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Corrosion Factor and Effects of Tin - Zinc Lead-Free Solder on Copper Substrate in Environmental Tests

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Abstract

We coated copper substrate with tin-zinc lead-free solder (Sn-9Zn and Sn-8Zn-3Bi), and then we performed the following corrosion tests: the salt mist test, the gas corrosion test, and the weathering test. Following the tests, we visually inspected specimen surfaces and cross-sections to determine the causes of corrosion and the extent of the corrosion to the base substrate.

By the surface condition of the Sn-Zn solder following the various tests, it was found that corrosive substances in the environment (such as sulfur and chlorine) reacted with the Zn in the solder to form corrosive products on the surface of the solder. After 18 months of the weathering test, cross-sectional analysis revealed that the Sn-Zn solder had been oxidized to a depth of 10um. However, the copper substrate underneath showed no evidence of corrosion. On the other hand, conventional Sn-Pb eutectic solder was oxidized to a depth of 20um, and the copper substrate also showed corrosion. We hypothesize that the corrosion of Zn in the Sn-Zn solder yielded a sacrificial corrosion effect by forming an intermetallic compound layer (Sn-Zn layer) between the base substrate and the solder. As a result, Sn-Zn solders exhibited corrosion resistance far superior to that of conventional Sn-Pb eutectic solder.

Introduction

Currently, research into the commercial adoption of lead-free solder is under way worldwide.[1-3] Typical examples of lead-free solder include Sn-Ag-Cu, Sn-Ag-Cu-Bi, and Sn-Zn. Among them, the Sn-Ag-Cu solder material exhibits the greatest level of reliability. However, Sn-Ag-Cu solder has a much higher melting point than conventional Sn-Pb eutectic solder, making it unsuitable for use with a variety of parts. Because of its advantageous melting point, which is close to that of conventional Sn-Pb solder, Sn-Zn solder has attracted attention as the next-generation candidate for lead-free solder. [4-5]

The diversification of our living environment has brought the use of electronic equipment to a wide variety of environmental conditions. Electronics equipment used near the seashore experiences degradation of electrical characteristics due to the ocean salt molecules. Electronics equipment mounted on vehicles or used near highways is subject to failure caused by exhaust gases polluting the atmosphere.

Data on the corrosion of metals and alloys have been provided in many reports. However, reports presenting data on the corrosion of solder materials are noticeably lacking. Tin, the primary constituent of solder material, forms a passive film on the surface, making solder quite resistant to corrosion.[6] However, the inclusion of metal additives changes its corrosion resistance characteristics. It can be anticipated that because Zn is a base metal its inclusion in Sn-Zn solder would degrade corrosion resistance. Corrosion could result in a loss of bonding strength between the solder and the base copper substrate, which is a component of the electronic parts leads. Results of the gas corrosion tests for Sn-Zn solder have also indicated formation of whisker-like needles in some reports[7]. These whiskers would short-circuit the electrodes, and must be confirmed in further testing.

The above-noted concerns mandate a thorough review of the corrosion resistance of Sn-Zn solder before its commercial adoption. As a result, we have carried out this research jointly with the "JIEP Project for Low-Temperature Lead-Free Solders and its Report on Questionnaire Survey" of the Japan Institute of Electronics Packaging (JIEP). This research carried out a variety of corrosion tests (the salt mist test, the gas corrosion test, and the weathering test) on the most typical types of Sn-Zn solder (Sn-9Zn and Sn-8Zn-3Bi). Following the tests, we observed the surfaces of the specimens with electron microscopes and elemental analysis equipment. Based on the results of these analyses, we have investigated the causes of corrosion and its effects on the base copper substrate.

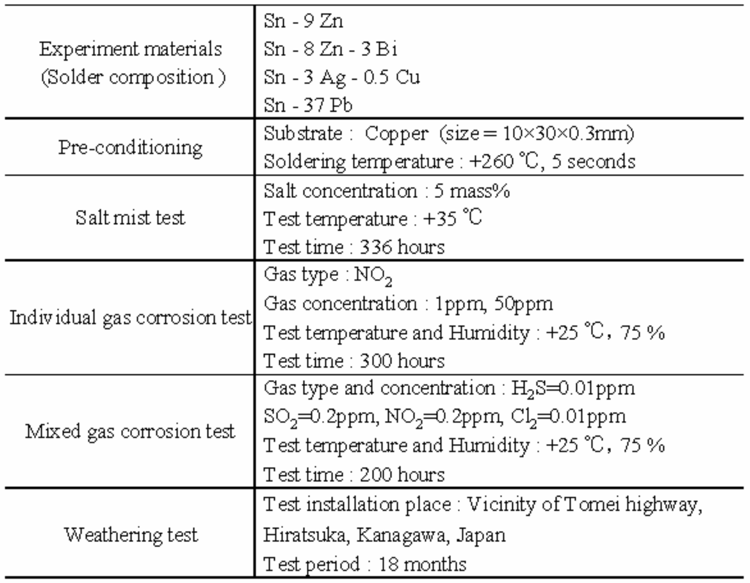
Experimentation

Solder Materials

Table 1 shows the solder materials that were evaluated, the specimen preparation conditions, and the corrosion test conditions. The solders used for evaluation were Sn-9Zn and Sn-8Zn-3Bi. Additionally, Sn-3Ag-0.5Cu and Sn-37Pb were used for the purpose of comparison.

A coating of the evaluation solder was applied to the copper substrate at 260°C for 5 seconds. Then, the coated copper substrate was washed with isopropyl alcohol (IPA), then with dichloromethane, and then once more with IPA.

Table 1 – Materials and Conditions for Experiments



Experiment materials (Solder composition)	Sn - 9 Zn Sn - 8 Zn - 3 Bi Sn - 3 Ag - 0.5 Cu Sn - 37 Pb
Pre-conditioning	Substrate : Copper (size = 10×30×0.3mm) Soldering temperature : +260 ℃, 5 seconds
Salt mist test	Salt concentration : 5 mass% Test temperature : +35 ℃ Test time : 336 hours
Individual gas corrosion test	Gas type : NO_2 Gas concentration : 1ppm, 50ppm Test temperature and Humidity : +25 ℃, 75 % Test time : 300 hours
Mixed gas corrosion test	Gas type and concentration : H_2S=0.01ppm SO_2=0.2ppm, NO_2=0.2ppm, Cl_2=0.01ppm Test temperature and Humidity : +25 ℃, 75 % Test time : 200 hours
Weathering test	Test installation place : Vicinity of Tomei highway, Hiratsuka, Kanagawa, Japan Test period : 18 months

Test Conditions

The salt mist test was performed using a neutral solution of saltwater with a concentration of 5 mass percent at 35°C (in accord with IEC-60068-2-11 standard). After the test, the specimens were washed with pure water.

The gas corrosion test was run at two different concentrations of NO_2 gas: 1ppm and 50ppm. This test was run based on reports of the formation of whisker-like metal products. Also, the mixture gas corrosion test (IEC 60068-2-60 standard, method 4) was performed in the simulated exposure environment of electronic equipment.

The weathering test was set up in the outdoor area of an ordinary building near the Tomei expressway in Hiratsuka City, Kanagawa Prefecture, Japan. The test was conducted over the course of 18 months (one year and a half).

After the test, the specimens were observed with an EPMA (Electron Probe Micro Analyzer) in surface and cross-sections, and elemental analysis was also performed. Additionally, rest potential was measured to determine the solubility reaction of the solder being evaluated. The rest potential measurement was done in a 0.1 M solution of KNO_3.

Test results and Discussion

Salt Mist Test

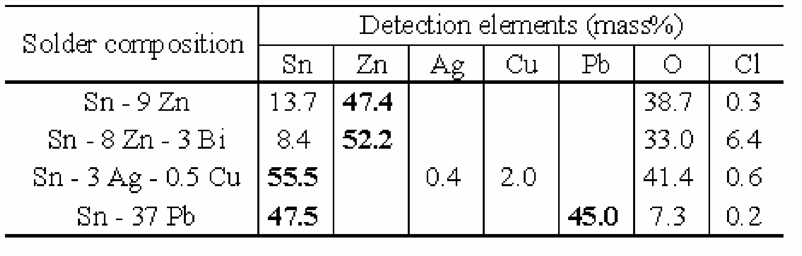
Following the tests, all of the solder surfaces were covered with white corrosion products. The surfaces of the Sn-Zn solders (Sn-9Zn and Sn-8Zn-3Bi) were completely covered with white corrosion products 96 hours after the start of the test. The surfaces of the other solders (Sn-3Ag-0.5Cu and Sn-37Pb) were covered more gradually with white corrosion products.

Table 2 shows the results of quantitative analysis of the specimen surfaces following the test. Post-test elemental analysis revealed large quantities of Zn with Sn-9Zn and Sn-8Zn-3Bi, quantities of Sn with Sn-3Ag-0.5Cu, and quantities of Sn and Pb with Sn-37Pb. Chlorine (Cl) and oxygen (O) were also detected.

Figure 1 shows a BE (Backscattered Electron) image of surface and cross-section of Sn-9Zn solder following the test. Corrosion products on the surface of the Sn-9Zn solder occurred selectively on the Zn areas. Corrosion was not found inside the solder or on the base copper substrate.

Following the salt mist test, basic zinc chloride ($ZnCl_2?4Zn(OH)_2$), which has good insulation characteristics, has been detected as a corrosion product.[8] The presence of this corrosion product leads us to assume that corrosion did not advance to the internal section of the solder because the corrosion product covering the surface suppressed the corrosion reaction.

Table 2 – Quantitative Analysis of Solder Surfaces after the Salt Mist Test for 336hr



Solder composition	Detection elements (mass%)						
	Sn	Zn	Ag	Cu	Pb	O	Cl
Sn - 9 Zn	13.7	**47.4**				38.7	0.3
Sn - 8 Zn - 3 Bi	8.4	**52.2**				33.0	6.4
Sn - 3 Ag - 0.5 Cu	**55.5**		0.4	2.0		41.4	0.6
Sn - 37 Pb	**47.5**				**45.0**	7.3	0.2

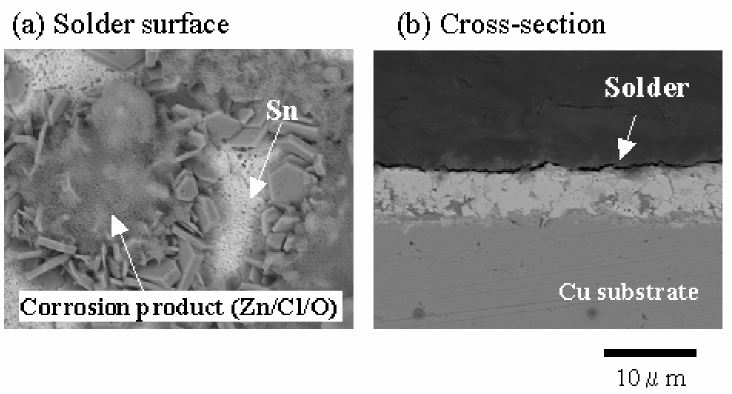


Figure 1 - BE Images of Sn – 9zn Solder Surface and Cross-Section after the Salt Mist Test for 336hr

Gas Corrosion Test

Surface observation

Figure 2 shows SE (Secondary Electron) images of specimen surfaces following the gas corrosion test. Following the test with 50ppm of NO_2 gas, the surface showed more advanced corrosion than in the other gas corrosion tests with lower concentration of NO_2.

Figure 3 shows a BE image and an EPMA elemental mapping image of the Sn-9Zn solder surface following the test with 1ppm of NO_2 gas. Results here, just as in the salt mist test, showed corrosion occurring selectively on the Zn areas. The corroded sections were found to have trace amounts of Cl. Because of this, the Zn corrosion can be presumed to be caused by trace amounts of Cl. However, it is not clear why Cl was detected even though we were performing an NO_2 gas corrosion test. It has been conjectured that trace amounts of the gas residue were left inside the test equipment. We also analyzed corrosion products that formed as protrusions on the surface of the Sn-Zn solder following the gas corrosion test with 50ppm concentration of NO_2 gas.

Figure 4 shows a SE image and an elemental mapping analysis. These results indicate that the main components of the corrosion products are Zn and O. These corrosion products are oxides and hydroxides of Zn.

Zinc oxide (ZnO) and Zinc hydroxide ($Zn(OH)_2$) have been reported as the oxide and hydroxide products formed.[9-10] Accordingly, the protruding corrosion products had low electrical conductivity. Because of this, we assumed that there was little probability of short circuiting resulted from these whisker-like occurrences.

The surfaces of the comparison solders (Sn-3Ag-0.5Cu and Sn-37Pb) formed corrosive products of Sn and Pb in the gas corrosion test with 50ppm concentration of NO_2 gas. Following the mixture gas corrosion test, all of the solder surfaces showed evidence of corrosion.

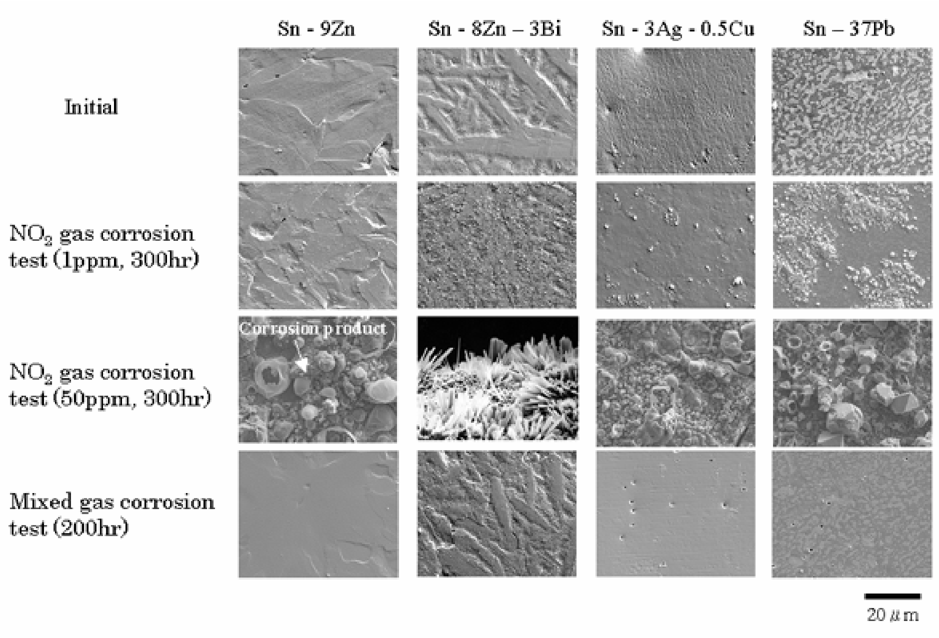


Figure 2 – SE Images of Solder Surfaces after the Gas Corrosion Test

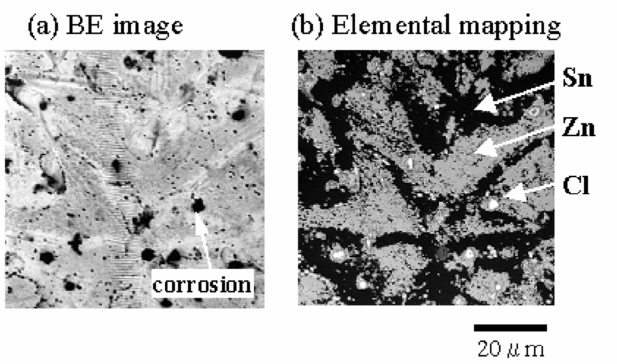


Figure 3 – BE Image and EPMA Elemental Mapping of Sn – 9Zn Solder Surface after the NO_2 (1ppm) Gas Corrosion Test For 300hr

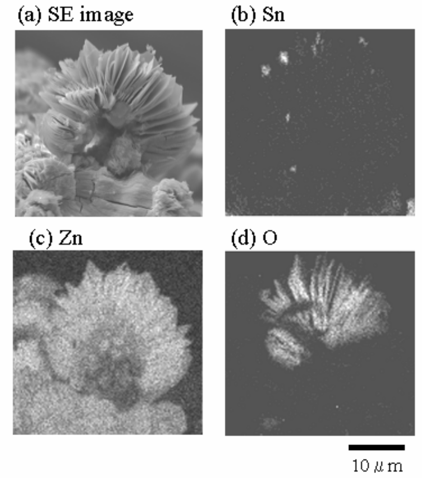


Figure 4 – SE Image and EPMA Elemental Mappings of Sn - 8Zn -3Bi Corrosion Products after the NO_2 (50ppm) Gas Corrosion Test For 300hr

Cross-Sectional Observation

Figure 5 shows cross-sectional observations following the gas corrosion test. Cracking and peeling were observed in the internal sections of all the solders following the gas corrosion test with 50ppm concentration of NO_2 gas.

Next, we observed the condition of the base copper substrate. With Sn-Zn solder, there was no evidence of corrosion to the base copper substrate. However, with conventional Sn-37Pb solder, the base copper substrate was eroded rather than corrosion. The lack of corrosion with Sn-Zn solder may be due to interaction between two factors. One of these factors is the sacrificial protection effect of the zinc component[11], and the other factor is the anti-corrosive effect of the Sn coating.

From the above, we surmise that the progression of corrosion in Sn-Zn solder occurs in the following process:

1. The Zn within the solder forms corrosion products on the surface of the solder.
2. The sacrificial protection effect of the Zn and the anti-corrosive coating of the Sn work to inhibit the progression of corrosion.
3. The progression of corrosion is suppressed, preventing the erosion of the base copper substrate.

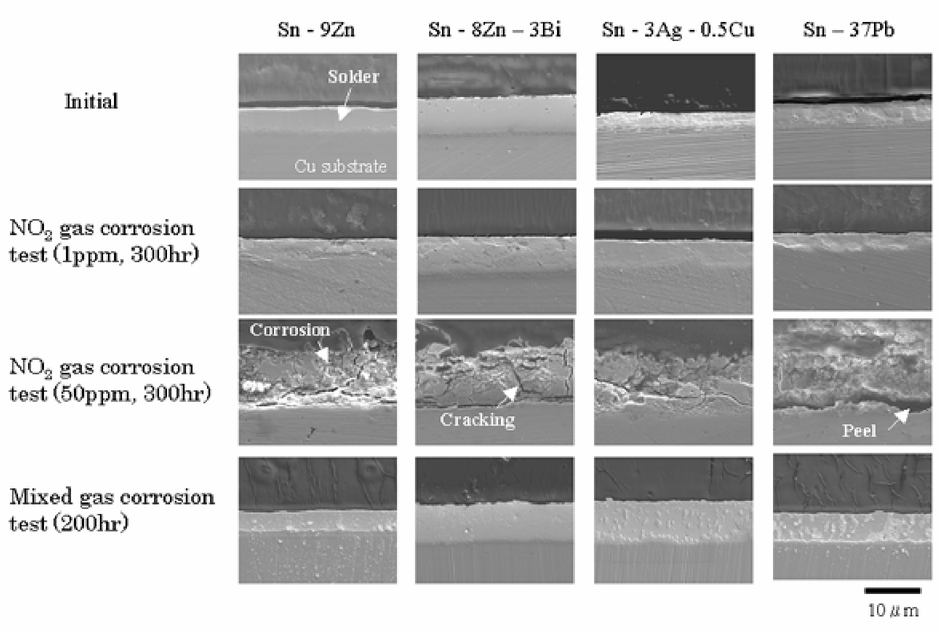


Figure 5 - Cross-Sectional SE Images of Solders after the Gas Corrosion Test

Weathering Test

Figure 6 and Figure 7 show SE images of the process of the weathering test, with solder surfaces in Figure 6 and solder cross-sections in Figure 7. The surfaces of all the solder materials gradually formed corrosion products starting from about one month after the beginning of the test. After eight months, the solder surfaces were completely covered with corrosion products. Elemental analysis was carried out to detect the corrosion products of sulfur (S) and chlorine (Cl) in the solder surfaces. The S component can be assumed to result from sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) gases, which are components of automotive exhaust and volcanic emissions and the Cl component, may be from sea salt particles, since the site of the weathering test was near the ocean.

We compared the specimen cross-sections after 1-18 months of the weathering test (Figure-7):

1. The Sn-Zn solders exhibited corrosion-induced internal vertical cracks. The base copper substrate did not exhibit any corrosion.
2. The Sn-3Ag-0.5Cu solder and the Sn-37Pb solder exhibited both corrosion and erosion.
3. The Sn-37Pb solder exhibited peeling between the solder and the base copper substrate.

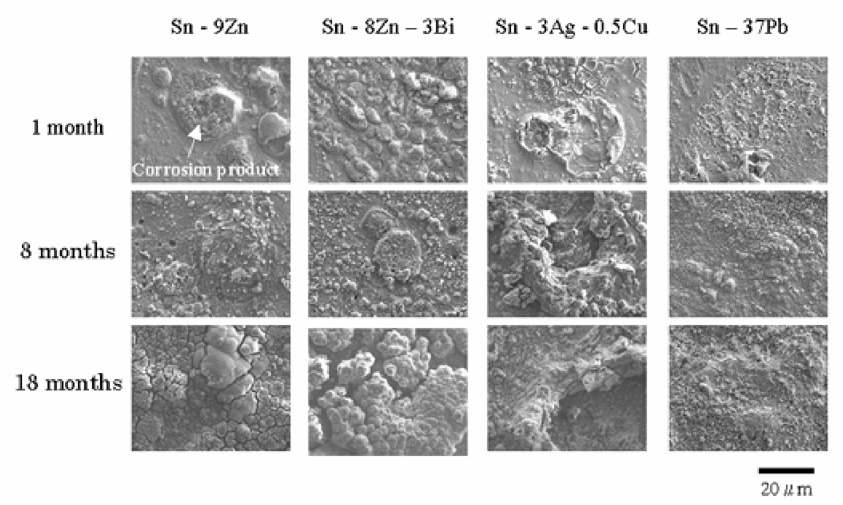


Figure 6 - SE Images of Solder Surfaces after the Weathering Test at Kanagawa for 1-18 Months

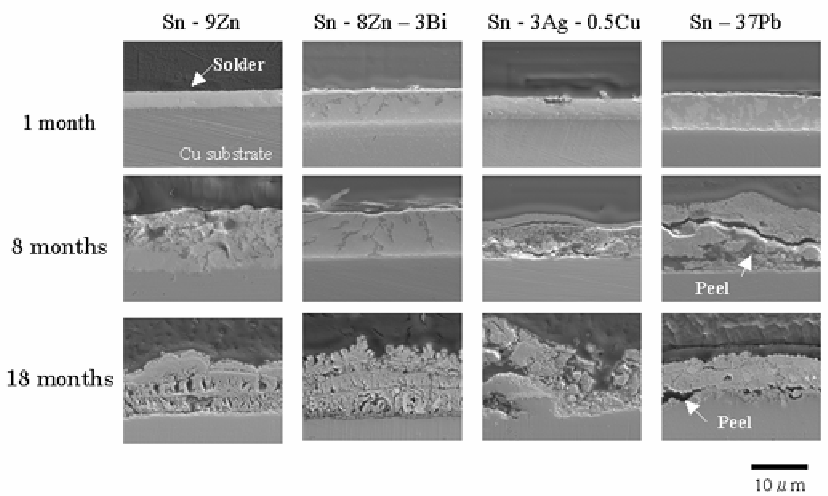


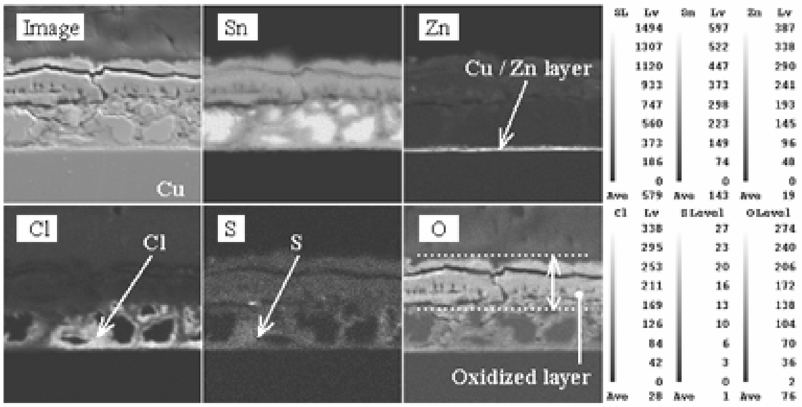
Figure 7- Cross-Sectional Se Images of Solders after the Weathering Tests at Kanagawa for 1-18 Months

Figure 8 shows elemental mapping images of the specimen cross-sections (Sn-9Zn and Sn-37Pb) after 18 months of the weathering test. The Sn-9Zn formed a Cu-Zn intermetallic layer (Cu-Zn layer) at the interface between the solder and the base copper substrate. This intermetallic layer suppressed the advance of Cl and S to the base copper substrate. However, the Sn-37Pb solder did not form an intermetallic layer, and as a result exhibited erosion to the base copper substrate.

Next, we compared solder oxidation in Sn-9Zn and Sn-37Pb. The Sn-9Zn solder was oxidized only near the solder surface. The Sn-37Pb solder, however, was oxidized throughout the solder. This difference is presumed to stem from the difference in the speed of the corrosion reactions. Sn-9Zn solder can be presumed to exhibit a slower corrosion reaction to the internal part of the solder than does Sn-37Pb solder.

Figure 9 shows a graph of the test time and the oxidation layer film in the weathering test. The graph presents a logarithmic display with the horizontal axis showing the test time, and the vertical axis showing the oxidation layer film. One month after the beginning of the test, the oxidation film was at 2um for both Sn-Zn- (Bi) and Sn-37Pb solders. However, after 18 months, the oxidation film increased to approximately 20um for Sn-37Pb solders, but only to 10um for Sn- Zn- (Bi) solder. This difference may be ascribed to the fact that with Sn-Zn solder the Zn forms a sacrificial protection effect and the Sn forms an anti-corrosive coating effect. On the other hand, the Sn-37Pb solder is thought to have oxidized because it lacks these protections.

(a) Sn - 9Zn



(b) Sn – 37Pb

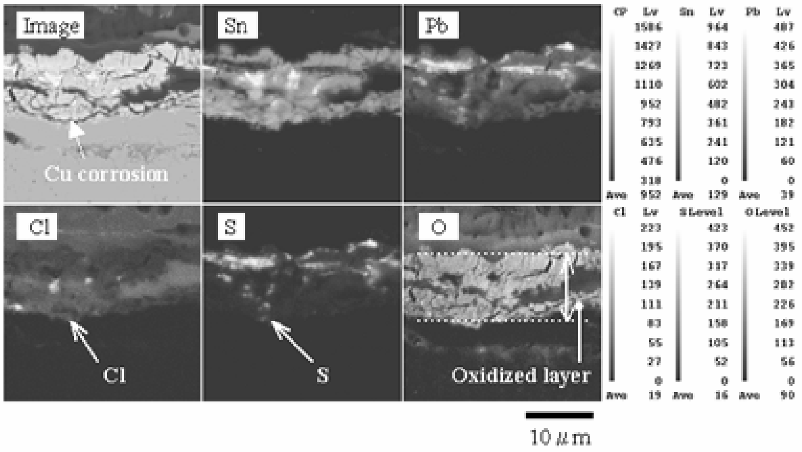


Figure 8 - Cross-Sectional EPMA Elemental Mappings Of Sn - 9Zn and Sn -37Pb Solders after 18 Months of the Weathering Tests at Kanagawa

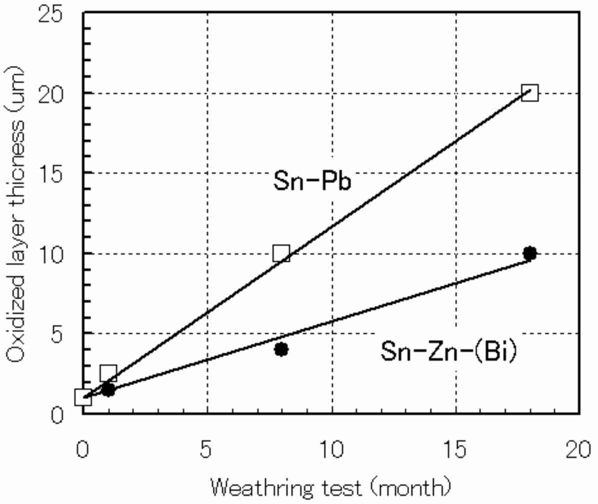


Figure 9 - Oxidized Layer Thickness of Sn - Zn and Sn -Pb Solders in the Weathering Test at Kanagawa up to 18 Months

Figure 10 shows a comparison of the rest potentials. The solubility reaction can be understood from the rest potential. Sn-Zn has the same rest potential as Zn, while Sn-3Ag-0.5Cu has the same rest potential as Sn. Sn-37Pb shows hybridization potential of Pb and Sn. From this, the solubility reaction of each solder can be assumed to progress in the following manner. (1) Sn-Zn based on Zn, (2) Sn-3Ag-0.5Cu based on Sn, and (3) Sn-37Pb based on Pb and Sn.

Sn-Zn solder in particular showed more base metals potential (activated characteristics) than the other specimens. From this we may conclude that the Zn took precedence in dissolving and so formed corrosion products. However, those corrosion products created a sacrificial protection effect that suppressed the corrosion reaction. In addition, the formation of an intermetallic layer (Cu-Zn layer) between the solder and the base copper substrate prevented the progression of the corrosion products. From these factors, we may assume that this solder evidences superior corrosion resistance to conventional Sn-Pb solder.

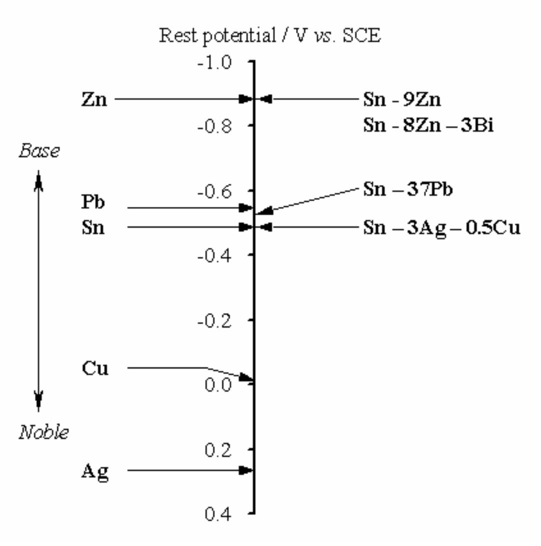


Figure 10 - Rest Potentials of Metals and Solders In 0.1 M KNO$_3$ Aqueous Solution At 25 °C

Conclusions

We performed a variety of corrosion tests to evaluate the corrosion resistance of Sn-Zn solders. Based on the results of these tests, we draw the following conclusions.

1. The progression of solder corrosion is based on reactions to corrosion factors (such as S and Cl) in the environment. In Sn-Zn solders (Sn-9Zn and Sn-8Zn-3Bi), the zinc component reacts to form corrosion products. In Sn-3Ag-0.5Cu solder, reactions are caused by the Sn component, and in Sn-37Pb solder, reactions are caused by both the Pb and Sn components.
2. With Sn-Zn solder, the Zn component selectively reacts with the corrosion factors in the environment to form corrosion products on the surface of the solder. As a result, Zn shows a sacrificial protection effect based on forming those corrosion products. In addition, an intermetallic compound layer (Cu-Zn layer) forms at the interface between the solder and the base copper substrate, suppressing the advance of corrosion products. Because of this, Sn-Zn solder exhibits much higher corrosion resistance than the conventional Sn-37Pb solder.
3. Since the corrosion products of Sn-Zn solders are Zn oxides and hydroxides, these products exhibit a low electrical conductivity. We believe that there is little likelihood of electrode gap short-circuiting caused by the growth of whisker-like corrosion products.
4. With Sn-Zn solder, the material Zn is easily affected by corrosion factors because Zn is an activated material. When using Sn-Zn solders in commercial products, one must take into consideration the actual usage environment.

Acknowledgments

This research was carried out jointly with the Japan Institute of Electronics Packaging ”JIEP Project for Low-Temperature Lead-Free Solders and its Report on Questionnaire Survey”. We would like to express our appreciation to the project members who evaluated this research, including the professor Tsukui of Tokai University, Mr. Sasaki of the Reliability Center for Electronic Components of Japan, and Mr. Kato of the Oki Engineering Co. Ltd. We would also like to express our sincere gratitude to Mr. Toyoda of the Senjyu Metal Corp. for his cooperation in supplying us with specimens and products.

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Corrosion Factor and Effects of Tin - Zinc Lead-Free Solder on Copper Substrate in Environmental Tests

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IPC Printed Circuit Expo/ APEX / ECWC 10

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Table of Contents

1. Background

2. Experimental Method

- Solder materials and test conditions

3. Test Results and Discussion

- Observation and elemental analysis
- Corrosion factor of solder materials

4. Summary

Background

1. Practical application of lead-free solder:

-Sn-Ag-Cu solder is widely adopted (melting 216C -220C)

-Sn-Zn (-Bi) : Low melting point (198C -193C)

2. Problem:

- No corrosion data of lead-free solder
- Zn is a base metal in Sn-Zn solder

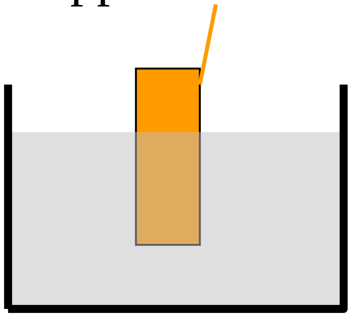
3. What's new in the present work:

- Corrosion factor and resistance of solders (Sn-Zn, Sn-Ag-Cu and Sn-Pb) under various corrosion tests
- Effect of base copper substrate

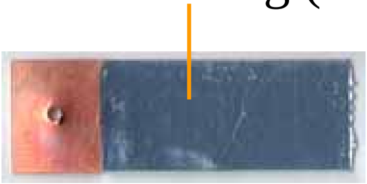
Experimentation

Experiment materials (Solder composition)	Sn - 9 Zn
	Sn - 8 Zn - 3 Bi
	Sn - 3 Ag - 0.5 Cu
	Sn - 37 Pb
Pre-conditioning	Substrate : Copper (size = 10×30×0.3mm) Soldering temperature : +260 ℃, 5 seconds

Solder Materials and Pre-conditioning



Pre-conditioning



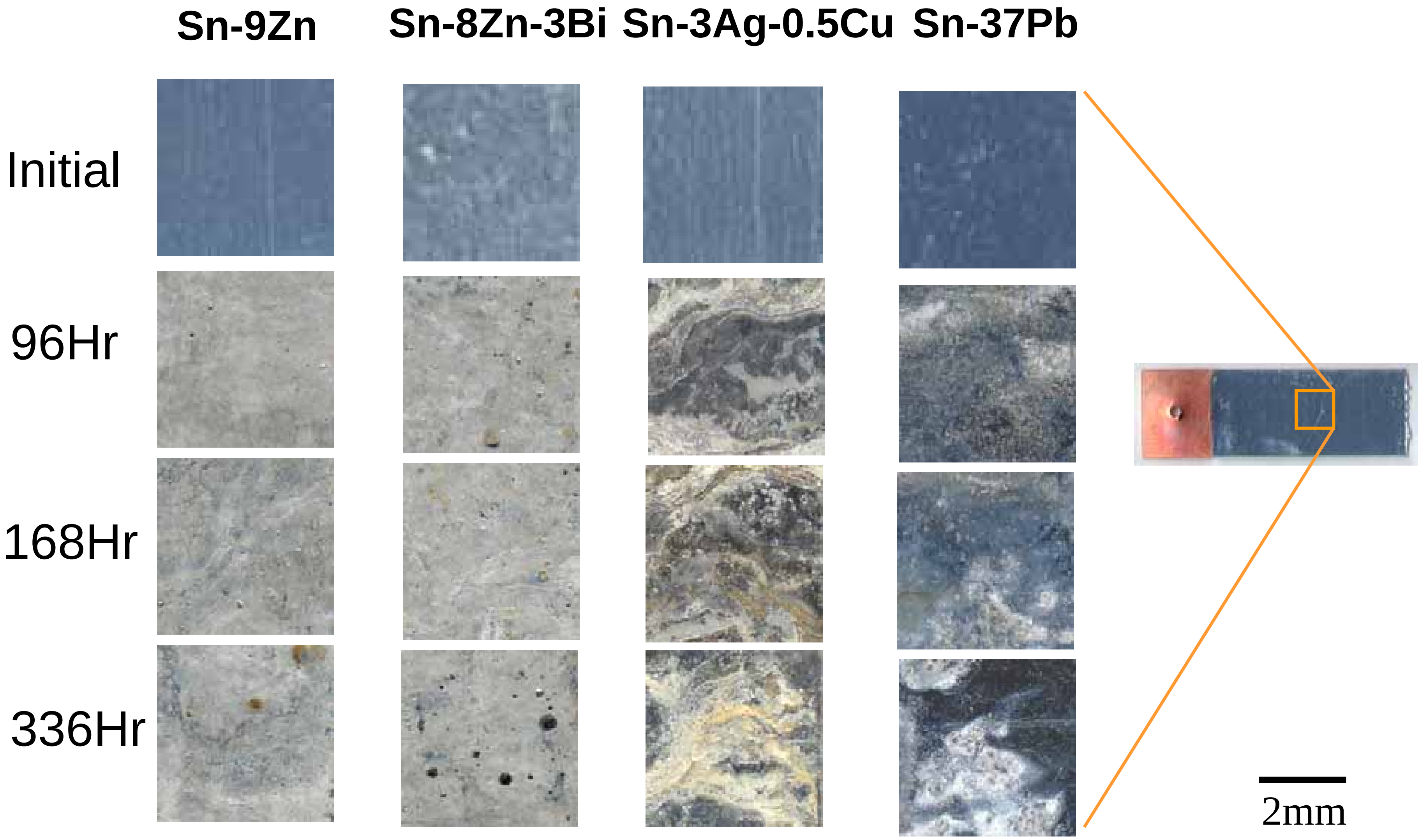
Size : 10 x 30 mm

Specimen

Corrosion Test Conditions

Salt mist test	Salt concentration : 5 mass% Test temperature : +35 **℃** Test time : 336 hours
Individual gas corrosion test	Gas type : NO_2 Gas concentration : 1ppm, 50ppm Test temperature and Humidity : +25 **℃,** 75 % Test time : 300 hours
Mixed gas corrosion test	Gas type and concentration : H_2S=0.01ppm SO_2=0.2ppm, NO_2=0.2ppm, Cl_2=0.01ppm Test temperature and Humidity : +25 **℃,** 75 % Test time : 200 hours
Weathering test	Test installation place : Vicinity of Tomei highway, Hiratsuka, Kanagawa, Japan Test period : 18 months

Solder Surface after Salt Mist Test

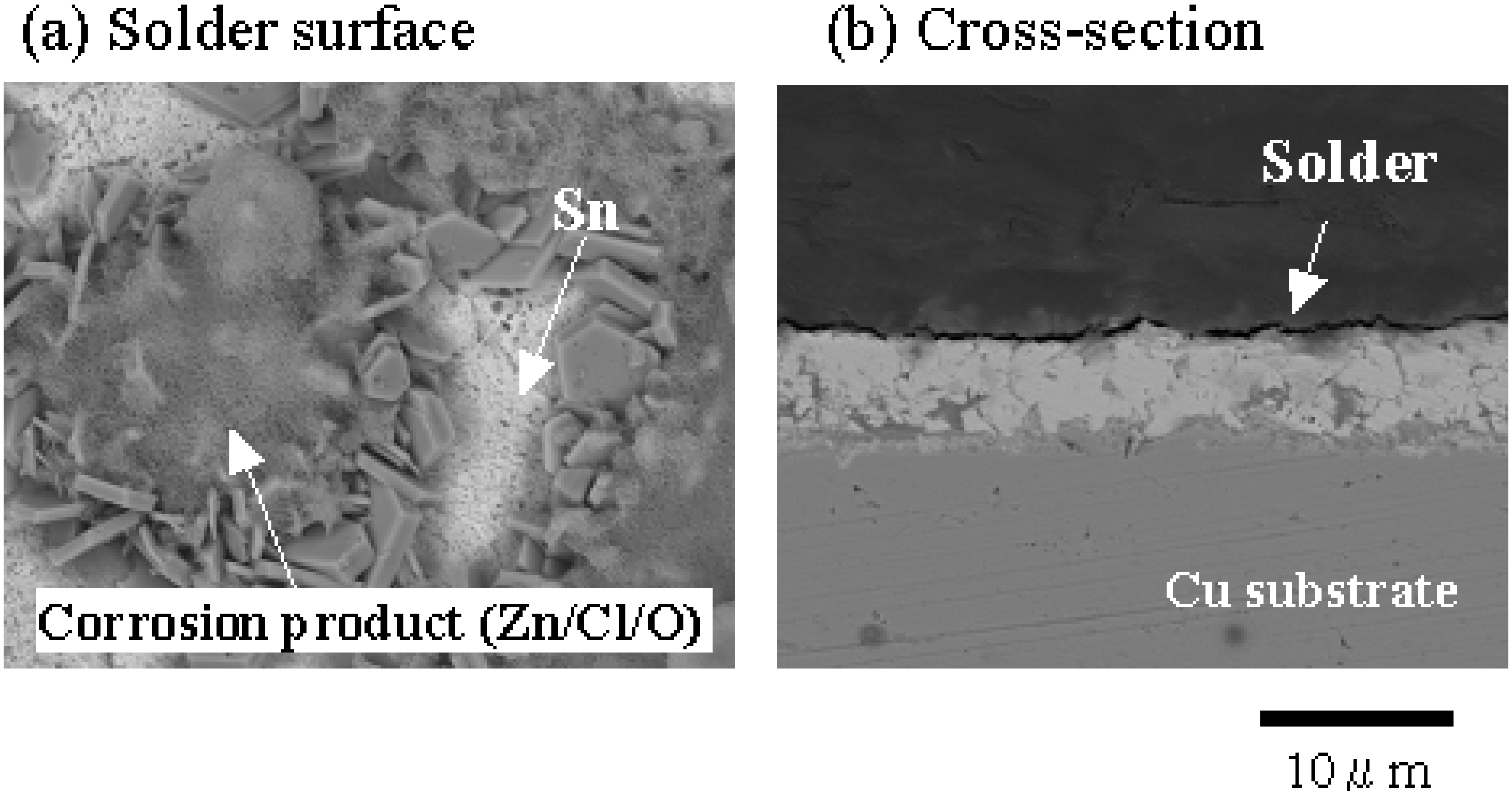


Quantitative Analysis after Salt Test

After salt mist test for 336hr

Solder composition	Detection elements (mass%)						
	Sn	**Zn**	**Ag**	**Cu**	**Pb**	**O**	**Cl**
Sn - 9 Zn	13.7	**47.4**				38.7	0.3
Sn - 8 Zn - 3 Bi	8.4	**52.2**				33.0	6.4
Sn - 3 Ag - 0.5 Cu	**55.5**		0.4	2.0		41.4	0.6
Sn - 37 Pb	**47.5**				**45.0**	7.3	0.2

Sn-Zn solder after Salt Mist Test

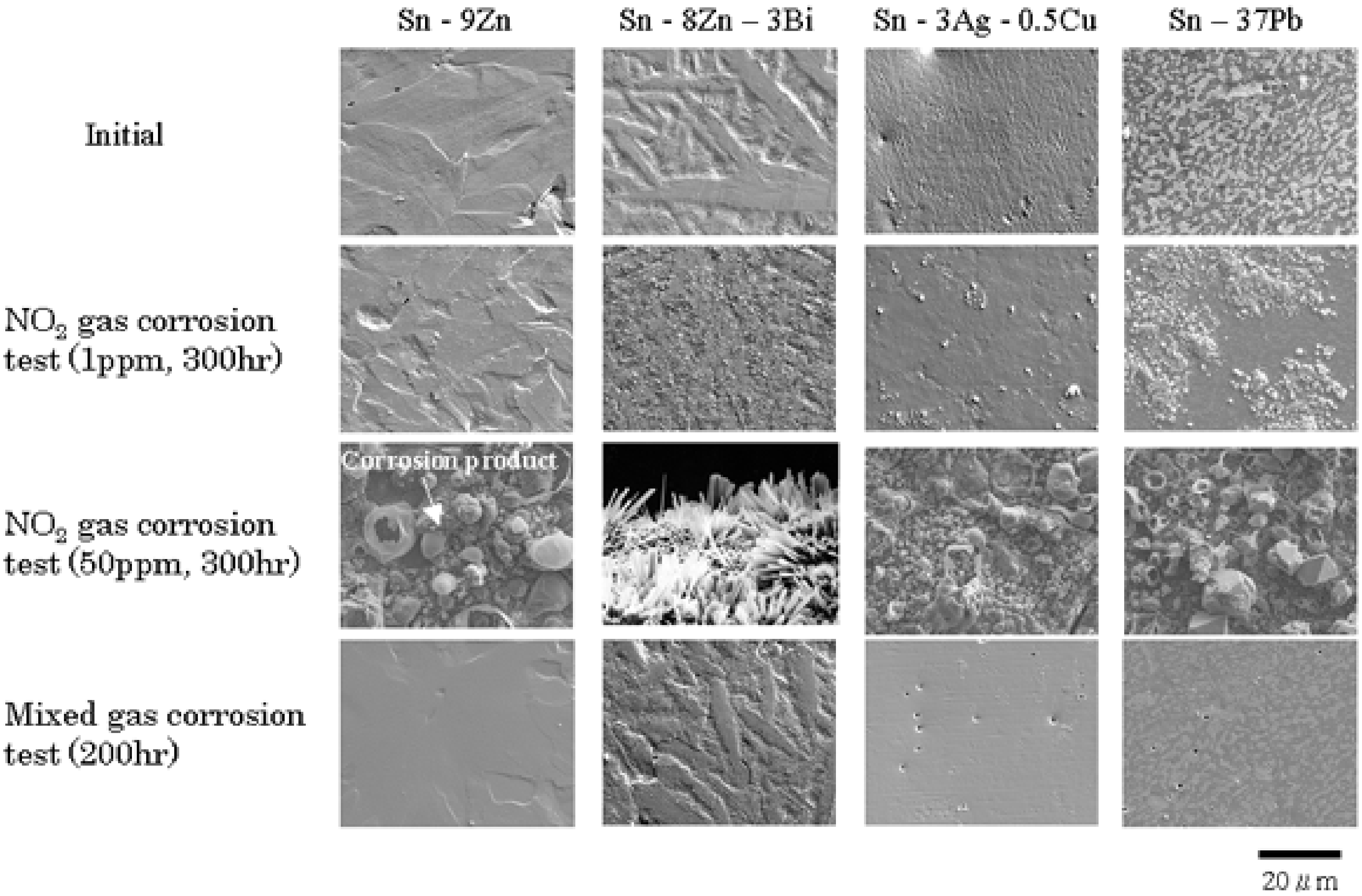


(a) Solder surface

(b) Cross-section

After salt mist test for 336hr

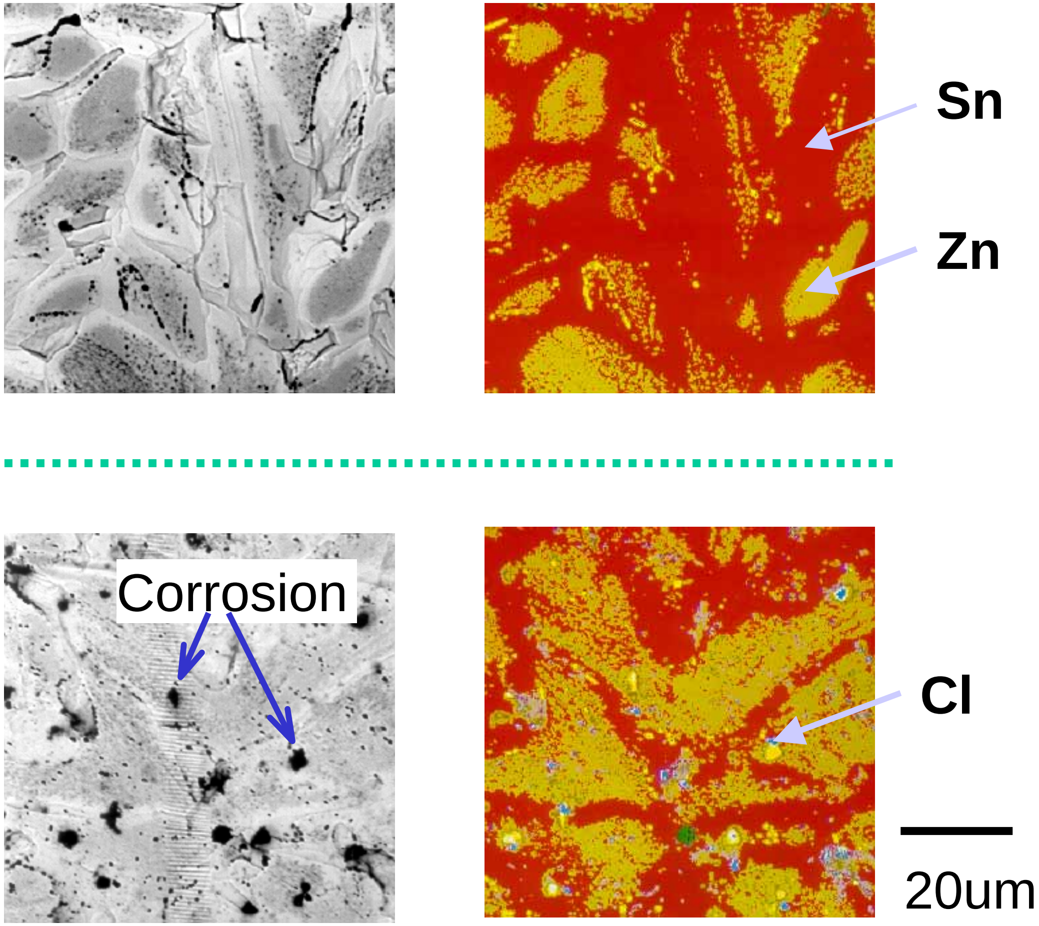
Solder Surface after Gas Test



Sn-Zn Surface after Gas Test

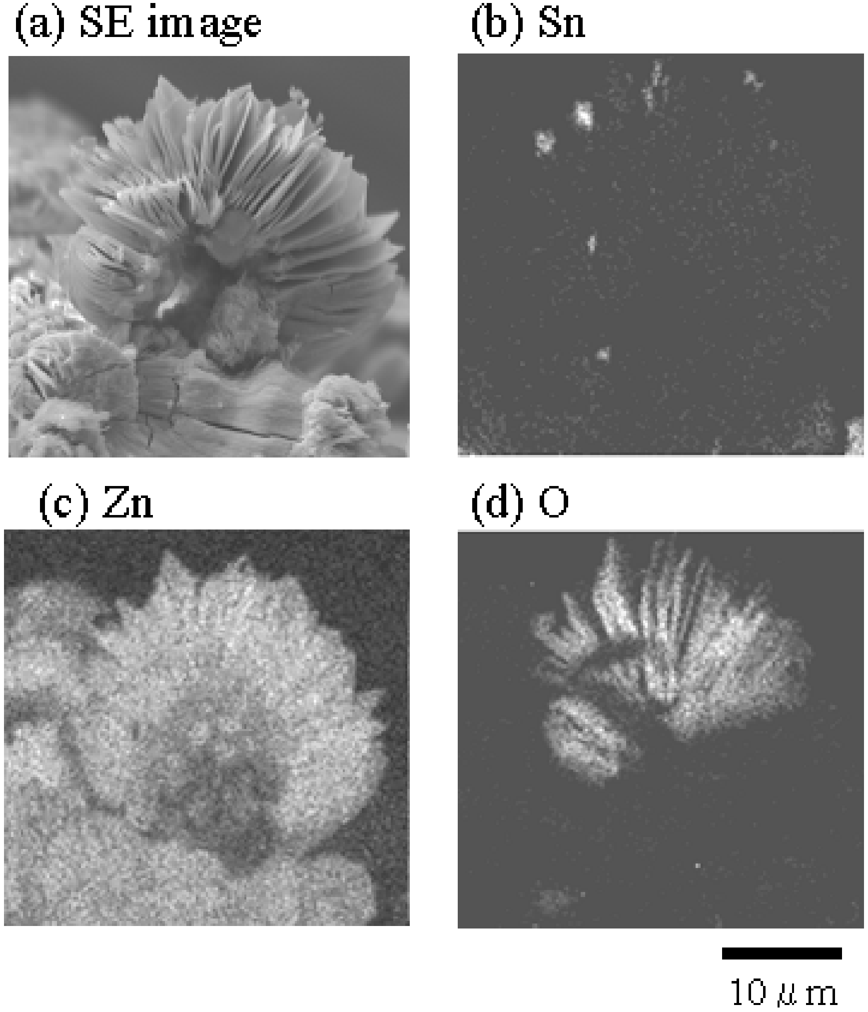
Initial

NO_2 gas test
(1ppm, 300hr)



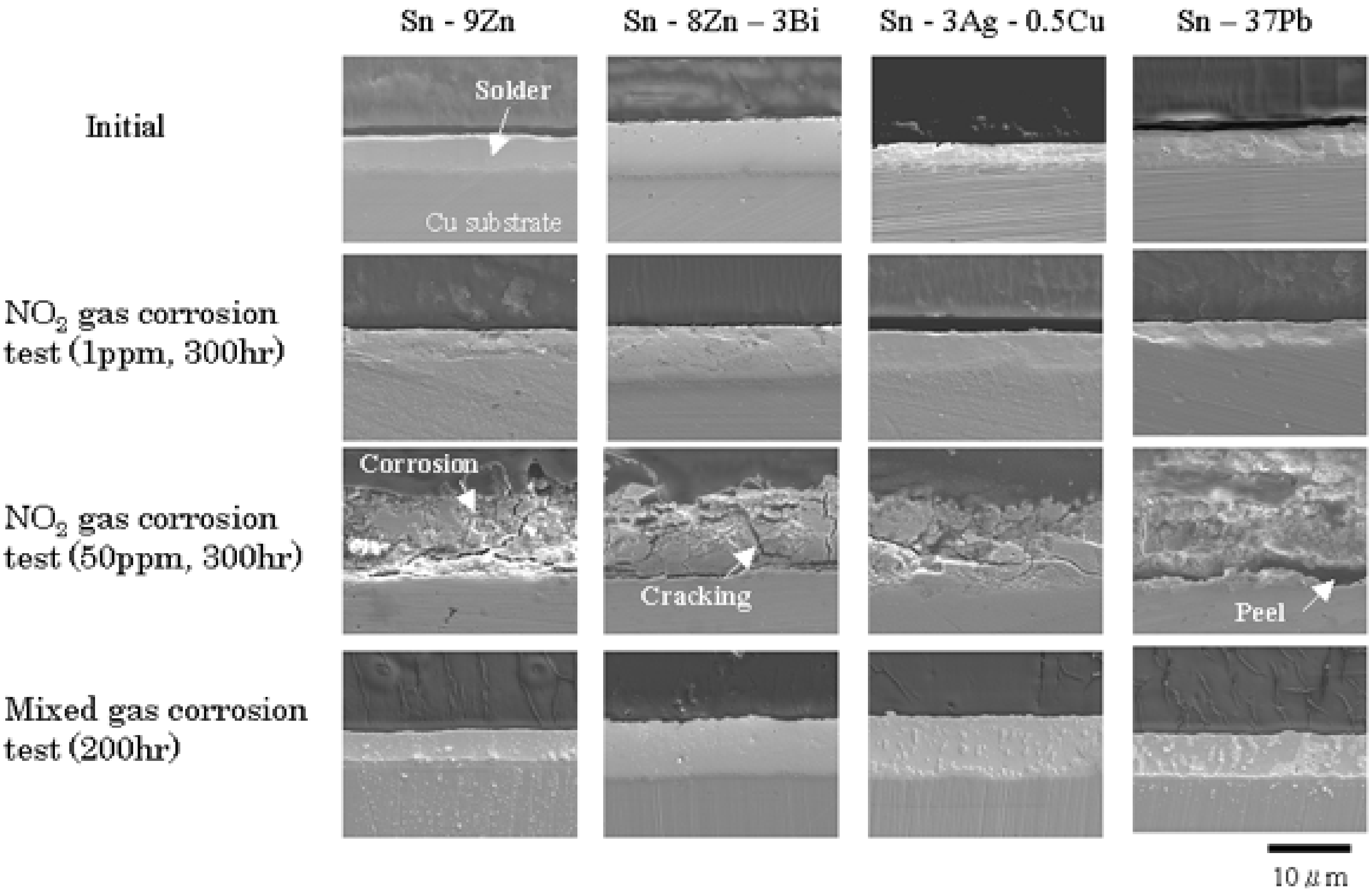
BE image **Elemental mapping**

Sn-Zn Corrosion Products

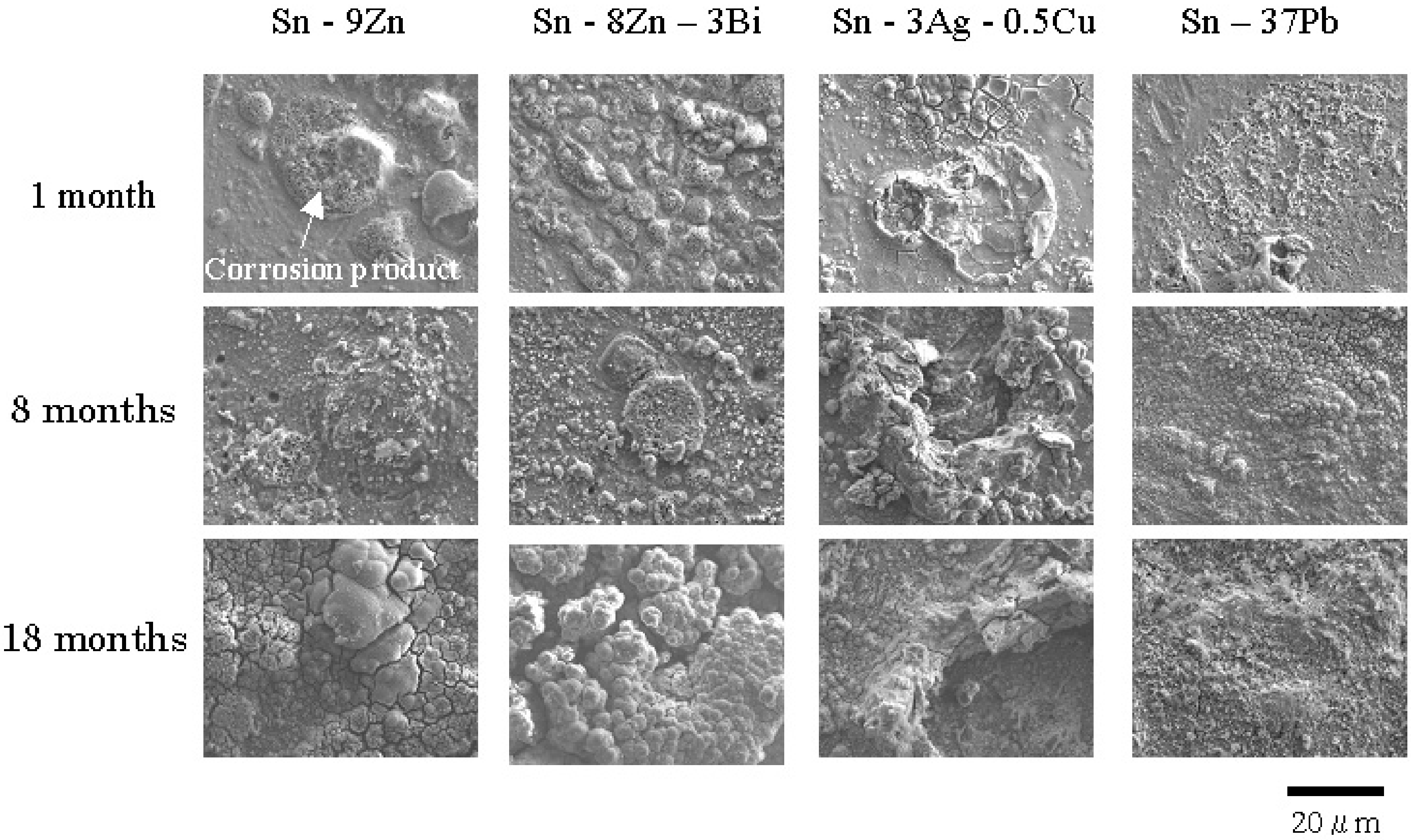

(a) SE image
(b) Sn
(c) Zn
(d) O

NO_2 gas test (50ppm, 300hr)

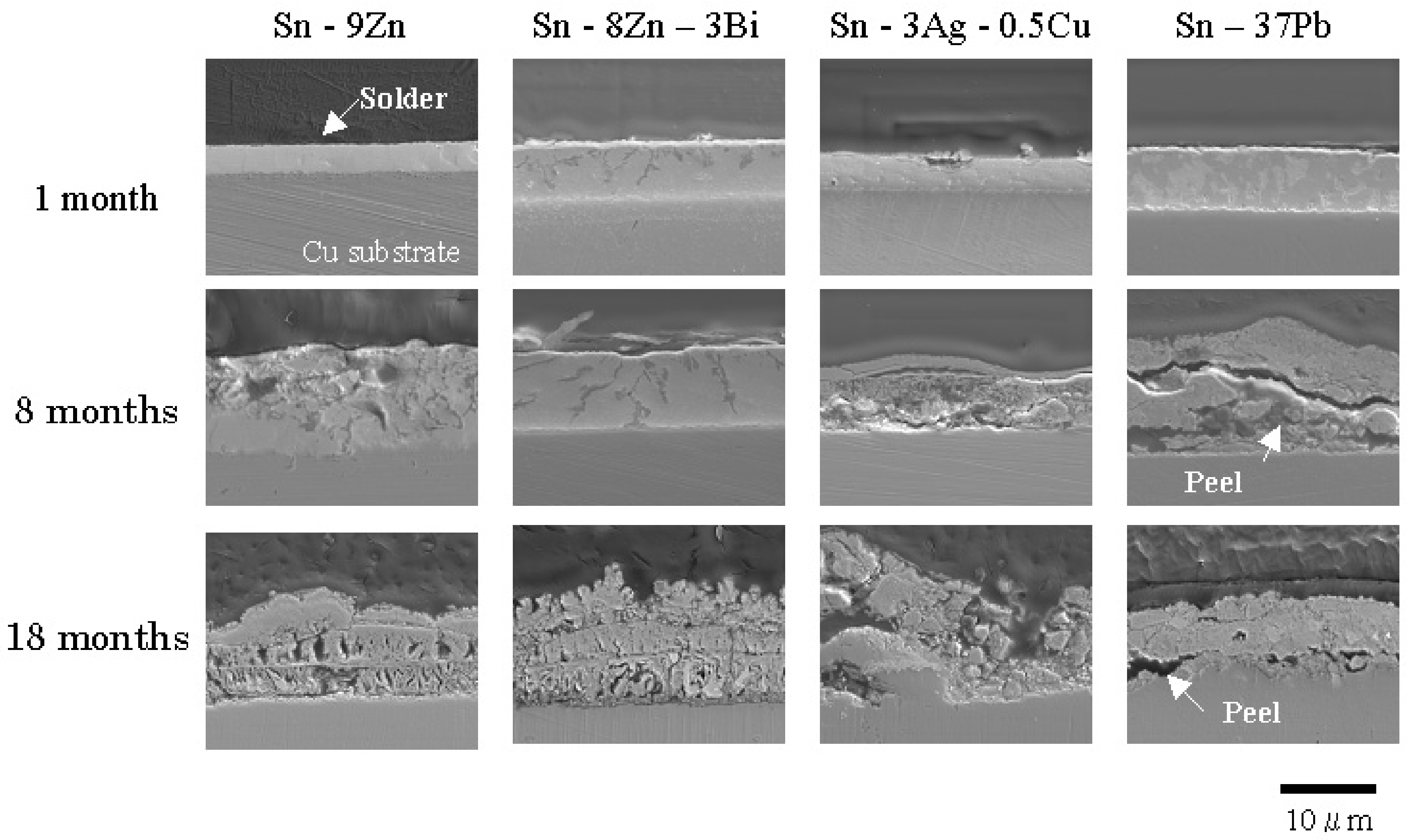
Cross-sectional Image of Solder



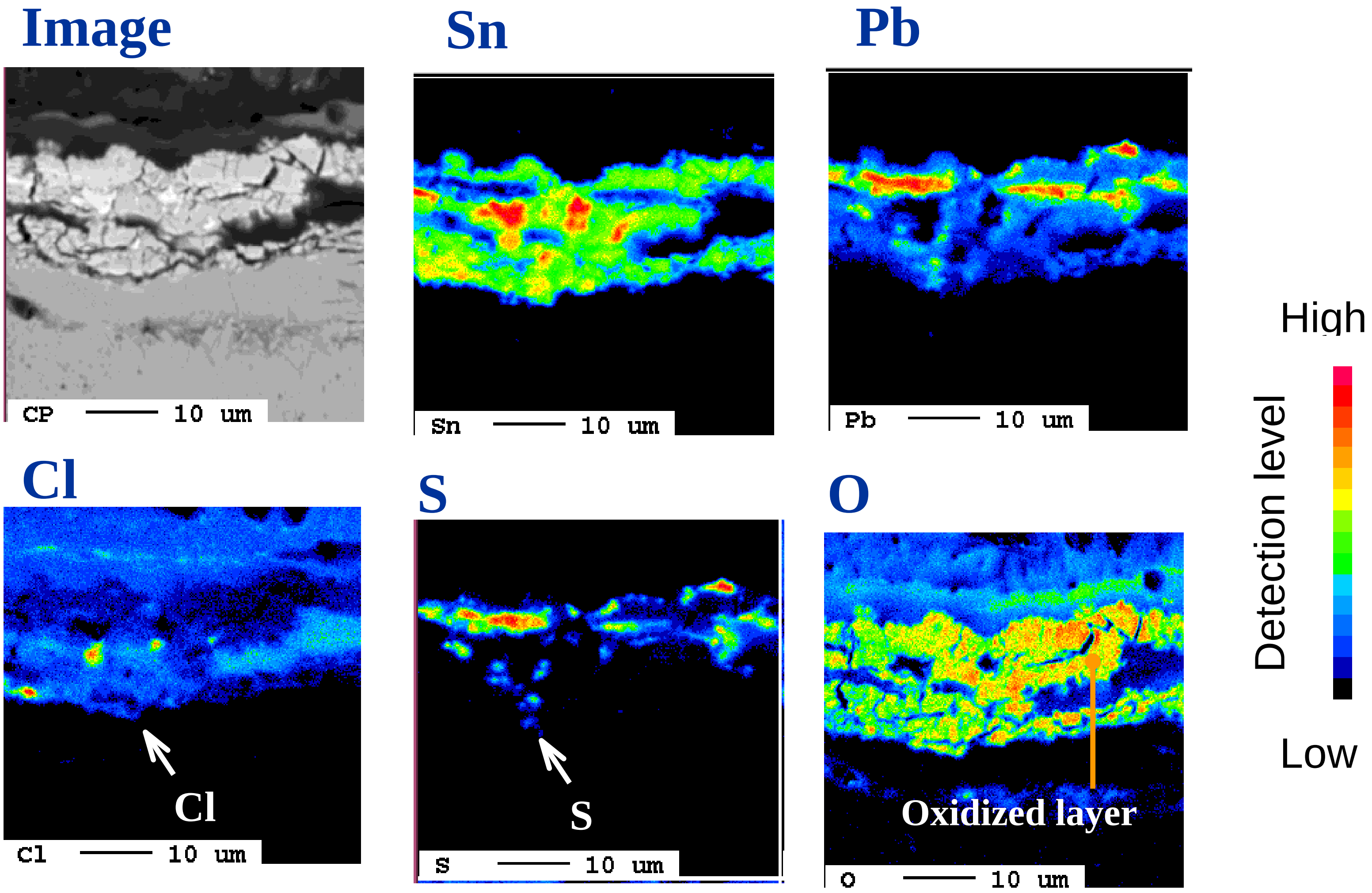
Solder Surface after Weathering Test



Cross-sectional after Weathering Test

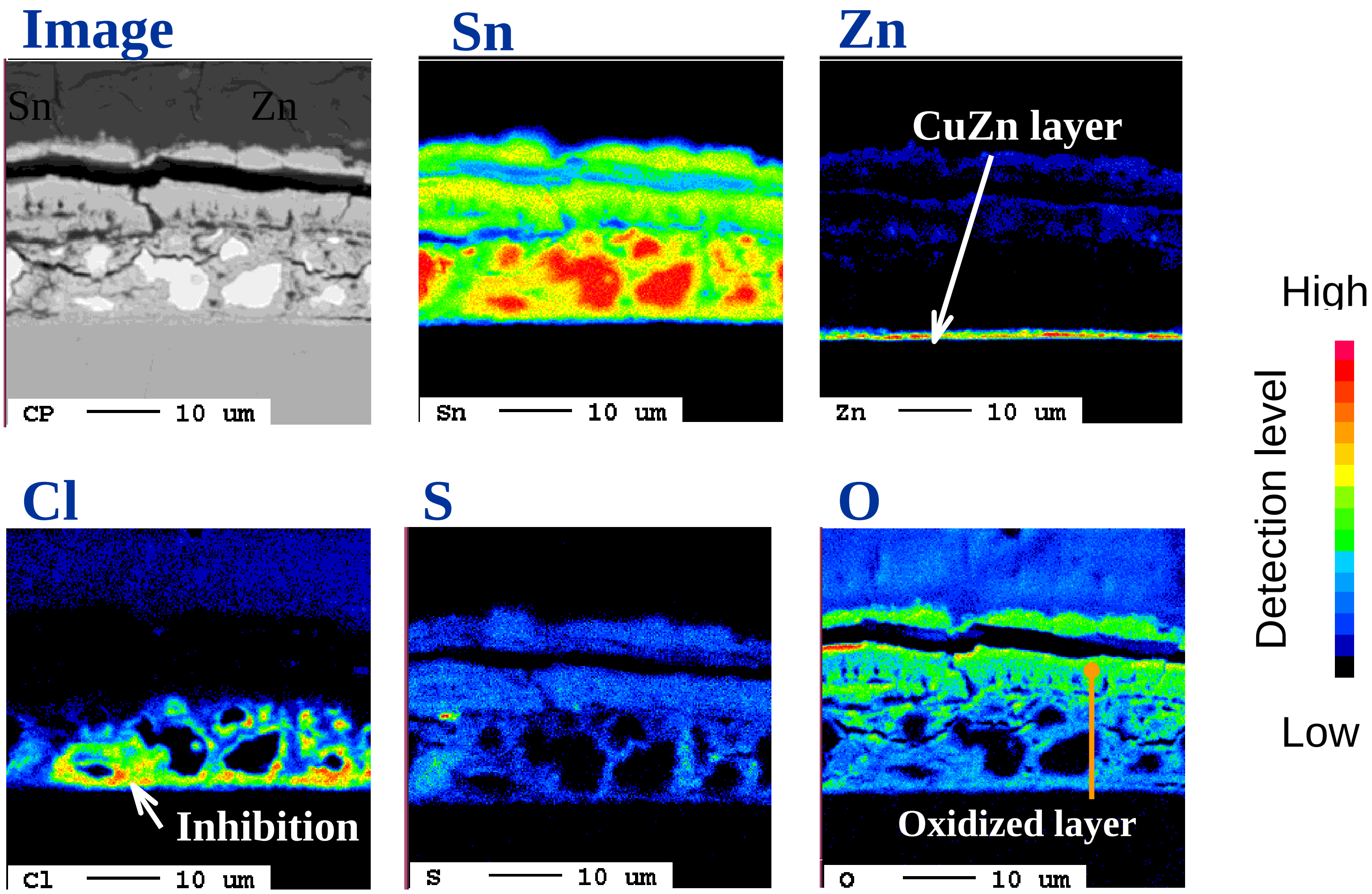


Elemental Mapping of Sn-Pb



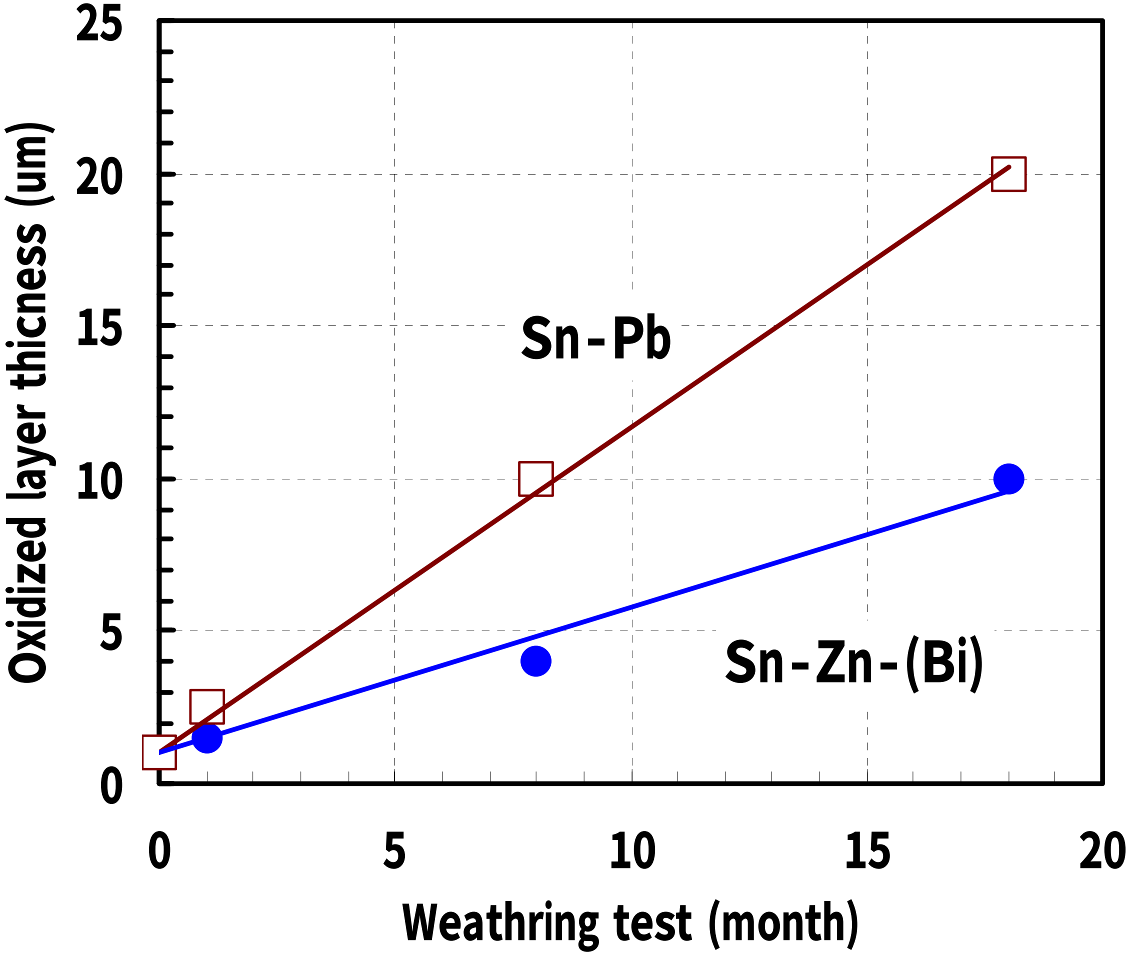
After weathering test for 18 months

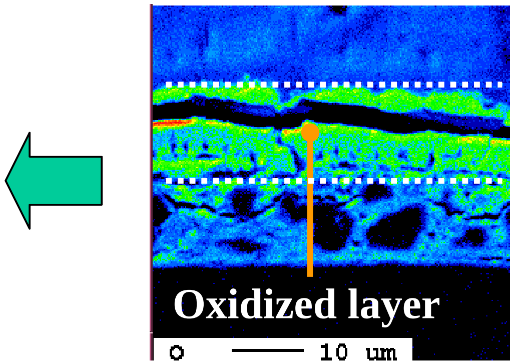
Elemental Mapping of Sn-Zn



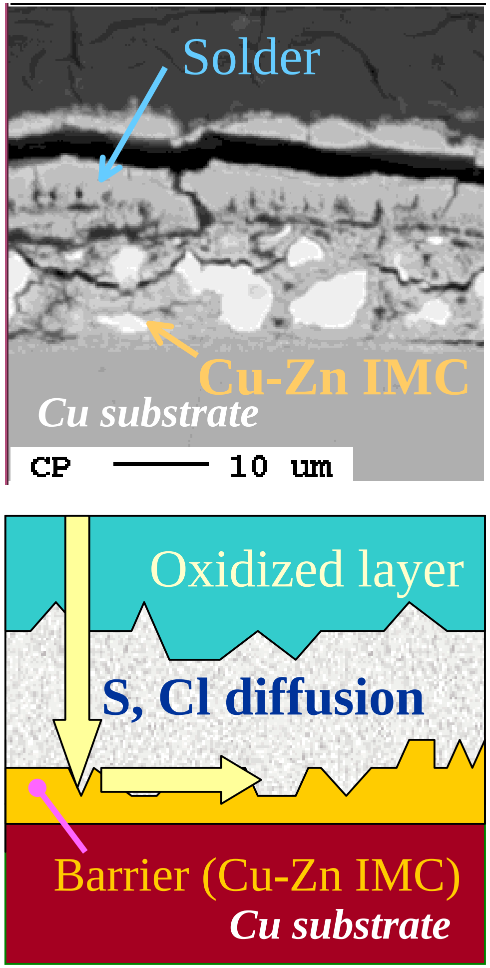
After weathering test for 18 months

Oxidized Layer Thickness of Solder





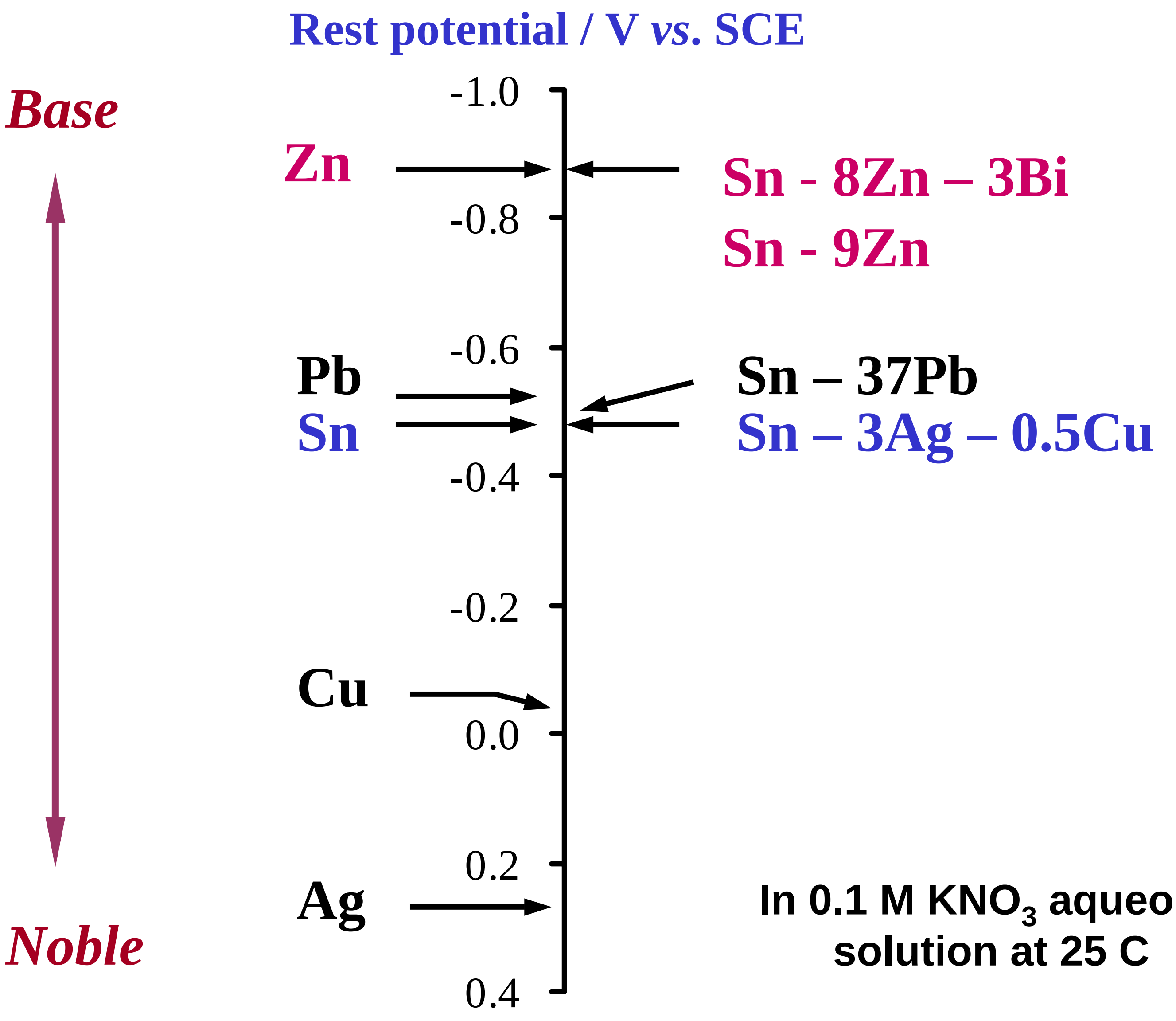
Corrosion Factor of Solder Materials



Cross-sectional image after weathering test

- **Corrosion factor of solder:**
  - Sulfur (S), Chlorine (Cl)
- **Corrosion reaction to solder:**
  - Sn-Pb: Fast
  - Sn-Zn: Slow
- **Corrosion to copper substrate:**
  - Sn-Pb=*Cu-Sn IMC: No barrier*
  - Sn-Zn=*Cu-Zn IMC: Barrier*
- **Corrosion resistance:**
  - Sn-Zn: Better than Sn-Pb

Rest Potentials of Solders



Base

Noble

Zn

Pb

Sn

Cu

Ag

Sn - 8Zn – 3Bi

Sn - 9Zn

Sn – 37Pb

Sn – 3Ag – 0.5Cu

In 0.1 M KNO_3 aqueous solution at 25 C

Summary

- Zn in Sn-Zn solder selectively reacts with the corrosion factors (S, Cl) in the environment
- However, Sn-Zn solder exhibits higher corrosion resistance than conventional Sn-Pb solder

- Zn in Sn-Zn solder shows a sacrificial protection

- Formation of an intermetallic compound layer (Cu-Zn layer) at the interface solder and the copper substrate

Acknowledgments

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Thank you for your attention

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