Substitute Materials for Complete Elimination of Hazardous Substances - Study of Whisker Growth on Lead-Free Plating -

● Seiki Sakuyama ● Michinori Kutami

(Manuscript received January 20, 2005)

To elucidate the mechanism of tin (Sn) whisker growth on lead (Pb)-free plated electrodes, we studied their growth behavior. Concerning the structure in which Sn whiskers originate, we determined that the whiskers are created by the recrystallization of Sn when the Sn grain size of whisker sources is coarser than that of the surrounding grains. We also found that there is a more than 700-hour period of latency before the whiskers appear in Sn plating, which correlates with the incubation period of Sn recrystallization. The longer the latency period of the plating, the greater the danger of needle-like whiskers growing. We also observed that needle-like whiskers grow most easily under the conditions of 25°C plus the application of external stress. We therefore chose those conditions for a probability test of Sn whisker growth.

1. Introduction

In the midst of increasing awareness of environmental problems around the world, many regulations concerning hazardous materials are being established, for example, the waste electrical and electronic equipment (WEEE) directive and the end-of life vehicles (ELV) directive in the European Union (EU). Furthermore, the Restriction of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) directive will add new restrictions when it comes into effect in July 2006. This directive will prohibit the sale in Europe of all products that use any of six materials (lead, mercury, hexavalent chromium, cadmium, polybrominated biphenyls [PBB], and polybrominated diphenyl ethers [PBDE]), except for some exempt products.

Many parts that contain these six materials are being used in home appliances, information equipment, and many other electronic devices. It goes without saying that a system for verifying that those components do not contain hazardous materials should be established, but the development of substitute parts and materials and the maintenance of part and material reliability is also important. A point that particularly requires attention is identifying which problems will arise concerning device characteristics and quality when these hazardous materials are eliminated.

Of the six materials mentioned above, lead (Pb) has the most diverse uses. Some example uses of Pb and its alloys are given in **Table 1**.1) Some of the many advantages offered by Pb are that it is softer, has a lower melting point, and is cheaper than most other ordinary metals. These are the reasons for its wide use, for example, as a material for soldering and a colorant and stabilizer for PVC (polyvinyl chloride). In electrical products, the greatest use for lead is in solder. Since the reporting of Pb pollution of ground water in the United States in 1988, the necessity for Pb-free soldering has been exclaimed and awareness of the problem has increased worldwide. Much research on Pb-free solders is in progress in Japan and other countries, and products that use tin-silver (Sn-Ag) or tin-zinc (Sn-Zn) alloy solder are currently on the market.[2),3)] On the other hand, tin-lead (Sn-Pb) alloys are used to plate electrical connections such as LSI lead pins and the electrical junctions of connectors. It is of course necessary to eliminate Pb from those plating materials as well, but it is known that Sn whiskers grow from the surface of Pb-free plating layers. These whiskers can create unwanted electrical shorts between electrodes. Little information on these Sn whiskers has been reported, and the mechanism of their growth remains unexplained.

In this paper, we report on a study of the relation between whisker growth and recrystallization as a step toward explaining the Sn whisker growth mechanism — an achievement that will open the way to Pb-free solder plating.

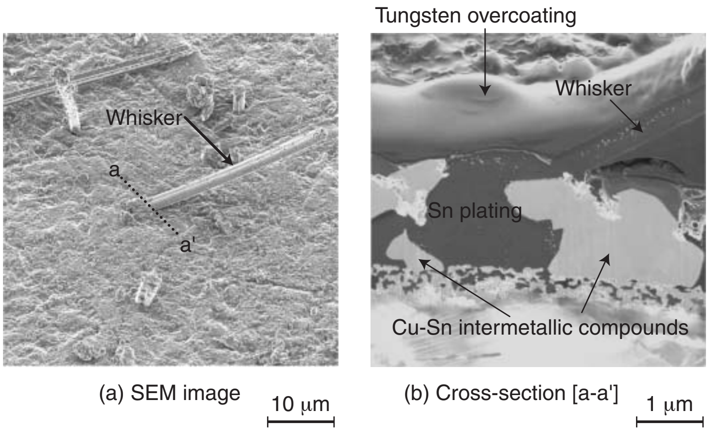
Table 1
Types and usage of lead and lead compounds.

Type	Usage
Metallic lead	Solder (joint material, plating)
Lead monoxide	Glass, rubber vulcanization
Lead dioxide	Storage batteries
Lead tetroxide	Glass, anti-corrosion paint
Lead titanate, lead chromate	Pigments
Lead acetate	Pigments, dyestuffs
Lead stearate	Stabilizer of PVC

2. Sn whiskers

A SEM image of a whisker growing from Sn plating and a SIM image cross-section of this plating are shown in **Figure 1**. In 1948, it was discovered that the telephone line failures that had been frequent up to that time were caused by electrical shorts created by Sn whiskers growing from the plating of capacitor plates. That brought attention to these whiskers. Many of these whiskers have a diameter of about 1 μm and grow to a length of more than 1000 μm. Concerning the whisker growth mechanism, dislocation theory, surface energy theory, and recrystallization theory have been suggested, but experience points to recrystallization theory as the most suitable of those.[4)] Many of the details, however, remain unknown. The melting points and recrystallization temperatures of various metals are presented in **Table 2**.[5)] The recrystallization temperature of a metal is typically from 0.35 to 0.60 of its melting point (Tm+273[K]); and Sn, cadmium (Cd), and zinc (Zn) — which have low melting points — recrystallize near room temperature. Therefore, we believe there is more opportunity for whisker growth to occur for these three elements compared to other metals.

For component electrode plating, Sn-alloy plating is in wide use because of its excellent



(a) SEM image (b) Cross-section [a-a']

Figure 1
SEM image and SIM image cross-section of whiskers on Sn plating.

solderability. Previously, whisker growth has been controlled by adding a small amount of Pb (5 wt% or more) to the Sn.6),7) However, because of restrictions on the use of Pb, it is being replaced with simple Sn plating or with Sn plus 1 to 3 wt% of copper (Cu), silver (Ag), or bismuth (Bi). Unfortunately, the growth of whiskers cannot be controlled in any of these plating compositions, and whiskers occur with high probability from the plated electrodes of components that have been subjected to externally applied stresses, especially those that occur during bending, cutting, and insertion.8)

Therefore, we evaluated whisker growth in relation to the following parameters that are considered to affect growth on the Sn and Sn-Cu replacements for Sn-Pb: external stress in the plating layer, base metal, temperature, and time.

Table 2
Melting points and recrystallization temperatures of various metals.

Metal	Melting point: Tm (°C)	Recrystallization temp. (°C)
Fe	1535	350 ~ 500
Ni	1455	530 ~ 660
Cu	1083	200 ~ 250
Al	660	150 ~ 240
Mg	651	150
Zn	419	7 ~ 75
Cd	321	~ 25
Sn	232	-7 ~ 25

Table 3
Plating details.

Base metal	Brass (40Cu/Zn), phosphor bronze (C-5191P)
Under plating	Ni (2 μm) or none
Surface plating	Bright Sn, mat Sn, bright Sn-2wt%Cu
Plating thickness	2, 5, 10 μm

3. Experiments

3.1 Plating samples

In the experiments, 40 × 5 × 0.1 mm brass (40 Cu/Zn) and phosphor bronze (C-5191P) plates were used as the plating base metals. The surfaces were plated with bright Sn and bright Sn-Cu. In addition, the base metals were plated with 2 μm of Ni. Surface platings of 2 μm, 5 μm, and 10 μm were used for all cases. The plating details are shown in **Table 3**.

3.2 Method of applying external stress and evaluation conditions

The apparatus shown in **Figure 2** was used to apply external stress. The two ends of each sample were fixed in place, and the moving part was adjusted to cause a 1.95 mm displacement in the sample. The resulting stress in the samples was 2.5 GPa, and the experiments were performed with the plated surfaces in this state. The samples were kept at 25, 50, and 130°C, and the maximum stress-application time was 2500 hours.

3.3 Whisker growth observation

Whisker growth and length were observed in a 0.84 × 0.62 mm area. Whisker growth was observed with a digital microscope (VHX, Keyence), and the lengths were measured with a scanning electron microscope (SEM: S-4700,

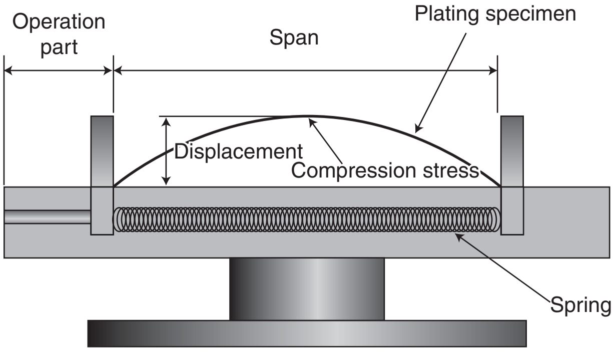


Figure 2
Bending stress tool for whisker test.

Hitachi). The observations were made on the compression side of the samples with the stress applied. The length threshold for counting the number of whiskers was 30 µm. The maximum whisker length in the observation area was measured at the same time.

3.4 Cross-section observation

We used focused ion beam equipment (FIB: SMI9200, Seiko Instruments) to make the cross-section and a scanning ion microscope (SIM) for the observations. For the conduction processing, carbon was sputtered onto the sample surface and the place where the cross-section was made was protected by a tungsten layer. The angle of observation was 60 degrees.

4. Results and discussion

4.1 Sn whisker growth

Bending stress was applied to Sn and Sn-Cu plating on phosphor-bronze base metal, and the whisker growth rate was measured. The results are shown in **Figures 3** and **4**. The Sn-Cu plating exhibited whisker growth just two hours after the stress was applied, and the growth stopped within 24 hours. On the other hand, whisker growth was observed on the Sn plating after about 720 hours, and the growth of even late-appearing whiskers stopped after about 2000 hours. In addition, the whiskers on the Sn plating were about 10 times as long as those that grew in the short period on the Sn-Cu plating. From **Figure 5**, we can see that the Sn-Cu plating has finer grains than the Sn plating, which facilitates atom mobility. Furthermore, we can infer that the application of external pressure produces the short-period whisker growth. The fact that finer grains facilitate recrystallization suggests that the whiskers appear when recrystallization occurs.$^{5)}$ To confirm the recrystallization state, we performed FIB treatment from the surface on the area where the whiskers appeared in order to observe their source. The results are shown in **Figure 6**. We found that whiskers grew from grains that were about 10 times the diameter of the surrounding grains. Furthermore, there were voids inside these coarse grains, suggesting that the whiskers grew as fast as atoms could be supplied from the surrounding crystal.

The time when the whiskers appeared was strongly related to the time between the plating process and the application of the stress. The Sn-plated samples that were stressed immediately after plating exhibited whisker growth about 720

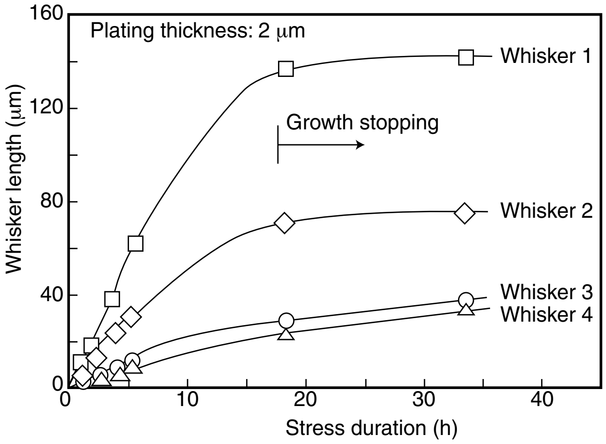


Figure 3
Whisker growth on stressed Sn-Cu plating at 25°C.

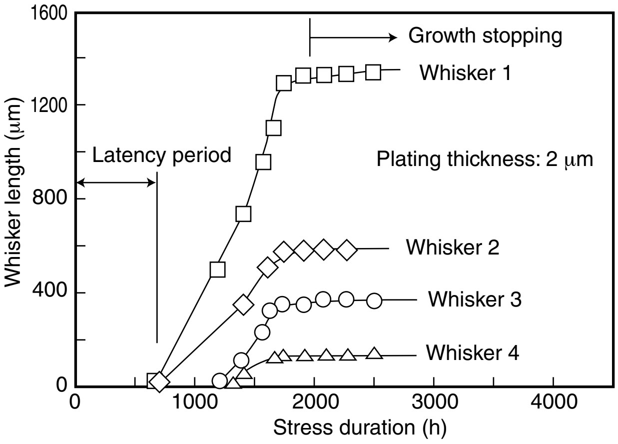


Figure 4
Whisker growth on stressed Sn plating at 25°C.

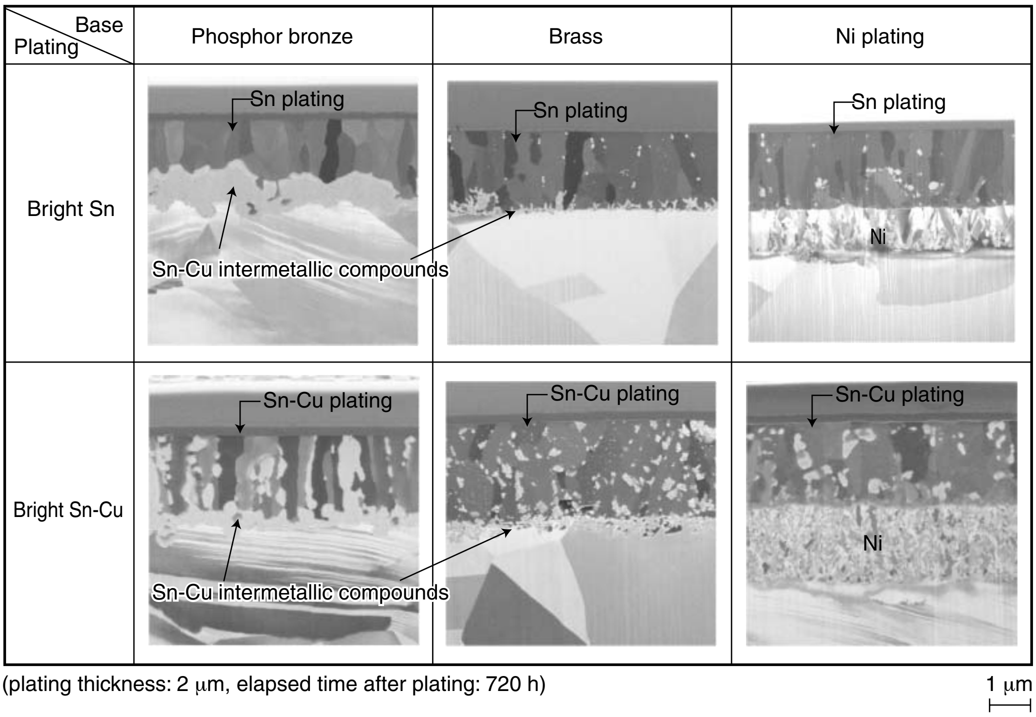
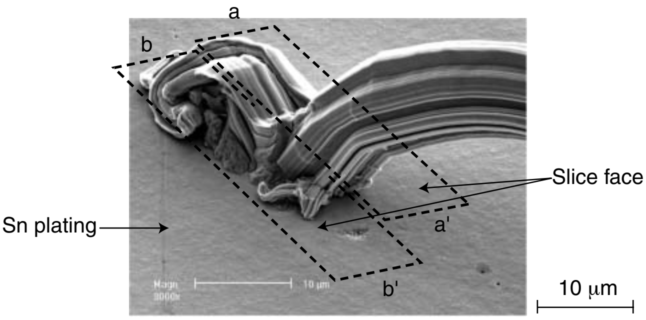
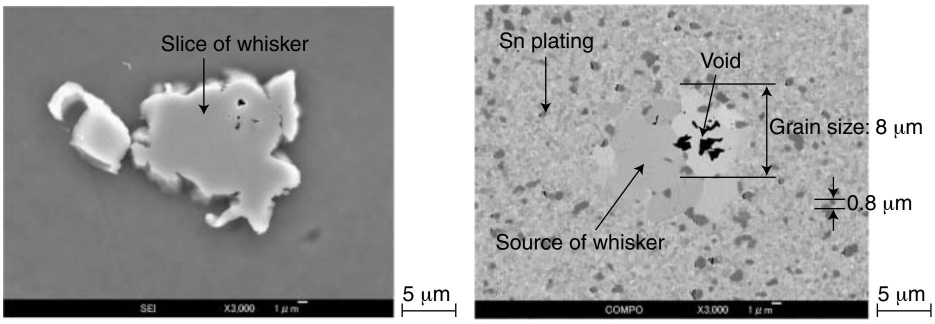


Figure 5
Cross-sections of Sn and Sn-Cu plating.



(a) Sn whisker



(b) Slice surface of a-a'
(SEM image)

(c) Slice surface of b-b'
(composite image)

Figure 6
Sn whisker and slice surfaces. (c) shows the whisker source.

hours after the start of stressing (Figure 4). However, the Sn-plated samples that were stressed starting 1500 hours after plating exhibited only a brief period of whisker growth several hours after the start of stressing (**Figure 7**). These results indicate that the latent period for whisker growth begins at the time of plating, which suggests a close relationship with the incubation period of recrystallization. Therefore, when evaluating whisker growth, the amount of time that has passed since the plating process is important.

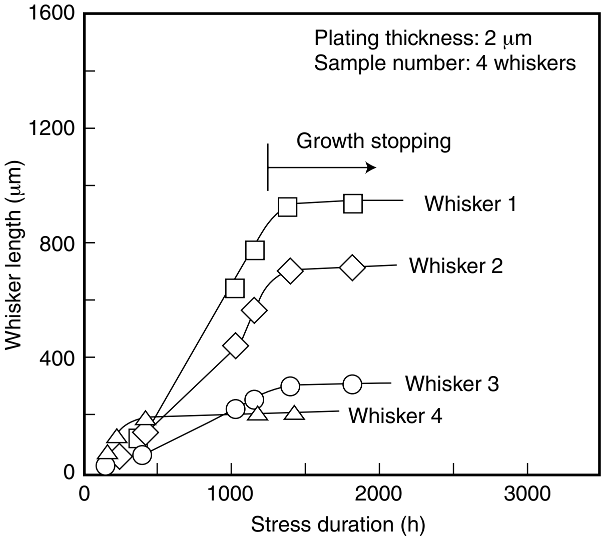


Figure 7
Whisker growth on samples that were stressed starting 1500 hours after Sn plating. (Temperature: 25°C)

4.2 Effects of base materials

The rates of whisker occurrence on samples of Sn-plated brass, Sn-plated phosphor bronze, and Ni-treated base metal plated with Sn are shown in **Figure 8**. When the base metal was plated with Ni, no whiskers longer than 30 μm were observed. The sample prepared by direct plating on phosphor bronze, on the other hand, exhibited whiskers longer than 1000 μm. Many whiskers appeared on the samples of plated brass, but they were shorter than the whiskers on phosphor bronze. Cross-section photographs are shown in Figure 5. In the case of the Ni-plated base, the barrier effect of the Ni controls the diffusion of Cu and Sn between the plating and base metal. In addition, the plating on phosphor bronze exhibited the most growth of the intermetallic-compound layer, which creates the compression stress within the plating layer that is inferred to be the cause of long whisker growth.[9)]

The results of Auger electron spectroscopy (AES) for an Sn-plated brass sample are shown in **Figure 9**. There are Zn and oxygen atoms at the grain boundaries of the Sn crystals. The creation of defects in the plating surface caused by the diffusion of Zn from the brass base metal is considered to be the reason for the many whiskers that appear.[7)]

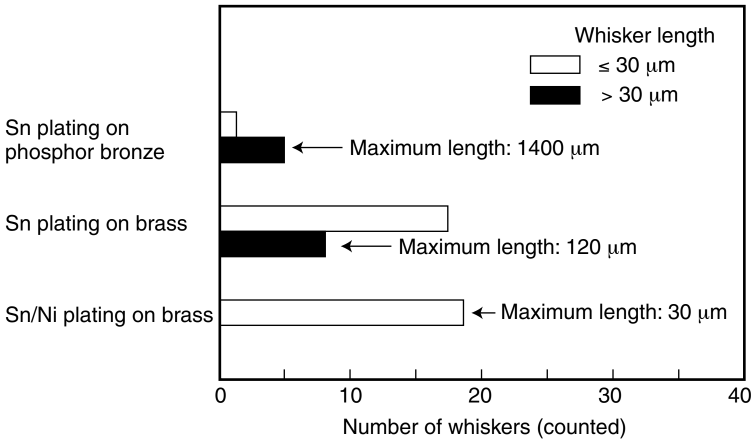
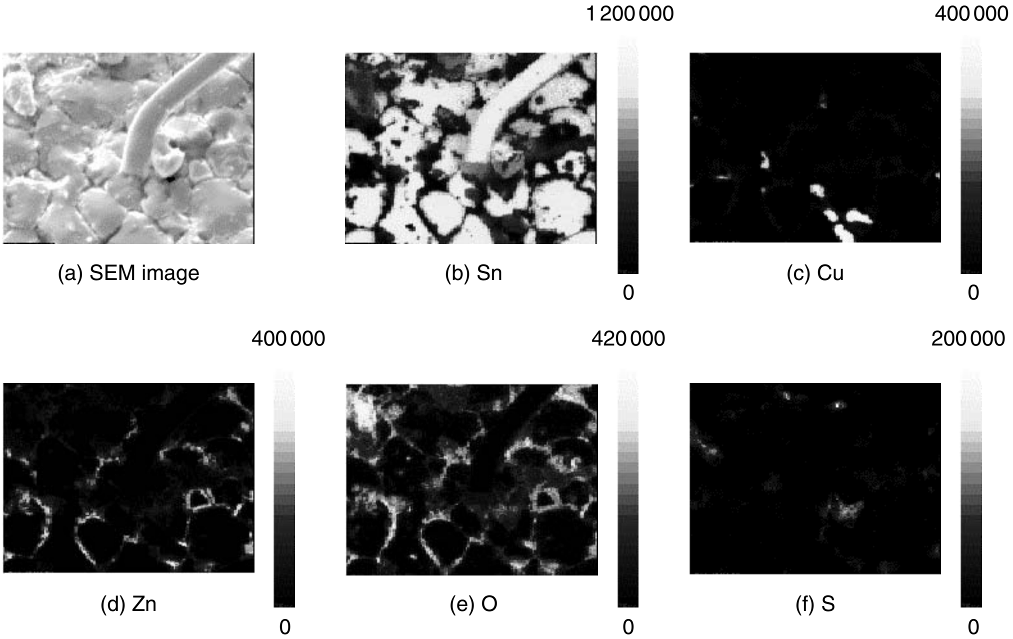


Figure 8
Maximum whisker length and number of whiskers on each base metal.



(a) SEM image (b) Sn (c) Cu
(d) Zn (e) O (f) S

Figure 9
AES and SEM images of Sn plating surface on brass.

These facts suggest that the formation of a diffusion control layer such as Ni plating is necessary to prevent whisker growth because the occurrence of whiskers is affected by the diffusion of Cu and Zn atoms from the base metal.

4.3 Effects of temperature

We investigated the relation between temperature and whisker formation of an Sn-plated phosphor bronze sample after adding a bending stress (**Figure 10**). At higher temperatures, short, nodule-shaped whiskers appeared; at lower temperatures, long, needle-like whiskers appeared. The recrystallization time is short when the temperature is high, which promotes whisker growth. However, we assumed that long whiskers did not form at higher temperatures because the heat relaxed the stress. Our results suggest that the most harmful needle-like whiskers easily appear at 25°C, which is the temperature at which much equipment is operated. Furthermore, the results discussed in Section 4.1 suggest that it is also important to confirm when whisker growth ends.

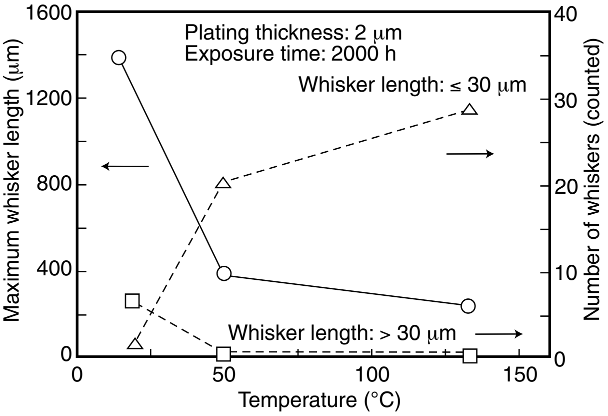


Figure 10
Relationship between temperature and whisker growth of Sn plating on phosphor bronze after adding bending stress.

5. Conclusion

The results of our study of the growth of whiskers from the surface of Pb-free Sn plating are summarized by the following:

1) The Sn whisker growth originates in an increase in grain diameter due to recrystallization, so Sn whiskers appear as the result of recrystallization driven by internal stress in the plating layer. There is a period of latency from the time an external stress is applied to the appearance of whiskers. Also, the longer the latency period of the plating, the greater the danger of harmful long, needle-like whiskers growing.
2) When brass is used for the base metal, zinc diffuses into the plating surface; with phosphor bronze as the base metal, Cu diffuses. In both cases, the diffusion causes whisker growth. Ni base plating prevents copper and zinc diffusion from the base metal and thus controls whisker growth.
3) At room temperature (25°C), the probability for growth of needle-like whiskers is high. In a high-temperature environment, relaxation of a plating's internal stress tends to increase the appearance of short nodule-like whiskers.

Because highly poisonous Pb has been much used in the past, the introduction of substitute materials such as Pb-free plating has become a necessary environmental measure with respect to the materials used in electronic equipment. A result of the elimination of Pb is the growth of Sn whiskers. Fujitsu is proceeding with various kinds of evaluation research with the objective of preventing damage from these whiskers. Ni under-plating restricts, but does not prevent, whisker growth on Sn plating. Therefore, before Ni-Sn-plated parts can be used, they must be externally stressed at 25°C and then inspected to check that their whisker growth has stopped, which would be very costly and time-consuming.

Finally, although we have focused on the problem of whisker growth here, the casual application of substitutes for other hazardous materials is highly likely to reduce product quality, so we believe that adequate evaluation must precede the application of such substitutes.

References

1) M. Saitou and K. Miyasaka: Leading Part of Chemical Restriction. (in Japanese), *Nikkei Ecology*, 11, p.23-51(2003).
2) T. Suga, ed.: Lead-free Solder Technology. (in Japanese), fourth edition, Nikkan Kogyo Shinbun, Ltd., Japan, 2003.
3) Y. Takahashi: Trend of Electronics Assembly Technology as Torchbearer of the 21 Century Environmental Revolution. (in Japanese), *Journal of High Temperature Society*, **30**, 1, p.16-23 (2004).
4) K. Yamabe: Whisker is Now. Current Research and View of Whisker. (in Japanese), *Metal*, **49**, 6, p.2-9, 1975.
5) J. Watanabe and Y. Saitou: Basic Metallic Material, fourth edition. (in Japanese), Kyoritsu Shuppan Co., Ltd., Japan, 1979, p.159-174.
6) R. Yamazaki: Whisker Grows in Metal. (in Japanese), *Surface Technology*, 73-3, p.112-116, 1973.
7) R. Kawanaka et al.: Role of Lead in Growth Suppression and Growth Mechanism of Tin Proper Whisker. (in Japanese), *Journal of Japanese Association for Crystal Growth*, **10**, 2, 1983.
8) N. Edanami: Whisker Test of Connectors, Examination Report for Practical Use of Lead-free Solder 2003. (in Japanese), Japan Electronic Industry Development Association, p.11-31, 2003.
9) George T. T. Sheng et al.: Tin whisker studied by focused ion beam imaging and transmission electron microscopy. *Journal of Applied Physics*, **92**, 1, p.64-69, 2002.

Seiki Sakuyama received the B.S. degree in Metallurgy from Akita University, Akita, Japan in 1989. He joined Fujitsu Laboratories Ltd., Atsugi, Japan in 1989 and has been engaged in research and development of solder-joint techniques and solder materials for electronics packaging. He is a member of the Japan Institute of Metals and the Japan Institute of Electronics Packaging.

Michinori Kutami received the B.S. degree in Electronic Eng. from Saitama University in 1976 and the M.S. degree in Electrical Eng. from Tokyo Metropolitan University in 1978. He joined Fujitsu Laboratories Ltd., Japan in 1978 and has been engaged in research and development of droplet ejection device for printing, MEMS material techniques, LSI device materials and ecological techniques. He is a member of the Institute of Electronics, Information and Communication Engineers, Japan and the Institute of Life Cycle Assessment, Japan.