Controlling Voiding Mechanisms in the Reflow Soldering Process

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ABSTRACT

While a significant level of voiding can be tolerated in solder joints where electrical conductivity is the main requirement, voiding at any level severely compromises thermal conductivity. For example, in Light Emitting Diode (LED) lighting modules effective conduction of heat through the 1st level die attach to the substrate and then through the 2nd level attach to the heat sink is critical to performance so that voiding in the solder joints at both levels must be minimized. Voids in solder joints are the result of bubbles of gas that do not escape before the solder has solidified. While there is the possibility that air can be entrapped in the bond area during the reflow of solder paste the gases in the bubbles are generally considered to come mainly from the flux medium, by volatilization of solvents, as by-products of activator reactions with metal oxides, and from decomposition of resins and other constituents. Whether these gases escape from the solder joint or remain as voids depends on many factors including joint area and geometry.   Since areas of non-wetted substrate provide points of attachment for bubbles the solderability of the substrates and the activity of the flux are other factors that affect the incidence of voiding in the solder joint. Volatiles released during the time when the solder powder particles are melting and coalescing are the main source of bubbles so that the shape of the reflow profile can have a major effect on the incidence of voiding. In this paper, the authors will review the factors that influence the incidence of voids in small and large area solder joints that simulate, respectively, the 1st and 2nd level joints in LED modules and discuss mitigation strategies appropriate to each level. They will also report the results of a study on the effect on the incidence of voids of flux medium formulation and the optimization of the thermal profile to ensure that most of the volatiles are released early in the reflow process.

INTRODUCTION

There are two general types of voids that can form in a solder joint: shrinkage voids and gas voids. Shrinkage voids are the consequence of the reduction in volume that occurs when most common solders change from liquid to solid. If the solder behaves as a eutectic and solidifies isothermally in a single stage, with the solid growing uniformly outwards from within the fillet, all the reduction in volume is accommodated on the outside surface. The only consequence is that the final fillet is a little smaller than that which originally formed in the liquid state with no internal voids.

The situation is complicated if the solder alloy does not behave as a eutectic and solidifies over a range of temperature with more than one stage of solidification. The Sn-3.0%Ag-0.5%Cu alloy, commonly known as "SAC305", is an example of a solder that exhibits such non-eutectic behaviour. Solidification begins at around 219°C with the growth of primary tin (Sn) dendrites which continue to grow as the solder cools to 217°C when the remaining liquid, enriched in silver (Ag) and copper (Cu), solidifies as a eutectic.   Pools of molten solder can be isolated within the network of primary tin dendrites so that when they solidify the reduction in volume has to be accommodated as a void.   Voids formed in this way have an irregular shape that reflects the shape of the solidification front that formed them and, because they occupy interdendritic spaces, a high aspect ratio.   If these shrinkage voids intersect the surface they can appear as a crack-like contraction cavity or shrink hole.
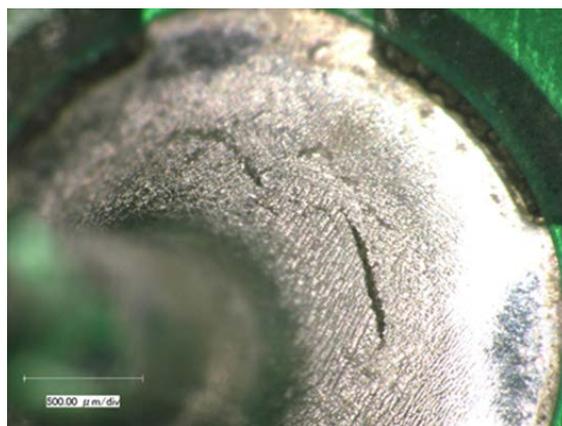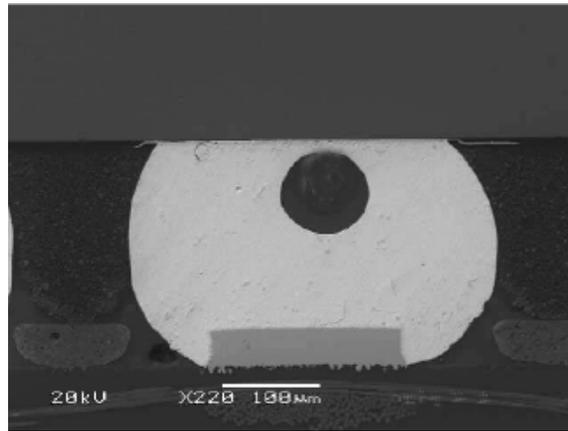

Figure 1-Shrinkage void in SAC305 that has intersected the surface of the solder fillet to form a contraction cavity

Figure 2-Typical void resulting from the entrapment of a bubble of gas within the solder

Gas voids are the result of a bubble of gas being trapped within the solder. The shape and size or these voids is determined by the balance between the pressure of the gas and the surface tension of the molten solder and so they are usually nearly perfectly spherical with a generally smooth interior surface. Exceptions to that rule occur when the bubble is attached to one of the joint substrates that has not been wetted by the solder, and when the equilibrium diameter is greater than the joint gap.
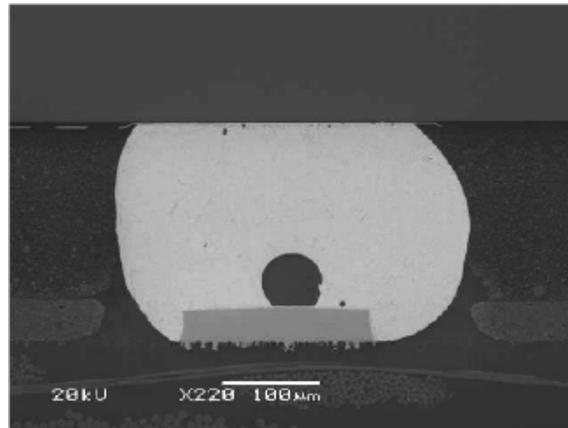
Figure 3- Void in which the gas bubble has attached to a non-wetted area of the pad

The gas that forms the void can come from a variety of sources, including the volatilization of moisture trapped in defects in the copper plating of the PCB and the decomposition of organics co-deposited during electroplating. The only type of void considered in this paper is that occurring in reflow soldered joints that result from the entrapment of volatiles released from the flux medium of the solder paste, either directly from its constituents or produced as result of fluxing reactions between the activators and surface oxides.

A bubble of gas in molten solder is in a thermodynamically unstable situation. The bubble creates an additional surface in the solder, which means that the free energy of the system is higher than it would be if the gas had escaped. That extra free energy provides a driving force for large bubbles, which have a smaller surface area-to-volume ratio, to grow at the expense of smaller bubbles. However, if this occurs only by gaseous diffusion through the liquid the process is very slow. Faster growth can occur by coalescence if the bubbles are being moved by other forces so that they come into contact with other bubbles. In such a contact the smaller bubble will be absorbed into the larger bubble with a net reduction in the area of the gas/solder interface. In reflowing solder paste there is sufficient movement for that to occur so that voiding in solder joints typically occurs as a relatively small number of larger bubbles.

Once reflow has been completed and the molten solder is quiescent, the only force that can move a bubble any significant distance in the time that the solder is molten (the Time Above Liquidus or TAL) is gravity. There is a buoyancy force acting on the bubble equal to the weight of the solder displaced (Archimedes principle). That gravity is a factor in void elimination is confirmed by the observation that voids tend to stay suspended in solder joints made in the zero gravity conditions of the International Space Station [1].

The buoyancy force works only in one direction, upwards, and if the geometry of the joint means that there is no route for

escape in that direction the bubble will remain trapped in the joint. It is for this reason that the incidence of voids tends to be highest in joints with a large aspect ratio such as those between large silicon chips and substrates.
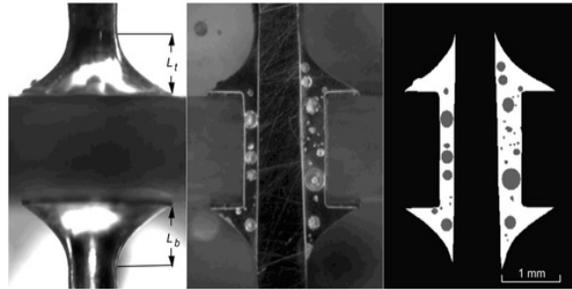

Figure 4- Gas bubble suspended in a solder joint made in zero gravity conditions [1].

The other factor that can prevent a bubble from being pushed out of a solder joint by the buoyancy force is the blockage of the escape route by solder that has already solidified. The likelihood of gas bubbles being trapped by solidified solder is increased if they are generated late in the reflow cycle and if there is a prolonged TAL. If the escape route is not impeded by the joint geometry, gas released early in the period that the solder is molten will escape before the joint starts to solidify.

VOID MITIGATION STRATEGIES

For a particular bubble, assuming the mass of the gas contained is fixed, the size of the bubble at a given temperature depends on the surface tension of the solder and the atmospheric pressure. This situation is described mathematically by the Young-Laplace equation which can be expressed in the form:

$$P_b = P_a + 2\gamma/r \qquad (1)$$

r = Bubble radius
γ = Surface tension of the bubble/solder interface
P_b = Pressure in the bubble
P_a = Atmospheric pressure

The surface tension acts against the pressure limiting the size that the bubble can reach for a given atmospheric pressure. It is clear therefore that if the surface tension can be reduced the over pressure that can be sustained is reduced and for a given mass of contained volatiles the bubble can increase in size.

In actual production conditions the incidence of voiding depends on a variety of factors, from the formulation of the solder paste to its storage and handling and to the conditions during its final reflow (Figure 5).
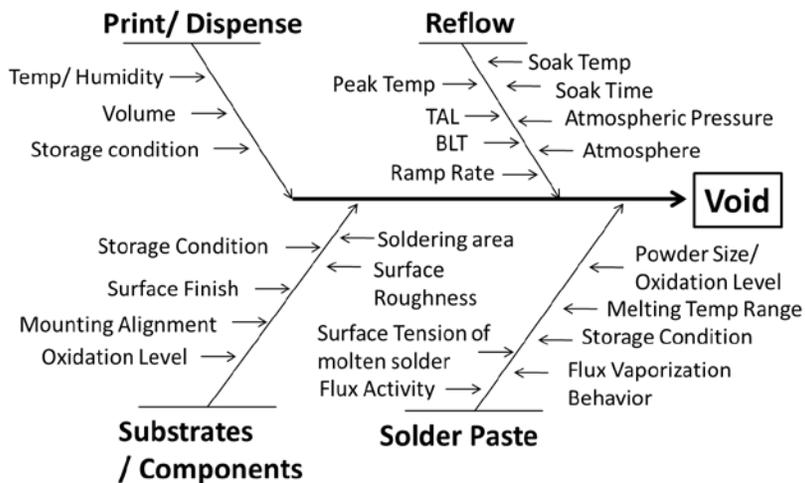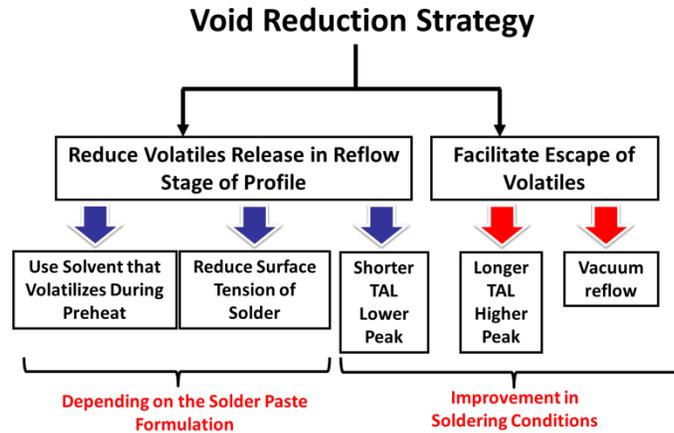

Figure 5- Factors that influence the formation of voids during soldering processes,

The key elements of void mitigation are materials selection and process controls. These considerations extend beyond the solder paste itself to the surfaces of the substrates and the components that are the substrate for the solder joint.

Figure 6- Void mitigation strategies in soldering

The starting point in void minimization in mitigation strategies is that voids are the result of bubbles of gas generated during the reflow process being trapped within the solder. The gas comes either directly from the constituents of the flux medium or is produced as result of fluxing reactions between the activators and surface oxides. The size that a gas bubble can reach and the ease with which it can break through the surface of the solder and escape is affected by the surface tension of the solder. The two approaches to void minimisation are therefore:

1. Reduce volatiles released in the reflow stage of profile
2. Facilitate escape of volatiles that are formed.

CONTRIBUTION OF SOLDER PASTE FORMULATION

Formation of volatiles can be tracked by thermo gravimetric analysis (TGA). For example, the weight loss of two kinds of solder paste flux medium, Flux A and Flux B, as a function of temperature at a heating rate of 50°C/minute in an air atmosphere is plotted in Figure 7.
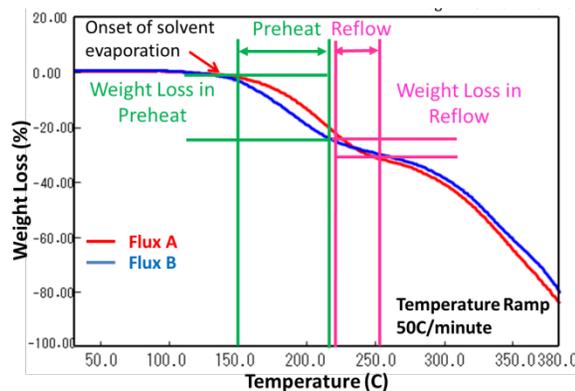
Figure 7- TGA of two types of solder paste flux mediums

The results summarized in Table 1 show that weight loss in the Flux B during the reflow stage of the profile was more than twice that of Flux A. It would be expected that with less gas being generated at the time when the solder is molten the opportunities for bubble entrapment should be reduced.

Table 1- Weight loss of flux medium during reflow

Flux Medium	Total % Weight Loss in Reflow	% Weight Loss in Preheat	% Weight Loss in Reflow
Reference	16.26	62	38
Low Voiding	17.5	85	15

A lower surface tension of the molten solder means a larger bubble, which is more likely to intersect the surfaces of the molten solder so that the entrapped gas can escape. In soldering processes, for a given solder the surface tension is largely determined by the effectiveness of the flux and in the first instance that is determined by its formulation.

If minimizing surface tension is an objective then it is necessary to have a method of measuring it. In the flux optimisation experiments reported here, the surface tension was measured by a method based on the use of a wetting balance [7]. In this method, the size of the meniscus formed against the non-wetting surface of a glass rod is measured as the difference between the upward force registered by a wetting balance and the force that would be expected from the simple displacement of the rod (the buoyancy force). Knowing the diameter of the glass rod the surface tension can be calculated from that force difference.
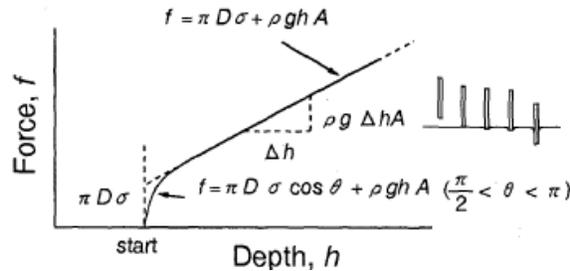

Figure 8- Principle of surface tension measurement method [6]

The force, f, registered by the wetting balance is the sum of the surface tension force and the buoyancy force acting on the non-wetting rod as it is immersed in the solder:

$$f = \rho g h A - \pi D \gamma cos\theta \qquad (2)$$

where D is the diameter of the rod, γ is the surface tension, θ is the contact angle, ρ is the density of the solder, h is the depth of immersion of the rod, and A is the cross-sectional area of the rod. When the contact angle on the non-wetting surface reaches π radians the only force increase registered as the rod is immersed more deeply is that due to buoyancy. By extrapolating the buoyancy force back to zero depth the value $\pi D \gamma$ can be obtained, from which the surface tension can be calculated.

The experimental set up is illustrated schematically in Figure 9. A 4mm glass rod fixed to the head of the wetting balance [8] is immersed in molten Sn-0.7Cu-0.05Ni+Ge solder [9] in a solder bath set at 240°C at a rate of 0.5mm/s to a depth of 20mm. A reference surface tension was measured in air in the absence of any flux.

(a)   (b)
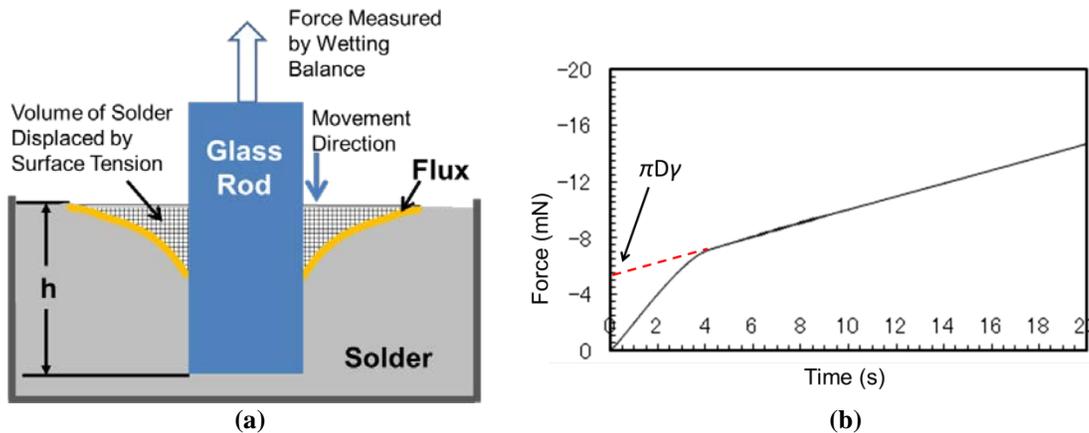
Figure 9- Schematic illustration of the set up for the measurement of the surface tension of the solder (a) and typical result of a surface tension measurement experiment (b)

When the test was used to measure the effect of the flux medium a consistent quantity of the medium was applied to the end of the glass rod by pressing the rod into a 6.5mm diameter 0.2mm thick deposit of flux medium that had been printed onto a ceramic plate. When the rod was lifted the 0.2mm thick layer of flux remained attached to it.

The results summarized in Figure 10 indicate that a significant reduction in surface tension was achieved by reformulation and this would be expected to contribute to reduced voiding in the way described earlier.
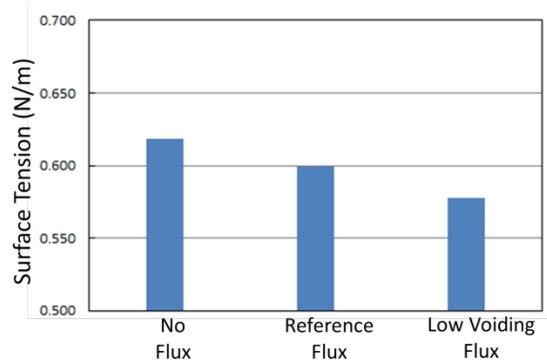
Figure 10- Results of surface tension measurement

Some confirmatory tests with the low voiding flux formulation were conducted with two types of components. To simulate a semiconductor power device a 19mm square copper plate was mounted on a conventional PCB substrate with 120µm thick solid printed paste. (Figure 11). The other component used was a 0.5mm pitch CSP132 with 300µm SAC305 solder balls mounted with 120µm solder paste (Figure 12).
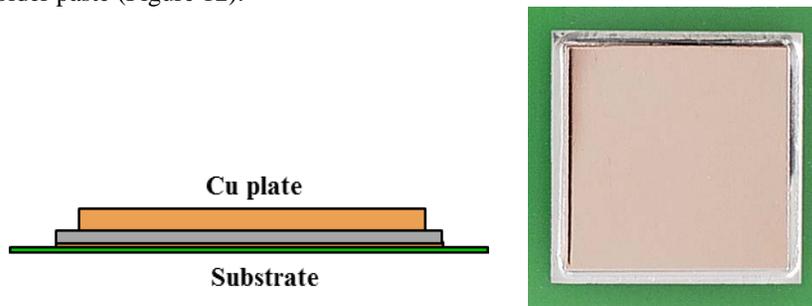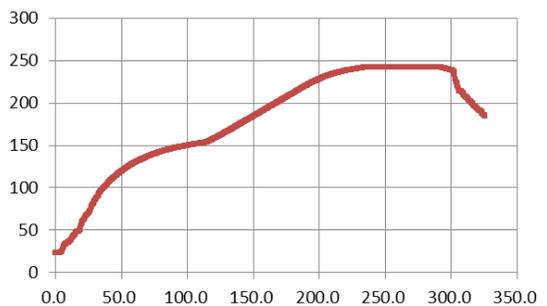

Figure 11- Simulated power semiconductor
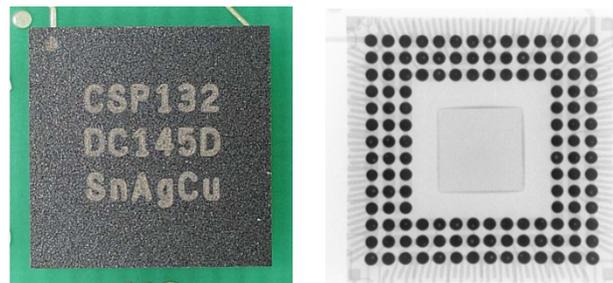
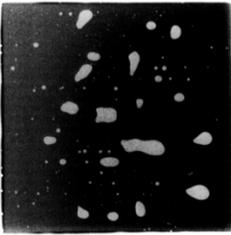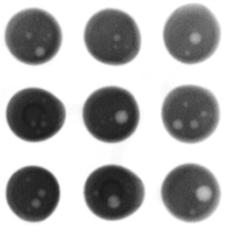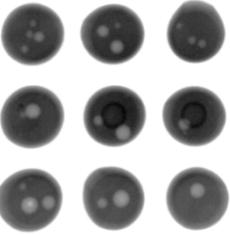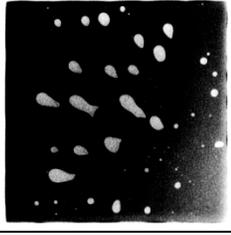
Figure 12- CSP132 test component

The solder paste alloy was the Sn-0.7Cu-0.05Ni+Ge alloy which has the additional advantage of eutectic freezing behaviour, which can also contribute to void minimization [11]. The reflow profile provided a time above the 227°C liquidus of 90 seconds (Figure 13).

Figure 13- Reflow profile for flux formula evaluation

The results of the void mitigation efforts described above are illustrated in Figure 14. In both cases the targets of <10% and <5% voiding were achieved. In addition, the superior performance of the solder paste formulated for low voiding was

confirmed with the chip components. The small beneficial effect of reflowing in a nitrogen atmosphere can probably be attributed to the protective effect that it has on the solder, minimizing the amount of oxidation that the flux has to deal with so that more flux activity is available for surface tension reduction.

| Large Thermal Pads		BGA Balls	
Reference	Low Voiding	Reference	Low Voiding
Air: 6.0% Voids	Air: 4.2% Voids	Air: 5.7% Voids	Air: 4.9% Voids
N2 : 5.7% Voids	N2 : 2.8% Voids	N2 : 5.1% Voids	N2 : 3.8% Voids

Figure 14- Effect of flux medium on voiding in solder joints

VOID MITIGATION BY REFLOW CONDITIONS

The first step in void mitigation is the elimination from the formulation of the solder paste flux medium ingredients that would not start to volatilize or decompose to create gas until late in the reflow profile. That can be achieved by using solvents that largely evaporate during preheat or very early in the reflow stage of the profile. The other ingredients in the flux medium, the resins, activators, and thixotropic agents, and stabilizers should remain stable with minimal release of volatiles, particularly during the latter part of the profile when the solder is molten (TAL).

However, since it is impossible to eliminate completely the possibility of the release of gas from late in the reflow, especially in voids attached to non-wetted areas that might contain trapped flux, measures have to be taken to facilitate the escape of the bubbles before solidification begins. To determine what techniques might be effective in minimising voids it is necessary to consider the ways in which a bubble can escape and the factors that might prevent its escape.
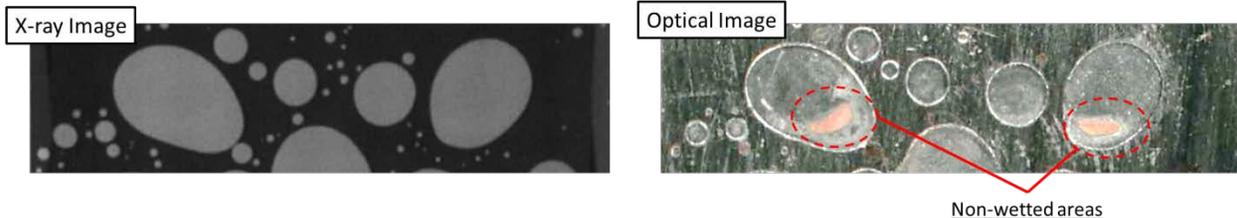
Figure 15-Typical X-ray and optical images of voids

Methods of reducing the likelihood of voids in solder joints emerge from the preceding consideration of the way in which they form. To reduce the incidence of voids the solder paste formulation should:

- have reduced volatile release during reflow (the period when the solder is molten),
- use solvents that volatilizes during the preheat stage of the reflow profile, and
- reduce the surface tension of the solder.

However, whether the full benefits of the contributions of solder paste formulation to void reduction are achieved is very dependent on the characteristics of the reflow profile, in particular the timing and duration of the reflow stage that is commonly known as the Time Above Liquidus or TAL.

EXPERIMENTAL PROCEDURE

For the evaluation of the effect of reflow profile on voiding in large pads 10mm square QFN with a Sn finish were mounted on a conventional PCB substrate with 130um thick solder paste. Two types of reflow profiles were used, one with a short TAL and a low peak temperature and the other with a long TAL and a high peak temperature (Figure 16).
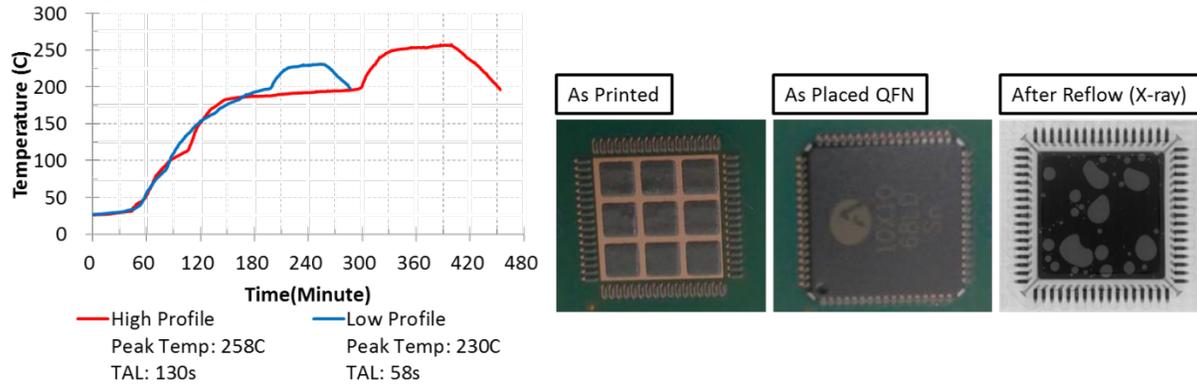

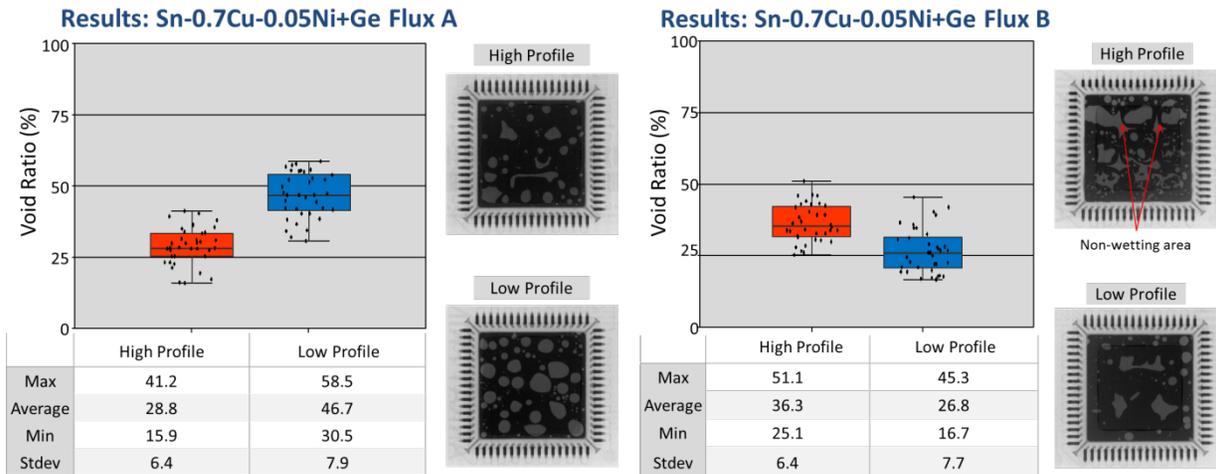**Figure 16- Reflow profiles and components for large thermal pad voiding evaluation**

Results: Sn-0.7Cu-0.05Ni+Ge Flux A

	High Profile	Low Profile
Max	41.2	58.5
Average	28.8	46.7
Min	15.9	30.5
Stdev	6.4	7.9

Results: Sn-0.7Cu-0.05Ni+Ge Flux B

	High Profile	Low Profile
Max	51.1	45.3
Average	36.3	26.8
Min	25.1	16.7
Stdev	6.4	7.7

Figure 17– Effect of reflow profile on the voiding in large thermal pads in Sn-0.7Cu-0.05Ni+Ge with Flux A (Left) and Flux B (Right)

Results for the Sn-0.7Cu-0.05Ni+Ge alloy with the Flux A medium shows that the longer TAL and higher peak temperature reduce the incidence of voiding. The high incidence of voiding with the lower profile is thought to be due to the inferior wetting that left a lot of non-wetted areas to which a bubble could attach and less time for the trapped bubble to escape from the molten solder during the TAL. The lowest average voiding was achieved with the combination of the low profile and Flux B, which had been formulated for maximum release of volatiles during preheat or in the early stage of reflow and high activity to achieve good wetting with minimum incidence of non-wetted areas to which a bubble could attach. The higher incidence of voiding with the combination of Flux B with the high reflow profile is thought to be due to the higher incidence of non-wetted areas because of the exhaustion of flux activity during the longer TAL. Because Flux B was formulated for maximum release of volatiles during preheat there was less solvent available to maintain flux mobility and activity during the long TAL when reoxidation of the joint substrates could occur.

Certainly good wetting of the substrates is essential so that there are no non-wetted or dewetted areas that can provide attachment points for a bubble such that in Figure 3. In the case of small solder joints, e.g. BGA and solder bumps, the surface tension of molten solder is so high that buoyancy force is not enough to detach the voids from non-wetted areas.

In Figure 18 is an example of the situation that can occur in a small solder joint where a bubble attached to a non-wetted area contains from flux residue. With an extended TAL the flux residue will continue to generate volatiles so the void will grow while the solder remains molten.
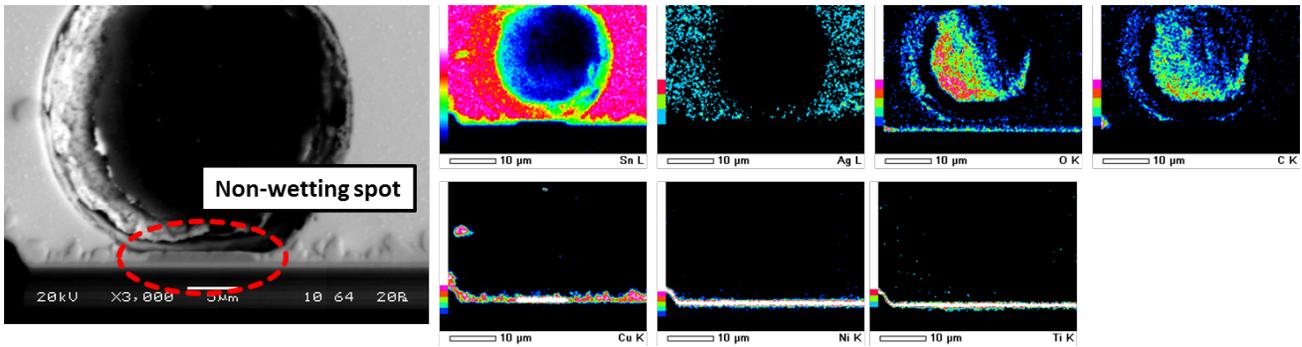
Figure 18- Typical example of a non-wetted area and flux residue entrapped in the void in a small solder joint

For the evaluation of voiding in small joints, 100µm solder bumps were prepared on Ti/ Ni/ Cu under bump metallization (UBM) with SAC405 ROL0 type 5 paste.   The assembly was reflowed with profiles with TAL that ranged from 50 seconds to 210 seconds (Figure 19).
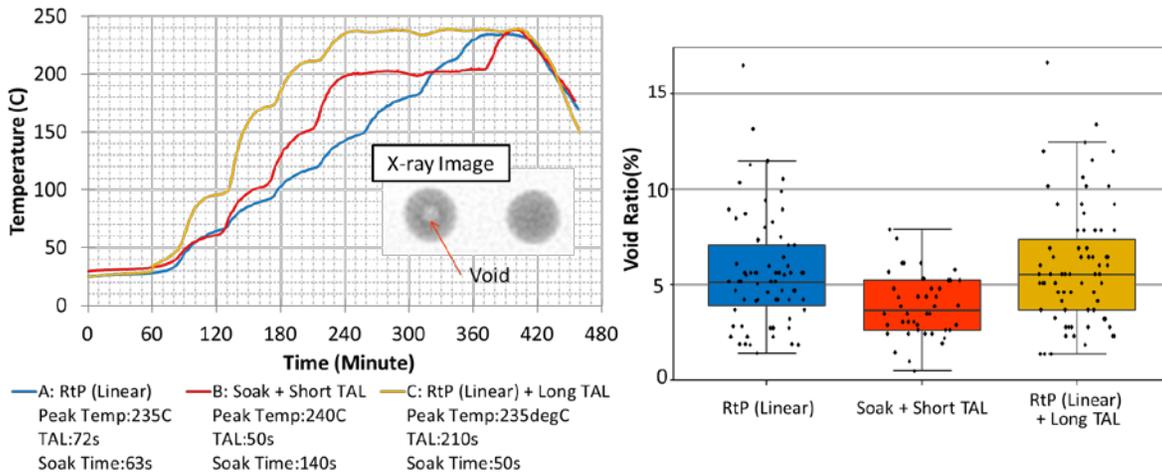
Figure19- The effect of the type of reflow profile on the voiding level in small joints

The results show that a smaller void area can be achieved with shorter TAL as this minimizes the vaporization of flux volatiles during the reflow stage of the profile. The results of RtP (Ramp to Peak) and RtP + Short TAL profiles indicated that preheat appears to be effective in reducing the incidence of voiding as this allows excess volatiles to escape before reflow begins. Therefore, as expected, for small solder joints, a shorter TAL and a lower peak reflow temperature might well minimize the likelihood of gas being generated by decomposition of flux constituents in voids trapped at non-wetted areas.
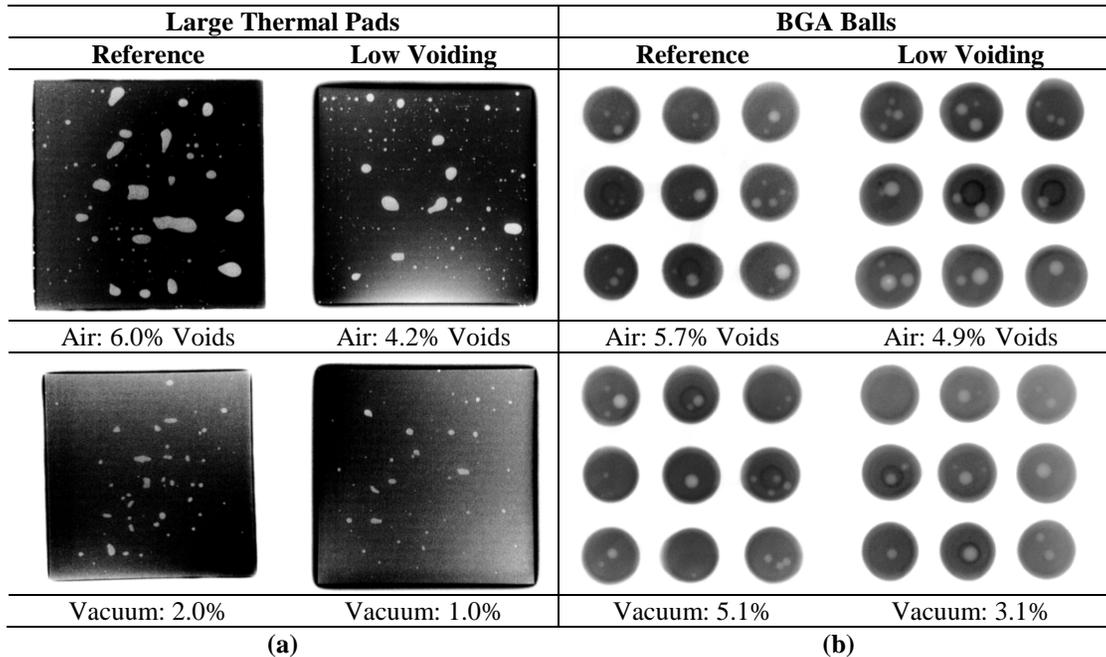
VOID MITIGATION BY VACUUM REFLOW
The only external force that can act on the bubble is gravity through buoyancy. The magnitude of the buoyancy force increases with the size of the bubble so anything that increases the size of the bubble will increase the likelihood of escape.

Apart from reducing surface tension, the only way that bubble size can be increased is by reducing atmospheric pressure. Since the product of pressure and volume remains constant (Boyle's Law) if the atmospheric pressure is reduced the volume of the gas at constant temperature increases. As explained earlier, in the case of a gas bubble in a liquid the balance is complicated by the surface tension of the gas/bubble interface.   Without the effect of surface tension the lowering of the pressure around the molten solder from normal atmospheric of 101kPa to 10kPa would result in an approximate doubling of the bubble diameter.   If the pressure is reduced to 1kPa the bubble diameter would increase by a factor of 4. With the limiting effect of surface tension on the bubble size for a given pressure reducing as the bubble size increases the reduction in atmospheric pressure will result in an even larger increase in bubble size.

There are two effects of increasing bubble size that could be expected to increase the likelihood of the contents of the bubble escaping.   Simple geometric considerations mean that the larger a bubble is the more likely it is to encounter and merge with another bubble. And the larger the bubble the more likely it is that it will contact an external surface of the solder and escape.   Since the buoyancy force is related to the volume of solder displaced that force increase with the cube of the

diameter of the bubble so there is a rapidly accelerating driving force for the elimination of the bubble. A doubling of the bubble size results in an eight fold increase in volume and hence the buoyancy force. Quadrupling the diameter increases the buoyancy force by a factor of 64.

Vacuum reflow equipment that is capable of reducing the pressure to which the still molten solder is exposed to 1 - 10kPa is now commercially available. For the evaluation, the test vehicle was that described in Figure 16 with some additional confirmatory tests conducted with 1608 and 2125 chip resistors and capacitors.

Large Thermal Pads		BGA Balls	
Reference	**Low Voiding**	**Reference**	**Low Voiding**
Air: 6.0% Voids	Air: 4.2% Voids	Air: 5.7% Voids	Air: 4.9% Voids
Vacuum: 2.0%	Vacuum: 1.0%	Vacuum: 5.1%	Vacuum: 3.1%
(a)		**(b)**	

**Figure 20- Effect of flux medium on voiding of large area solder joint (a)
and effect of flux medium on voiding in CSP (b)**

Table 2- Effect of flux medium on voiding of chip components in vacuum reflow

Component	Voiding Incidence			
	Reference		Low Voiding	
	No.	%	No.	%
CR1608	9/200	4.0	0/200	0.0
CC1608	2/200	1.0	0/200	0.0
CR2125	30/270	11.1	0/270	0.0
CC2125	3/270	1.1	0/270	0.0

The results in Table 2 indicate that vacuum treatment during TAL can significantly reduce the voiding level especially in large thermal area pads and can minimize the voiding level for both large and small solder joints. It is likely that most of the voids remaining after vacuum reflow are those attached to non-wetted areas.

CONCLUSIONS
While it is not possible to completely eliminate voids they can be minimized by a systematic approach based on recognition of the factors involved in the generation of voiding and their mitigation. In the study reported in this paper, the beneficial effects of the following factors were demonstrated with target voiding levels being achieved.

- modifying the formulation to minimize the release of volatiles during the part of the reflow profile when the solder is molten
- optimizing the formulation for reducing the surface tension of the solder
- maximizing the chance of escape from the molten solder by prolonged TAL
- vacuum treatment while the solder is molten

Incidentally, the benefit of a nitrogen atmosphere was confirmed.

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