227
Density (kg/m^3)	8.4	7.3	7.3	7.5

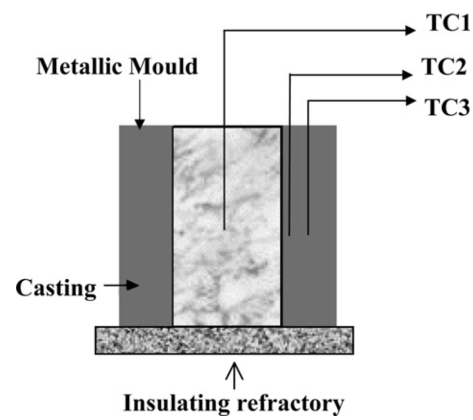

Fig. 2. Schematic sketch of experimental set up for solidification.

Table 2
Thermal properties of mould materials

Property	Copper	Stainless steel
Thermal conductivity (W/m K)	383	16
Specific heat (J/kg-K)	385	570
Density (kg/m^3)	8.9	7.9

Fig. 2 shows the schematic sketch of the experimental set up. Both casting and mould were instrumented with K-type thermocouples (TC1, TC2 and TC3). Moulds made of copper and stainless steel were used in the experiment to achieve different cooling rates. The thermal properties of the mould material are given in Table 2. Experimentally measured temperatures were used as input for inverse analysis for the calculation of heat flux transients. The mathematical details of the inverse analysis for estimation of heat flux transients are given in Ref. [14]. The alloys used in the simulation study were used in the solidification experiments as well. The cast specimens were sectioned and subjected to microstructure study for analyzing the effect of mould variables on the microstructure of various solder alloys.

3. Results and discussion

3.1. Simulation study

Fig. 3 shows the variation of arrest time with heat transfer coefficient for various alloys simulated. The effect of heat transfer coefficient on arrest time is significant when it is increased from 1000 to 2000 $W/m^2 K$ where as the effect is gradual during its increase from 2000 to 4000 W/

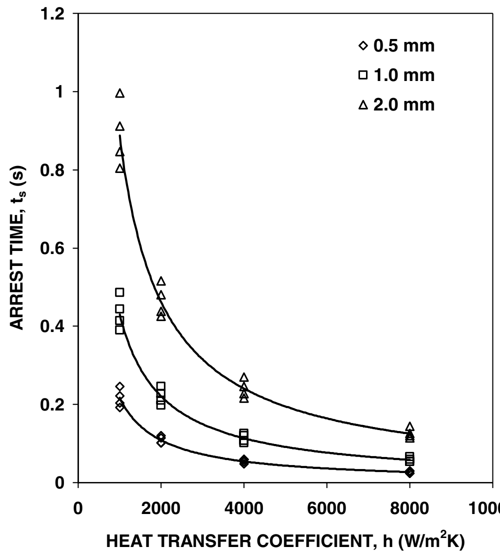

Fig. 3. Variation of arrest time (t_s) with heat transfer coefficient (h) for various solder droplet sizes.

m^2 K or higher. For example, the arrest time for a spherical drop of 0.5 mm radius of Sn–0.7Cu alloy is 0.192 s at 1000 W/m^2 K heat transfer coefficient, 0.102 s at 2000 W/m^2 K, 0.048 s at 4000 W/m^2 K and 0.024 s at 8000 W/m^2 K. The decrease in arrest time is 0.09 milliseconds per unit increase in heat transfer coefficient during its increase from 1000 to 2000 W/m^2 K. The corresponding values for the decrease in arrest time are 0.027 and 0.006 milliseconds during the increase of heat transfer coefficient from 2000 to 4000 W/m^2 K and 4000 to 8000 W/m^2 K, respectively. Thus, there is a significant drop in arrest time for increase in heat transfer coefficient from 1000 to 2000 W/m^2 K and the drop is gradual for the further increase in heat transfer coefficient. A similar behaviour is observed in other alloys also. The effect of heat transfer coefficient on arrest time during solidification of solder alloys is summarized in Table 3.

The variation of arrest time with heat transfer coefficient is expressed by a power relationship of the type

$$t_s = m(h)^{-n} \quad (1)$$

where t_s is the solidification or arrest time, h is the heat transfer coefficient and is a measure of thermal contact conductance and m and n are constants. The values of constant m are 593, 331 and 216 for droplets of size 2, 1 and 0.5 mm, respectively. The corresponding values of exponent n are 0.94, 0.96 and 0.999, respectively. As the size of the spherical droplet decreases the value of n approaches unity. This indicates that for very small spherical droplets arrest time decreases linearly with increase in heat transfer coefficient according to the equation:

$$t_s = m(h)^{-1} \quad (2)$$

To quantify the effect of heat transfer coefficient and thermal properties of solder on arrest time, the following dimensionless parameters are defined:

Table 3
Effect of heat transfer coefficient on arrest time for various solder alloys

Solder alloy	Droplet size (mm)	Decrease in solidification time in milliseconds per unit increase in heat transfer coefficient (in W/m^2) from		
		1000–2000	2000–4000	4000–8000
Sn–37Pb	0.5	0.126	0.03	0.0075
	1.0	0.24	0.06	0.015
	2.0	0.48	0.123	0.0315
Sn–9Zn	0.5	0.108	0.027	0.0075
	1.0	0.216	0.054	0.015
	2.0	0.432	0.117	0.03
Sn–0.7Cu	0.5	0.09	0.027	0.006
	1.0	0.192	0.048	0.012
	2.0	0.378	0.105	0.0255
Sn–3.5Ag	0.5	0.102	0.024	0.0075
	1.0	0.204	0.051	0.0135
	2.0	0.408	0.105	0.027

$$\text{Heat transfer parameter,} \quad \phi = hr/k \quad (3)$$

$$\text{Arrest time parameter,} \quad \beta = r^2/(\alpha t_s) \quad (4)$$

In the above parameters k and α represent the thermal conductivity and thermal diffusivity of the solder alloy, r is radius of the spherical drop under study, h is the heat transfer coefficient at the interface and t_s is the solidification time or arrest time. The parameters ϕ and β have the same significance as Biot and Fourier numbers.

Fig. 4 is a plot of variation of β with ϕ. It is observed that all three lead-free solders under study behave in the similar manner and the behaviour of these alloys can be expressed by a single best fit equation. On the other hand, the conventional lead–tin alloy behaviour is different and cannot be expressed by the equation derived for lead-free

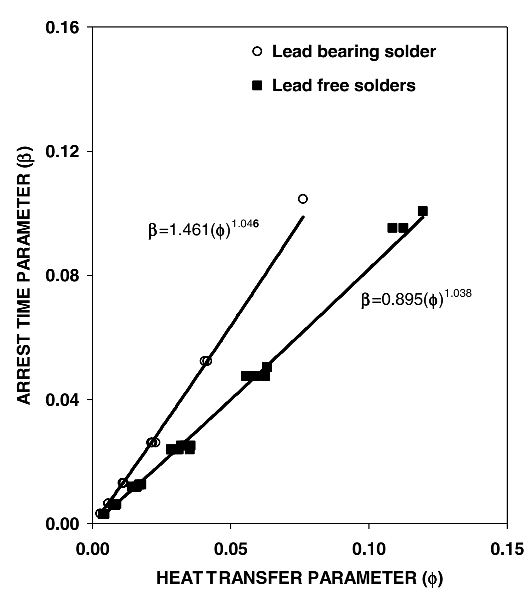

Fig. 4. Variation of arrest time parameter (β) with heat transfer parameter (ϕ) for solder alloys.

solders. The best fit equations for lead–tin and lead-free alloys are given below:

$$\beta = 1.461(\phi)^{1.046} \quad \text{[Sn–37Pb alloy]} \tag{5}$$

$$\beta = 0.895(\phi)^{1.038} \quad \text{[all lead-free alloys]} \tag{6}$$

It is evident that the arrest time depends not only on solder properties and its physical dimensions but also on the interfacial contact conductance. The solidification time of solder droplet depends on three important parameters: (i) thermal diffusivity, a material property (ii) size or radius of solder droplet and (iii) interfacial conditions, quantified by heat transfer coefficient. A small arrest time is preferred in case of lead-free alloys as it results in finer microstructures leading to better mechanical properties. Thermal diffusivity, being a material property, is fixed once the alloy is selected. The size of the solder drop depends on the quantity of solder required for the interconnection. Hence it is necessary to obtain the required heat transfer coefficient that would yield the right microstructure and mechanical properties.

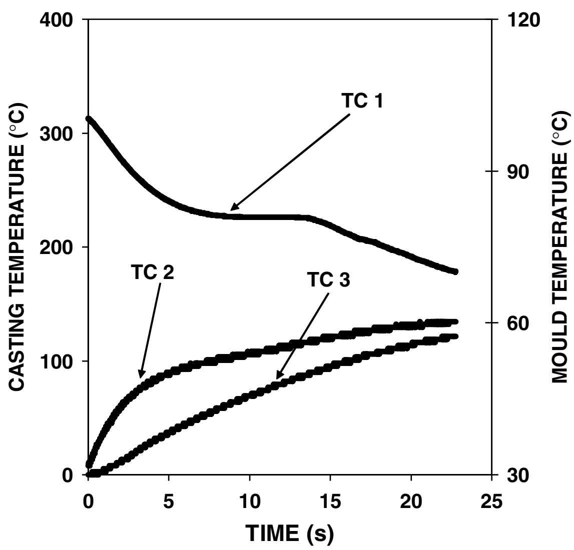

Fig. 5. Typical casting and mould thermal history during solidification of solder alloy (Sn–0.7Cu).

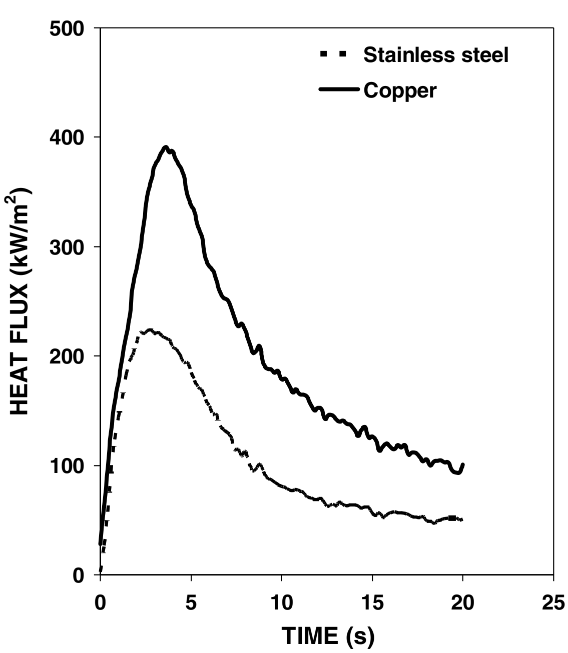

Fig. 6. Variation of heat flux with time during solidification of Sn–37Pb solder alloy.

3.2. Solidification experiments

Typical thermal history for the casting and mould during the solidification of solder alloy are shown in Fig. 5. Figs. 6 and 7 show the variation of heat flux transients with time for a lead based solder and a lead free solder alloy, respectively. The results of thermal analysis are presented in Table 4. The average flux was calculated by using the relation:

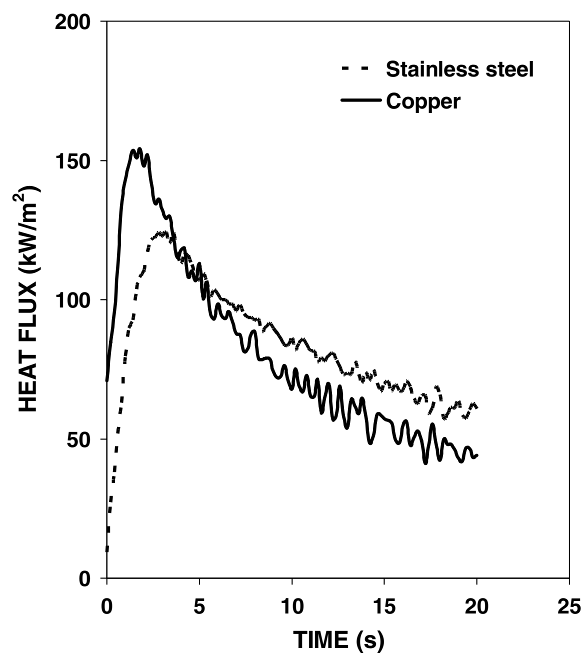

Fig. 7. Variation of heat flux with time during solidification of Sn–3.5Ag solder alloy.

Table 4
Thermal analysis results for solder solidification

Solder	Mould	Arrest time (s)	Eutectic temperature (°C)	Average heat flux (kW/m^2)
Sn–37Pb	Copper	13	183	195.77
	Stainless steel	18	183	105.65
Sn–9Zn	Copper	13	197	259.11
	Stainless steel	28	198	103.39
Sn–0.7Cu	Copper	7.3	227	175.11
	Stainless steel	18	227	118.51
Sn–3.5Ag	Copper	11	219	114.13
	Stainless steel	17	220	99.37

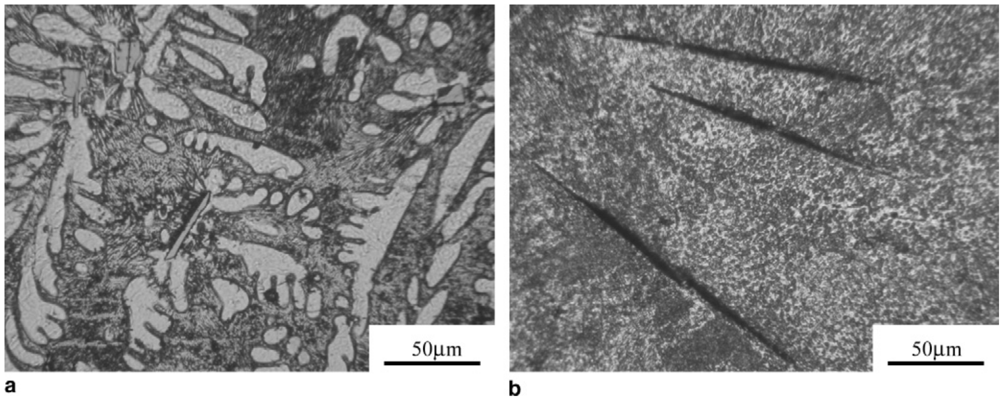

Fig. 8. Photomicrographs of: (a) Sn–3.5Ag solder and (b) Sn–9Zn solder alloys cast in stainless steel mould.

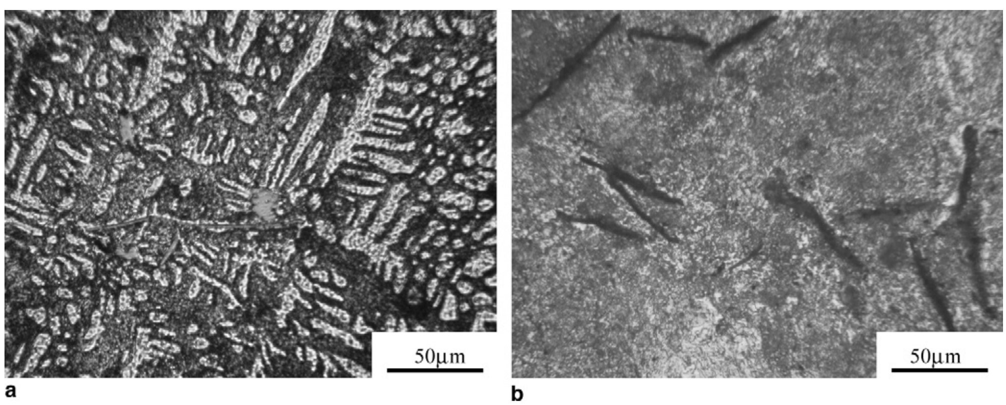

Fig. 9. Photomicrographs of: (a) Sn–3.5Ag solder and (b) Sn–9Zn solder alloys cast in copper mould.

$$\bar{q} = \frac{1}{t_s}\int_0^{t_s} q\,\mathrm{d}t \quad (7)$$

where q and $\bar{q}$ represent the instantaneous and average values of interfacial heat flux, t_s is the solidification time. The effect of mould material on the solidification behaviour is evident from thermal analysis data. The high thermal conductivity copper mould takes away the heat from the molten solder alloy rapidly than low thermal conductivity stainless steel mould. This is reflected in lower arrest time values and higher average flux values for the various alloys solidified in copper mould in comparison with those solidified in stainless steel mould. Heat flux transients for alloys cast in copper moulds were significantly higher than those cast in stainless steel mould. For instance, peak flux values recorded for conventional tin–lead and lead-free Sn–Cu eutectic solders cast in copper moulds were 387 and 332 kW/m^2, respectively. Corresponding values of peak flux when cast in stainless moulds were only 224 and 214 kW/m^2, respectively.

Figs. 8 and 9 show the photomicrographs of solders solidified in stainless steel and copper moulds. As expected, the specimens solidified in copper moulds showed finer micro structural features than those cast in stainless steel moulds. For example, finer dendrites are observed in the Sn–Ag solder solidified in copper mould and smaller Zn rich rod phases are found in the Sn–Zn solder solidified in copper mould. On the other hand, for the same alloys when cast in stainless steel mould, the coarser features are observed. Similarly Zn rich rods are longer in the alloy cast in stainless steel mould.

4. Conclusions

1. The heat transfer coefficient affects the arrest time significantly. There is a significant drop in arrest time for the increase in heat transfer coefficient from 1000 to 2000 W/m^2 K and the drop is gradual for the further increase in heat transfer coefficient.
2. For small solder volumes the arrest time decreases linearly with increase in heat transfer coefficient.
3. The solidification behaviour of Sn–Pb solder can be expressed by $\beta = 1.461(\phi)^{1.046}$ where as that of lead-free solders can be expressed by $\beta = 0.895(\phi)^{1.038}$ where β and ϕ are arrest time and heat transfer parameters, respectively. Solidification time of the solder droplet is thus affected by thermal diffusivity, size of solder alloy and the interfacial heat transfer.

4. Samples cast against high thermal conductivity copper mould showed lower arrest time and higher heat flux transients where as those solidified in low thermal conductivity stainless steel mould showed higher arrest time and lower heat flux transients. Microstructural features of the specimens cast in the copper mould are finer compared to those solidified in stainless steel mould.

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