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Inert Soldering With Lead-Free Alloys: Review And Evaluation

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Abstract

Using nitrogen to create an inert atmosphere during soldering of conventional Sn/Pb alloys has become a generally accepted practice in the assembly of electronics. There seems to be little doubt in the minds of the user that nitrogen improves the process. However, its cost-effectiveness and technical necessity are still frequently questioned. One reason being that the benefits of nitrogen are difficult to evaluate since they are often process specific and reliability based.

The introduction of the lead-free debate has intensified the need for accurate and specific information on this topic. A review of published data, reports, and experts' opinions generally come to the conclusion that the need for a controlled atmosphere in lead-free soldering is even greater than with traditional Sn/Pb alloys. These reports are contrasted and studied in this review.

In addition, a series of wetting balance tests were performed to assess performances of lead-free solders with varying atmosphere. It was found that limiting the oxygen level in the atmosphere improves wettability and can even allow for the reduction of lead-free process temperatures (superheat temperatures) with certain benefits.

The Move Towards Lead-Free

Lead has been used for thousands of years. The toxic properties of lead were slowly discovered with the progress of medicine and chemistry in the former centuries. Among the toxic metals, lead is far from being the worst. However, it still has been widely used (e.g. for paint pigments and gasoline additives) in modern society. In the past decades, lead use has became a public health issue, and progressively lead has been banned from many of its common uses.

Now this movement has reached the solder of electronic assemblies. The real question is whether lead in solder is a real threat or not for human health or for the environment. The answer to that question is still unclear, but the move towards lead-free solder is well on its way. Even if the European Directives, initially scheduled to be in force by 2004 or 2008, are not immediately approved, the assembly industry has to be prepared to switch to lead free sooner or later.

Legislation constraints in Europe and Japan may soon not be the driving force of the move towards lead-free manufacturing. In Japan, the green label has proved to be a strong selling argument to the consumer. Will this become a global trend? If consumers strongly favor 'green' products, an increase of lead-free production may primarily be a result of sales pressures. Marketing reasons rather than regulatory ones will probably push the lead out of assembly lines in the near future.

The Chemist Point of View

Higher Processing Temperatures - A significant amount of work has been done to find a substitute for the common eutectic Sn/Pb alloy. However, the search for a "drop in" replacement failed to discover any alloy having the same chemical properties. Because of this, the question of finding the proper alloy has become rather complex and has been widely discussed. The new alloy must be judged on a variety of properties including: availability, toxicity, process conditions, and melting temperature to name a few.

All candidates to replace Sn/Pb are centered on the inclusion of tin because of its very specific properties. So far, the industry seems to be to converging to tin/silver/copper mixtures, as well as other binary and ternary combinations based on tin. Unfortunately, all of these combinations have noticeably higher melting temperatures than the traditional tin-lead mixture. The temperature issue is one of the most difficult problems faced in the lead-free soldering transition.

Tin-zinc eutectic may be the outsider of this race. Its melting temperature is only 6°C above Sn/Pb. Of course zinc, being strongly electronegative, is much more prone to oxidation than silver or copper. Special precautions have to be taken against this, but soldering without a drastic temperature increase is an invaluable bonus. Some Japanese companies have chosen this approach. To meet demand in Japan, on major solder manufacturer has installed in Japan a production facility for 3 tons per month of Sn/Zn solder paste.[1] Bismuth use may also help avoid the temperature issue, but the “lifting” effect needs to be addressed.

There is a definite move toward a standard alloy in the US and Europe. The best candidates are combinations of the above mentioned metals: Sn, Ag and Cu.[2,3] All of those combinations have melting points ranking from 34 to 44°C above Tin-lead eutectic. Due to this fact, electronics manufacturers will most likely have to face a non-negligible increase in their processing temperatures.

Increased Oxidation & Flux Issues - Higher processing temperatures are a serious issue for the PCBs as well as for the components. Since electronic soldering has been done, the technology has been stabilized around the melting point of tin-lead. Reflow ovens and wave soldering processes will need to be modified to account for the new solder materials. Once this is done, the greatest impact of the increased operating temperature, an increase in oxidation, will be seen.

The science of soldering relies heavily wetting, which is reduced by oxidation. An overall increase in oxidation will adversely affect soldering. One could state that a 10-degree temperature increase is small, but considering Arrhenius law, the growth in reaction rate is exponential and thus very significant in terms of oxide layer thickness.

To reduce the effect of oxidation and allow for sufficient wetting, flux is used in soldering. Flux formulations are often delicate blends of carefully chosen organic compounds and solvents. The tolerance of those organic compounds to elevated temperatures is fairly limited. Organic compounds are prone to "cook" or "bake" in high temperatures thereby loosing the chemical properties for which they have been added to the flux. The solvents will also evaporate faster when the temperature is raised.

In reference to lead-free soldering[4], it was found that higher preheat temperatures promote slumping, the spread of solder paste, and a more rapid deactivation of the acids used in fluxes. It can also be added that at higher temperatures, the flux layer protecting the metal will be thinner, thus increasing the potential oxidation rate of the solder as well as of the metal on the pads or leads being soldered. Moreover, the components of the flux will also oxidize and/or polymerize. After soldering, this may leave a brownish and hard to remove mix of chemically undefined compounds. Whether those compounds are or not a threat to the reliability of the end product is an open question.

The Benefit of an Inert Atmosphere - Flux and solder paste manufacturers do not remain inactive when facing the challenge of the higher temperatures required by lead-free solders. They continue to modify and experiment with new and stronger flux formulations. Increased solid content and higher boiling temperature solvents are common answers. However, newer and stronger formulations may raise some issues related to the post-soldering residue formation. These residues may be more difficult to clean or may be harmful if left on the finished product. As we move towards more complex products and board designs, not cleaning potentially harmful residues may cease to be an option.

One solution to the increase of temperature and oxidation, while still allowing for the use of standard or less aggressive flux formulations, is to reduce the oxygen content in the solder step by inerting the reflow oven or the wave solder equipment. Providing a low ROL (Residual Oxygen Level) in the soldering area will help protect metal and flux against excessive oxidation while promoting better wetting. The only drawback to such an answer is the cost of the nitrogen used for inerting. Although nitrogen consumption of soldering equipment has been greatly lowered, the added cost still requires that the use of nitrogen be fully justified.

Inert Soldering: Experts’ Opinions

Among the growing amount of literature dedicated to the lead-free issue, we have searched for published material related to nitrogen use and inert soldering. The information published is important and can help the assembler improve his knowledge of lead-free soldering in order to make the appropriate decisions.

Professional Press and Consultants

In a recent article,[5] the use of nitrogen is questioned in the reflow of Pb alloys. The article has the opinion that while an inert atmosphere in reflow may help, its cost may not be justified. However, for wave soldering, it gives a different analysis. It should be noted that the article does state that if the process window is significantly impinged upon, there should not be any hesitation to use an inert atmosphere.

In another article,[6] focusing on nitrogen atmosphere, develops a recipe as to when or when not to use N2 in Pb systems. The forgiving qualities of nitrogen may prove useful when certain conditions such as high temperature solder, fine pitch, complex assemblies, or high product reliability are involved. Lead-free soldering does involved high temperatures, and future products will involve smaller, more complex designs while using lead-free solders.

Gas manufacturers

Gas manufacturers generally admit that using nitrogen should be done selectively and based on process criterias. One particular benefit could be that nitrogen use for lead-free solder systems could allow soldering to be performed at just a few degrees above the solder melting point.[7] The objective being to reduce the heat stress seen by the component which is now among the predominant issues of lead-free soldering.

This is also supported by an example where six lead-free solders were tested with a clear focus on the "Superheat Temperature" (ST).[8] The ST can be defined as the difference between the melting point of the alloy and the process temperature used to solder it. Again, it is concluded that nitrogen can reduce the ST for reflow, therefore allowing for a reduction in the proposed increase in soldering temperature required with lead-free solders.

Flux and Solder Paste Manufacturers

These companies are directly on the forefront of the lead-free issue and most of the published data on this topic is coming from them. Various publications, as well as commercial technical brochures, generally indicate that flux and solder pastes are formulated to give good results with both air and nitrogen. Nitrogen atmosphere must be avoided [for cost reasons] but it might not always be possible.[9]

Others focus on the poor wetting properties generally encountered with lead-free alloys but state that the interest of nitrogen is marginal.[10] A slightly different opinion is to recognize that increased oxidation promotes nitrogen use, but then insist that for their own flux formulations, nitrogen is an advantage but is not essential.[11] Some opinions are more openly in favor of nitrogen stressing the poor wetting properties of the Sn/Ag/Cu series of alloys with commercial and especially no-clean fluxes,[12] or insisting on the possibility of using nitrogen to avoid cleaning issues.[13] A difference has to be made between reflow and wave soldering for which the nitrogen benefit of the former is apparently not discussed.[14]

Other interesting technical opinions encountered include: flux residues oxidizing during processing in air to a state where they are difficult to clean vs. N2,[9] nitrogen being used successfully for hot gas repair, and nitrogen reducing oxidation simplify the process control.[15] Nitrogen is also recommended in zinc-bearing solders.[16]

Equipment Manufacturers

Publications by these companies in the lead-free area are less common. One study did find the opinion of a manufacturer who is clearly in favor of nitrogen.[17] The main argument is that given the fact that we do not want to use active fluxes and subsequent cleaning, the quality of the nitrogen atmosphere may become even more important for Pb-free alloys than it has been with the standard Sn/Pb solder.

The same source also emphasizes the efforts made recently to lower the nitrogen consumption of reflow ovens and wave soldering machines. Figures are given to obtain a ROL of 150ppm. The typical consumption is now below 27Nm^3/h (1000 scfh) in reflow rather than the 55–80 Nm^3/h (2000-3000 scfh) commonly encountered in older N2-capable reflow ovens.

Users

Many assemblers are spending time testing lead-free solutions on part of their own production. For evident reasons, data is not willingly shared or published. Nevertheless, some indications can be found in the published material.

The majority of assemblers try to work without nitrogen for cost reasons.[11] Important R&D efforts have especially been made in Japan to obtain acceptable results using air, even in adverse conditions with Zinc containing solders.[18] However, others that have tried nitrogen have disclosed their experience concluding to the necessity to use inert atmosphere for telephone assemblies.[19]

Professional Organizations and Research Institutes

For these organizations, under less commercial pressure, the opinion is more widely in favor of nitrogen inerting for wave as well as for reflow. "Nitrogen inerting may become of critical importance in the future with the uptake of lead-free alloys."[20] Several sources report that the use of a nitrogen atmosphere can allow a reduction in the peak soldering temperature,[2,21] thus confirming that inert soldering is a possible way to address the issue of higher temperatures in lead-free soldering.

The use of nitrogen is also specifically stressed for complex boards with a high thermal demand and a large range of temperatures across the board.[20] Is it also stressed for varying finishes and thermal requirements.[2] For such boards, nitrogen is recommended.

The Cost Issue

It is generally agreed that lead-free implementation will unavoidably result in an increase of production costs. It might be interesting to analyze this cost increase in order to work to minimize it. In one example,[11] a simulation shows that the cost of the soldering material is less than 0.1% of the cost of the electronic end product. In fact, utilities or nitrogen are typically less than 0.1% of the finished product cost.

Another very interesting result of this simulation is a list of the most important contributors to the cost increase associated with lead-free implementation. At the top of this list, as far as this can be estimated, are typically the implementation costs for the new process, the slower cycle times applied to the new thermal profiles, and in particular the unavoidable reduction of product yields. Can nitrogen become a low cost insurance when implementing a new process with an unavoidably shrinking process window?

The Specific Case of Wave Soldering

One of the primary differences between wave and reflow soldering is the creation of dross. Dross is formed in wave soldering when the molten wave of solder comes in contact with the oxygen contained in the air. Naturally, the use of an inert atmosphere largely eliminates the creation of dross, preventing a large amount of solder from being wasted.

How does lead-free modify this situation? An interesting answer to that question can be found in research work performed some years ago in England.[23] Extracted from this reference, Table 1 shows the cost of the dross estimated for a commercial wave soldering machine with different solders while comparing air and nitrogen atmospheres. Sn/Cu, Sn/Ag, and a representative of Sn/Ag/Cu series are compared to the standard Sn/Pb solder. Using this data, dross savings in $/hr, are 66% to 130% higher for lead-free alloys than for standard Sn/Pb with virtually the same nitrogen costs (Table 2).

Table 1 - Estimated Cost for a Commercial Wave Soldering Machine With Different Solders

		Sn-40Pb	Sn-0.7Cu	Sn-2Ag-0.8Cu-0.5Sb (Castin)	Sn-3.5Ag	Sn-20In-2.8Ag
Metalprice ($/ton)		4140	6274	8730	10630	98504
Air	Dross produced at ITRI (g/hr)	25.3	28.7	19.8	22.8	-
	% of Sn-40Pb	100	113	78	90	100
	Dross produced in a commercial wave soldering machine (g/hr)	800	908	626	721	800
	$/hr	3.31	5.69	5.47	7.66	78.80
50 ppm O_2	Dross produced by ITRI (g/hr)	1.47	1.68	0.98	1.21	1.47
	% of Sn-40Pb	100	114	67	82	100
	Dross produced in a commercial wave soldering machine (g/hr)	40	45	31	36	40
	$/hr	0.17	0.28	0.27	0.38	3.94

Table 2 - Dross Cost Comparisons

		Sn-40Pb	Sn-0.7Cu	Sn-2Ag-0.8Cu-0.5Sb (Castin)	Sn-3.5Ag	Sn-20In-2.8Ag
Air	$/hr	3.31	5.69	5.47	7.66	78.80
N_2	$/hr	0.17	0.28	0.27	0.38	3.94
Savings	$/hr	3.14	5.11	5.20	7.28	74.86
	% SnPb	-	63%	66%	132%	-

Need for Quantitative Data

Using nitrogen to inert the atmosphere during soldering of conventional Sn/Pb alloys has become a generally accepted practice in electronic assembly. There seems to be little doubt in the minds of the user that nitrogen “improves” the process, however, its cost-effectiveness and technical necessity are still questioned very frequently. A reason being that the benefits of nitrogen are difficult to evaluate since they often are process-specific and reliability based. The introduction of the lead-free debate has intensified the need for accurate and specific information on that topic.

Higher temperature and the associated increase in oxidation, as well as expert opinion, seem to indicate that lead-free soldering with nitrogen might be necessary. However, most of the information reported above is qualitative, and of course there is a need for more quantitative data to support the comparison between air and nitrogen results.

Wetting Balance Tests

A key difference between air and nitrogen (or absence of oxygen) is the effect on oxidation and wetting. Since soldering is strongly influenced by the wetting force, it was decided to consider quantitative data on wetting to create measurable comparisons. Among the methods to obtain this quantitative data, the choice of the wetting balance method is most logical. It is a well-established method that easily gives precise and quantitative data, and it can easily be performed in different atmospheric conditions. The objective of this study was to perform tests that were close to the actual conditions encountered on the production floor. This study would complement another, extensive study on the same topic.[20]

It was decided to use plain copper adding a controlled level of pollution to be representative of what is commonly encountered in assembly lines. A decision was made not to use rosin based fluxes, as it looks too academic, but rather an organic flux that is representative of the industry standard for no-clean applications. The flux chosen (1.8% solids), is considered to have the highest level of quality on the European market. For the temperature range, 10°C superheat temperature, representative of the possibility to use the lower superheat temperature for lead-free solders, was used. Until components are improved for their thermal resistance, a 10°C superheat will prove attractive. Tests were also made at the standard (Sn/Pb) superheat of 30°C to get a comparative set of data.

Experimental Set-Up and Alloys Selection

The wetting balance used was a model ST40 from METRONELEC (see Figure 1). It was equipped with a dry box enclosure and nitrogen supply. With this apparatus, a ROL of 50 PPM O2 could be easily reached and monitored throughout the test. We also equipped it with a dedicated airlock system to introduce the test samples. With this device, a time of less than 10s was necessary to achieve the required ROL after introducing a new sample.

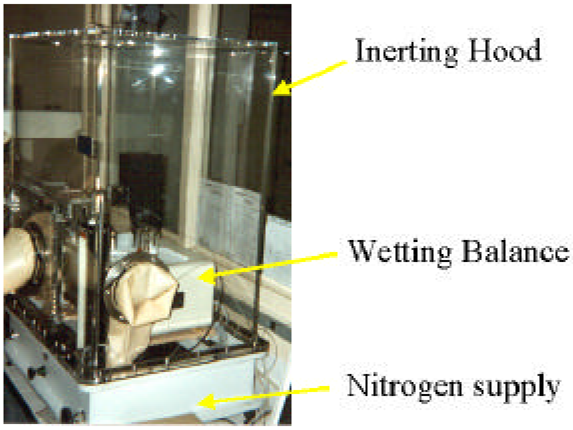


Figure 1 – Controlled Atmosphere Wettng Balance

The alloys were chosen according to their emergence as the best candidates for reflow applications. Those included SnAg eutectic (96.5Sn/3.5Ag) and a ternary Sn/Ag/Cu that is commercially available (95.5Sn/4Ag/0.5Cu) and as close as possible the ranges recommended by NEMI[2] and ITRI.[3] The superheat temperatures for the 96.5Sn/3.5Ag (melting point of 221°C) were 231±1°C and 251±1°C corresponding respectively to 10 and 30°C superheat. The Superheat temperatures for 95.5Sn/4Ag/0.5Cu (MP range of 216 - 219°C) were 229±1°C and 249±1°C corresponding again to 10 and 30°C above the liquidus point.

Sample Preparation & Test Procedure

To prepare for the best possible conditions, samples of plain copper were chosen according to ISO 1634-CU-ETP. After proper degreasing and cleaning by immersion in methylethylketone and 20% V/V nitric acid respectively, the samples were prepared according the French NFC 90 551 standard by immersion 30±0.5 sec. at 22.5±0.5 °C in a solution of 1.5 milligram/liter of sodium sulfur. All samples were stored 24 hours in controlled conditioned for proper aging. They were used within 4 hours after aging was complete. The carefully controlled sulfuration of the copper surface obtained by this treatment corresponds to the level III S.A.R. (Artificial Reference Sulfuration) according to NFC 90 551. It is representative of the pollution level that is commonly encountered in an assembly environment.

The test procedure was based on recommendations of J-STD-004 (IPC-TM-650, Test method 2.4.14.2 Liquid Flux Activity, and Wetting Balance method) with some minor changes. The solder pot temperature was modified according to the solder alloys and superheat tested. The sample preparation was as described above instead of a 10% fluoroboric acid dip. Lastly, the sample dimensions had to be adapted to the wetting balance used (coupons increased to 10mm x 0.6 mm instead of 6mm x 0.5 mm). For each Alloy/Superheat/Atmosphere combination, a sample set of 10 measures was recorded.

Test Results and Discussion

The mean values of the 10 recorded wetting balance curves obtained for each Alloy/ Superheat/ Atmosphere combination are given in Figure 2 and 3 for Sn/Ag and Sn/Ag/Cu solders respectively. As can be seen on both Figures, the wetting force is fairly constant and stable after a few seconds.

Maximum Wetting Force

The acceptance level of 150 micro-newtons/mm fixed by J-STD-004 is also reported on Figure 2 and Figure 3. For both solders it can be seen that the values obtained with a superheat of 30°C in air reach the acceptance level with only a small margin of safety. With 10°C superheat in air, the acceptance level is not reached, especially for the SnAgCu solder. On the other hand, the maximum wetting forces obtained under N2 are well above this acceptance level, especially with the Sn/Ag solder.

It is also noticeable that both curves with nitrogen and 10°C superheat are above the air and 30°C superheat curves. The difference between air and nitrogen is more important for Sn/Ag than for Sn/Ag/Cu. This may be related to the better wetting forces obtained in other work[25] with less silver-containing solders. This result is important and shows that with the help of nitrogen, the superheat necessary to obtain acceptable wetting can be noticeably lowered. Such a conclusion has already been reported in other literature.[20]

Time To Buoyancy and 2/3 Max. Wetting Force

A typical wetting balance curve is given in Figure 4. Wetting is usually characterized by the time ($T_{2/3}$) to reach a level of 2/3 of the maximum wetting force. As is often observed,[15] the wetting can be slow, unstable, or irregular, and it can then be difficult to precisely define the value of the maximum force. Some prefer to consider the time (T_w) to reach buoyancy of the tested sample (time to record exactly the buoyant force) while $T_{2/3}$ may prove easier for data analysis and comparison. Both measures were used to analyze the data.

The number of measures performed for these tests (10 for each Alloy/Atmosphere/Superheat) proves to be sufficient to allow a statistical treatment. For each Alloy/Atmosphere/Superheat and time (T_w and $T_{2/3}$), the mean value and standard deviation were calculated and then plotted as a probability density curve. An example is given in Figure 5. The results of this calculation are given in Figure 6 and Figure 7 for T_w and Figures 8 and 9 for $T_{2/3}$. The values for nitrogen are plotted as solid lines and air is plotted as a dotted line. The higher superheat (30°C) is in darker color (bold).

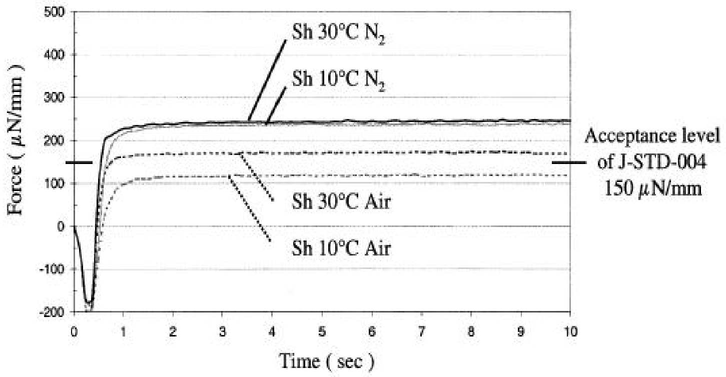
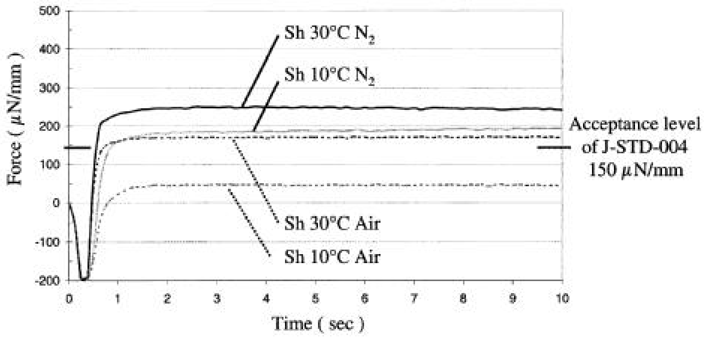


Figure 2 – Wetting Balance Cuves; Ally: Sn96,5 Ag3,5



Sh 30°C ⇨ Superheat 30°C
Sh 10°C ⇨ Superheat 10°C

Figure 3 – Wetting Balance Curves; Alloy: Sn95,5 Ag4 Cu0,5

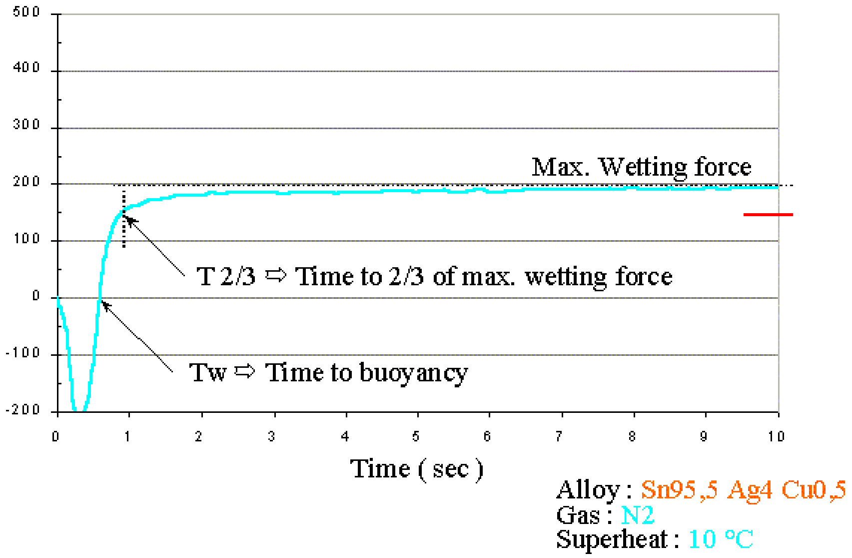
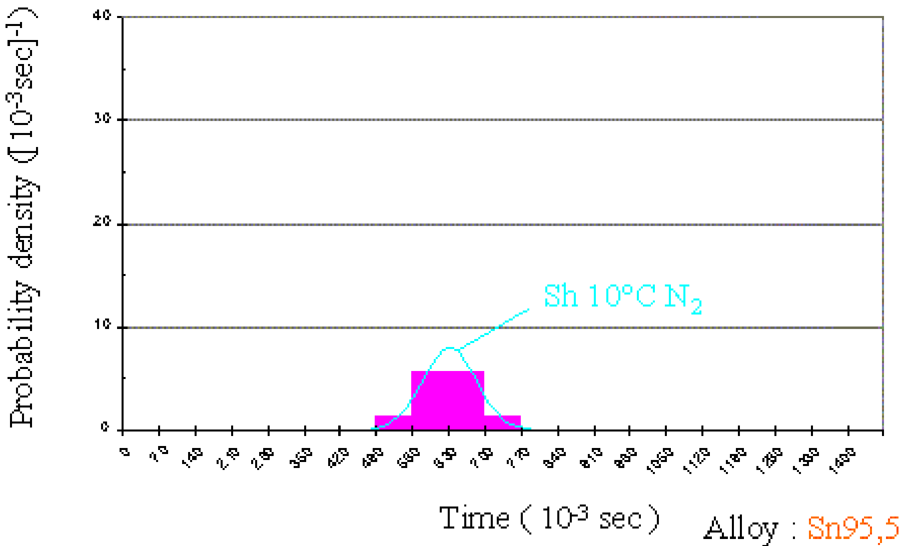


Figure 4 – Wetting Balance Curve



tw (10^{-3} sec)	n	%
0 - 70		
70 - 140		
140 - 210		
210 - 280		
280 - 350		
350 - 420		
420 - 490	1	10
490 - 560	4	40
560 - 630	4	40
630 - 700	1	10
700 - 770		
770 - 840		
840 - 910		
910 - 980		
980 - 1050		
1050 - 1120		
1120 - 1190		
1190 - 1260		
1260 - 1330		
1330 - 1400		

Alloy : Sn95,5 Ag4 Cu0,5
Gas : N2
Superheat : 10 °C

Figure 5 – Probability Density

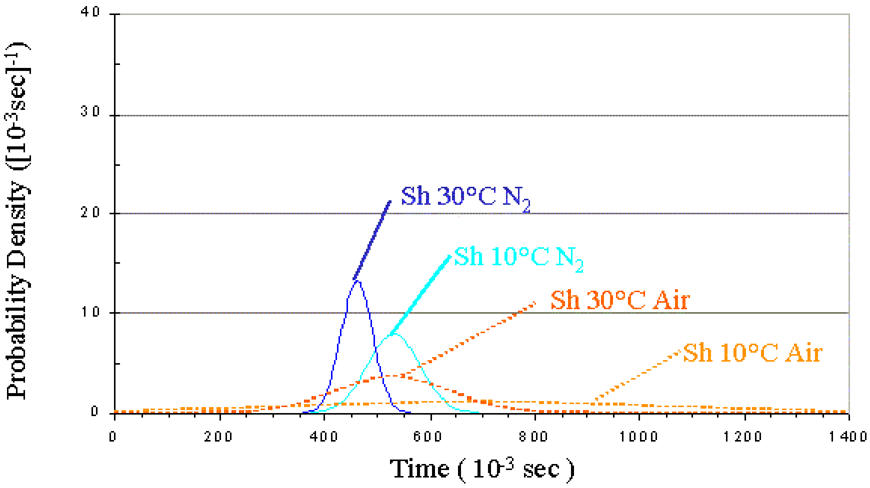


Figure 6 – Time to Buyoancy 9tw); Alloy: Sn96,5 AG3,5

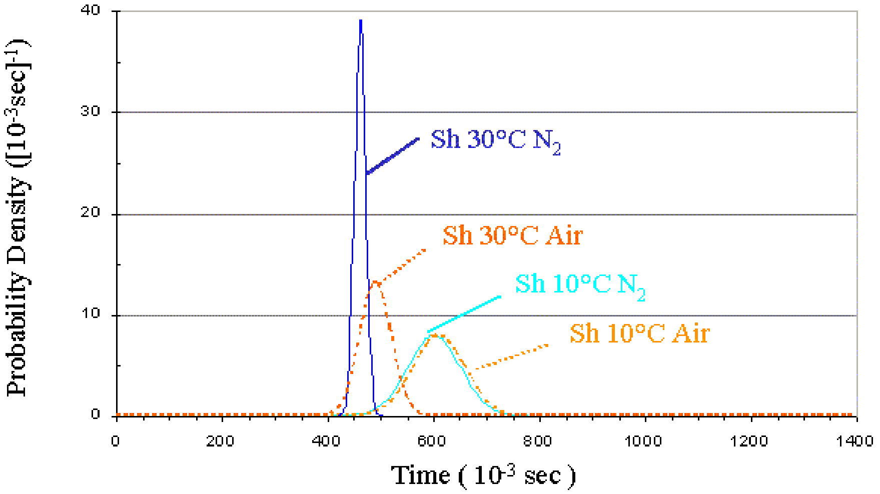


Figure 7 – Tme to Buyoancy (tw); Alloy: Sn95,5 AG4 Cu0,5

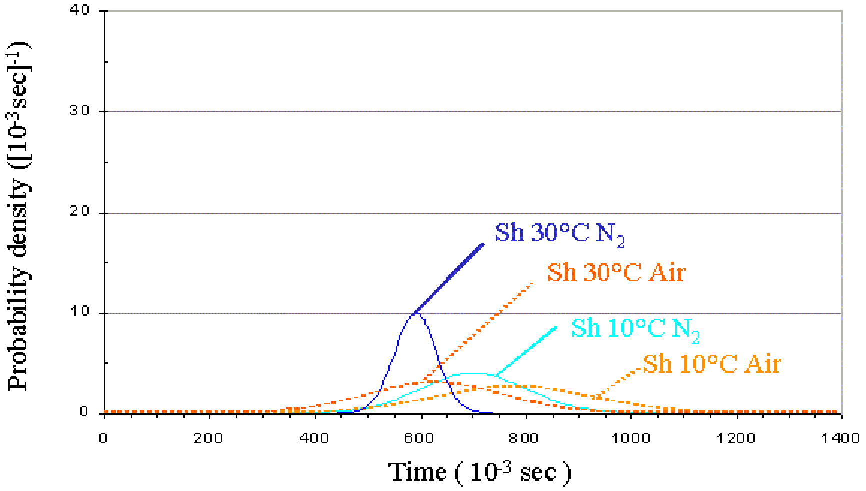


Figure 8 – Time to 2/3 Max Wetting Force; Alloy Sn96,5 AG3,5

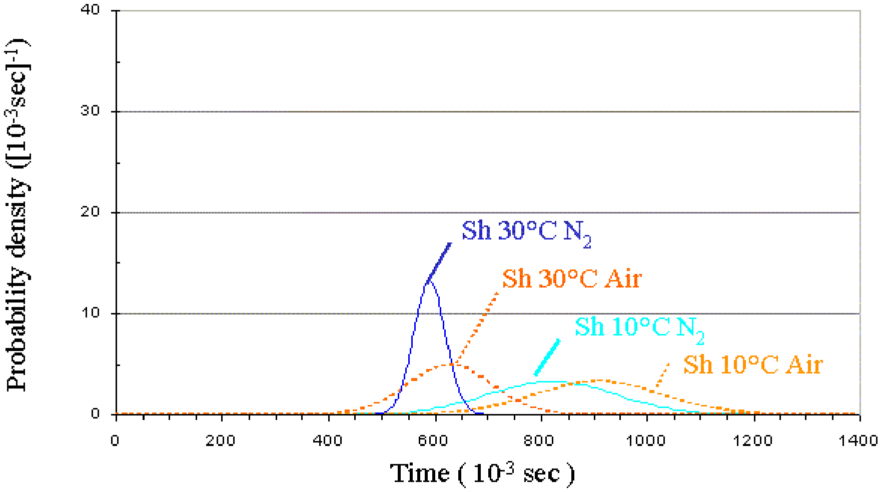


Figure 9 – Time to 2/3 Max Wetting Force; Alloy: Sn95,5 AG4 Cu0,5

These results clearly show that, in all considered cases and for the flux used in this experiment, the mean wetting times obtained with nitrogen are smaller than with air. In addition, the precision and repeatability of the results is noticeably better with nitrogen than with air. For the real application, this may suggest that for varying process parameters and solderability, nitrogen can forgive process flaws by expanding the process window.

Other conclusions indicate that in air, a reduced superheat of 10°C is insufficient to ensure good wetting conditions. Significantly better wetting values are obtained with Sn/Ag/Cu than with Sn/Ag. This is consistent with data published in.[20]

Conclusions

Lead-free soldering is technically possible and will probably be implemented for commercial ambitions before the real pressure of regulations exists. Nevertheless, the transition to lead-free soldering brings some significant issues that need to be properly addressed. Among them, the increase in the soldering temperature and the associated increase in oxidation which adversely impacts wetting, thermal resistance of SMDs, and the ability to clean.

Better wetting under nitrogen may even allow lead-free process temperatures to be close to current peak reflow temperatures if the thermal demand of the product is not a significant issue. This could eliminate certain component thermal shock issues altogether. The tests performed in this study bring quantitative data to support this opinion. Additionally, using nitrogen increases wetting while opening the process window.

The introduction of the lead-free debate has intensified the need for accurate and specific information on that topic. The various expert opinions on the use of nitrogen vary, but as lead-free specifications diminish the process window, the use of nitrogen might become essential despite the added cost. The need for a controlled atmosphere in lead-free soldering is greater than with traditional Sn/Pb alloys, but to what degree has yet to be determined.

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