The Relationship of Components, Alloys and Fluxes

Call it a love triangle – or a Bermuda Triangle. Either way, the best alloy may be determined by the end-application.

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LEAD HAS BEEN an indispensable element in solders due to its high ductility, reasonable mechanical strength, low eutectic melting temperature with tin, low surface tension and low cost. Lead-free soldering requirements are an earthquake to the lead infrastructure that has been evolving for several decades. Within the past few years, the relationship among components, alloys and fluxes has already reshuffled. Although the dust has not settled, a picture of this new relationship is emerging. Changes in alloys not only directly impact components and fluxes, but also the relationship between components and fluxes, which in turn impacts the alloys.

Alloys vs. Components

High temperature stability. Perhaps the biggest impact on components is the requirement of higher thermal stability. With mainstream solder for SMT changing from eutectic SnPb to higher melting temperature systems such as eutectic SnAgCu (217°C), eutectic SnAg (221°C) or eutectic SnCu (227°C), the soldering temperature inevitably has to be raised, with a consequent increase for component thermal stability. As reflected in IPC/JEDEC J-STD-020C, with an increase in melting temperature to 217°C from 183°C, the thermal stability requirement rises about 20°C. On the other hand, moisture sensitivity would drop one to three levels with 260°C reflow peak temperature, and new molding compounds would be desired to improve the performance – at additional packaging cost.[1]

The interaction between solder alloy and components is two-way. The impact of a high solder melting temperature is very harsh, particularly for large boards in applications such as servers or telecommunication systems in which the temperature gradient across the board can be greater than 40°C and the maximum temperature experienced by some components can be over 270°C. In other words, the thermal stability of components has to be upgraded to that temperature, unless the melting temperature of solder alloys is reduced. The latter appears to be an easier solution, and has been adopted by industry. TABLE 1 shows melting temperatures of some viable lead-free solders, including some low melting alloys. A 10° to 20°C decrease in melting temperature is sufficient to permit components to survive in large-board situations. Alloys such as Sn86.9Ag3.1In10, Sn88Ag3Cu0.5In8 or Sn89Zn8Bi3 are considered viable for this purpose. Bi57Sn42Ag1 and Bi58Sn are also possible

TABLE 1. Pb-Free Alloys and Solidus and Liquidus Temperatures

SOLDER ALLOY	SOLIDUS (°C)	LIQUIDUS (°C)	E=EUTECTIC
SnCu0.7	227	227	E
SnAg3.5	221	221	E
Sn95.5Ag3.0Cu0.5	217	221	
Sn95.5Ag4Cu0.5	217	220	
Sn95.5Ag3.9Cu0.6	217	220	
Sn95.5Ag3.8Cu0.7	217	219	
Sn95.5Ag3.5Cu0.9	217	217	E
Sn91.8Ag3.4Bi4.8	211	213	
Sn86.9Ag3.1In10	204	205	
Sn88Ag3Cu0.5In8	195	201	
SnZn9	199	199	E
Sn89Zn8Bi3	187	197	
Bi5742Sn42Ag1	139	140	
BiSn42	138	138	E

TABLE 2. Pb-Containing High Melting Temperature Solders[2]

SOLDER ALLOY	SOLIDUS (°C)	LIQUIDUS (°C)	REMARKS
PbIn19	260	275	
Pb88Sn10Ag2	267	290	
PbSn10.5	275	302	
PbSn10	275	302	
Pb92.5Sn5Ag2.5	287	296	
Pb90In5Ag5	290	310	
Pb90Ag5Sn5	292	292	MP
Pb95.5Ag2.5Sn2	299	304	
Pb92.86In4.76Ag2.38	300	300	MP
Pb92.5In5Ag2.5	300	310	
PbIn5	300	313	
PbSb2	300	320	
PbAg2.5	303	303	E
Pb93Sn3In2Ag2	304	304	MP
PbSn5	308	312	
Pb97.5Ag1.5Sn1	309	309	E
PbSb1.5	310	322	
Pb91Sn4Ag4In1	313	313	E
Pb98Sb1.2Ga0.8	315	315	MP
100Pb	327	327	MP

E = eutectic, MP = melting point

options. The latter has been used by IBM for wave soldering for three decades. However, the melting temperature of eutectic BiSn or near eutectic BiSnAg1 may be so low that their service temperature range is compromised.

1. Internal Solder Alloys

High melting solders. Due to the process hierarchy consideration, the internal solder joints of a package often need to be high in melting temperature so that the subsequent board-level assembly will not cause remelt of those internal joints. Remelt of internal solder joints may cause die drifting, solder extrusion and damage on wire bonding. With SAC alloys having a melting temperature around 217°C being adopted as a mainstream solder for SMT assembly, and with components possibly reaching 260°C upon reflow, internal solder joints should have a solidus temperature above 260°C, preferably above 280°C. **TABLE 2** shows some lead-containing solders with solidus no less than 260°C.[2] By considering alloys with melting temperatures as high as 500°C, still very few lead-free alloys meet this relaxed requirement, as shown in **TABLE 3**, and none are acceptable as a drop-in lead-free replacement for high-temperature, lead-containing solders.[2] Gaps in performance include melting temperature and range, solder wetting, solder ductility, mechanical strength, thermal fatigue, electromigration and cost. Due to these unresolved gaps, lead is exempted in certain RoHS applications: 1) solder joints with lead content greater than 85%, 2) pin-to-package connection with 80 to 85% lead and 3) lead used in flip-chip solder joints within packages.

Medium melting solders. For internal solder joint applications where remelting is not a concern, solder mechanical or thermal fatigue behavior becomes the focus. Frear et al. reported in 2001 that eutectic SnCu performed best in flip-chip applications.[3] Clech in 2004 analyzed some published data (**FIGURE 1**) expressing the correlations of characteristic life to cyclic shear strain range for bare chip assemblies for SnCu, SnPb and SAC assemblies by trendlines.[4] The analysis indicates that, under high cyclic shear strain range, eutectic SnCu with a higher ductility exhibits a longer characteristic life. The results suggest that, in low-strain applications, a more ductile solder experiences an earlier loss of structural integrity and therefore earlier failure. In high-strain applications, this faster creep deformation results in a shorter life than in low-strain applications. However, this deformation also avoids early cracking caused by excessively large strains, and therefore outlives solders with low ductility. On the other hand, more brittle solders such as SnAgCu or SnAg could not relieve the stress caused by large strains, and consequently suffer early cracking at weak spots of the system. In other words, the best alloy choice is determined by the end-application.

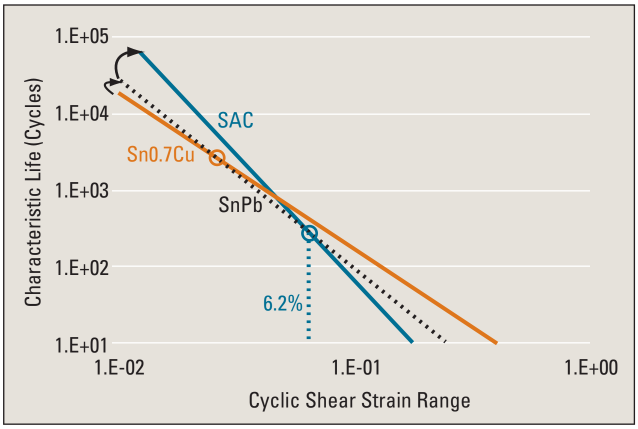

FIGURE 1. Correlations of characteristic life to cyclic shear strain range for bare chip assemblies: power-law trendlines for SnCu, SnPb and SAC assemblies.[3]

TABLE 3. Tentative High-Temp. Pb-Free Alloys, Solidus Temperature 260° to 500°C[2]

SOLDER ALLOY	SOLIDUS (°C)	LIQUIDUS (°C)	E=EUTECTIC
89Bi-11Ag-0.05Ge	260	360	
80Au-20Sn	280	280	E
88Au-12Ge	356	356	E
96.76Au-3.24Si	363	363	E
95Zn-5Al	382	382	E
55Ge-45Al	424	424	E
75Au-25In	451	465	
82Au-18In	451	485	

Alpha particle emission. An alpha particle is a nuclear particle that contains two protons and two neutrons. The alpha particle strips electrons from atoms such as ^{28}Si as it passes through the electron cloud of an adjacent atom, thus producing charge along their path, leaving a trail of electrons and holes. When enough electrons were knocked out of an IC and accumulated in a capacitor, it switched the capacitor from 0 to 1 or from 1 to 0 and resulted in a so-called "soft error." The distance an alpha particle travels through the semiconductor package ranges from 7 µm for Au to 24 µm for Si and 28 µm for polyimide. For high I/O devices, solder bumps have to be placed everywhere on the IC surface, hence a low alpha emission solder will be required.[5]

Within common solder constituents, lead has been identified as the primary source of alpha particles. Both ^{214}Pb and ^{210}Pb contribute to alpha emission, with ^{210}Pb being the primary source due to its considerably longer half life (**FIGURE 2**). Most of the elements involved in viable lead-free alternatives, either as major constituents or as possible minor additives such as tin, indium, silver, copper, antimony, zinc, germanium, nickel and gold, have no isotopes which will release alpha particles; all considered safe. Bismuth may have an issue due to the existence of radioactive ^{214}Bi, which will convert into stable ^{206}Pb in about 24 years. ^{212}Bi would also

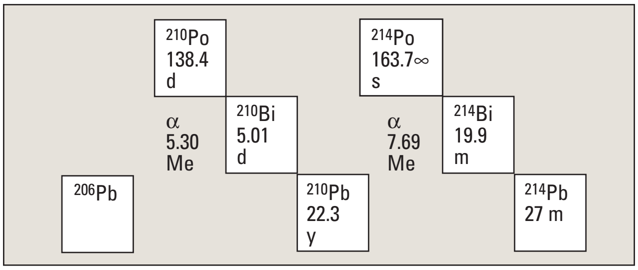

FIGURE 2. Secular equilibrium of lead.

TABLE 4. Effects of Mixed Alloys on Solder Joint Reliability

COMPONENT	MIXED ALLOY COMBINATION	OTHER CONDITIONS	IMPACT ON JOINT RELIABILITY
BGA	SnPb ball on Pb-free paste	Pb-free reflow profile	Large voids in joint
	Pb-free ball on SnPb paste	Reflow < 217˚C	Early crack at joint interface with board pad due to excessive strain at SnPb zone
		Reflow > 217˚C	Negligible impact on reliability if joint composition homogenized
SMT	SnPb finish in Pb-free paste	SAC paste	Pb may concentrate in the last cooled zone of joint and cause early failure
		SnBi paste	Early failure due to low melting ternary SnPbBi phase
	SnPb finish in Pb-free wave	–	Fillet lifting on topside joint
	Pb-free finish in Sn-Pb paste	Metal volume ratio of finish to paste is critical	Negligible effect, unless excessive amount of Ag, Au or Pd from finish dissolved in joint
	Pb-free finish in SnPb wave	–	Negligible effect

undergo alpha decay and cause concerns for soft error.[5]

Other than Bi-containing alloys, low alpha emission can be achieved by controlling lead impurity levels. The alpha emission rate of typical pure lead is about 10-10^2 count/cm^2/hr. Currently used solders have alpha emission levels from 0.05 to 0.01 count/cm^2/hr. (LC2 level). To reduce alpha emission rate from 10^2 to 10^{-2} count/cm^2/hr., the lead content in lead-free solders will have to be lowered by four orders of magnitude, or to 100 ppm or below. This is easily achievable, since tin is the primary source of lead contamination, and lead impurity in tin metal often ranges from 50 to 200 ppm. In other words, the requirement on maximum lead impurity permitted can be met by screening tin lots for lead content with a reasonably high pass rate. However, the same cannot be said for future requirements in which the alpha emission rate may need to be as low as 10^{-3} count/cm^2/hr. (LC3 level).[5]

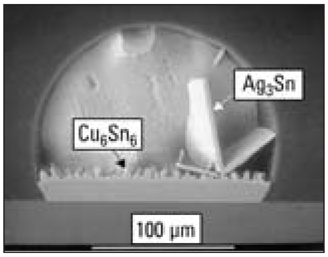

FIGURE 3. Intermetallic compounds formed in the solder joint of Sn95.5Ag3.8Cu0.7 on Cu.[9]

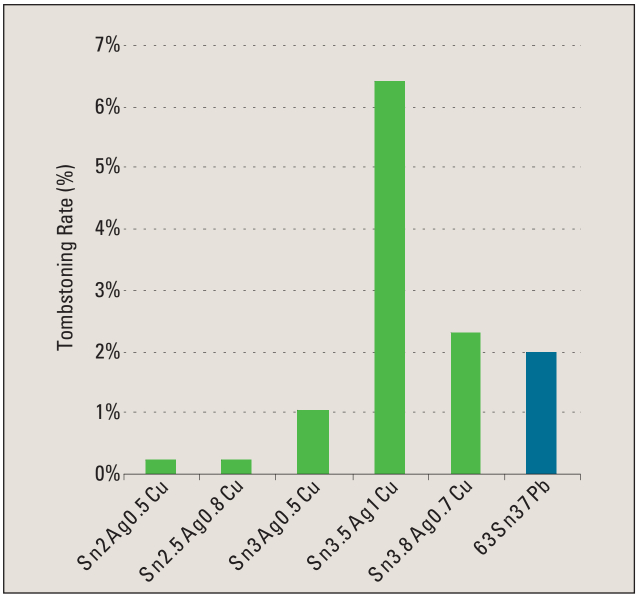

FIGURE 4. Tombstoning rate of solder pastes under vapor phase reflow. SAC and SnPb pastes were reflowed at 260˚ and 215˚C, respectively.

2. BGA Solder Balls

Fragility. Similar to SMT assembly applications, SAC has also been adopted for BGA solder balls. The alloys employed include SAC305, SAC387, SAC396 and SAC405. However, unlike other SMT components, the fragility of BGA SAC solder joints appears to be considerably poorer than that of BGA SnPb joints for both NiAu and OSP surface finishes, particularly in the former case. This difference manifests especially in the drop test. BGA SAC joint fragility has been attributed to inconsistent plating quality of the copper pad,[6] Kirkendall void formation,[7] low solder ductility and intermetallics.[8]

To resolve the issues, approaches have been taken to develop alloys with better resistance against fragility. The most popular approach is increasing the solder ductility by decreasing the Ag and Cu content; reducing Ag is the most effective means. While Ag down to 1.5 or 1% has been considered favorable, Date et. al. further claim the desired Ag content is 0 to 1%, with Cu at 0.5 to 0.7%. With NiAu BGA surface finish, those alloys outperformed SnPb in drop tests.

Adding small amounts of other elements is an attractive way to suppress intermetallic formation. Elements such as germanium, Ni and Zn have showed promising results. Zn has also reduced Kirkendall void formation by suppressing Cu3Sn formation on copper pads. Maintaining some Cu in lead-free solders is also considered helpful in curtailing intermetallic formation on NiAu.[8] The effect of adding additional elements varies depending on the type of finish involved.

Intermetallic plates. Ag in lead-free solders contributes to fragility of joints and to the formation of large intermetallic plates. **FIGURE 3** shows AgSn intermetallics plates formed in the solder joint of SAC on Cu after being reflowed twice at 260˚C and heavy etching.[9] The plates may grow across the entire solder joint, and may protrude out of the joint itself. The probability of AgSn plate formation is aggravated by slow cooling and thermal aging, and decreases with decreasing content of Ag. An IBM study indicated that the probability of large AgSn plates observed in solder balls with SAC alloys solidified at a rate of 0.02°C/sec. is 76/100 for SAC387, 9/200 for SAC309, 1/200 for SAC259 and 0/200 for SAC209. IBM noted that Sn97Ag2.3Cu0.5Bi0.2 is desirable for ball composition, with Bi added to prevent tin pest formation.[10]

3. Small Forms

With continuous miniaturization of electronics, discretes such as chip capacitors or resistors are also shifting toward 0402, 0201 or 01005. An immediate impact is the rapid increase in tombstoning rates. Although this problem can be countered by optimizing fluxes, designs or profiles,[11] the most effective approach is solder alloy optimization. **FIGURE 4** shows results of an Indium study on tombstoning rates of solder pastes. Tombstoning of SAC is affected by solder composition, and is dictated by the wetting at the onset of the paste melting stage. A maximal tombstoning rate is observed at the ternary eutectic composition Sn95.5Ag3.5Cu1. The tombstoning rate decreases with increasing deviation in Ag content from this composition. A DSC study indicates this is mainly due to the increasing presence of pasty phase in the solders, which results in a slower wetting speed at the onset of solder paste melting. Surface tension plays a minor role, as lower surface tension correlates with a higher tombstoning rate. SAC composition with a Ag content lower than 3.5%, such as Ag2.5, is more favorable to reduce tombstoning.[12]

4. Component Finishes

Lead-free surface finishes of components include Sn, SnBi, SnCu, SnAg, NiAu and NiPdAu. Among those, Sn is favored for passives, SnBi is common for leadframes, and NiPdAu is popular for pre-plated leadframes.

Sn is solderable and cheap. Concerns over tin whiskers (caused by compressive stress in the tin layer) must be addressed. Under isothermal conditions, the compressive stress generation is dominated by intermetallic compound (IMC) formation at grain boundaries whereas under temperature cycling conditions, stress generation is dominated by CTE mismatch between Sn and the metalization underneath. Measures shown relatively effective in curtailing tin whiskers include Ni-barrier plating, thin Sn layer, baking treatment and alloying with Bi.

NiPdAu is both wire bondable and solderable, and can be used on pre-plated leadframes without the need for selective plating. This simplified process results in a lower manufacturing cost than that of Sn plating when used on pre-plated leadframes. A tradeoff may be reduced joint strength due to reduced wetting.[13]

5. Components Assembled with Mixed Alloys

Whether a forward or backward compatibility situation, mixed alloys are inevitable during the transition. In general, lead contamination often significantly compromises reliability, and should be avoided when possible. **TABLE 4** lists mixed alloys at component assembly and their impact on solder joint reliability.

TABLE 5. Surface Tension of Some SAC Alloys vs. SnPb37[12]

SOLDER	SURFACE TENSION (N/m)
SnPb37	0.506
SnAg2Cu0.5	0.565
SnAg3Cu0.5	0.567
SnAg3.5Cu1	0.553
SnAg3.8Cu0.7	0.560

Components vs. Fluxes

1. Solder Bumping

Solder fusion on wafer. For electroplated or evaporated solder bumps on wafer, the bumps need to be fused with spin-coated fluxes to eliminate the porosity of the bumps or round up the bumps. The fluxes required for this process often are not significantly affected by lead-free. Fluxes used for fusing high lead solder bumps typically are also applicable for lead-free, Sn-rich solder bumps, such as SnCu0.7 bumps.

Paste bumping on substrate or wafer. Solder paste bumping is a low-cost process for wafer bumping or pre-solder bumping on substrates. Fine powder is required, either type 4, 5, 6 or 7, depending on the pitch and bump dimension desired. Converting from SnPb37 to lead-free (such as SAC) requires fluxes with better wetting and cleanability.

Ball mounting on wafer or BGA. Ball mounting on wafer or BGA employs printing or pin-transfer flux deposition, followed by ball placement and reflow. Converting to lead-free solders results in a higher ball missing rate or misalignment rate due to the poorer wetting of lead-free alloys. The flux residues are also harder to clean. Upgrading both aspects is essential for successful conversion.

Ball mounting on BGA socket. Solder bumping onto a socket is performed by printing paste or pin-transfer flux onto the pin head, followed by solder ball placement and reflow. The solder ball should form a bump by fully wetting the pin head, but wetting beyond the pin head can cause collapses. To confine solder wetting (and reduce cost), the surface finish of the pin is normally plated with nickel. For SnPb37 balls, it is not an issue to balance the wetting so that the ball wets sufficiently – but not excessively – on the pin head. For SAC solder balls, however, sufficient wetting often poses a challenge, and the flux activity needs to be improved.

2. Component Attachment

Small forms. Small form components such as 0402s or 0201s are prone to skewing, tombstoning or billboarding. Converting to lead-free may lessen or aggravate the problem, depending on the alloy employed (**FIGURE 4**). To help alleviate the problem and widen the process window, fluxes with slow wetting are desirable.

Large forms. Similar to the SnPb process, soldering large components or thick boards requires a long soak at reflow to minimize the temperature gradient across the board. However, if reflowing under air, soaking at around 200°C for lead-free reflow will result in much more severe oxidation on parts and paste than soaking at the typical 160°C for SnPb reflow. This inevitably requires improved flux oxidation resistance and flux capacity.

Old components. In one special situation, the problem is associated with lead-finished components but caused by lead-free requirement. Due to expected shortages of lead-finished components in the future, many of those parts are stocked for future repair or replacement. Those components suffer excessive oxidation, and hence poor solderability, when stored beyond their recommended shelf life. In this case, an aggressive flux must be used to address this heavily oxidized surface finish.

No-flow underfill. No-flow underfill is a solution for enhancing the drop test performance of CSP solder joints, and has been adopted for portable devices. By dispensing no-flow underfill onto CSP pads, then placing the CSP and reflowing, the flux in no-flow underfill will clean the oxide, solder will wet the pad and form a joint, and the underfill cure will be completed at the end of reflow cycle.

No-flow has been employed successfully in production for Sn63Pb CSP processing. However, converting to lead-free poses major challenges. First, lead-free solder wetting is poorer, and non-wetting often occurs with no-flow fluxing chemistry, particularly in the case of OSP finishes. Second, outgassing of the lead-free process also causes problems. One great challenge of no-flow underfilling is voiding and, accordingly, skew and chip drift caused by moisture. Sealing the space between the CSP and substrate with liquid underfill makes it very difficult for volatiles from the CSP and substrate to escape during reflow. This is particularly true for lead-free CSP assembly, for which reflow temperatures are considerably higher. The third challenge is reworkability. Underfill cured at a higher temperature often is more difficult to rework due to a more thorough curing reaction.

Until recently, no-flow underfilling for lead-free process has been a blank. This situation changed with the publication of Yin et al on new materials that meet the crucial requirements.[14]

Alloys vs. Fluxes

Higher activity fluxes. Lead-free alloys do not wet as well as SnPb37. This can be attributed to their surface tension being about 20% higher than that of eutectic SnPb (**TABLE 5**). Poor wetting results not only in poor solder spread but also in voiding, and hence becomes a major reliability concern. This inferior wetting power of lead-free alloys will have to be compensated through the development of more aggressive fluxes.

Lower activation temperature of fluxes. Among lead-free alternatives, BiSn52 or BiSn42Ag1 has a melting temperature around 138°C, and is particularly important for applications where parts cannot survive common soldering temperatures. To benefit from this low melting temperature, a flux with a low activation temperature is required. For a no-clean process, this presents a challenge, as higher activity at low temperature often demands the use of a more aggressive flux, while a benign flux residue after low temperature soldering process demands the use of a less aggressive flux.

Compatibility with reactive elements. As shown in **TABLE 1**, some lead-free alternatives contain reactive elements such as zinc or indium. This reactivity poses a compatibility issue between flux and solder in solder paste, and between flux residue and solder joints in a no-clean process. The compatibility challenge can be eased somewhat by adding bismuth into SnZn solder, and by keeping the indium content at or below 10%.

On the other hand, silver in solder has also been reported to catalyze dissociation of some covalent halide, which is often used as an activator in fluxes. This dissociated halide is reactive at ambient temperature, and thus can cause corrosion in solder paste. With silver being part of virtually all the vital lead-free alloys, designing a proper flux chemistry becomes crucial.

High melting temperature. The soldering process of high lead solders is often conducted between 300° and 380°C. Such temperatures are reaching the limit of thermal stability and cleanability of organic materials. As revealed in **TABLES 2** and **3**, lead-free alternatives for high lead solders virtually do not exist. On one hand, they are limited by the gap in alloy properties required compared with those of tentative candidates. On the other hand, even if some high melting alloys (**TABLE 3**) might be promising, it is extremely difficult to develop a flux that can survive a reflow temperature higher than 400°C. This limitation of organic materials in turn limits the possible options for high-melt lead-free solders.

Solder joint appearance and grain size. Compared with eutectic SnPb, the solder joint appearance of lead-free alloys is typically dull and not smooth. This is attributed to the large dendrite formation caused by the strong crystallization tendency of high tin solders. Regardless, a joint with small grain size, or small dendrites, is still desirable for better creep resistance and fatigue resistance. Although the formation of grain is a metallurgical behavior of solder, the presence of flux on the surface of molten solder may affect the grain size by affecting the nucleation of solder. Hypothetically, fluxes that tend to induce the solder nucleation are expected to result in a greater number of grains, smaller dendrites and, consequently, smoother solder surface. The opposite would be expected for fluxes that tend to hinder the nucleation formation of solder. Yin et al reported that the microstructure of flip-chip SAC solder bumps can be affected by flux chemistry and cooling rate, with higher cooling rates resulting in a slightly finer microstructure in both grain and dendrite size. However, the effect of flux chemistry exhibits a greater effect than the cooling rate. Therefore, selecting a flux may not only affect solder wetting, but also may affect the microstructure of solder joints.[15]

Lead-free conversion is a complicated process. It impacts the electronics infrastructure, and causes interlinked chain reactions among components, alloys and fluxes. Although solder alloys may initiate that chain reaction, its impact on components and fluxes rebounds and affects the path of alloy developments. The interaction between components and fluxes further complicates their impact on alloys. Successful execution of lead-free conversion requires the concurrent change and improvement of components, alloys and fluxes. **PCD&M**

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