IN HOUSE DROSS RECOVERY- DO YOU KNOW WHAT YOU ARE PUTTING BACK IN YOUR SOLDER BATH?

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ABSTRACT

Over the last 3 years, several large OEMs and CEMs have purchased inexpensive equipment to melt entrapped metal from solder dross skimmings, and returning this material to their wave soldering or selective soldering systems. This results in a significant reduction in the volume of bar solder consumed. With the still increasing trend towards lead free utilization and higher pot temperatures, dross management becomes a greater issue.

In this process, small ingots of solder are produced by using pressure to separate liquid metal from the oxide/metal mixture skimmed from the solder bath. After the entrapped metal is removed, the remaining oxides are returned to solder suppliers for further recovery. Analysis of these ingots show that there is a significant change in the ratio of tin/silver in SAC alloys, and the ratio of tin/lead in Sn63 alloys. This means that the ratio of tin to silver and tin to lead may be changing in the wave or selective soldering pots.

Analysis of the amount of dross included in the ingots produced using this method was compared to a number of commercially available brands of bar solder. Data indicates that the lack of post treatment of this recycled material results in an order of magnitude increase in the amount of included dross.

INTRODUCTION

Wave or machine soldering was patented in 1958 by the Electrovert Company.[1] Wave soldering revolutionalized the process of soldering through hole components to printed wire boards. The number of components that can be soldered per man hour increases exponentially versus soldering with a hand held iron using cored wire.

One drawback of the wave soldering process is the generation of solder dross. Dross is oxidized metal that is incapable of forming intermetallic compounds with the metallization used on circuit boards and component lead finishes. It is generated wherever molten (liquid phase) solder alloy is exposed to oxygen from the atmosphere. Dross can be observed as a dark grey (Sn/Pb dross) or a gold tinted (high Sn, Pb free dross) solid material on the surface of the solder bath. Dross fines are also dispersed throughout the solder bath.

Many plated through hole (PTH) technology roadmaps call for thicker boards with multiple layers of copper.[2] These boards require more heat and higher wave heights to assure complete hole fill. Dross production accelerates exponentially as the temperature of the solder pot increases. Also, dross generation accelerates as higer turbulance is used to increase the wave height to accommodate thicker boards.[3]

Solder dross that adheres to the surface of a printed circuit board is an unacceptable cosmetic defect. It is a dull, grainy material that does not melt when heated above the alloy melting point. Dross included in a solder joint will make the joint less thermally and electrically conductive and more prone to mechanical and thermal cycling failure. Because dross is less dense than molten solder it is commonly found on the surface of a solder bath, it is easily picked up by through hole component leads protruding from the bottom side of the circuit board.[4]

Dross is removed from the molten bath by manual skimming. Solder dross skimmings are normally collected in steel pails and sold to materials recyclers who consolidate and/or process large volume batches. In the skimming process, unoxidized molten solder alloy is entrapped in the dross. The first step in recovering good metal from this dross is a process called sweating. The dross and entrapped metal are heated above the melting point of the entrapped metal, and the liquid metal is separated from the solid dross oxides using pressure.

After sweating the dross, commercial solder recycling process includes multiple refining steps and an accurate analysis of the alloy, before it is added to a batch of J-STD-006 compliant solder alloy. In house dross recovery systems only use the first step without any further refining or chemical treatment or alloy verification. This paper will discuss some of the differences in commercially available bar solder and material that was recycled in house by two Contract Electronics Manufacturers.

DROSS INCLUSION MEASUREMENT

Quantitative Method

Two experimental methods were used to determine dross inclusion in alloys recycled by two different Contract Electronic Manufacturers. One method used a variant of the Archimedes principal to determine the density of the castings. The second method was a well known test called the dross inclusion test.[5]

The first experiment was to measure the densities of samples of recycled metal and the metal oxide that it was seperated from and the density of virgin bar solder.

Multiple ingots of recycled 63/37 Tin (Sn)/Lead (Pb) metal (Figure 1) were carefully weighed. A glass cylinder with a smooth continuous lip was filled until a miniscus began to form on the upper edge of the lip, indicating that the cylinder was completely full. The last fraction of a gram of water was carefully added with a micro-pipette. The cylinder filled with water was weighed with a calibrated Sartorious balance capable of measuring to the nearest 0.01 gram. (Figure 2).

Figure 1. Cast Ingots of Recycled 63/37 Alloy

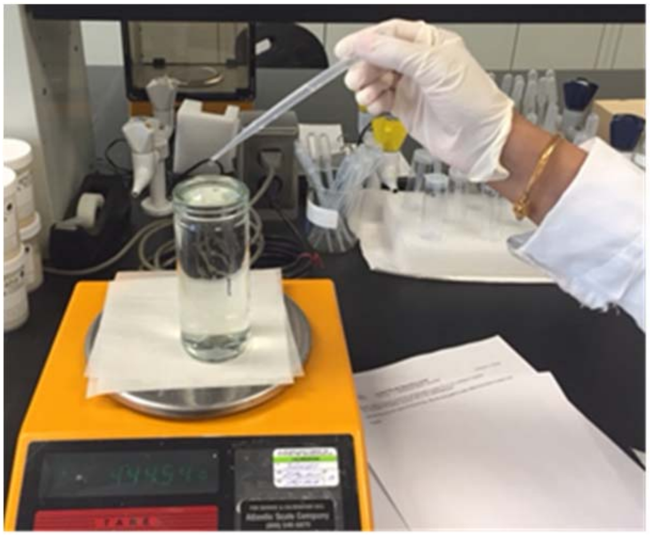


Figure 2. Filling the Glass Cylinder

The cylinder was then emptied and completely dried around the top and outside. The weighed sample of the recycled metal was placed in the jar. The jar was then re-filled to the same level as the example shown in Figure 2 and weighed. Assuming that the water weighed 1 gram/cc, the volume of the recycled material was calculated using the following equations:

Weight of jar full of water = $W_1 + J_m$ where W_1 was the weight of the water in the full jar and J_m was the weight of the empty jar.

The weight of the jar containing the recycled sample and filled with water = $W_2 + J_m + I_m$ where W_2 is the weight of the water and $\mathbf{I_m}$ is the weight of the metal ingot. Taking the difference of these two weights, then subtracting the weight of the ingot gives you the difference in the weight (or volume) of water. This is equal to the volume of the ingot.

$$(W_2 + J_m + I_m) - (W_1 + J_m) = W_2 - W_1 + I_m$$

The density of the ingot is calculated by dividing its weight by its volume.

Simular measurements were made with dross that was remaining from the metal extraction process and compared with virgin bar solder. The results are in Figure 3.

	grams/cc
Reference Density of Virgin 63/37	8.40[6]
Average Density of Recycled Metal	8.18
Average Density of Metal Oxide	6.62

Figure 3. Density of Materials

To solve for the weight of dross in the recycled metal, the following two equations needed to be solved:

X * 6.62 g/cc + Y * 8.40 g/cc = 8.18 g/cc
X+Y=1
X = % Dross by weight in Sample
Y = % 63/37 Alloy by weight in Sample
Solution:
X=1-Y
(1-Y) * 6.62 + Y * 8.40 = 8.18
6.62-6.62Y + Y * 8.40 = 8.18
1.78 * Y = 1.56
Y = 87.6% by weight
X = 12.4% by weight

To calculate the volume of dross included in the recycled material, 12.4% x 8.40/6.62 (the ratio of the densities of pure solder and dross) = 15.7% by volume.

A benchmark of several samples of 63/37 alloy bar solders was carried out several years ago to determine an entitlement level of included dross. Although no IPC standard exists for dross inclusion, this benchmark could be used by the J-STD-006 committee as a starting point to evaluate if a standard could be established.

In this experiment, 7 brands of Sn63 bar solder from 5 different companies were kept in a static dipping pot for 4 hours at 500°F (260°C). The accumulated dross at the surface was skimmed and weighed. The skimmings were then fully treated for maximum metal recovery. The weight percent of the skimmings and recoverable metal is reported in Figure 4.

Material	Solder Pot Grams	Dross Removed Grams	% of Dross	Metal in Dross	% Metal In Dross
Brand 1	7848	32.6	0.42	17.4	53.4
Brand 2	5703	116.8	2	99.4	85.2
Brand 2	5755	147.6	2.56	91.7	62.5
Brand 4	5499	111.5	2.03	88	78.9
Brand 5	5355	131.6	2.46	131.6	80.7
Brand 6	7573	88	1.16	64.4	73.2
Brand 7	10694	79.4	0.74	62.9	79.2

Figure 4. Dross from Benchmark Study[7]

The largest amount of dross recovered from this benchmark was 2.56%. 62.5% of this skimmed material was recoverable metal. After 4 hours in the molten state, 1-.625= .375 X .0256 = 0.96% of the highest drossing sample was in the form of oxide. Based on this benchmark, in house recycled alloy contains an order of magnitude more included dross than commercially available solder alloy.

DROSS INCLUSION MEASUREMENT

Qualitative Method

As a quality assurance protocol, Alpha has developed a dross inclusion test method. This test is simple and quick and uses four visual standards as acceptance criteria for bar solder.

The method involves melting a 1 kilo sample of bar solder into a 150 mg glass beaker. 4 ml. of a rosin bearing wave soldering flux, similar to the IPC ROL0 standardis added to inhibit dross development during the test.. A glass stirring rod is used to disperse any dross that may be included in the sample. The four visual standards are shown in Figure 5.

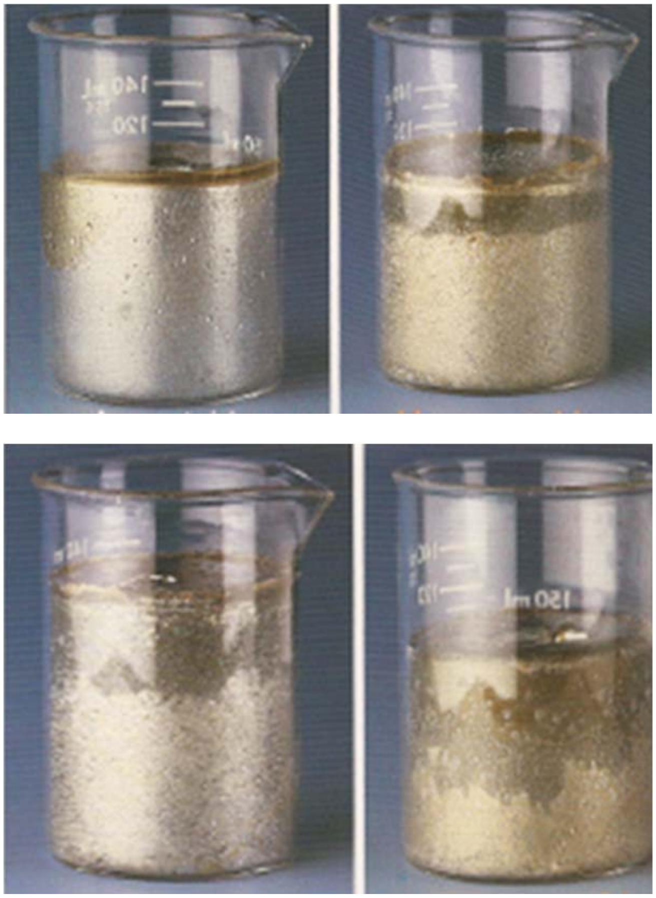


Figure 5. Clockwise from upper left- “Acceptable”. All three others are unacceptable.

The upper left visual standard is the only acceptable example. The other three are considered unaccepable because of the easily observed darker coloured dross in the sample.

Dross inclusion tests were run on two separate samples of recycled metal obtained from two different Contract Electronic Manufacturers (CEMs). One CEM uses 63/37 Tin/Lead in a commonly used wave soldering machine. The second CEM uses a lead free alloy designated as SAC 0307 (0.3% Silver, 0.7% copper, balance tin). There were several samples of the recycled tin/lead, but only one sample ingot of the lead free alloy in this study.

The result from the qualitative dross inclusion test for the tin lead recycled material is shown in Figure 6. The labaoratory manager who supervised this test rated is as unacceptable per the visual standard. Relatively large quantities of dross are visible throughout the sample. This sample was from the same lot of material pictured in Figure 1.

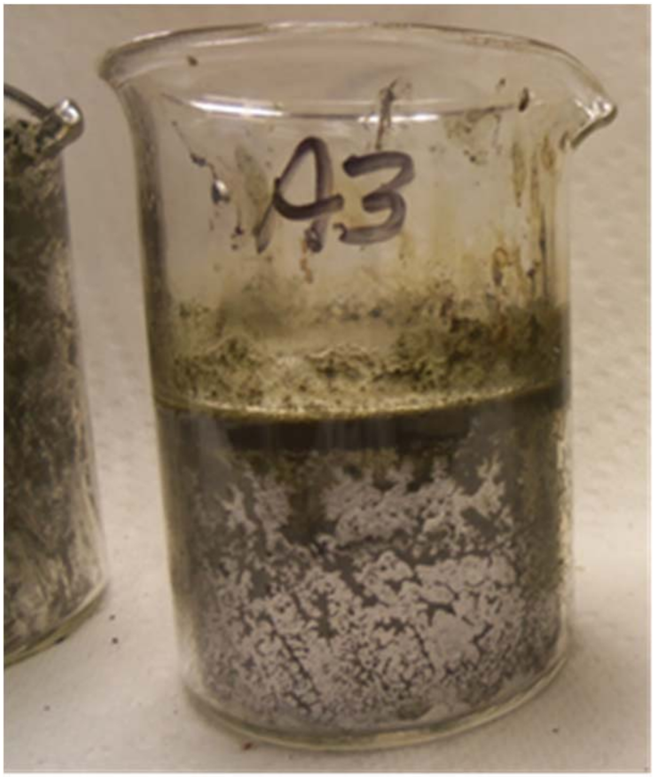


Figure 6. Dross inclusion Test Result from Recycled Sn 63 Ingot.

The result of the qualitative dross inclusion test using the recycled SACX 0307 ingot is shown in Figure 7. It appears that there is even more included dross in this sample, but the quantitative test was not repeated before the dross inclusion test was performed. Because of the destructive nature of the qualitative dross inclusion test, the quantitative test was no longer possible. Again, per the visual standard in figure 4, this sample would be considered unacceptable for excessive dross inclusion.

Figure 7. Qualitative Dross Inclusion Recycled SAC 0307

ALLOY CONTENT

Tin Lead Recycled Ingots

Each element in a tin bearing solder alloy has a different oxidation rate at a given temperature. In the binary Sn63/Pb37, elemental tin is oxidized to stannic oxide (SnO_2) at a faster rate than lead is oxidized to PbO_2.[8]

In the tertiary alloy of tin, silver and copper, tin is also the least noble of the three elements. Because of tin's lower nobility, the ratio of tin to lead in 63/37 and the ratio of tin to silver in a SAC alloy shift as tin oxides in higher concentrations than the original wave solder alloy. As skimmings (good metal and dross) are removed, the concentration of ratio of tin to lead and tin to silver is reduced.

To test this hypothesis, an elemental analysis of CEM in-house recycled alloy and the recovered oxides from the recycling process was undertaken. Figure 8 shows the tin content of each of the 6 ingots of recycled Sn/Pb, plus the tin content in the dross/oxide separated during the recycling process.

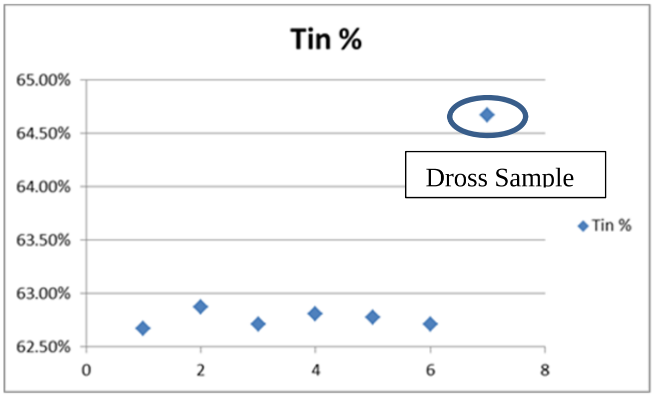


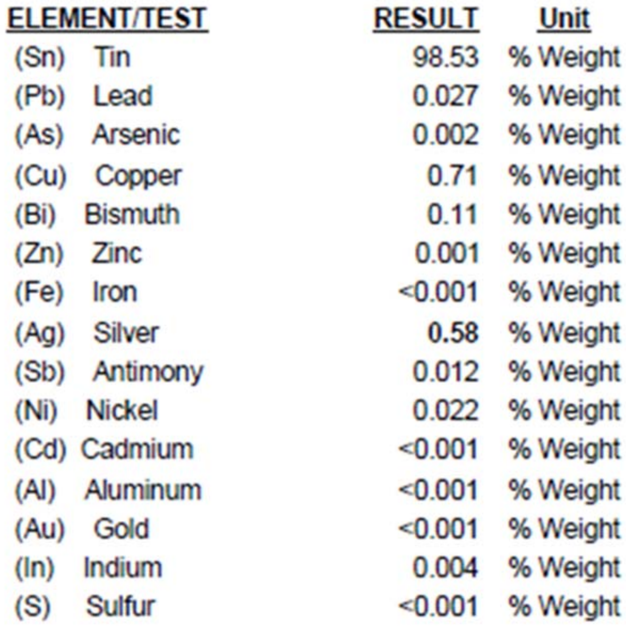
Figure 8. Assay of 6 Recycled Ingots and Recovered Dross

The 6 metal **s**amples all have measurably lower tin content than the nominal 63%. Although J-STD-006 calls for +- 0.5%, and the alloy is still above the lower spec limit of 62.5%, there is a consistant pattern of a lower tin content. This is confirmed by the significantly higher tin content in the oxide content of 64.6%

ALLOY CONTENT

SAC 0307 Recycled Ingots

Elemental analysis of the recycled SAC 0307 ingot was undertaken. Silver and copper were measured using X-ray flourescence. All other elements were measured using optical emission. This alloy has a nominal silver content of 0.3% silver. Per the latest IPC standard, J-STD-006C, any element with less than 1% nominal content shall have a tolerance of +- 0.1%. Figure 9 shows the analysis results of the recylded ingot of SAC 0307.



ELEMENT/TEST		RESULT	Unit
(Sn)	Tin	98.53	% Weight
(Pb)	Lead	0.027	% Weight
(As)	Arsenic	0.002	% Weight
(Cu)	Copper	0.71	% Weight
(Bi)	Bismuth	0.11	% Weight
(Zn)	Zinc	0.001	% Weight
(Fe)	Iron	<0.001	% Weight
(Ag)	Silver	0.58	% Weight
(Sb)	Antimony	0.012	% Weight
(Ni)	Nickel	0.022	% Weight
(Cd)	Cadmium	<0.001	% Weight
(Al)	Aluminum	<0.001	% Weight
(Au)	Gold	<0.001	% Weight
(In)	Indium	0.004	% Weight
(S)	Sulfur	<0.001	% Weight

Figure 9. Elemental analysis of recycled SAC 0307

The silver content in the ingot rose from a nominal 0.3% to 0.58%, well above the J-STD-006C upper limit of 0.4%.

Again, as was the case for the recycled tin/lead, the less noble element in the alloy, tin, is preferentially oxidized at a higher rate than the more noble element, silver. Tin oxidizes at a higher rate than silver at any given temperature or concentration of oxygen available to react with the molten solder alloy. Because less silver is being oxidized, the ratio of silver to tin increases in the solder bath as metal oxide (dross) is skimmed from the system.

CONCLUSIONS

Recycling metal has always been an important consideration since wave soldering became a viable process in 1958. It is an important part of the through hole assembly processes, obviously much more so with respect to classic wave soldering because of the grater rate of dross generation due to larger surface areas of molten solder exposed to oxygen.

However, simply sweating molten alloy from metal oxide may not create solder alloy required for high reliability, mission critical assemblies. Shifting ratios of tin to lead and tin to silver was found in the small number of samples tested. These results were expected, based on the thermodynamics of the oxidation of key elements in tin/lead and one SAC alloy.

The addition of material to wave and selective soldering pots without traceable certificates of analysis should be an area of concern for high reliability aerospace, medical, military, telecom infrastructure and automotive applications.

Adding low density material with reduced levels of tin to a plated through hole process, because of the presence of included metal oxide is something else to consider. In house recycled metal can contain unacceptable amounts of included oxides was shown in this study, but more data needs to be developed to confirm these initial findings.

FUTURE WORK

Further samples of recycled material from other sources is a top priority to confirm the early findings from this study. Samples of SAC 305, a very commonly used alloy, will be analyzed for quantitative dross inclusion using the density measurement method before this paper is presented, but the data is not yet available.

Elemental analysis of recycled SAC 305, and the accompanying dross are also planned to confirm the trend for silver content to increase in the wave or selective soldering bath as the mixture of tin and silver oxides are skimmed to reduce the issues of excessive dross in a through hole assembly process.

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