Another chance for Tin-Copper as a Lead-free Solder

– KEITH SWEATMAN looks at Nihon Superior's Nickel-Modified Tin-Copper Eutectic

The Advantages of Tin-Copper

Since the Reid bill, presented to the US Congress in 1991, first alerted the electronics industry that it might have to give up the lead-containing solders on which it had always depended, the tin-copper eutectic (Sn-0.7Cu) was identified as one of the most likely candidates for the replacement of the industry standard, the tin-lead eutectic (nominally Sn-37Pb). The advantage of a eutectic alloy is that, like a pure metal, it should freeze isothermally (i.e. at a single temperature) and so the tin-copper eutectic was seen to have the potential to be an economical and environmentally friendly solder.

Toxicity is the primary concern driving the elimination of lead, and the fact that copper is generally regarded as non-toxic is a key advantage. Most of world's drinking water is conveyed through copper pipes.

The other driving force for the elimination of lead has been the need to safely and economically recycle scrapped electronic equipment, and copper has the advantage of not introducing another element into the system. Virtually all electronic circuitry already has a substantial amount of copper in the tracks of the printed circuit board (PCB) and the component terminations. The more elements there are to deal with, the more complex and expensive the recycling process becomes. Copper can be removed from tin, where it is likely to end up in the recycling of electronic circuitry, relatively easily and cheaply using simple kettle refining methods.

Another concern in the current climate of environmental sensitivity is the availability of resources, and the fact that there is sufficient copper available to meet any new requirement for lead-free solder, without the need for increased mining operations, is another significant advantage.

Having only two constituents the tin-copper system is relatively easy to manage in the solder baths required by some soldering processes such as dip, wave and selective soldering. Some alternatives with three and four elements are difficult to keep in balance, as each element has its own rate of reaction with the soldered substrates and with air.

A related benefit is that because it is already close to saturation at typical soldering temperatures the alloy has a relatively low dissolution rate for copper. In soldering processes such as dip, wave, selective soldering and rework, copper PCB tracks and component terminations are in contact with molten solder for several seconds. If the rate of copper dissolution is high the erosion can reduce the reliability of the assembled circuit.

Copper also happens to be the cheapest alloying addition, other than lead, that does not introduce other complications. Zinc, for example, can be, and is, used as an alloying addition to tin to make solders, but the reactivity of the resulting alloy imposes severe limitations on its application.

Tetsuro Nishimura, President of the Japanese solder maker Nihon Superior Co., Ltd.

Some encouragement for the belief that the tin-copper eutectic would be a viable lead-free solder was provided by the fact that it had already been fairly widely used as a replacement of tin-lead in the soldering of copper potable water reticulation systems.

Lowering the melting point of the solder is one of the objectives of the alloying addition, but the benefit of copper is relatively small, reducing the melting point only 5°C from that of tin (232°C) to 227°C. It was originally thought that it would be necessary to find a lead-free solder with a melting point as close as possible to that of the tin-lead eutectic it was replacing (183°C), but it has been found subsequently that the melting point is only one of the factors that determine the temperature that has to be used in a soldering process. In wave soldering, for example, the temperature range found to be necessary to get satisfactory results with the tin-silver-copper eutectic is 250-265°C, which is much the same as those used with the alloy based on the tin-copper eutectic described later in this article, despite the fact that the melting point of the tin-silver-copper eutectic is 10°C lower.

The Limitations of the Basic Tin-Copper Eutectic

Given the above advantages, it might be expected that the tin-copper eutectic would have quickly been estab-

lished as the preferred lead-free solder. Indeed it was included, with the tin-silver-copper eutectic, as one of the lead-free solders recommended by industry consortia in Europe (IDEALS) and America (NEMI) although, because of its higher melting point, only for wave soldering.

However, the results with SnCu0.7 were generally unacceptable, showing poor joint fillet shape and the high temperatures/times needed to effect soldering caused deterioration of the board materials.

At the temperatures that PCB components can tolerate, the alloy lacks the fluidity necessary in wave soldering for filling the plated- through holes of PCBs and the draining of excess solder from the "bridges" between adjacent joints, that otherwise create short circuits. And when it solidified the tin-0.7% copper alloy did not look like the eutectic it was supposed to be, but had a coarse cracked surface with the outline of primary _-tin dendrites apparent in the surface. In an attempt to get better fluidity the solder bath temperature was increased but, that resulted in damage to board materials. And even then the quality of the soldering was unsatisfactory.

In trials with the tin-copper eutectic in the Hot Air Solder Levelling (HASL) of PCBs, another major market for solder, similar problems were encountered and it was widely believed that the change to lead-free solder would mark the end of HASL as a PCB finish.

The consequence of these unfortunate experiences with the tin-copper eutectic was that it became widely

Diary

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accepted that the tin-silver-copper eutectic, or alloys close to that composition, would become the main replacement for tin-lead solder in the coming lead-free era. Tin-copper was relegated to some low technology dipping process where cost was the major consideration.

Turning the Tin-Copper Eutectic into a User-Friendly Solder

Given the potential advantages of the tin-copper eutectic there should have been a strong incentive to improve its properties. However, most of the electronics industry and its suppliers seemed content to accept that the tin-silver-copper eutectic would be the standard lead-free solder and concentrated on exploring variants within the constraints of the patents that already covered that system.

Tetsuro Nishimura, now President of the Japanese solder maker Nihon Superior Co., Ltd, was, however, convinced that it should be possible to improve the properties of tin-copper eutectic. As a metallurgist Tetsuro knew that there were examples of the properties of eutectics being improved by minor ternary additions to create industrially important alloys. He therefore began a systematic study of possible additions to the tin-copper eutectic.

One of the phases in the tin-copper eutectic is an intermetallic, Cu6Sn5, with some distinctly non-metallic characteristics, and the fact that the microstructure of the tin-copper eutectic contains a lot of primary _-tin, which in theory should not be present, suggests that solidification was being inhibited by difficulty in nucleating the intermetallic phase. If this could be improved, the result might be a much more user friendly solder. A search of known tin-based intermetallics revealed a nickel-tin intermetallic, Ni3Sn2, which has the same close packed hexagonal structure as Cu6Sn5 and almost the same lattice constants, suggesting that nickel atoms could be incorporated fairly easily into Cu6Sn5. The resulting disturbance to the crystal structure might facilitate the earlier nucleation necessary for the alloy to behave as a true eutectic.

This hypothesis was confirmed with the discovery that an addition of less than 0.1% nickel dramatically changed the appearance of the as-cast alloy. When in 1999 this modified alloy was tried in a wave soldering line, on which an unsuccessful attempt had been made to solder VCR boards with the unmodified tin-copper eutectic, the effect was dramatic. The incidence of bridges fell to a level comparable with that obtained with tin-lead solder, good soldering could be achieved at a temperature of 255°C and, as a bonus, the solder fillet was smooth and bright, disproving the widespread belief that lead-free solder joints are inevitably dull and grainy.

This development is protected by patents in Japan and most other developed countries

Sn-0.7Cu

Sn-0.7Cu+Ni

Effect of a controlled addition of nickel on the appearance of the tin-0.7% copper alloy

News of this alloy, offered to the market by Nihon Superior under the brand name "SN100C" quickly spread and by the end of 2004 there were more than 600 wave solder machines in more than 16 countries around the world using this alloy in commercial production with more machines being commissioned every month.

A similar dramatic difference was noted when in 2002 this nickel-modified tin-copper eutectic was tried in a vertical HASL machine. Good results could be obtained at a temperature of 265°C, only a little higher than had been used with tin-lead. Hole clearance and bridge elimination was good and the finish was smooth, bright and shiny. Similar results were obtained in subsequent trials on horizontal HASL lines and there are now more than 20 lines around the world using this process commercially with more lines being commissioned every month. An unexpected bonus is that the uniformity of the nickel-modified tin-copper eutectic HASL finish is better than typically obtainable with tin-lead solder. Given that the non-uniformity of the coating thickness

was one of the characteristics that was limiting the application of HASL to surface mount boards this improvement should open up new opportunities for HASL as a PCB finish.

Although initially developed for wave soldering, the nickel-modified tin-copper eutectic also offers promise in reflow soldering. The melting point is 10°C higher than that of the tin-silver-copper eutectic that is being widely promoted for this application, but in a good forced- convection oven the nickel- modified tin-copper alloy can be reflowed with a profile having a peak temperature of around 245°C. (A temperature often used for the reflow of the tin-silver-copper eutectic.) The same smooth bright fillets are obtained in reflow as in wave soldering and "SN100C" is being adopted by a number of companies who prefer to use the same alloy for both reflow and wave soldering.

Other Advantages of the Nickel-Modified Tin-Copper Eutectic as a Lead-free Solder

The performance reported above would by itself be sufficient to justify the widespread adoption of the nickel-modified tin-copper eutectic as a lead-free solder but there are other advantages that further strengthen the case.

In wave soldering, the economics of the process are greatly affected by dross losses and Nihon Superior's nickel-modified tin-copper eutectic has a low dross rate, typically around half that of tin-3.0% silver-0.5% copper.

The pot of wave soldering machines has been traditionally constructed of stainless steel which is resistant to erosion by tin-lead solder. All the high-tin lead-free solders are more aggressive towards stainless steel, but this seems to be increased by the presence of silver and is further increased by the phosphorus that is commonly added to tin-silver-copper alloys in an attempt to reduce drossing. The problem is being addressed by the use of solder baths constructed of titanium or of stainless steel with erosion-resistant coatings or surface treatments, but these add to the cost of the equipment. The nickel-modified tin-copper eutectic has been found to be much less aggressive towards stainless steel and many wave soldering machines using this alloy in production have only plain stainless steel solder baths.

Reference was made earlier to the erosion of copper tracks and component terminations by lead-free solders. As well as being a reliability issue the eroded copper contaminates the solder bath. If the rate of erosion is low enough, as it is with the nickel-modified tin-copper eutectic, the copper content can be kept within specification by the use of a top-up alloy with a lower copper content. However, if the rate of erosion is too great, that technique is not sufficient and part of the solder bath has to be removed periodically, often monthly, and replaced by copper-free solder to keep the composition within specification.

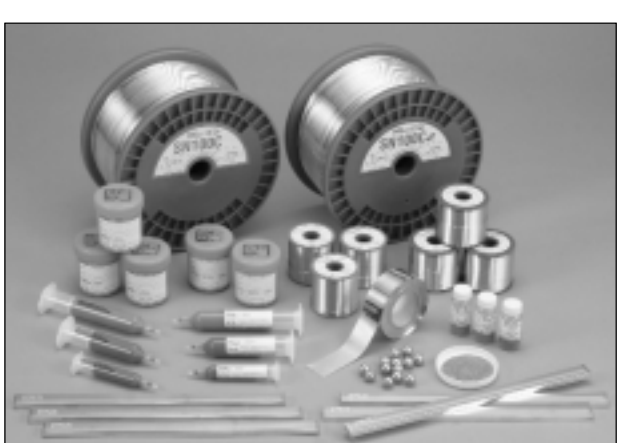
Solder consumption is also affected by the amount of solder in each joint. The high fluidity of the nickel-modified tin-copper eutectic usually results in the classical concave fillets. By contrast the tin-silver-copper alloy fillets tend to be convex and, over the millions of joints produced each year on a typical line, the extra solder can be significant.

The above factors all contribute to the cost of running a wave soldering line and comparisons on parallel lines over a year indicate that the cost of running a line with the nickel-modified tin-copper eutectic is typically at least half that of a similar line using the tin-3.0% silver-0.5%copper alloy.

The Market Choice

In the Japanese electronics industry, already about 40% converted to lead-free, Nihon Superior's "SN100C" has captured a substantial and growing share of the market. In Europe, which is still less than 10% converted, the alloy has captured an even larger share of the lead-free wave soldering market and virtually all of the lead-free HASL market. And it is in Europe that the nickel-modified tin-copper eutectic has established a position in the reflow market. The American market is still in the very early stages of conversion to lead-free but, despite the heavy promotion of the tin-silver-copper alloys there is strong interest in Nihon Superior's nickel-modified tin-copper eutectic which is already being reflected in adoption for commercial production. Usage in other Asian countries reflects the choices in the Japanese, European and American markets for which much of the production is done and many of the 600+ lines running the Nihon Superior alloy are located in countries such as China, Thailand, Malaysia and Indonesia.

The Nihon Superior development of a nickel modification process gives the tin-copper eutectic the chance of establishing its rightful place as one of the main solders for electronic assembly in the coming lead-free era.



Nihon Superior SN100C products