SAND99-0463J

2/01/99

RECEIVED
MAR 03 1999
OSTI

Solder Contamination

Paul T. Vianco
Sandia National Laboratories

There are two sources of contamination in solder alloys. The first source is trace elements from the primary metals used in the as-manufactured product, be that product in ingot, wire, or powder form. Their levels in the primary metal are determined by the refining process. While some of these trace elements are naturally occurring materials, additional contamination can result from the refining and/or forming processes. Sources include: furnace pot liners, debris on the cutting edges of shears, rolling mill rollers, etc. The types and levels of contaminants per solder alloy are set by recognized industrial, federal, military, and international specifications. For example, the 63Sn-37Pb solder purchased to the ASTM B 32 standard can have maximum levels of contamination for the following metals: 0.08(wt.)%Cu, 0.001%Cd, 0.005%Al, 0.25%Bi, 0.03%As, 0.02%Fe, and 0.005%Zn[1].

A second cause of contamination in solders, and solder baths in particular, is their actual use in soldering operations. Each time a workpiece is introduced into the bath, some dissolution of the joint base metal(s), protective or solderable coatings, and fixture metal takes place which adds to contamination levels in the solder. The potential impurities include Cu; Ni; Au or other noble metals used as protective finishes and Al; Fe; and Zn to name a few. Even dissolution of the pot wall or liner is a source of impurities, typically Fe.

The size of solder baths can range from several hundred grams to hundreds of kilograms (one pound to several thousand pounds) depending upon the facilities. The larger the solder source, the longer the source can operate before contamination limits are exceeded. It must always be presumed, however, that use of a solder bath will cause its contamination levels to increase above the original specifications of the alloy. Therefore, a balance must be struck between the potentially detrimental effects that the contaminants have on solderability (manufacturability) and solder joint reliability versus the cost of replenishing or replacing the solder bath.

Common contaminants of solder joints are Au, Fe, Ni, Cu, As, and Sb. While the solder is molten, these elements will remain in solution as long that the saturation point is not reached. When the saturation level is exceeded, the contaminant will precipitate out. Typically, precipitation results in the formation of binary intermetallic compound particles with the Sn component of the solder. Those particle chemistries are $AuSn_4$, $FeSn_2$, Ni_3Sn_4, Cu_6Sn_5, As_3Sn_4, and Sb_2Sn_3. Shown in Figure 1 is the solidified microstructure of a solder having a Cu content which exceeds the solubility limit of Cu in Sn (0.3–0.7 wt.%). Cooling causes the precipitation of large Cu_6Sn_5 intermetallic compound particles. The particles have a needle morphology if viewed perpendicular to the growth axis, or appear as hexagonal "donuts" if viewed along the axis of crystal growth. Gold contents that exceed the solubility limit may result in the appearance of $AuSn_4$ particles which have a needle-like morphology as shown in Figure 2. The $AuSn_4$

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

phase may also have a blocky appearance. In the case of Sn-Pb solders, Sn-Pb-$AuSn_4$ ternary phase particles may be observed to form in the bath [2]. Excessive Sb and As contents in solder result in the formation of Sb_2Sn_3 and As_3Sn_4 intermetallic particles, respectively, both having a blocky morphology. An example of an Sb_2Sn_3 intermetallic compound particle is shown in Figure 3. Metals such as Cd, Zn, Al, and Bi simply exist as elemental particles at concentrations that exceed their respective solubility limits in Sn or Sn-based solders.

Also, particulates that result from solder dross (oxidized solder) and carbon particles from charred flux can become suspended (not necessarily dissolved) in the solder and find their way into the solder joint. Therefore, they are also considered as contaminants.

It is often not clear as to the maximum levels of contaminants that are permissible in a solder bath. This topic has not been thoroughly documented with respect to the impact had by *specific* contaminant levels on the manufacturability and reliability of solder joints. Such documentation which does exist, pertains largely to the assembly of electronic products. Shown on the right-hand side of Table 1 are the maximum allowable contaminant ranges for a solder bath per the IPC 815A (electronics) specification. The maximum limits for virgin alloys – taken from ASTM B 32 - are shown in the center column. The IPC limits provide a conservative guideline for structural soldering practices since such joints often have larger gaps and can be soldered with more active fluxes.

Some practices can be performed periodically to remove contaminants from the solder bath so as extend the life of the solder source. In the case of solder particulates such as dross and flux residues which generally float on the solder surface, occasional skimming of the bath's surface will prevent the accumulation of this matter. Elemental metal contaminants such as Cu, Ni, etc., that form intermetallic compound particles can be removed from the bath by a procedure that is based upon the fact that the solubility limits of impurities in the solder depend upon the solder temperature: the lower the temperature, the smaller is the amount of contaminant that remains in solution. As the solder is cooled to just above its liquidus temperature, contaminants are forced to precipitate from solution. The precipitated particles are simply removed from the surface and/or bottom of the solder bath. Then, the bath is returned to its nominal operating temperature and replenished with new material.

A novel approach to purifying a solder bath of Cu, Au and other contaminants is through the additions of Sn^{4-}-salts such as $SnCl_4$ or $SnBr_4$[3]. The salts dissociate into their respective ions. A valence exchange between the Sn^{4-} and Cu or Au to form Cu^{2-} and Au^{2-}, respectively, allows the contaminants to then combine with the halide ions and subsequently float to the bath surface for removal.

In summary, contamination levels can impact the manufacturing and reliability of solder joints. Although contaminant levels in virgin solder do come under several US and international specifications, only a few guidelines have been presented on acceptable contamination levels in working solder baths. Those guidelines pertain to the more stringent conditions required for electronics assembly and may be overly conservative (and costly) to follow in some structural applications. In the continued absence of such data, best practices would be to assure, first of all, that process development engineers and operators appreciate the fact that solder baths do indeed become contaminated with

use. Secondly, those same personnel should be aware that solder joint quality on outgoing product or assemblies will degrade if produced with overly contaminated solder. An evaluation of solder joints that exhibit poor solderability (hole fill and/or spreading), discolored fillets, or fillets that appear "unusually" rough should include the possibility of solder contamination as one amongst many potential causes of these degradation modes.

References:
[1] *Standard Specification for Solder Metal*, B 32-96, 1996, *Annual Book of ASTM Standards.* American Society for Testing and Materials (ASTM), West Conshohocken, Pa.

[2] Seen, H. and Becker, G. 1986. "The Effect of Impurity Elements on the Soldering Properties of Eutectic and Near-Eutectic Tin-Lead Solders," *Brazing and Soldering* No. 11: p.4.

[3] [164] Israeli patent #74438/3, *Method for Purifying Soft Soldering Melt*, inventor: Baruch Blumen.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

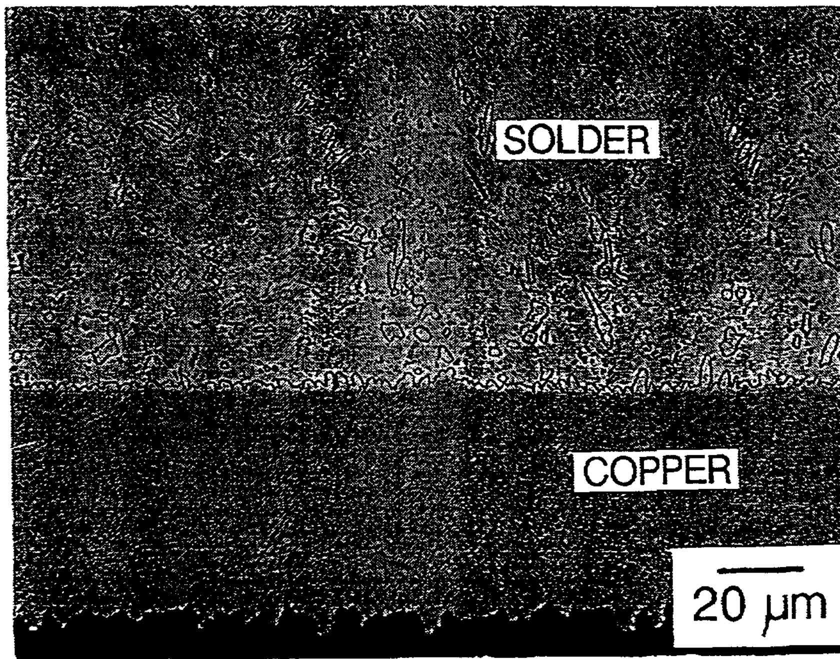

Fig. 1 Microstructure of a Sn-Ag solder containing a 4 wt% Cu content which exceeds the solubility limit of Cu in Sn, resulting in the formation of Cu_6Sn_5 particles.

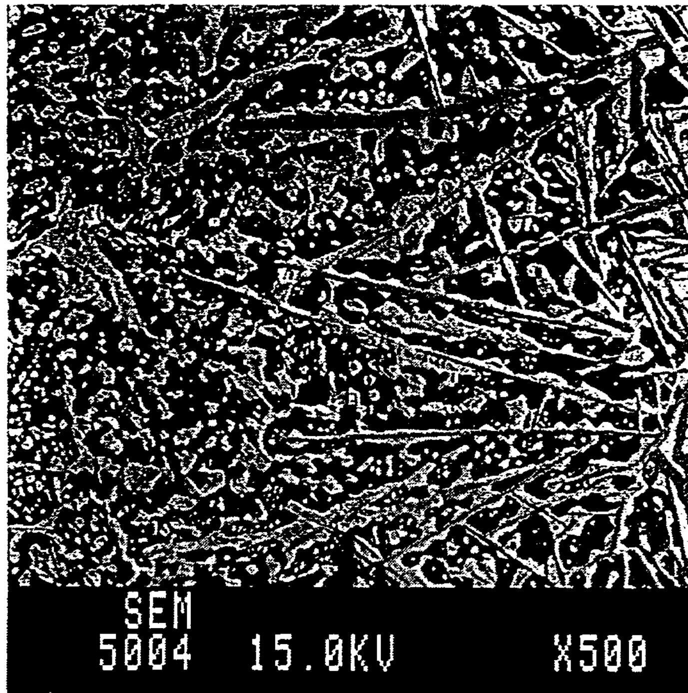

Fig. 2 The formation of $AuSn_4$ needle structures in Sn-Pb solder.

Fig. 3 Blocky Sb_2Sn_3 intermetallic compound particles.

Contaminant	Maximum concentration in virgin solder, %[a]	Maximum concentration in solder bath, %[b]
Copper	0.08	0.75/0.30
Gold	—	0.50/0.20
Cadmium	0.001	0.10/0.005
Zinc	0.005	0.008/0.005
Aluminum	0.005	0.008/0.006
Antimony	0.2–0.5	0.50/0.50
Iron	0.02	0.02/0.02
Arsenic	0.03	0.03/0.03
Bismuth	0.25	0.25/0.25
Silver	0.015	0.75/0.10
Nickel	—	0.025/0.01

Notes:
a. ASTM B32.
b. Per IPC-S-815A.

Table 1 Impurity limits for virgin solder (ASTM B 32) and maximum concentrations in working Sn-Pb solder baths (IPC-S-815A) *(used with permission, ASM International)*