A Study on Copper Dissolution in Liquid Lead Free Solders under Static and Dynamic Conditions

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Abstract
During lead-free wave soldering or rework operation for through hole components, high rate copper dissolution may occur to printed wiring boards. It is widely believed that Sn-Ag-Cu (SAC) lead-free alloys, the currently most popular alloys in the electronic industry, have more than twice the rate of copper dissolution compared to the Sn-Pb eutectic (63Sn-37Pb) solder alloy. In this study, copper dissolution was evaluated with four lead-free alloys (SAC305, K100LD, SC995e, SN100C) at temperatures 245, 260, 280 and 300°C with time duration of 20, 60, 300 and 600 seconds. Results show that K100LD and SN100C have the lowest rate of copper dissolution. A unique dynamic copper dissolution testing was also performed to investigate effects of liquid solder dynamic flow speed, time and temperature on dissolution kinetics. These dynamic tests involved three different sample motion speeds of 2, 5 and 15 ft/min at temperatures of 245, 260 and 280°C with time duration of 20, 60 and 300 seconds. Our unique test setup clearly demonstrated that alloy selection and process window definition are critical for lead-free soldering for through hole component assembly and repair operation.

Introduction
Lead-free alloys, based on Sn-Ag-Cu (SAC) ternary near eutectic composition, such as SAC 305 and 405, have become the most popular alloys in the electronic industry for surface mount technology (SMT) and plated through holes (PTH's) assembly processes. According to the 2007 European Lead-free Soldering Network Report, SAC alloys have been used in 59% of these applications by Q2 of 2007.[1] As most industries have successfully transferred to lead-free design and assembly for their products without much unpleasant glitch, some remaining issues, such as tin whiskering, lead-free solder joint rigidity, and high rate copper dissolution, still confront with many companies and industries, who take reliability of their products and service as their highest priority.[2]

Erosion of copper pads due to copper dissolution is a common phenomenon during soldering. Industry has accumulated a great amount of knowledge on the copper trace thickness requirements and wave-soldering processes with Sn-Pb eutectic solder alloys. However, many recent publications indicate that SAC alloys are characterized with more than twice the rate of copper dissolution when compared with the Sn-37Pb solder alloy.[3 4 5 6 7] Copper dissolution rates depend not only on solder alloy composition, but also on time, temperature and dynamic conditions of molten solder during wave soldering. In general, the data show that SAC 305 and similar lead-free alloys, based on Sn-Ag-Cu ternary eutectic composition, consistently have a significantly higher copper dissolution during wave soldering and rework for PTH components.

In recent years, industry and academia have turned for help with additional alloying elements, such as Ni, Co, Fe, rare earth elements, to reduce the copper dissolution rates in molten solder with some limited success. In this study, we investigated four lead-free alloys (SAC305, K100LD, SC995e, SN100C) at elevated temperatures for time period ranging from 20 seconds up to 10 minutes. Copper dissolution kinetics in these four molten solders were measured both at static and dynamic conditions. The purpose of this evaluation was to gather experimental data for better lead-free wave soldering process window development and qualification of wave solder alloys to substitute SAC or Sn-Cu alloys in wave-soldering processes. With the knowledge of copper dissolution kinetics under static and dynamic conditions, we would be able to establish guideline for solder alloy composition optimization and criteria for selection of copper-erosion resistant lead-free alloys for wave and rework soldering processes.

Experimental Materials and Procedures

Copper Dissolution at Static Conditions
Four Pb-free solder alloys and one SnPb eutectic solder alloy were selected for the copper dissolution evaluation tests: SAC 305 (Sn96.5Ag3.0Cu0.5), K100LD, SC995e, SN100C, Sn/37Pb. K100LD is a low-cost (silver-free) lead-free alloy developed by Kester, containing tin and copper with the inclusion of metallic dopants to control the grain structure and the copper dissolution. SC995e (Cobalt 995, Sn99.5/Cu0.5/Co) lead-free solder alloy is manufactured from electrolytically processed tin and other elements, with melting point at 228°C and a recommended operating temperature range of 260-270°C.

SN100C is a lead-free solder alloy developed by Nihon Superior, mainly comprised of tin, copper, and a small amount of nickel**.** It basically is a Sn-Cu eutectic based lead-free alloy without silver or bismuth.

Oxygen free copper coupons with size of 25.4 x 12.7 x 0.546 (mm) (1" x 0.5" x 0.0215") were used as the test samples. Solder alloys were melted in five solder pots. Volume of solder in each pot was about 393 cm^3 (24 in^3), which is equal to a mass of 2,012 gram (7.86 lb) and 1,689 gram (6.60 lb) for SnPb and Pb-free alloys respectively. The reason to choose such large volume solder pots is to minimize the effect of solder alloy composition changes due to the copper dissolution of test copper coupons. Tests were conducted at four different temperatures, 245°C, 260 °C, 280 °C, and 300 °C for Pb-free alloys and at 245 °C for SnPb eutectic alloy. Immersion of copper coupons was performed at four time durations of 20, 60, 300 and 600 sec. Schematic test assembly is presented in the Figure 1.

Before tests, copper coupons were cleaned in the ultra-sonic bath with acetone, then with isopropanol (5 min. each). Each test group was consisted of three copper coupons to minimize measurements and test variation (measurement errors) such as sample setup, temperature of solder alloy and immersion speed. Samples were immersed up to 2/3 of the coupons length. Top side of coupons was covered by Kapton tape to protect copper surface, which would be used as a reference during copper dissolution evaluation (see Figure 2). A magnetic clamp was used to hold the samples. After clamping, samples were dipped in the Qualitek 735-11 water soluble flux for 10 seconds then allowed to dry near the molten solder. Average temperature drift of the molten solder alloys was in the range of ±2°C. Before samples were submerged into the molten solder, they were placed directly above the solder, allowing the heat from the solder to further dry and activate the flux. While this was occurring, the oxide layer was completely removed from the solder (scrapped off using a spatula). Once the oxide layer was removed, samples were submerged according to specific test time duration. After test completion, samples were removed from solder pots, quenched in the water bath, mounted in epoxy compound and then ground approximately 1/16 inch deep. Polished samples were evaluated using 2D optical stage under magnification of 200X. Three measurements were taken at fixed locations on soldered side and at random locations on unsoldered side. The soldered side measurements were taken at 2.5mm, 4mm, and 5mm from sample's edge. The unsoldered side measurements were taken at random locations. Copper dissolution was calculated as a difference in copper thickness from soldered and unsoldered side.

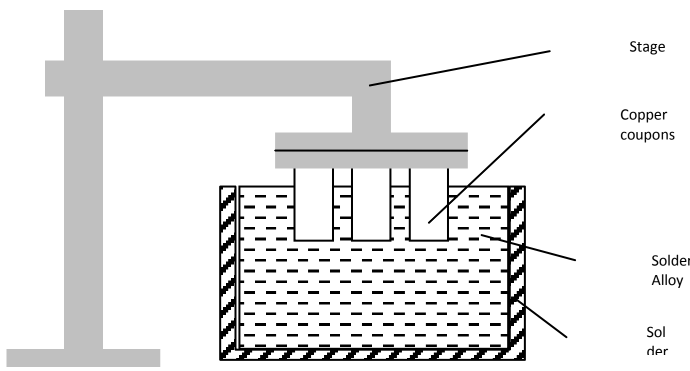

Figure 1 Experimental setup of the copper dissolution experiments.

Figure 2 Copper test coupons, clamp set and copper dissolution test in progress.

Copper Dissolution under Dynamic Conditions

Evaluation of copper dissolution under dynamic conditions was conducted using the Pb-free solder alloy K100LD, with the SnPb eutectic as baseline. Dynamic flow test conditions were achieved by circular movement of copper coupons in the solder pod with controlled speed. Schematic test assembly is presented in the Figure 3. Tests were conducted at four different temperatures, 245 ^{o}C, 260 ^{o}C, and 280^{o}C. Immersion of copper coupons was performed at three time durations of 20, 60, and 300 sec. Three different motion speeds were applied: 4, 8 and 16 ft/min. Copper test coupons were prepared using the same procedures described for the static study. Difference was only related to the protection of the back side of coupons, which were protected by Kapton tape to avoid effect of different dynamic conditions at front and back sides of the coupon. The samples were submerged according to specific test time duration at the specific speed of motion.

The copper dissolution rates of these lead-free alloys are then compared in static and dynamic conditions to find the best candidate solder alloys, with the slowest copper-dissolution kinetics in variation manufacturing conditions.

Experimental Results and Discussions

An optical sample after dissolution testing is shown in Figure 4. It is clear that the portion of sample with direct contact to molten solder loss quite an amount of copper during the test. The unsoldered portion (protected by the tape and from immersion into the liquid solder) has original smooth surface and thickness. Figure 5 provides even more dramatic illustration of how severe the copper dissolution can be in molten solder at 280°C for 10 minutes, particularly for SAC305 (Sn-Ag-Cu) alloy, which loss 1/3 of the original mass. The advantage in terms of dissolution rates for the K100LN over SAC305 is clearly demonstrated in Figure 5. In addition, it can be seen that the copper dissolution front surface is more curved for SAC305 than for Sn-Cu based alloy K100LN, indicating the preferred location or orientation of fast dissolution kinetics for Sn-Ag-Cu alloy in general.

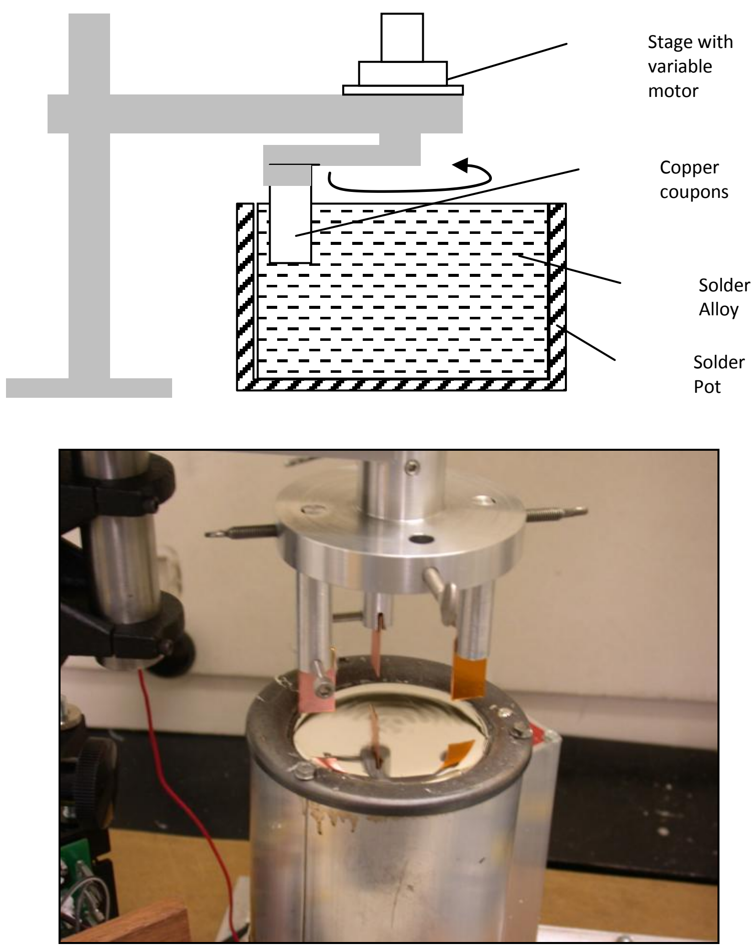

Figure 3. Experimental setup of the dynamic copper dissolution experiments.

Figures 6-9 present test results of copper dissolution for SAC 305, SC995e, K100LD, SN100C and Sn/37Pb alloys at 245°C, 260°C, 280°C and 300^{o}C. Comparison of test results at temperature 245^{o}C, presented in Figure 6, show that SAC 305 and SC995e alloys are characterized with much higher rates of copper dissolution.

K100LD and SN100C alloys show much lower rates of copper dissolution, equivalent to the dissolution rates of SnPb eutectic alloy at this temperature. Recommended wave soldering temperature range for K100LD and SN100C alloys is 260-270 ^{o}C [8]. Analyzing test results at temperatures from 260 to 300^{o}C, as shown in Figures 7-9, it can be seen that both K100LD and SN100C still have significant advanatge over the SAC305 and SC995e. Figure compares the copper dissolution rates vs. temeperatures for these alloys. It is clear that significant increase in the rate of copper dissolution with higher temperature happens to all these alloys (note, SnPb alloy was tested only at 245^{o}C as a reference point). Compared the copper dissolution rate for Sn-Pb eutectic alloys at 245°C, the best alloys, K100LD and SN100C still dissolve 1.8 and 2.7 times more copper at 260°C and 280^{o}C respectively.

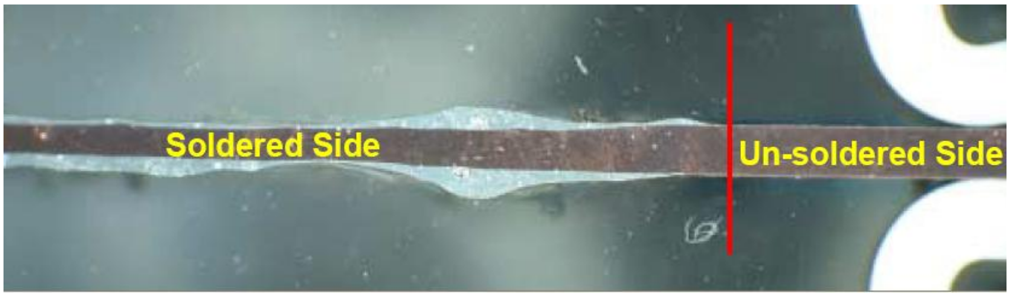

Figure 4. Test coupon after copper dissolution test.

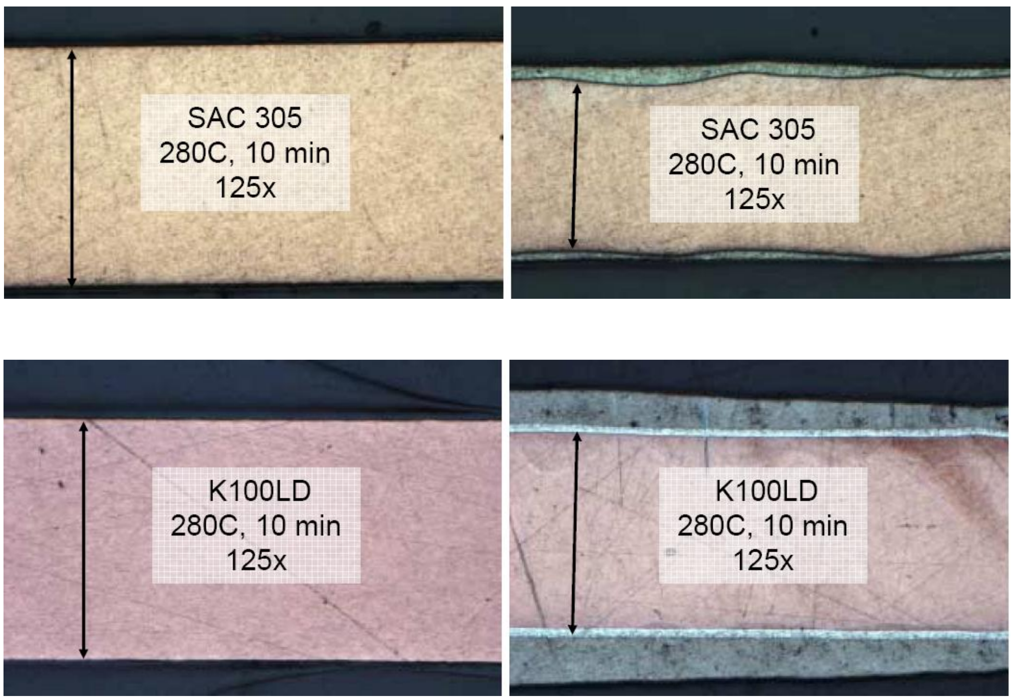

Figure 5. Comparison of unsoldered and soldered parts of test samples after copper dissolution tests in SAC305 and K100LD solder alloys.

Averaged rates of copper dissolution calculated for time durations of 100 to 600 seconds are presented in Figure 10 and in Table 1. It can be seen that at 245^{o}C, K100LD and SN100C have copper dissolution rates of 0.8 and 0.73 relatively to the Sn-Pb solder. On the other hand, SAC 305 and SC995e have relative rates of 1.98 and 1.64 respectively. Increasing the temperature to the recommended range of 260-270°C for lead-free wave soldering, increases the relative rates of copper dissolution to 1.3-2.0 for these two alloys, K100LD and SN100C. It is apparent that SAC305 can have up to 7 times the copper dissolution rate at 300 °C compared with a normal Sn-Pb eutectic wave soldering (usually at 245°C to 250°C)

From these results, it is clear that the two Pb-free alloys, K100LD and SN100C, can be recommended for Pb-free wave soldering process with a great improvement on reduction of copper erosion on the PCBs. For mission critical applications, selection of a good Pb-free alloy for wave soldering with a relatively low copper dissolution rate would increase the chance to form sound solder joints. However, a real wave soldering process is characterized with the dynamic flow of liquid solder alloy and, as a result, could have significantly higher rates of copper dissolution when compared with static conditions.

Table 1. Relative rate of copper dissolution compared with rate of SnPb eutectic alloy at 245°C.

Temperature °C	Relative rate of copper dissolution for Pb-Free alloys			
	K100LD	SN100C	SAC305	SC995e
245	0.80	0.73	1.98	1.64
260	1.50	1.30	2.30	2.10
280	2.23	2.13	4.40	3.33
300	3.33	3.20	7.00	4.50

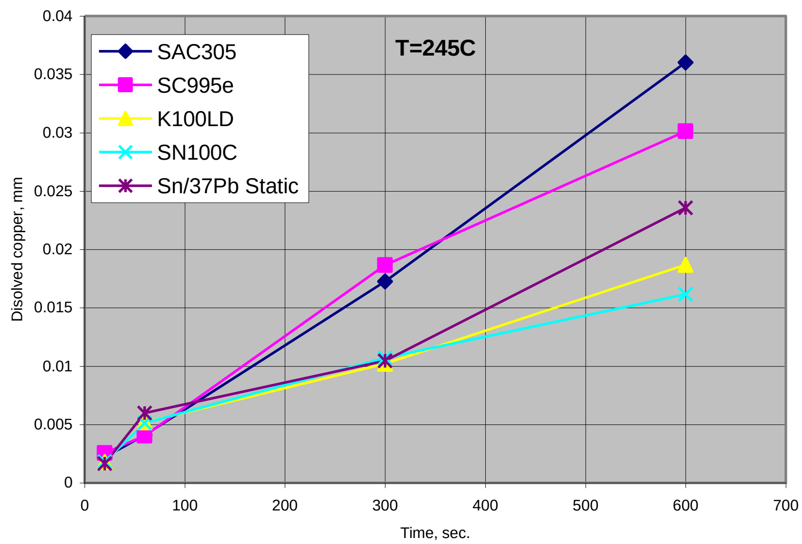

Figure 6. Comparison of copper dissolution test results conducted at 245°C.

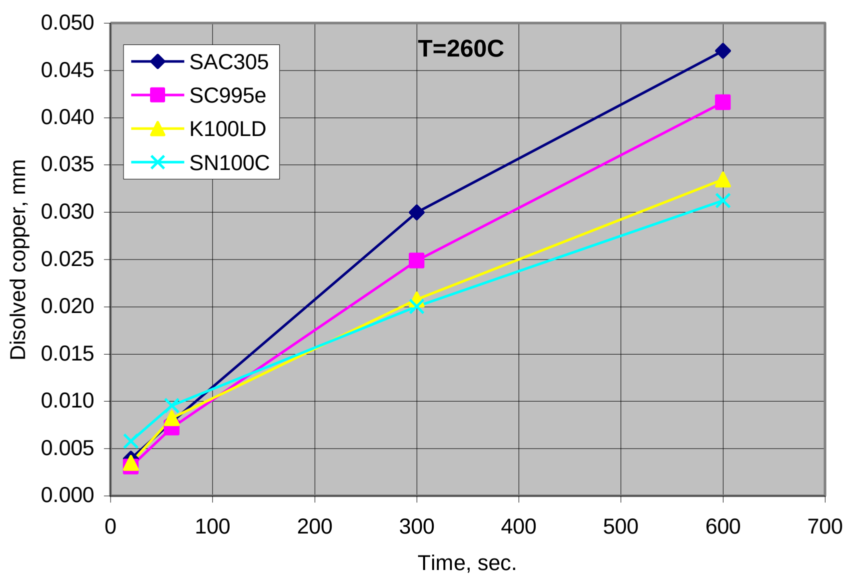

Figure 7. Comparison of copper dissolution test results conducted at 260°C.

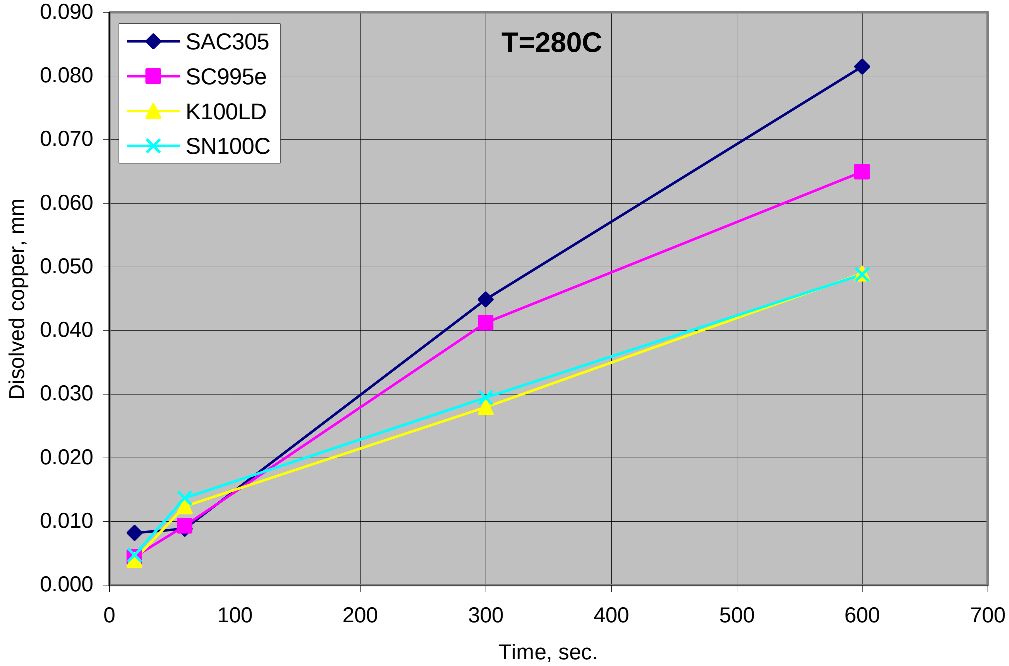

Figure 8. Comparison of copper dissolution test results conducted at 280°C.

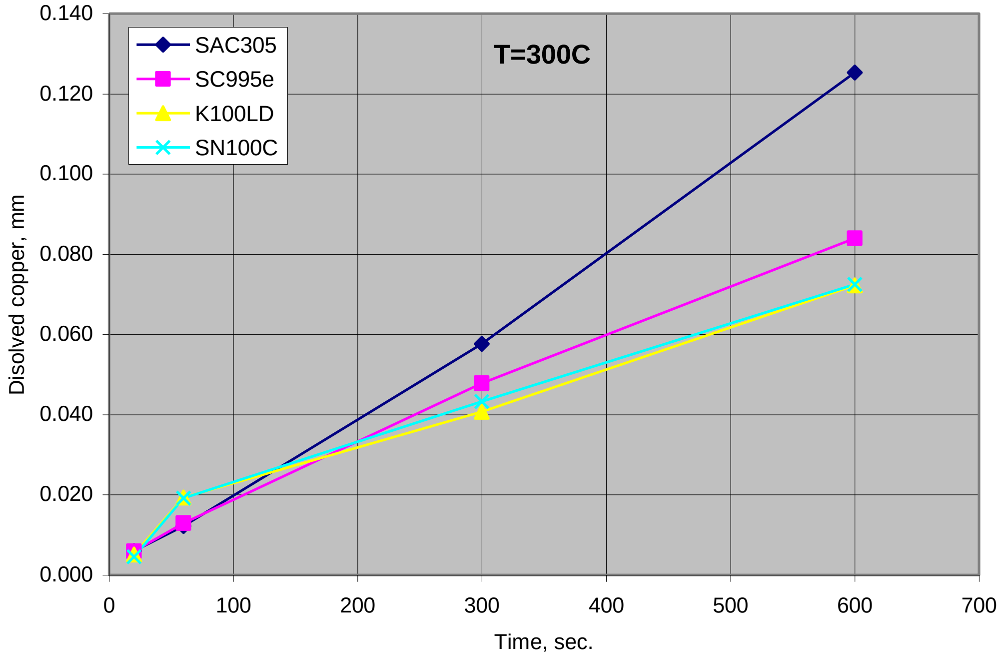

Figure 9. Comparison of copper dissolution test results conducted at 300°C.

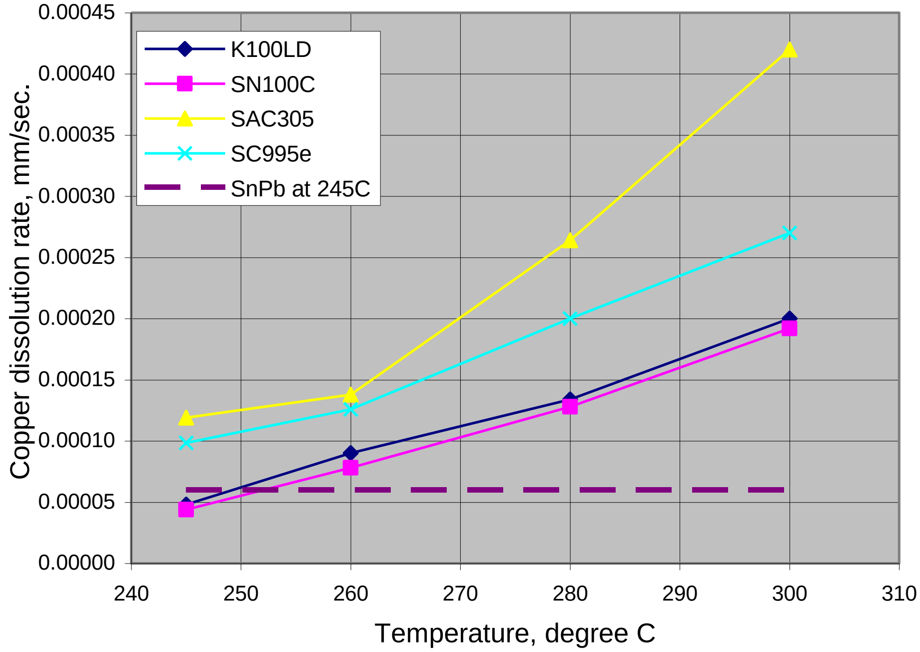

Figure 10. Copper dissolution rates for Pb-free alloys. Average Copper dissolution Rates for 100-600 sec duration.

As an example to examine the dynamic condition effect on the copper dissolution rate, the alloy K100LD was subjected more tests under dynamic conditions. Comparison of copper dissolution behavior as function of time for static and dynamic conditions and at speeds of 2, 5 and 12 ft/min (0.61, 1.52, and 3.66 m/min) at temperatures 245, 260 and 280^{o}C are presented in Figures 11 to 13. It is clear there is a significant increase in the dissolution rate under dynamic conditions. The calculated rates of cupper dissolution based on obtained data are presented in Figure 14 for alloy K100LD at different temperatures and dynamic speed. Again, here it is even more clear that that flow speed of liquid solder has significant effect on rate of cupper dissolution, indicating the dissolution under static condition may not be enough to establish an alloy selection criteria. With a moderate motion speed of 2 ft/min, the copper dissolution rate, compared with static conditions, is up to 4.5 times in average at all tested temperatures. Increasing speed of solder flow up to 12 ft/min would further increase dissolution rate up to 10 folds. It should be pointed out that the temperature effect on copper dissolution rate is almost constant from 245^{o}C to 280^{o}C, which is equal 2.4 times, regardless static and dynamic conditions (different motion speeds).

In real wave soldering process, the speed of solder flow varies from 3 up to 8 ft/min. It can be seen that for most recommended temperature of wave soldering process at 250-260^{o}C, copper dissolution rate is in the range of 0.0002~0.0006 mm/sec. The experimental data of copper dissolution during dynamic conditions can be used for determining wave soldering process window to select optimum temperature, speed of solder flow and time of contact with molten solder, to avoid issues associated with copper dissolution during lead free wave soldering. In addition, as demonstrated in previous section, a good copper-erosion resistant lead-free alloy, such as K100LD and SN100C at a moderately high temperature, not too much higher than 250^{o}C, with help of a favorable flux system is capable to perform as well as the traditional Sn-Pb eutectic alloy in wave soldering.

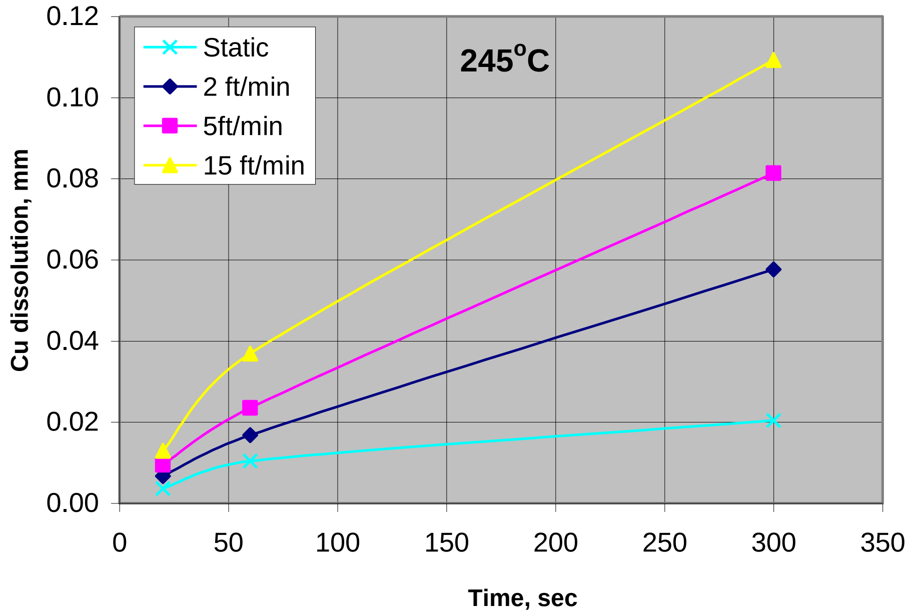

Figure 11. Copper dissolution at dynamic conditions as function of time at 245°C for K100LD alloy.

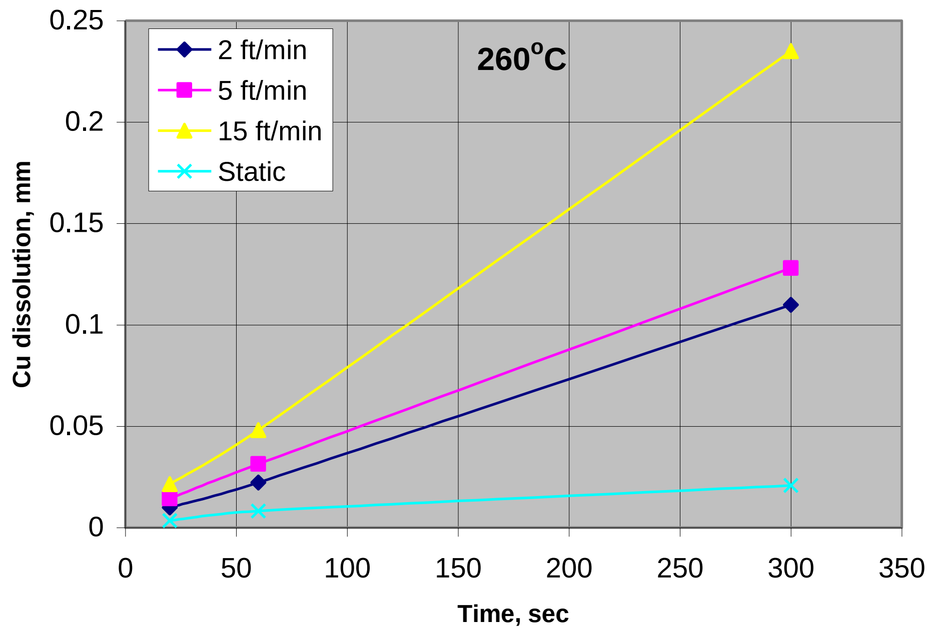

Figure 12. Copper dissolution at dynamic conditions as function of time at 260°C K100LD alloy.

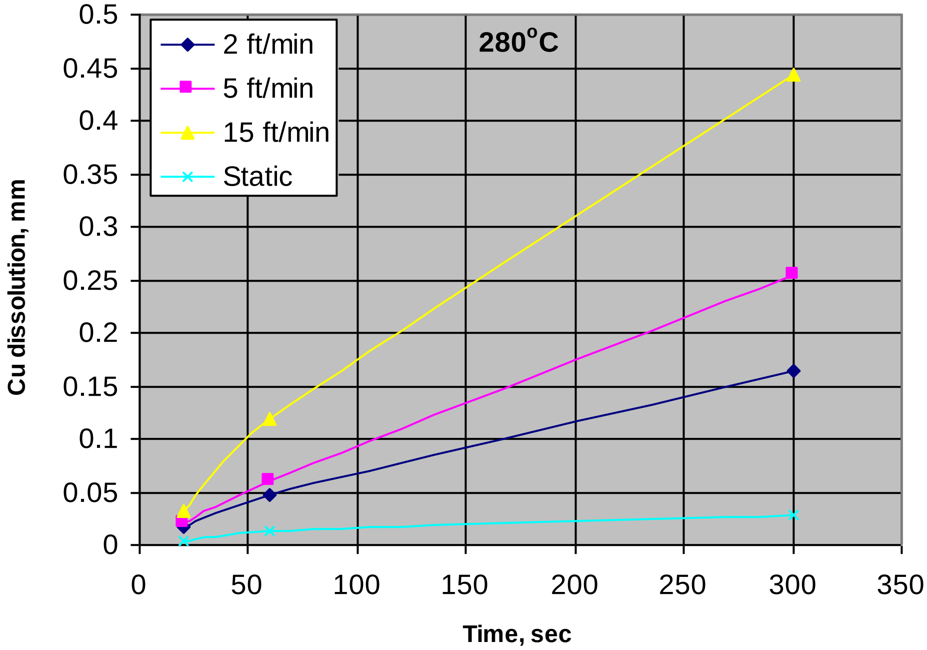

Figure 13. Copper dissolution at dynamic conditions as function of time at 280°C K100LD alloy.

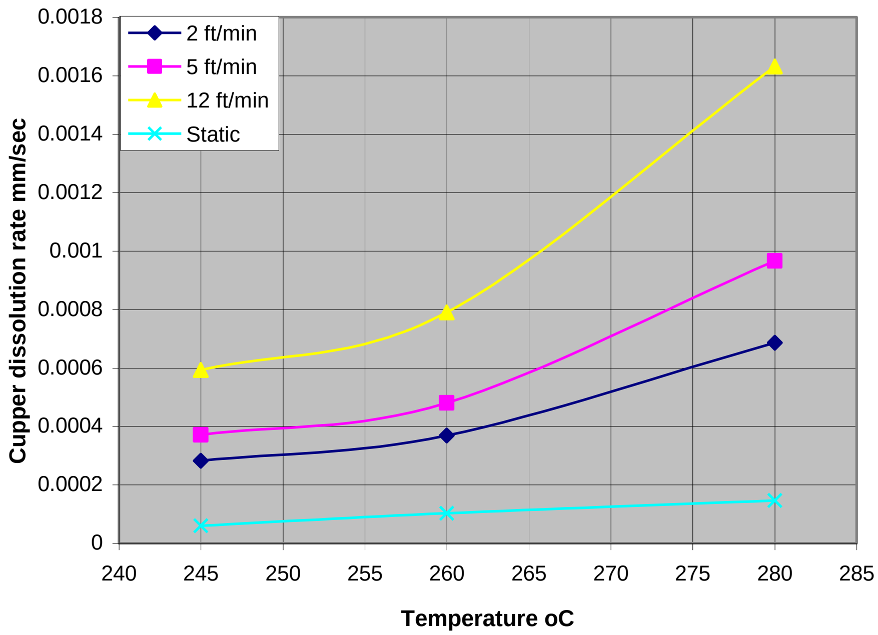

Figure 14. Copper dissolution rate as function of temperature for different dynamic (2, 5, 12 ft/min) and static conditions for K100LD alloy.

Conclusions

Copper dissolution performance was investigated with four lead-free alloys (SAC305, K100LD, SC995e, SN100C) at temperatures up to 300°C with time duration to 10 minutes under static and dynamic conditions. The following conclusions can be drawn from this study:

1). The lead-free Sn-Cu based alloys without Ag , but with additions of other elements, K100LD and SN100C, have much lower rate of copper dissolution compared to Sn-Ag-Cu alloy, SAC 305. The rate for copper dissolution for K100LD and SN100C is comparable to Sn-Pb alloy at moderately high temperature below 260 °C. On the contrary, SAC305 could have a 7 times higher dissolution rate at 300 °C compared to the Sn-Pb alloy at 245 to 250 °C.

2). Increase in liquid solder flow speed increases dissolution rate significantly; as much as 10 folds with a solder flow rate of 12 ft/min compared to in static condition was observed; indicating the exposure to liquid solder during wave soldering should be kept as short as possible.

3). Temperature increase leads to a higher copper dissolution rate with an almost constant factor from 245^{o}C to 280^{o}C (2.4 times) regardless static and dynamic condition (at different motion speed).

4) With the knowledge of copper dissolution kinetics under static and dynamic conditions, it is possible to establish guideline for solder alloy composition optimization and criteria for selection of copper-erosion resistant lead-free alloys for wave and rework soldering processes.

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