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EFFECTS OF REFLOW ATMOSPHERE AND FLUX ON TIN WHISKER GROWTH OF Sn-Ag-Cu SOLDER

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ABSTRACT

Sn whisker growth behavior of Sn-Ag-Cu solder fillets, on lead-frames of quad flat packages (QFPs), on OSP printed circuits boards during 85°C/85% relative humidity (RH) exposure was evaluated. Three different concentrations of halogen activated flux (Sn-3.0wt%Ag-0.5wt%Cu) were soldered in an air and an inert N_2 reflow atmospheres. The lead frames of QFPs were metalized with Sn plated Cu and Fe-42wt%Ni (alloy 42). Sn whiskers were observed on the surface of solder fillets of the QFPs joints reflowed with halogen flux in air atmosphere. Substantial amount of Sn oxides were formed for those solder fillets with whisker growth and the amount of Sn oxides increased with the halogen content. Sn oxide formation apparently enhanced whisker formation. The combination of air reflow atmosphere and high halogen flux was the worst for oxidation of solder fillet resulting in Sn whisker formation, regardless of electrode lead frame for Cu and alloy 42. In contrast, an inert N_2 reflow atmosphere prevented the Sn whisker formation of Sn-Ag-Cu solder fillets, for all conditions of current work.

Key words: Sn whiskers, Sn-Ag-Cu solder, Corrosion, N_2 atmosphere, heat/humidity exposure

INTRODUCTION

The Tin Whisker phenomena can have a serious negative affect on electric circuits reliability; its mechanism, however, is still conclusively unknown. Since the first tin whiskers were reported by K. G. Compton, et al [1], in 1951, many researchers have been attempting to discover the root-cause and further define the mechanism. A series of papers have discussed this issue, and attempted to propose solutions to mitigate tin whisker formation [2]. Among them, it was discussed that alloying tin with lead (Pb) was an effective method for Sn whisker mitigation [3]. However, with the ROHS Legislation, the removal of lead was required in the electrics industry on July 1, 2006 . At the same time, with electronic devices tend to downsizing day by day, the tin whisker problem has drawn unprecedented attention again because Sn whiskers may often cause short circuits. Although the mechanism of tin whisker formation was not clarified until now, there are many beneficial results from various aspects. Using different combinations of substrate, making a barrier layer (i.e., under-layer and flash coat on plating), thickness of electrodeposited plating, and heat treatment etc., have been investigated the mechanism of tin whiskers growth and mitigation methods on electroplated Sn films [4-8]. In addition, recent research has reported that Sn whiskers also formed on solders not only electroplated Sn films [9]. Typically, because the wetting of lead-free solders are poor, as compared to Sn-Pb solders, thus high activity flux is required to get good wetting. Such active agents containing Cl or Br can cause corrosion on service. It is considered the corrosion of solders may become a trigger of whisker formation. Consequently, one needs to control processing conditions during reflow as well as flux compositions for preventing the formation of Sn whiskers on lead-free solder joint. In this work, the follwing were investigated: 1.) Sn whisker formation on solders, 2.) effects of process atmosphere, i.e., a N_2 atmosphere and an air atmosphere in reflow and 3.) the effects of three kinds of fluxes on Sn whisker formation and oxidation behavior for solders.

EXPERIMENTAL PROCEDURES

The present work characterized by Sn plated QFPs soldered with three different concentrations of halogen based RMA (Rosin Mildly Activated) flux with Sn-3.0Ag-0.5Cu were used, i.e., halogen free (HF), HF added 0.4%HBr-based activator, and added 0.8%HBr-based activator, respectively. Solder pastes were printed on Cu pads of OSP (Organic Solderability Preservative) finished PCB. The QFPs were assembled on PCBs and were soldered in an air and an inert N_2 (≦500ppm O_2) reflow atmosphere. The QFP had 100 lead frames of Cu leads as well as alloy 42 electrode lead frames with Sn plating. These samples underwent reflow at peak of 240°C. After that they were cooled at 4.3°C/s of cooling speed. Figure 1 shows a QFP joints after reflow soldering.

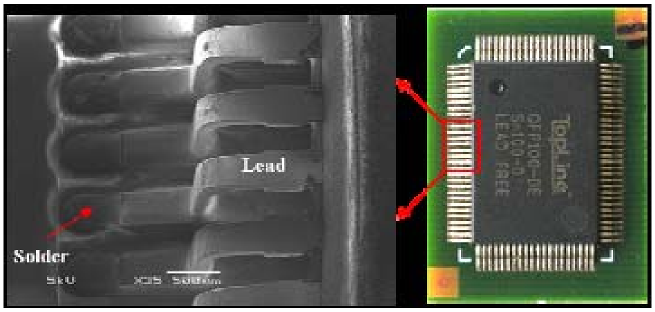


Fig. 1 An example of QFP joints after reflow soldering.

Twelve combinations were used for the above conditions. Heat, temperature and humidity exposure tests were carried out up to 1000 hours without cleaning the residual flux during reflow. Holding temperature was 85℃, and relative humidity was 85%.

Microstructures were examined by SEM (Scanning Electron Microscopy) and FIB (Focused Ion Beam microscopy) after these samples were exposed to 85℃/85% RH ambient for 1000 hours. The element composition was identified by EDS (Energy Dispersive Spectroscopy) and EPMA (Electron Probe Micro Analysis).

RESULTS AND DISCUSSIONS

Effects of Reflow Atmosphere and Flux on Sn Whisker Occurrence

To investigate effect of reflow atmosphere on Sn whisker growth, Sn plated QFPs were observed on solder fllets holding 1000 hours in 85℃/85% RH. Those QFPs were soldered in an air and a N_2 atmosphere, respectively.

Figure 2 show surface morphology of solder fillets of QFPs holding 1000 hours in 85°C/85%RH ambient observed by optical microscope.

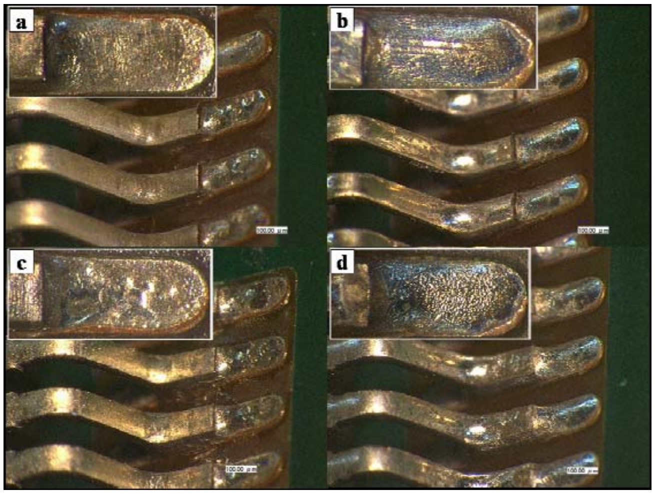


Fig. 2 Surface morphologies of solder fillets after 1000 hours in 85°C/85%RH ambient for the case with HF+0.8%HBr activated flux: (a, c) are soldered in air, (b, d) are soldered in N_2 atmosphere, and (a, b) are with Cu electrode lead frames, (c, d) are with 42 alloy electrode lead frames.

Magnified images of the solder fillets are shown on the upper left corner, respectively. Image (a, c) are soldered in air, substantial island-like microstructures were observed in the solder fillets, and wetting of solder fillets are poor compared with N_2 samples (b, d). In contrast, apparent fine microstructure and relative good wetting were obtained in the case of N_2 atmosphere. Fig. 3 shows typical surface morphologies of solder fillets for Cu lead frames of QFP holding 1000 hours in 85°C/85%RH ambient.

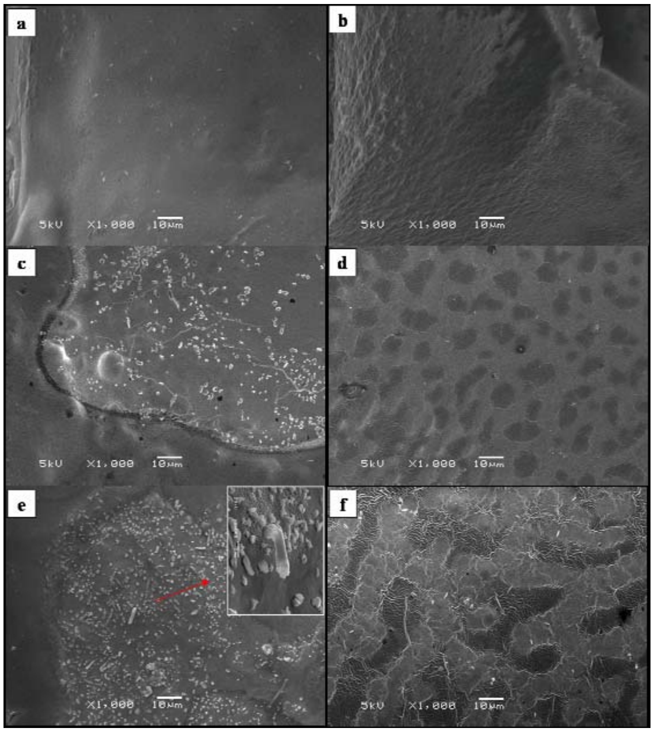


Fig. 3 SEM images of solder fillets soldered in air/N2 atmospheres after 1000 hours in 85°C/85%RH for the case of Cu electrode lead frames: (a, c, e) soldered in air atmosphere, (b, d, f) soldered in N2 atmosphere; (a, b) are with HF flux, (c, d) are with HF+0.4%HBr activated flux, (e, f) are with HF+0.8%HBr activated flux.

Images (a, c, e) show surface morphologies of solder fillets that were reflowed in an air atmosphere. Images (b, d, f) show those in a N_2 atmosphere. No Sn whisker were observed on the surface of solder fillets with halogen free flux (a, b). In contrast, island-like microstructures consisted of nodules, where white spots were formed on the surface of solder fillets, for those 0.4 % HBr activated samples that were soldered in air (Fig. 3 c). For those soldered in N_2 atmosphere, clear surface microstructures were obtained (Fig. 3 d), and the island-like microstructure was not formed. Further activated samples of 0.8% HBr, 10 μm Sn whiskers were formed for samples soldered in air (Fig. 3 e). Whisker formation was not observed for samples soldered in N_2 atmosphere (Fig. 3. f). Sn whiskers grow from white spots, island-like microstructures. In the same way, typical surface morphology of solder fillets for the case of alloy 42 lead frames of QFP are shown in Fig. 4. Similar results were obtained where Sn whiskers were not formed on solder fillets with halogen free flux or with N_2 atmosphere. Sn whiskers were not formed in all conditions of halogen free samples, regardless of process atmosphere and lead frames.

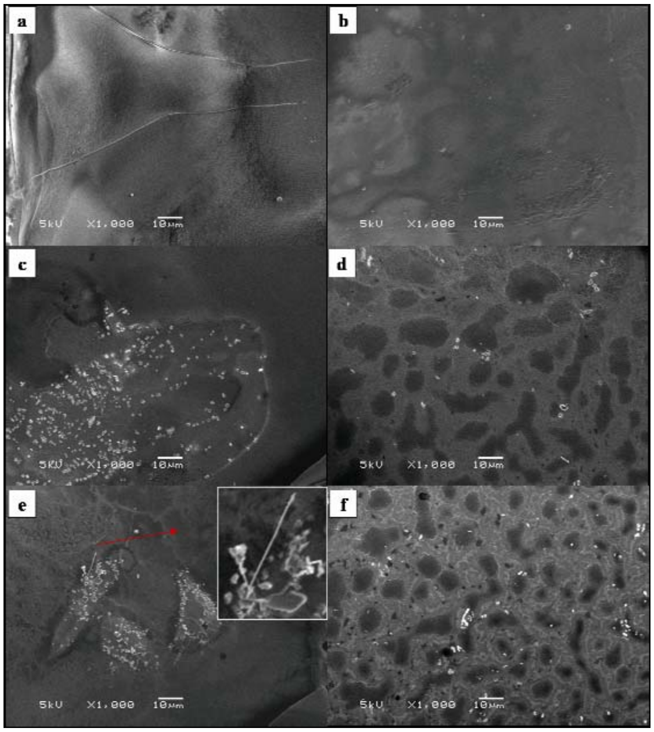


Fig. 4 SEM images of solder fillets soldered in air/N2 atmospheres after 1000 hours in 85°C/85%RH for the case of 42 alloy electrode lead frames: (a, c, e) soldered in air atmosphere, (b, d, f) soldered in N2 atmosphere; (a, b) are with HF flux, (c, d) are with HF+0.4%HBr activated flux, (e, f) are with HF+0.8%HBr activated flux.

For all conditions in the current work, the maximum length of Sn whiskers formation on solder fillets of QFP are summarized in Table 1.

Table 1 Sn whisker formation on solder fillets of the QFP after 1000 hours in 85°C/85%RH.

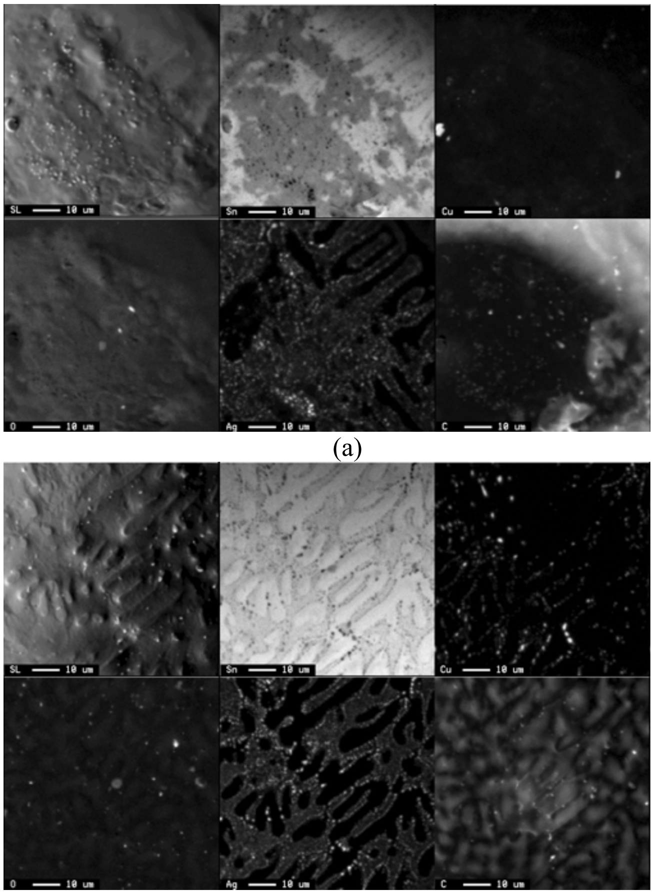
location	Atmosphere	Electrode	HF01	HF01+0.4%	HF01+0.8%
Solder fillet	Air	Cu	-	≦5 μ m	≦10 μ m
		42 alloy	-	≦5 μ m	≦15 μ m
	N_2	Cu	-	-	-
		42 alloy	-	-	-

* "-" mean no Sn whisker observed.

No Sn whisker formed in all samples of the case of N_2 atmosphere and of halogen free flux noticeably. However, in the case of air atmosphere reflow, 5μm Sn whiskers were observed in samples of 0.4%HBr activated flux regardless of lead frame. For samples of 0.8% HBr activated flux, 10μm Sn whiskers were formed for the Cu lead frames and 15μm Sn whiskers were formed for the lead frames of alloy 42. With increasing halogen concentration in flux, the propensity of Sn whiskers formation is increased. The lead frames of alloy 42 sample show less favorable results than those of Cu lead frames. These results clearly show that a nitrogen reflow atmosphere and halogen free flux have a great effect on suppressing Sn whisker formation on solders.

Effects of Reflow Atmosphere and Flux on Oxidation

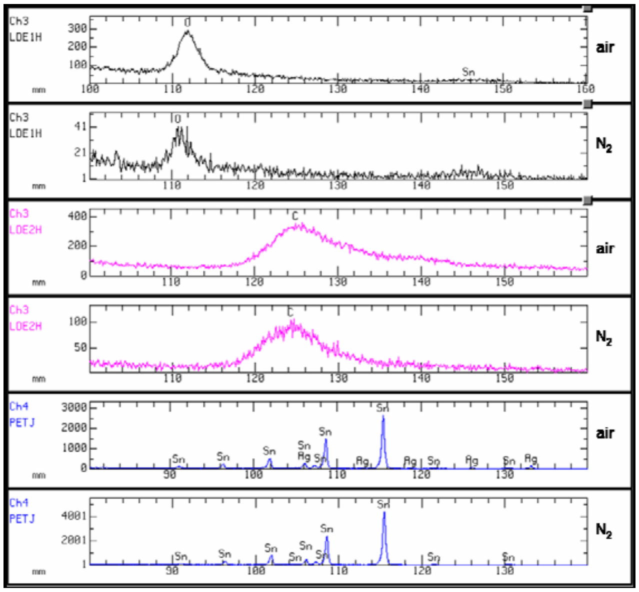
To investigate the process atmosphere effect on solders, elemental analysis of solder surfaces were identified by EPMA. For the case of 0.8HBr activated flux reflowed in air Fig. 5 (a) shows the oxidization of surface microstructures more severe than those in N_2 reflow (Fig. 5 b&c); also, shows Sn chipping and areas of high C (carbon) concentrations around the white islands-like microstructures. Those white islands-like microstructures consist mainly of Ag, Sn and O (Fig. 6).



(a)

(b)

Fig. 5 Elemental analysis of solder surfaces for the case with 0.8HBr flux by EPMA: (a) soldered in air, (b) soldered in N2 atmosphere,



(c)

Fig. 5 Elemental analysis of solder surfaces for the case with 0.8HBr flux by EPMA: (c) qualitative elemental analysis of solder surface

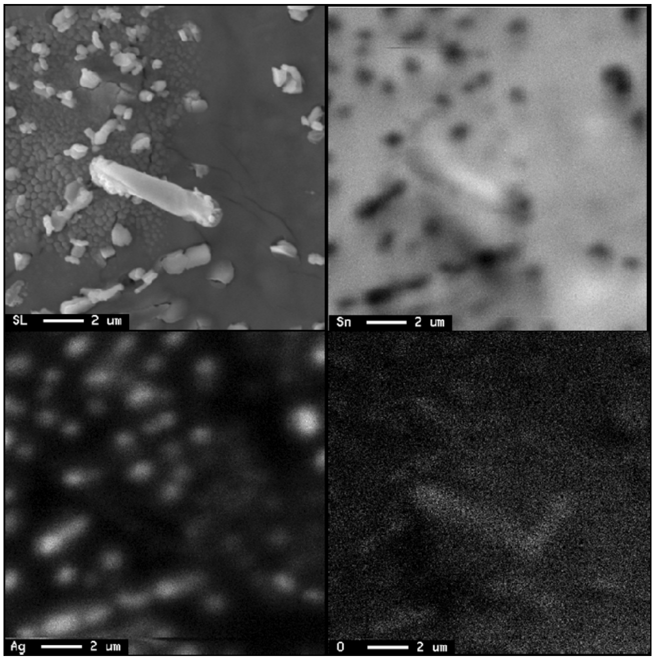


Fig. 6 Elemental analysis of white-spots microstructure formed on the solder surface for air condition by EPMA.

It is theorized that solder oxidization affected the eutectic microstructure of Sn-3.0Ag-0.5Cu solder. This caused a deformation and exposed island-like spots on the surface of solder fillets. To keep phase equilibration, Sn atoms diffused to the direction of low energy; the result was Sn whisker growth on these oxidized solder surfaces. Consequently, the N_2 reflow atmosphere has a suppressive effect on solder oxidization, thereby dramatically inhibiting the formation of Sn whiskers.

Investigate analysis of the oxides of the solder fillet, i.e., cross-sections of the oxidized area with the island-like white spots microstructures, were examined by FIB and EDS (Fig. 7). From image (c, e), it is well illustrated that the solder was oxidized below the islands-like microstructures. In other words, the oxide penetrated deeply into the solder fillet.

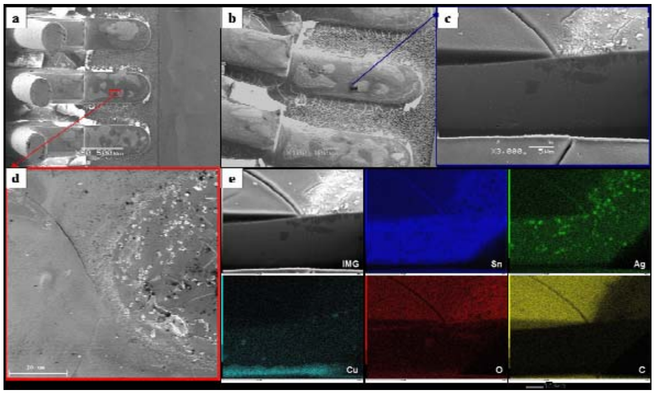


Fig.7 Oxidation of Solder fillet was examined by FIB and EDS: (a) an SEM image of solder fillets before fabricated by FIB, and (d) is magnified image of squared area; (b) a tilting image after fabrication by FIB, (c) magnified cross-sectional image fabricated by FIB; (e) elemental analysis of the cross-section by EDS.

The Cross-sectional microstructures of solder fillet are examined for investigating effects of N_2 atmosphere and flux on oxidization of solder fillets. Figure 8 show the cross-sectional microstructures of solder fillets for the case of 0.8%HBr activated flux after conditioning in an 85℃/85% RH ambient for 1000 hours.

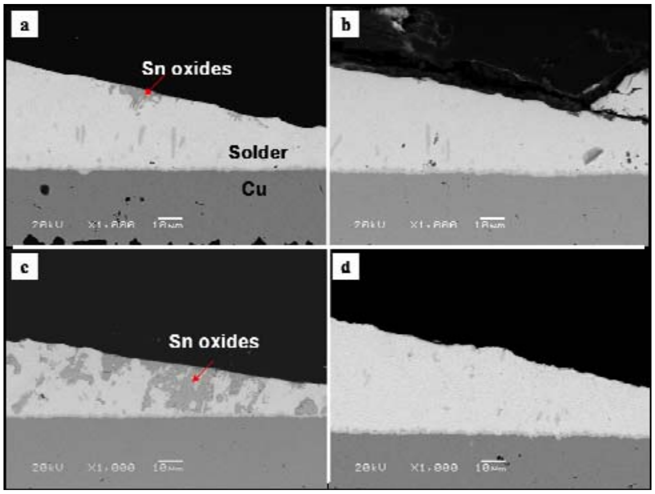


Fig. 8 Cross-sectional microstructures of solder fillet with HF+0.8%HBr activated flux after 1000 hours in 85°C/85%RH: (a, c) soldered in air atmosphere, (b, d) soldered in N2 atmosphere; the electrode lead frames for (a, b) is Cu, and the lead frames for (c, d) is 42 alloy.

Fig. 8 (a, c) show the cross-sectional microstructures of solder fillets were soldered in air atmosphere. With the exception of typical Sn-Ag-Cu ternary alloy microstructure were composed of primary β-Sn grains surrounded by a Ag_3Sn/Cu_6Sn_5/β-Sn eutectic network, Sn Oxides were examined by EDS (Fig. 9).

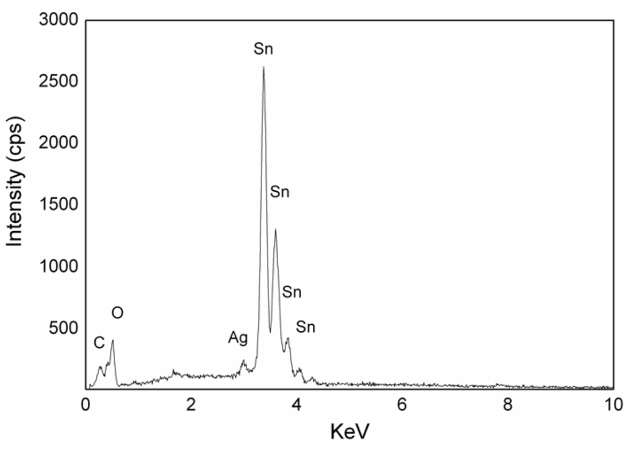


Fig. 9 EDS analysis of cross-sectional microstructures of solder fillet with HF+0.8%HBr activated flux for 42 alloy electrode lead frame after 1000 hours in 85°C/85%RH.

Comparing samples reflowed in N_2 and air atmospheres, a large amount of Sn oxides penetrated into solder fillet with the air soldered parts. With the N2 atmosphere, a small amount of Sn oxides were detected at solder surface or the cross area between solder surface and Cu pad. This is attributed to the fact that N_2 atmosphere prevents diffusion of oxygen into the molten solders, thus no oxide formation. No visible Sn oxides were observed in the cross-sectional microstructure of solder fillets after holding 1000 hours in 85°C/85% RH for the case of 0.4% HBr flux and halogen free flux reflowed in air, regardless of lead frames of Cu or Alloy 42. Sn oxides increase with increasesd halogen concentration of flux. These results indicate that halogen free flux has a suppressive effect on the oxidation of solders. To clarify the reason for the formation of Sn whiskers, cross-sectional microstructures of Sn whiskers were examined by FIB and EDS. Figure 10(c) show a typical cross-sectional microstructures of Sn whiskers on solder fillet of QFP soldered in air with 0.8HBr activated flux. It can be seen that Sn oxide be formed around the Sn whiskers.

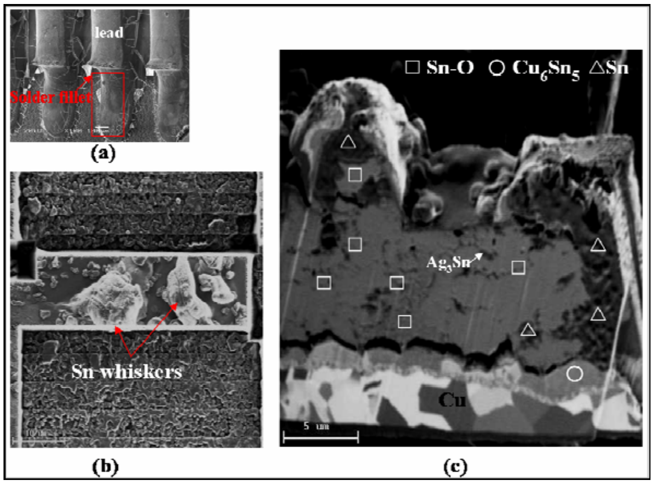


Fig. 10 Cross-sectional microstructure of Sn whiskers on solder fillet of QFP for soldered with HF+0.8%HBr activated flux in air after 1000 hours in 85°C/85%RH ambient. (a) Solder fillets of a QPF joints. (b) Sn whiskers morphology on a solder fillet during FIB micro-sampling process. (c) The cross-sectional microstructures of Sn whiskers were obtained tilting the micro-sample backward 60 degree after fabrication by FIB, and elemental compositions were analyzed by EDS.

The formation of Sn oxides result in volume expansion about 29~34% (Table 2) [5].

Table 2 Theoretical differential volume for oxidation products of Sn

Material	Molar Free Volume (CC/mole)	Excess Molar Volume (%)
Sn	16.2	----
O_2	0	----
OH	**0**	----
SnO	**20.9**	**14.5**
SnO_2	**21.7**	**11.3**
SnO2-hydrated	**36**	**40.7**

Consequently, that Sn oxides formed can be the source of compressive stress act on Sn grains. To release this stress, Sn whiskers grow from the Sn surface. Easy to understand this mechanism, a sketch map of Sn whisker formation on solders induced by oxidization as drawn in Fig. 11.

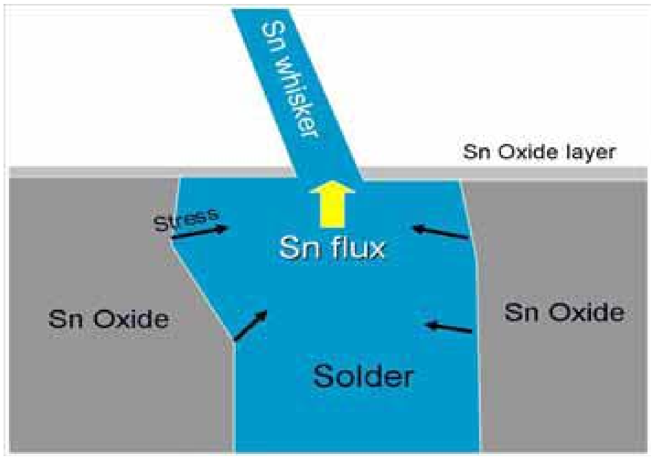


Fig. 11 The mechanism of Sn whiskers formation on solder fillet induced by oxidization.

Under this mechanism, the higher corrosive samples grow Sn whiskers more easily. Because the Sn oxides formation is accelerated by the activated solders, and the compressive stress act on Sn grains also be promoted. In the case of alloy 42 lead frames of QFP samples, this compressive stress to be accelerated by coefficient of thermal mismatches between materials of solder fillet and lead frames of QFP additionally. Table 3 lists thermal expansion coefficients of typical material on electronic packaging.

Table 3 Thermal expansion coefficients of typical materials on electronic packaging

Cristal	Thermal expansion coefficient (10^{-6}/K)
Sn	23.0
Cu	16.5
Ni	13.3
Zn	39.7
Alloy 42	4.5~6.5[25]
Cu_6Sn_5	16
Cu_3Sn	19
Ni_3Sn_4	14

Comparing with Cu, the coefficient of thermal expansion mismatches of alloy 42 is larger, susceptible to generation mismatch strain result in the formation of Sn whiskers. We speculate the lead frame of alloy 42 combined solder fillets worse than Cu lead frames of those for Sn whisker formation on QFP solder fillets. Further investigation is required to clarify effect of lead frame material on Sn whisker growth in future.

Consequently, it is demonstrated that an inert N_2 atmosphere and halogen free flux have the great effect on suppressing Sn oxides formation on solder fillet, so that restrained the formation of Sn whiskers regardless of lead frame.

CONCLUSIONS

In this work, Sn whiskers formation on solders fillet of QFP soldered on PCB with three different concentrations of HBr activated fluxes in air/N_2 process atmosphere were evaluated during 85℃/85% RH ambient exposure. Sn whiskers formed on solder fillets induced by oxidizations were investigated. Oxidization induced Sn oxides along wit lack Sn area and rich C area on solder fillet to generate stress concentration locally. This excess stress concentration became the source of compressive stresses that act on Sn grains. To release this stress, Sn whiskers were incubated and then grow up on solders surface. In addition, HBr activated fluxes have an accelerative effect on solders oxidization, thereby increasing Sn whiskers growth on solder fillets. In contrast, N_2 atmosphere effectively restrain the formation of Sn oxides, and suppressing Sn whisker growth for all conditions in the current work, although flux activated with 0.8%HBr. In conclusion, we proposed that combining inert N_2 reflow atmosphere and halogen free flux is one of the mitigating methods for Sn whiskers formation on Sn-Ag-Cu solders. To establish more reliable reflow process, further investigation is required to optimize the N_2 gas flow and to find the other atmosphere condition.

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