ADVANCES IN THE RESEARCH OF A SN/CU-NI COMPOSITE SOLDER PASTE FOR HIGH TEMPERATURE USE

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ABSTRACT

Continued research on a prototype paste, consisting of a composite mixture of SN100C (Sn-0.7Cu-0.05Ni+0.01Ge) commercial solder powder and Ames Lab's gas atomized Cu-10Ni, wt.%, powder is being completed to improve the reliability and survivability of PCB and SMT solder joints operating under extreme temperatures (< 500°C). The designed paste is predicted to be nearly 4,000 times less expensive than the currently available HTLF (high-temperature lead-free) solder Au-20Sn, wt.%, and able to withstand higher temperatures while still maintaining a standard commercial processing temperature of 250°C. The paste performs using liquid-phase diffusion bonding (LPDB) of the high-melting Cu-10Ni powders into the low-melting SN100C to form the room-temperature stable intermetallic compound (IMC) $(Cu,Ni)_6Sn_5$. The nickel addition to this high-temperature phase increases joint ductility by suppressing the transformation of the IMC into the brittle low-temperature phase that would otherwise occur. Current research includes exploring the effect that powder size has on void formation in the joint. Existing results suggest that this composite solder could be a superior "drop-in" replacement for the Pb-based high-temperature solders that will soon be eliminated by RoHS restrictions.

Key words: high-temperature solder, liquid-phase diffusion bonding, Pb-free solder, RoHS

INTRODUCTION

In June of 2016, a study was published by Oeko-Institut e.V. and Fraunhofer-Institut IZM, approved by Eunomia Research & Consulting, to provide "technical and scientific support" for the EU's assessment of renewal requests for extended expiry dates for high-temperature high-Pb solders. An extension of three years has been recommended by the consultants for continuation of RoHS Exemption 7(a) due to the fact that "the substitution and elimination of lead in LHMPS [lead-containing high melting point solders with at least 85% of lead content] generally is still scientifically and technically impracticable." In the report (Ref. 1), Freescale et al. discusses their issues with finding a suitable high-temperature lead-free (HTLF) alternative for their semiconductors because "lead is the unique element which has practical qualities of melting point, electrical conductivity, thermal conductivity, mechanical reliability and chemical stability with an ideal balance." Freescale et al. also say they plan to use "careful scrutiny" of any new LHMPS alternatives, "so as to maintain the required high quality of components in the process, to avoid failure in the field, so that such new technology can be adopted." Several other companies, including the Die Attach 5 or DA5 - a partnership between Bosch, Infineon, Freescale, STM, and NXP – support these claims as well.

The diagram in Figure 1 was provided to the RoHS consultants of Ref. 1 as a way of explaining their difficulty in acquiring a LHMPS alternative. Freescale et al. used the figure to explain the lack of availability of lead-free solders with a solidus temperature of 250 °C or greater. In the figure, the shaded blue box indicates the desired regime for LHMPS alternatives.

One of the most readily-known applications of electronic systems being subjected to increased temperature is involved with downhole oil-drilling. With the average geothermal gradient at 25°C per kilometer of depth, the deeper the oil industries drill into the earth, the more resistant solder must become to higher temperatures[2]. Many other industries also require high temperature electronics, with some seeking solders operable up to 800°C (e.g. Freescale[1]). Examples of these industries include the automotive[2], aerospace/avionics[2], acoustic[1], and high-strength magnet[1] industries. Movements such as the "more electrical aircraft", or MEA, place control systems closer to engines and actuators of vehicles, exposing vulnerable integrated circuitry to high heat, and thus, failure[2]. In addition, these newer electrically-powered vehicle systems are powered by very high densities of energy, resulting in extensive Joule heating of their integrated circuitry[2]. Yet another industry affected by RoHS Exemption 7(a) is the producers of large speaker systems, which require close proximity of solder joints to the high temperatures of their magnetic coils in order to prevent vibrational fatigue of each speaker's fragile wires. These industries and more are patiently awaiting the announcement of a practical "drop-in" Pb-free solder replacement.

Figure 1: Relationship of several solder types and their melting temperatures[1]

Despite a lack of a "drop-in" replacement thus far, there are a few options for the purpose of high-temperature circuitry use that are currently available commercially. Examples of these products include: Senju's SAC305/Cu (RAM) powder paste blend[3], Indium Corp's Gold/20Sn and BiAgX alloys[4], Ormet's Sn-Cu/Bi blend[5], and AIM's M8 Solder Paste[6]. Senju Metal Industry Co.'s (SMIC) solder has a processing temperature of ~ 245°C, an operating temperature of ~ 250°C or higher, and contains Sn, Ag, and Cu.[3] Indium Corp's Au-20Sn has a processing temperature of ~330°C, can be used at ~ 250°C, and contains a large amount of Au with Sn[4]. Indium Corp's BiAgX solder alloy has a processing temperature of ~ 325°C, an operating temperature of 262°C, and contains Bi, Ag, and an undisclosed material[4]. Ormet Circuits Inc.'s Sn-Cu/Bi alloy has a processing temperature of ~170°C, an operating temperature of ~260°C, and contains Sn, Cu, and Bi[5]. Notice that many of the solders commercialized so far for this purpose tend to have a processing temperature above their post-processing operating capabilities. In addition, there has been a trend in these high-temperature solders so far to include bismuth, mostly for strengthening purposes. However, bismuth has posed certain limitations on its high-temperature capabilities with its tendency to void at phase boundaries and its low melting temperature (271°C)[7,8].

In this document, a patent-pending composite solder paste designed by the collaboration of Ames Lab and Nihon Superior will be discussed for its potential use in HTLF operations. On the diagram of Figure 1, this prototype composite solder paste falls into the category of a "Sn system + high melting temperature type metal". It has been formulated according to the composition of a commercial paste, SN100C, sold by Nihon Superior. With its application of liquid-phase diffusion bonding (LPDB), the results of this study will explore the potential for a literal "drop-in" replacement for high-lead solders, while also increasing the capable operable temperatures to 450°C and beyond.

EXPERIMENTAL PROCEDURE

The Ames composite solder paste prototype is formed by blending Ames Lab's gas-atomized Cu-10Ni (wt. %) powder and Nihon Superior's commercial SN100C (Sn-0.7Cu-0.05Ni+0.01Ge, wt.%) powder. The blend is then compounded with a typical flux and solvent to form a solder paste. In this experiment, the size of the SN100C powder particles was tested for its effect on solder joint porosity of the composite paste. Table 1 shows the different composite paste powder blends tested.

Table 1: Paste Blend Combinations Tested

	Cu-10Ni Powder		SN100C Powder	
Blend	Size	Content	Size	Content
A	20-38 μm	13 vol%	20-38 μm	87 vol%
B	20-38 μm	13 vol%	5-15 μm	87 vol%

Each blend from Table 1 was spread onto a copper block to form a single-sided solder paste joint (Fig. 2). Figure 3 contains the set-up of the solder joint reflow on an electrically-powered hot plate. A stainless steel plate was placed between the stainless steel clamp holding the copper block and the hot plate surface to act as a heat sink in order to maintain a consistent hot plate temperature for reflow. A thermocouple was also clamped to the setup to monitor the temperature of the solder during the experimental runs. Figure 4 shows the reflow profile for each run with a peak reflow temperature of 250°C held for one minute. Each blend was tested twice for consistency.

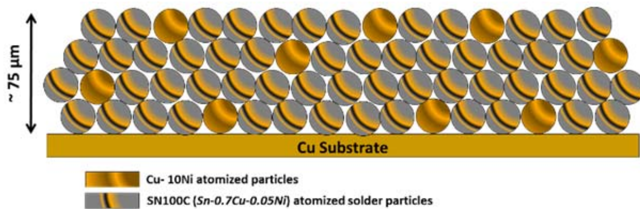

Figure 2: Ames composite solder paste concept, showing the blend of two alloys

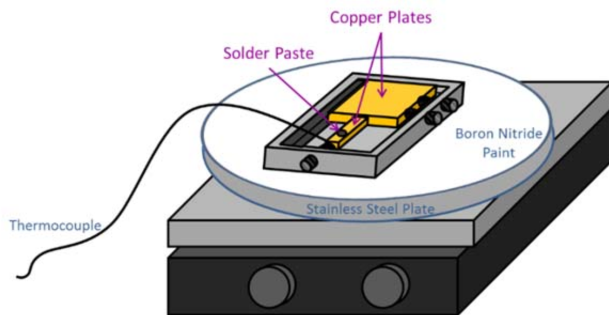

Figure 3: Experimental setup of copper blocks and paste on a hot plate for single-sided joint

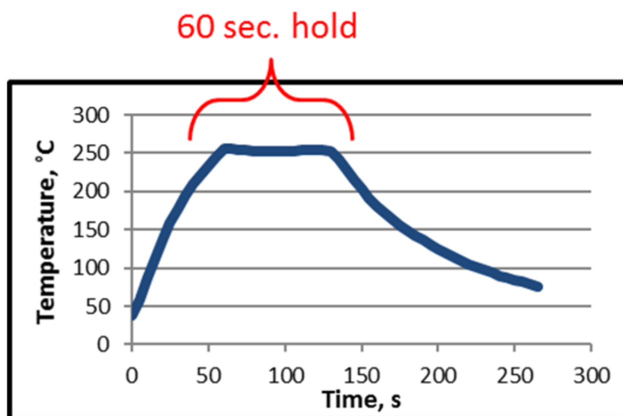

Figure 4: Reflow profile applied to each paste blend combination on the hot plate setup

RESULTS

The following images in Figures 5 and 6 are short segments of the cross-sections of the resulting single-sided solder paste joints viewed under a scanning electron microscope (SEM) in backscatter mode. In the images, the color red highlights any voids or porosity in the joint. The cross-section of Paste Blend B clearly seems to have lower porosity than Paste Blend A. Using quantitative metallography of at least 15 SEM images of the resulting joint from each reflow run, it was found that the images of Paste Blend A contain an average of 3.73 area % porosity and the images of Paste Blend B contain an average of 0.87 area % porosity.

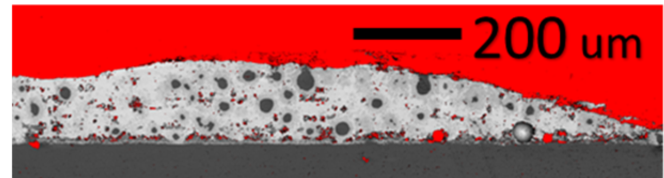

Figure 5: Cross-section of Paste Blend A

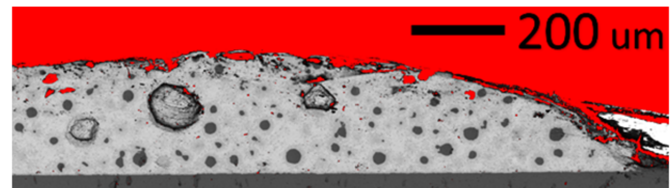

Figure 6: Cross-section of Paste Blend B

A closer view of the solder interfaces (Figs. 7 and 8) also revealed a much smoother substrate bond when using the Type 6 powder than when using the Type 4 powder. In addition, the intermetallic compound or IMC $(Cu, Ni)_6Sn_5$ (the light gray phase in Figures 7 and 8) seems much more dispersed in the Sn matrix phase for the Type 6 powder.

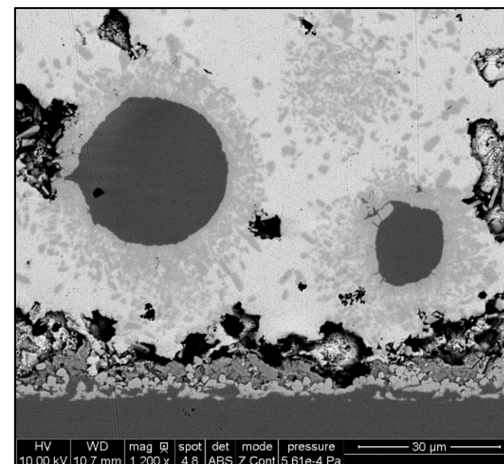

Figure 7: Interface of Paste Blend A - containing Type 4 SN100C

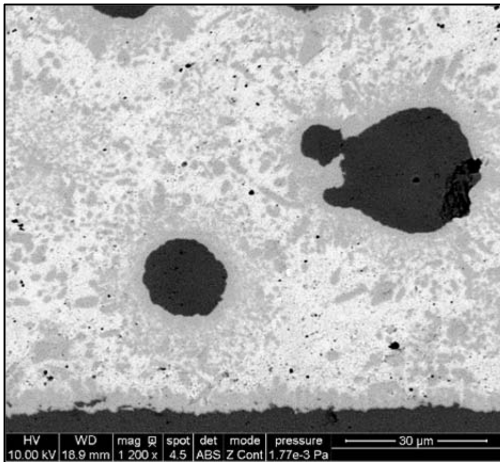

Figure 8: Interface of Paste Blend B - containing Type 6 SN100C

When a double-sided solder paste joint was created using Paste Blend B (Fig. 9), the interface remained connected and smooth. The porosity with the double-sided joint also remained low, averaging porosity in less than 1% of the image area.

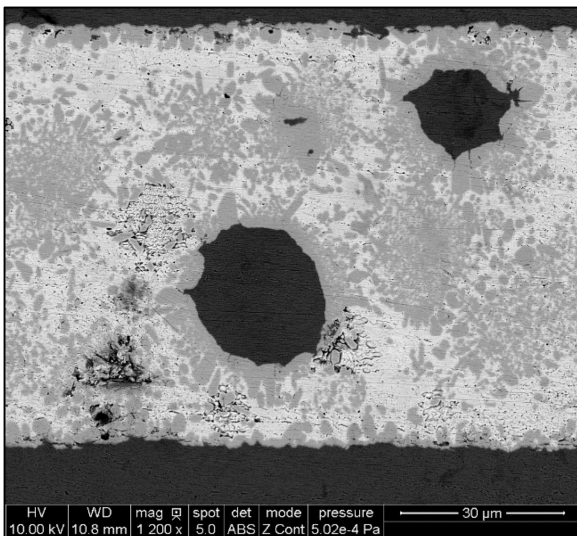

Figure 9: Cross-section of a double-sided joint using Paste Blend B (Type 6)

Energy dispersive spectroscopy (EDS) was performed on the joint in Figure 9 to determine the consistency of the phase compositions with previous values from the composite paste. The compositions of the filler phase, the residual Sn, and the IMC surrounding the filler phase all remained consistent. Previously, the IMC phase lining the substrate lacked the desired Ni content to inhibit a brittle and allotropic phase transformation. However, with the Type 6 powder paste blend, the Ni was able to diffuse into this area, as desired, to create the same desired ductile IMC that surrounds the filler phase in Figure 9. The phases, their compositions, and their identities in each micrograph are listed in Table 2.

Table 2: Average EDS results of phase compositions

Weight %	Sn	Cu	Ni
Filler Phase (dark gray)	0.44	88.1	11.5
Residual Sn (white)	99.6	0.39	0.01
IMC (intermediate gray)	55.9	40.5	3.62
Substrate	0.32	99.7	0

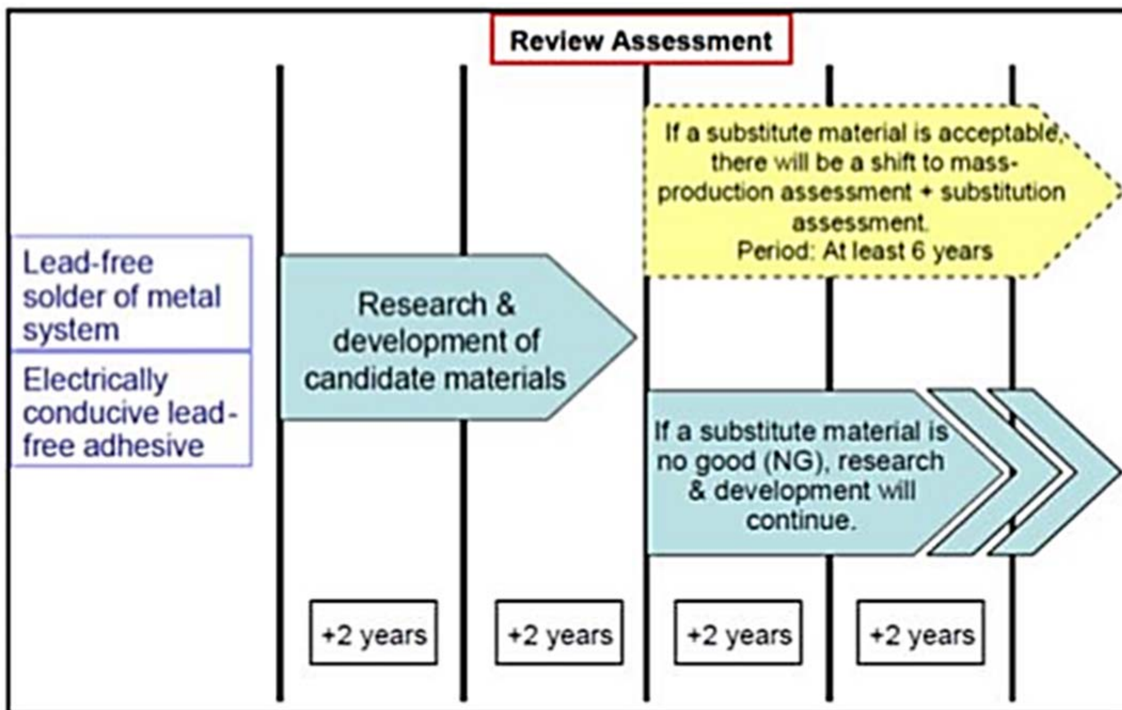

Figure 10: Diagram depicting the expected time for a LHMPS alternative to become commercially available[1]

DISCUSSION

With the likely extension of RoHS Exemption 7(a), companies will have a bit of extra time to determine a way to remove lead from their high-temperature electronic products[1]. Despite most requests for an extension of five years, the RoHS consultants of Ref. 1 have recommended a three-year extension due to their opinion that a five-year extension may "not be in line with the stipulations of Article 5(1)(a)."[1] In other words, the consultants believe that a suitable replacement for LHMPS may be available within the next three years, so granting five years would be excessive and would not further the progress of the EU's RoHS directive.

Freescale/NXP et al. provided the diagram in Figure 10 to help explain their reasoning behind a desired five-year extension to Exemption 7(a)[1]. Unlike the consultants, they believe it could take over six years before a suitable replacement can be found on the market[1]. However, the Ames composite paste design has the potential to greatly reduce this time period. With its patent already pending, the Ames composite paste is a step ahead. The composite paste is designed for rapid insertion into normal PCB assemblies. Since the overarching concept of the paste is to simply modify an existing commercial solder paste (SN100C) with the addition of a small amount of Cu-Ni powder, the process of accommodating the switch to this paste would be nearly negligible. In addition, very similar processing parameters of those previously used in industry could still be implemented successfully.

The current research seeks to combat known defects, specifically porosity and voiding, found in joints formed with similar composite solder pastes[9]. From the results of the current experiments, the Ames composite paste blend with the varying sizes of powders (Paste Blend B) was found to provide a considerable difference in the amount of joint porosity present after reflow. The reduction of porosity with the smaller SN100C powder size most likely resulted from a maximized surface area of the Sn alloy, which increased the melting and wetting rates of the solder powders together. The smaller powders of the low-melting metal alloy allowed for better penetration of tight spaces between the larger Cu-10Ni powders, similarly effecting the wetting of the substrate. By being able to melt and reach the surfaces of the filler powders quicker, the tin alloy could completely engulf the filler powders before the gaseous flux could become trapped by the isothermal solidification of the newly-formed bonding IMC by liquid-phase diffusion bonding (LPDB)[10]. When the flux does become trapped, especially with a larger ratio of Cu-Ni:Sn alloy, flux residue is left in the joint, forming small spherical gaseous voids[10].

In addition to the decrease in joint porosity, the smaller powders sizes provided a few extra benefits. For example, the spread of the intermetallic compound seems more dispersed in the joint made with the smaller powders (Fig. 5 vs. Fig. 6). This quicker spread of the IMC should aid in the eventual goal of expanding the IMC across the entire joint interface. When the entire joint consists of a network of the nickel-modified IMC with possibly some residual pockets of Cu-Ni, the strength and ductility of the joint should improve. The composite solder paste joint will then take on the properties of a $(Cu,Ni)_6Sn_5$ matrix (T_m=525°C[10])

containing pockets of a stronger and more highly conductive Cu-Ni phase.

The addition of nickel to the copper powders through pre-alloying before gas atomization provides the stability needed for the hexagonal form of Cu_6Sn_5 to maintain its crystal structure, rather than transform into the more brittle monoclinic form of the phase upon cooling from high temperatures[11]. Therefore, the discovery of the Ni-modified Cu_6Sn_5 at the substrate/solder interface was also an added benefit to using smaller powders, as previous experiments with the larger SN100C powders resulted in a lack of Ni in this same area. This pre-alloying of the filler powders is the key difference between the Ames composite solder paste design and that of others, placing nickel at every area where a bond will be created via IMC and preventing the formation of un-modified Cu_6Sn_5 (which will cause joint brittleness when cooled) and other undesired IMCs such as Ni_3Sn_4 (a brittle and less conductive phase)[10].

CONCLUSION

From this experiment, two blends of Cu-10Ni composite pastes with varying Sn-alloy powder sizes were tested for their porosity. On average, the paste containing the smaller SN100C powder size (Type 6, 5-15 μm) resulted in solder joints with less porosity. The smaller powder size also helped create a more complete bond with the joint's substrate. The compositions of the phases were all as desired, including the previously unmodified (with Ni) IMC phase lining the Cu substrate.

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