

Mechanism of Whisker Growth caused by Corrosion of Solder

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Abstract

Recently semiconductor devices are used in more strict circumstances of humidity and temperature. In these circumstances, we have high risk that great number of whiskers will occur and grow by corrosion of solder. However, this type of whisker will be not almost studied including its mechanism. In the first step of this study we tried to make tin whisker grow by residual stress of corroded solder. We succeeded in growth of whiskers by corroded solder. Maximum length of whisker was observed to be 400 micron-meter. And in the second step, we observed these whiskers using high resolution SEM and TEM. Observed whiskers were located between two corroded solders. In these observations, it was concluded that these whiskers occurred and grew by residual stress of corroded solder and inter-metallic compound. And new mechanism of whisker growth was proposed. We noticed the risk for application of lead-free solder to these strict circumstances.

Key words; whisker, solder, corrosion, residual stress, lead-free

1. Introduction

Recently, miniaturization and high performance of electronics accelerate the increase of mounting density of electronic parts to the printed wiring board. Moreover, the circumstances (temperature and humidity) that these are used are becoming more strict, especially in car electronics. The risk of whisker growth caused by solder corrosion is increasing.[1][2] Then in this paper we studied about whisker growth caused by solder corrosion attacked by the flux residue.

2. Experimental procedure

Comb-type wiring boards were prepared. These were dipped into molten tin solder after flux coating. Without rinse these were held in 85C-85% chamber for 0-2000h.. After holding, whiskers and corroded conditions in these specimens were observed. Two kinds of wiring boards were adopted; Cu-OSP and Ni/Au electroless plating. Used flux content is WW Rosin-23.9wt% IPA-75wt% Diethyl amine HBr salt -1.1wt%. Fig.1 shows PWB and example of observed whiskers. Almost whiskers are located at the edge of wiring.

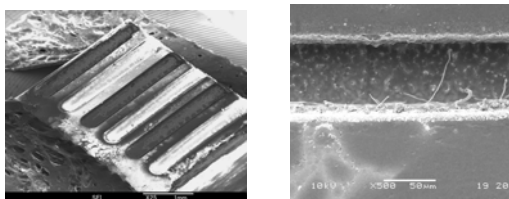


Fig.1 SEM images of PWB and the example of whiskers

3. Experimental results

Fig.2 shows the relation between holding time and whisker maximum length, numbers.

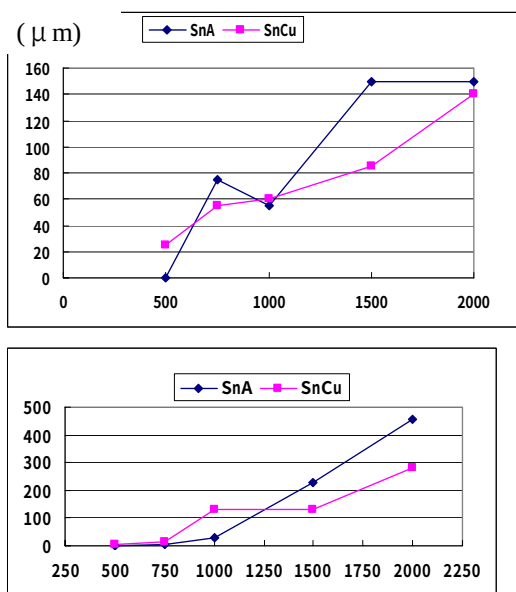


Fig.2 Relation between holding time (h) and whisker maximum length (upper figure) / whisker number (bottom figure)

In this figure SnA stands for Ni/Au, SnCu for Cu OSP. Holding time is the longer, length and number of whiskers are the larger. Maximum length is about 150 μm on 2000h. Substrate materials (Cu or Ni/Au) does not have an great effect on whisker growth. Then, we observed the cross-section of whisker using Ni/Au plated substrate. Fig.3 shows the whisker of which we observed its cross section. Its root swells a little. This sample was cut with micro-tome and polished with FIB (Focused Ion Beam).



Fig.3 SEM image of observed whisker

This whisker is located at the side of Cu-wiring.

Fig.4 shows SEM image of sectioned whisker that grows at slightly lower position from the shoulder of Ni plated Cu-wiring.

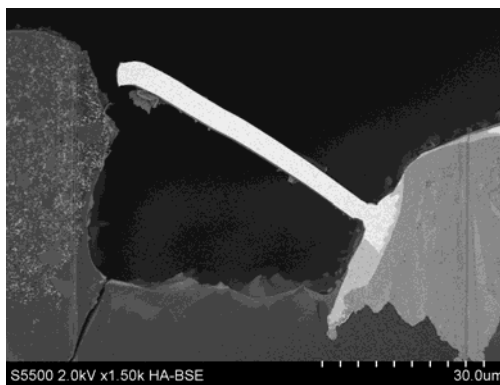


Fig.4 BSE image of sectioned whisker

Almost all whiskers were located at the same position. Fig.5 shows the enlarged image of its whisker root.

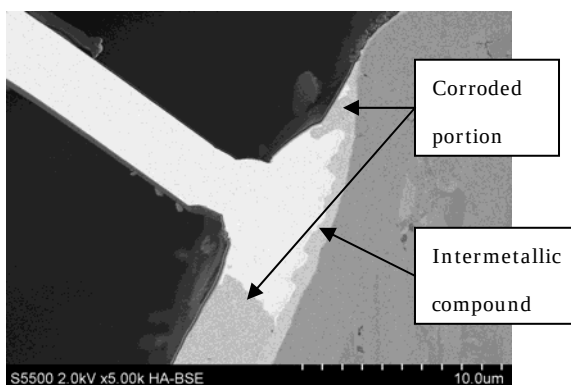


Fig.5 BSE image of whisker root portion

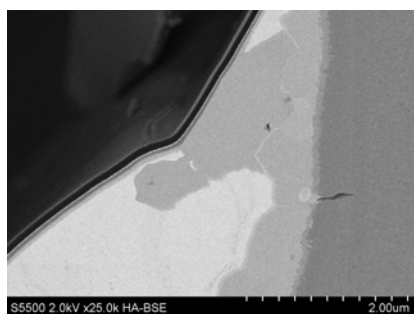


Fig.6 BSE image of upper side in whisker root

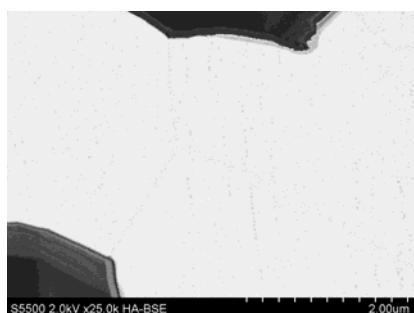


Fig.7 BSE image of whisker root portion

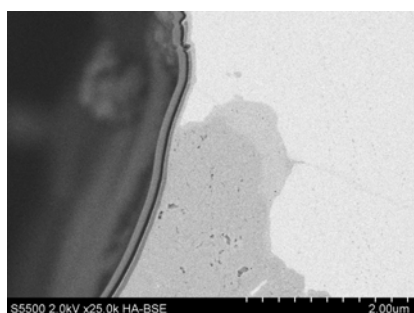


Fig.8 BSE image of lower side in whisker root

Enlarged BSE images are shown in Fig.6 (upper side), Fig.7 (root portion) and Fig.8 (lower side).

As subsequently analyzed, the white portion of whisker and its root (Fig.7) are tin and gray zones of upper (Fig.6) and lower (Fig.8) are porous tin-oxide. These porous tin-oxides are the corroded materials by flux residue. Based on Fig.7 it will be considered that whisker grows from Y-shaped tin grain. In Fig.5 some inter-metallic compound layer exists between plated Ni and tin. We can suggest that as holding time passed, corroded zone of upper and lower side and inter-metallic compound were in progress,

and so whisker grew by this compression stress.

Fig.9 shows the enlarged BSE image of Fig.8.

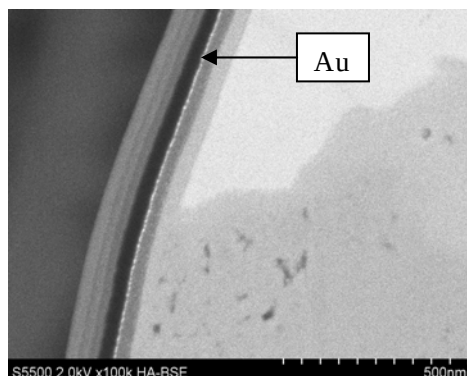


Fig.9 Surface image of lower side in whisker root

In this image, the thin white surface layer shows evaporated Au layer for SEM observation. We can observe two layers under this Au layer. These layers were analyzed in detail afterward.

Then TEM observation was conducted on the same position as shown in Fig.10, 11, 12, 13.

Fig. 10, 11, 12, 13 show each the upper portion, root portion, whisker and lower portion.

From these images we can suggest that whisker is single crystal and tin crystals of its root are composed with many stressed sub-grains. This will be the result of compression stress by growth of corroded portion and inter-metallic compound.

In corroded portion we can observe many voids as shown in Fig.9 and 13.

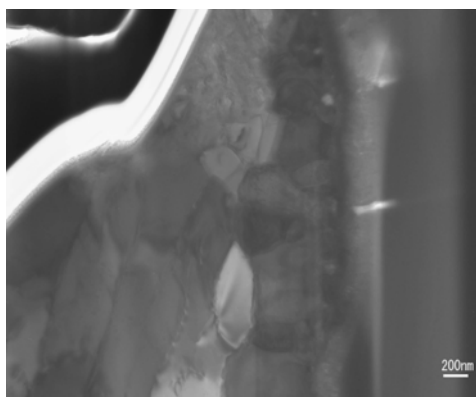


Fig.10 TEM image of upper portion in whisker root

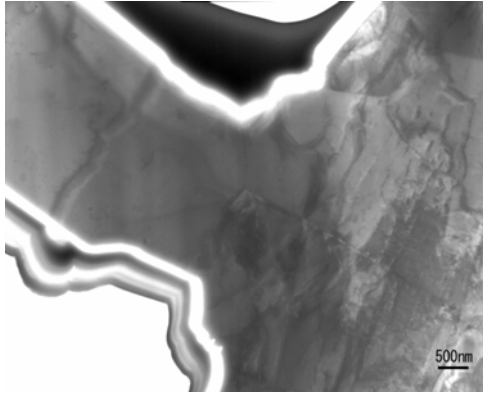


Fig.11 TEM image of whisker root

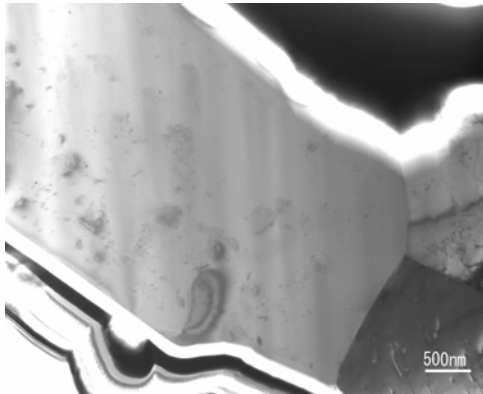


Fig.12 TEM image of whisker

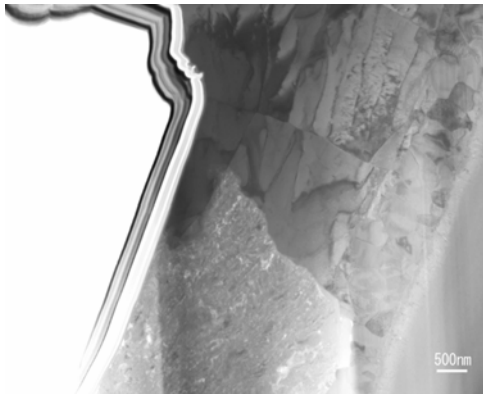


Fig.13 TEM image of lower portion in whisker root

Moreover, Fig 14 shows the enlarged surface layers(HAADF-STEM image). As mentioned before, two layers under Au evaporated layer were observed, and analyzed with EDX.

Results of EDX are shown in Table 1.

The upper layer under Au will be considered a flux residue as content is carbon. The lower layer is tin-oxides.

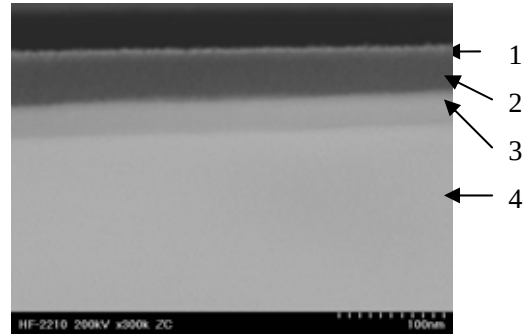


Fig.14 HAADF-STEM image of surface layers
(Figures show EDX analysis points)

Table1 EDX analysis results of Fig.14

	Au	Sn	O	C
1	18.1	3.0	8.0	70.9
2	1.0	11.8	8.6	78.6
3	-	66.0	34.0	-
4	-	100.0	-	-

Fig.15 shows diffraction results of surface layers.

The first layer is C-rich amorphous material.

Therefore, it is considered as the flux residue.

The second layer is nano-order tin-oxide grains.

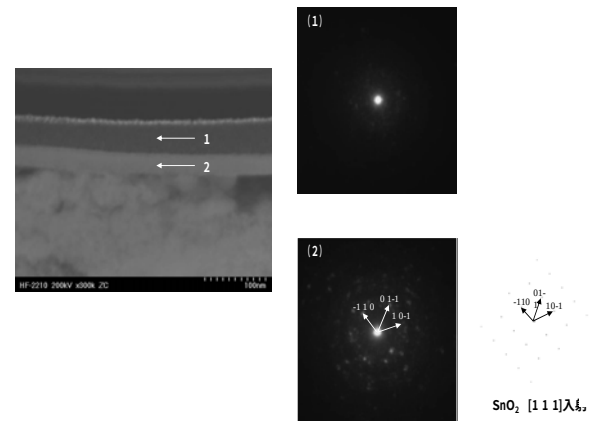


Fig.15 Diffraction results of surface layers

Then, EDX and diffraction analysis were conducted at the corroded portion of Fig.13. Fig.16 shows analysis points and Table2 shows the results of EDX.

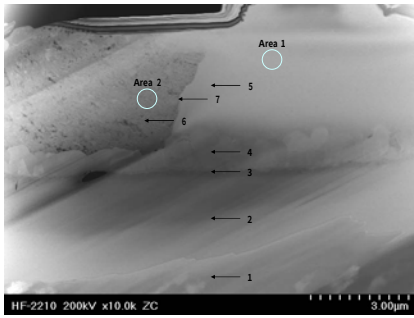


Fig.16 HAADF-STEM image of Fig.13

Table2 EDX analysis results of Fig.16

	Cu	Ni	P	Sn	O
1	100.0	-	-	-	-
2	-	90.2	9.8	-	-
3	-	25.1	73.5	1.4	-
4	-	49.0	-	51.0	-
5	-	-	-	100.0	-
6	-	-	-	82.0	18.0
7	-	-	-	82.6	17.4

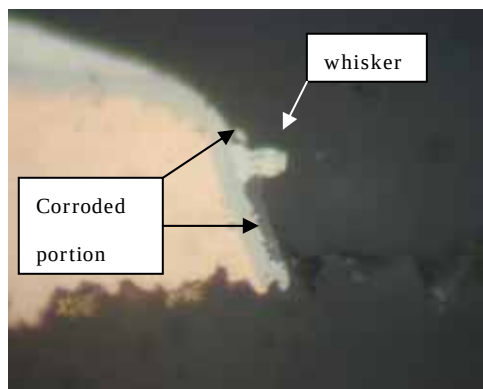
In Fig.16 Area-1,2 are each tin and corroded zone. Analysis points 6,7 show corroded zone.

These corroded materials were SnO₂ based on diffraction patterns in which grain size was 100nm order.

4. Discussion

We reported the analytical results of whisker grown by corrosion of solder so far.

Fig. 17 shows the optical microscope image of its cross-section.



**Fig.17 Optical microscope image of
Cross-section of whisker root**

From this photo we can recognize that the whisker grows from tin surrounded by the corroded upper and lower portion. Taking these factors into consideration, the following growth mechanism will be suggested.

During holding in high humidity and temperature chamber, corrosion of tin solder starts and progresses by active atom(Br) of flux residue from the shoulder and the root. On the other hands, inter-metallic compound grows toward tin solder. By growth of corroded portion and inter-metallic compound, residual tin is compressed, and a re-crystallized grain occurs and grows at the surface by its stress. As corrosion mechanism of solder, the local cell mechanism between tin and Ni or Cu will be considered.

To observe this corrosion mechanism of solder, the following experiment was conducted.

A solder ball (760 μm diameter) coated with flux was reflowed on Cu plate. Without rinse these plates were held in 85%-85C chamber for 0-1000h. After holding these, progressing conditions of corrosion were observed. Fig.18 shows these progressing conditions of corrosion. Tin solder began to corrode from 100h. As shown in these photographs the corrosion points are near Cu plate. From these figures corrosion make progress by local cell mechanism between solder and Cu metal. Active atom(Br) in flux will be considered to play a leading role of corrosion. In the case of the position far from Cu plate we could not observe any corrosion in spite of existence of flux. In case of Fig.17 we can observe two corrosion points- the shoulder and the lower part of wiring metal. So, wiring metal will expose at these points in air.



Fig.18 Optical microscope images of corrosion (holding time; 0-1000h)
(the upper is 0h ,the second is 30h, the third is 100h, the fourth is 300h, the bottom is 1000h)

As a risk of electronic parts, maximum length of its whisker will be important to be predicted.

We tried to get some longer whiskers, changing the reflow process and the other conditions

.We observed over 400 μm length whisker caused by corrosion. To get the longer whiskers it will be important that thickness of solder is large. In the case of Fig.17 thickness of solder was about 5 μm . Fig 19 shows the example of over 400 μm . Fig.20 shows the cross section of the root of this whisker. In this case thickness of solder was about 30 μm . The source volume of tin for whisker is larger than that in Fig.17.

Therefore, the position where whisker caused by solder corrosion occurs will be considered to be the following conditions.

- (1) the position where Cu or Ni exist near lead-free solder and these metals are exposed in air.
- (2) the position where residual flux including active atoms exists
- (3) the position where this electronic parts are used in high humidity and temperature
- (4) thickness of solder is the larger, the longer whisker grows

Next, as compression stress to make tin atoms diffuse, we can consider two causes; inter-metallic compound and corroded material.

To clarify the contribution of these two factors, we have to study moreover.

However, considering from TEM images (Fig.11,13), inter-metallic compound will be a great contribution to compression stress of tin sub-grain.

5. Conclusions

We could grow intentionally whiskers caused by solder corrosion, and observed them using SEM and TEM. The following conclusions were got.

1. By holding the soldered substrate covered with flux residue in high humidity and temperature chamber, whiskers caused by corroded solder grew. Holding time was the longer, its whisker length became the longer.

2. We analyzed the whisker, using SEM and TEM. The whisker grew from tin grains surrounded by inter-metallic compound and corroded tin. This tin grains included many sub-grains.

3. We could get some whiskers of over $400\text{ }\mu\text{m}$ length. In this whisker thickness of tin solder was higher.

4. We made an experiment on solder corrosion, using reflowed tin solder on Cu plate. Solder will be suggested to corrode by local cell model between solder and the other metals (Cu, Ni).

5. We proposed its whisker growth mechanism. During holding in high humidity and temperature chamber, corrosion of tin solder starts and progresses by active atom(Br) of flux residue from the shoulder and the root. On the other hands, inter-metallic compound grows toward tin solder. By growth of corroded portion and inter-metallic compound, residual tin is compressed, and a re-crystallized grain occurs and grows at the surface by its stress.

An illustration of this model is shown in Fig.21.

6. References

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- [2]P.Oberndorff,M.Dittes,P.Crema,P.Su and E.Yu; "HumidityEffectson Sn Whisker Formation" IEEE Trans. EPM Vol.29 pp239-245 2006

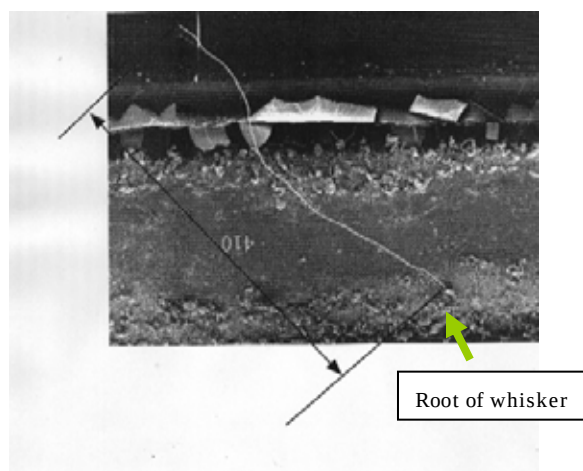


Fig. 19 Example of long whisker($410\text{ }\mu\text{m}$)



Fig.20 Cross section of the long whisker root(Fig.20)

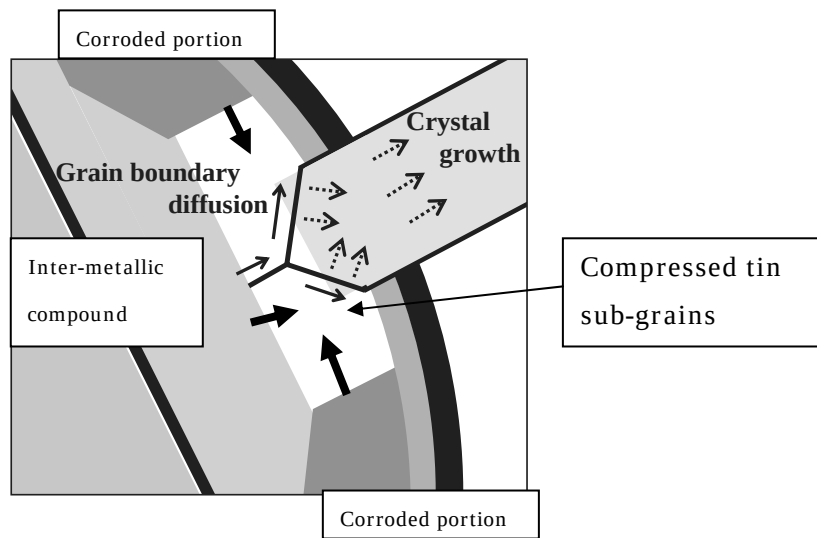


Fig.21 illustration of whisker growth mechanism