

Factors leading to ionic migration in lead-free solder

Hirokazu Tanaka*

*I*onic migration (also known as electrochemical migration) is an electrochemical phenomenon related to chemical solutions and electric potential. The reaction mechanisms of ionic migration can be classified into three processes: anodic dissolution, mass transfer, and cathodic deposition. In particular, the anodic dissolution process of alloys used in lead-free solder exhibits different characteristics depending on the electrode potential and the forming location of the passivity film that is produced by the surface texture of the component materials.

Accordingly, the factors leading to ionic migration under investigation by this report are those factors stemming from cathodic deposition characteristics, anodic dissolution characteristics, and the surface texture and rest potential of lead-free solder. The results of this investigation indicate that lead-free solder suppresses the cathodic deposition reaction by forming a stable passivity film that prevents the anodic dissolution reaction. These results indicate that lead-free solder can be considered more reliable than conventional leaded solder with regard to ionic migration.

1. Introduction

Practical applications of lead-free solder have been proliferating throughout the world, requiring evaluation studies on how ionic migration (hereafter, “migration”) affects insulation reliability. Current reports indicate that lead-free solder is free of migration problems,¹⁾ but verification can be considered necessary for such components as silver (Ag) and copper (Cu), in which migration occurs relatively quickly.

Migration in electronic materials is caused by electrochemical phenomena related to chemical solutions and electric potential. Involved in migration are deposition reactions and metal ion transfer reactions induced by such factors as metal dissolution reactions, diffusion, and migration. Migration is especially likely to occur when electronic devices using high-density mounting are affected by both materials and environmental conditions. When migration occurs, it causes changes in electrical characteristics and results in equipment failure.

Let’s now consider migration from the aspect of materials. Alloys, which have binary components added to the metals, have a large number of complexly interconnected factors such as electrode potential and the stability and forming location of the passivity films*¹ of both metals.

The main component of lead-free solder, tin (Sn), is itself a metal with superb corrosion resistance due to the passivity film it forms.²⁾ However, adding various alloy elements can degrade the corrosion resistance (dissolution characteristics).

The alloys Sn-Ag, Sn-Cu, and Sn-Bi currently being

promoted for lead-free solder applications utilize the noble metals silver (Ag), copper (Cu), and bismuth (Bi). Another alloy, Sn-Zn, utilizes the base metal zinc (Zn) with tin, and so we can assume that the conditions leading to migration in this alloy are likely to differ from those in the noble metal alloys.

For these reasons, we first investigated the surface texture, electric potential, and anodic dissolution characteristics of lead-free solder and considered the factors leading to migration. We used the water drop test*² to examine the migration resistance of lead-free solder by looking at the form of migration deposits and the changes in current during the actual migration process. We also examined the composition of the migration deposits using elemental analysis.

2. Surface texture and mechanisms leading to migration

2-1 Anodic reaction and mechanisms leading to migration

“Migration” refers to a phenomenon in which metal ions are transferred from one metal electrode to the opposite metal electrode. This process results in metal or alloy deposits. The transfer occurs between the electrodes of devices such as printed circuit boards (PCBs) when an electric field is impressed in the presence of moisture such as dew condensation adhering between the electrodes.

Migration is classified as either dendrite or conductive anodic filament (CAF) depending on the shape of the deposits and the conditions leading to the occurrence.^{3), 4)} “Dendrite” refers to dendritic-shaped metal or metal-oxide deposits on the surface of PCB insulation. “CAF”

* Technical Development Headquarters

refers to metal or metal-oxide deposits in the shape of elongated fibers deposited along the glass fibers of the interior of the PCB insulation panel. (Photo 1)

There are three processes leading to migration: (1) anodic reaction (metal dissolution), (2) cathodic reaction (metal or metal-oxide deposits), and (3) inter-electrode reaction (metal-oxide deposits).

- (1) Anodic reaction (“M” stands for metal.)
- $M \rightarrow M^{n+} + ne^{-}$ (1)
- $H_2O \rightarrow \frac{1}{2}O_2 + 2H^{+} + 2e^{-}$ (2)
- $M + H_2O \rightarrow MO + 2H^{+} + 2e^{-}$ (3)
- (2) Cathodic reaction
- $Mn^{+} + ne^{-} \rightarrow M$ (4)
- $O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$ (5)
- $2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$ (6)
- (3) Inter-electrode reaction
- $2M^{+} + 2OH^{-} \rightarrow M_2O + H_2O$ (7)

Considering the mechanisms by the type of reaction, we find that the electrolytic reaction of water causes the area around the anode to become acidic due to H^{+} ions forming from type (2) reactions, while the area around the cathode becomes alkaline due to OH^{-} ions forming from type (5) and (6) reactions.⁵⁾

Fig. 1 shows Pourbaix potential–pH diagrams of the main materials used for lead-free solder.⁶⁾ As you can see from the diagrams, when a pH shift toward acidity occurs, there is a greater tendency for metal ions to form, promoting a metal dissolution reaction at the anode. A shift toward an alkaline pH causes a metal deposition reaction at the cathode due to the formation of hydroxides and metal oxides. The reaction shown in formula (5) forms the driving force of the migration reaction.⁷⁾ Oxygen gas, which makes up approximately 21 percent of the atmosphere, dissolves in the electrolytic solution, and because of the high oxygen reduction reaction (affinity for electrons) of this dissolved oxygen, electrons are captured at the cathode.

In this way, the process leading to migration is comprised mainly of anodic dissolution and cathodic deposition reactions, and the speed of those reactions is affected greatly by the characteristics of the materials.

2-2 Surface texture of solder materials

Photo 2 shows three scanning electron microscope (SEM) images of the surface of lead-free solder and one back-scattered electrode image. Photo 2 (a) of Sn-3.5Ag shows the intermetallic compound (Ag_3Sn) phase forming as a product of the reaction between Sn and Ag, with the Ag_3Sn phase dispersed throughout the Sn component. Similarly, Photo 2 (b) shows the intermetallic compound (Cu_xSn_x) phase forming from Sn and Cu, with (Cu_6Sn_5) minutely dispersed throughout the Sn component.

No intermetallic compound is formed in Sn-58Bi (Photo 2 (c)) or in Sn-9Zn (Photo 2 (d)), and the photos show the binary phase texture of Sn-Bi and Sn-Zn.

The above evidence indicates that the surface texture of materials known as lead-free solder differs according to the composition of the alloy materials and their intermetallic compounds. These textures are affected by the electrode potential and the formation of a passivity film, and appear as characteristics leading to the occurrence of migration.

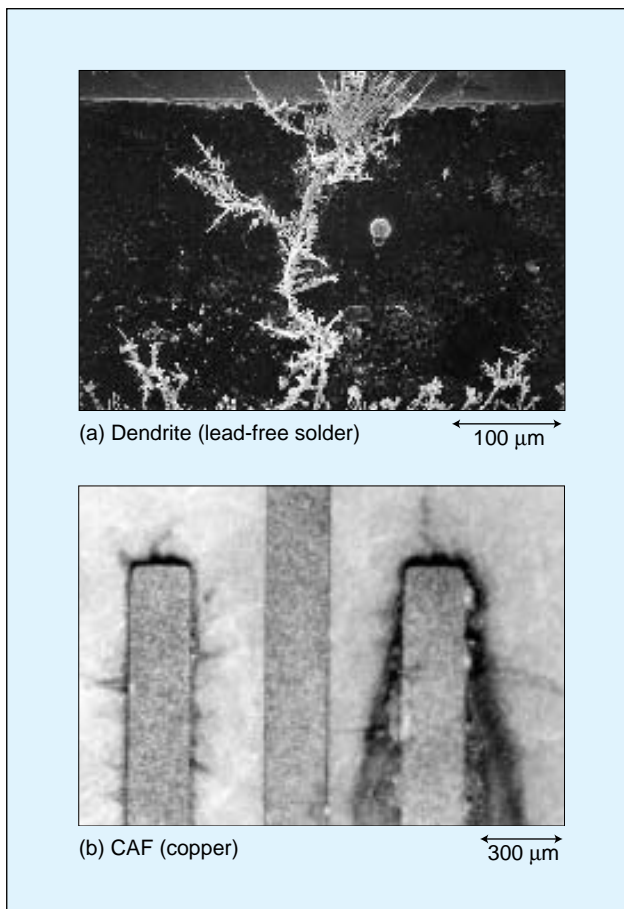


Photo 1 The forms of ionic migration

Reactions (1) and (2) are thought to be mechanisms leading to dendrite formation. Metal dissolving at the anode*³ (positive electrode) is deposited on the cathode*⁴ (negative electrode). These dendrites consist of pure metal or metal oxide deposits growing toward the anode, and result in short circuits between the electrodes. Reactions (1), (2), and (3) are all thought to be mechanisms leading to CAF formation. Here, too, metal dissolving at the anode results in metal or metal-oxide deposits between the electrodes, and the growth of these deposits results in short circuits between the electrodes.

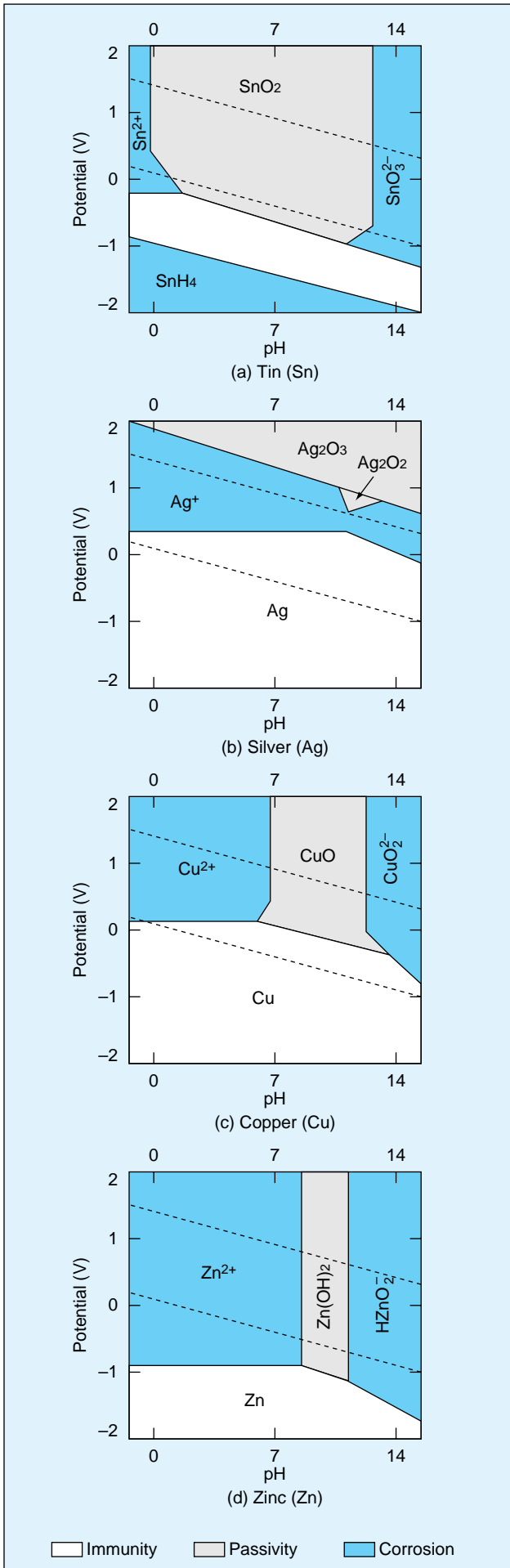


Fig. 1 Pourbaix potential-pH diagrams for main materials used for lead-free solder ⁶⁾

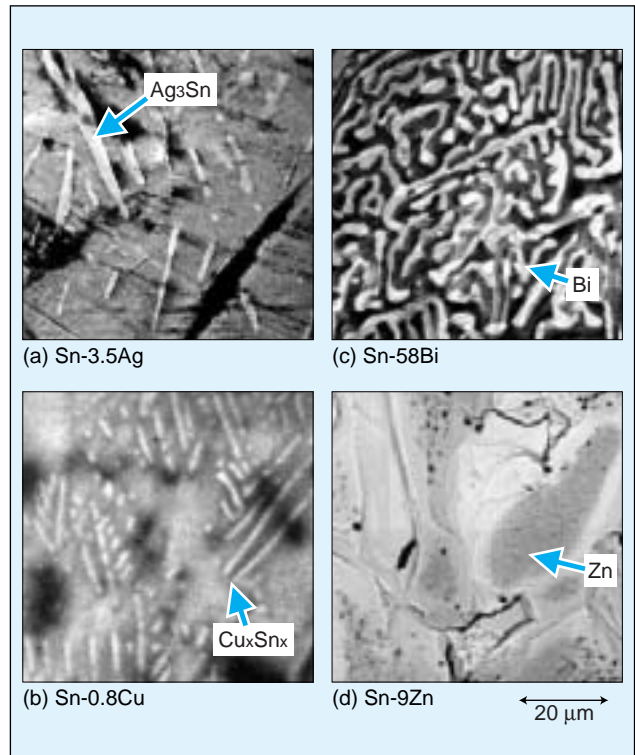


Photo 2 SEM images of solder surfaces (back-scattered electrode image, Sn-9Zn only)

3. Analysis of anodic dissolution characteristics

3-1 Experiment method

We investigated anodic reactions from the aspect of differences in electrode potential and metal dissolution characteristics stemming from differences in the surface texture of each type of solder.

Table 1 shows materials and measurement conditions for the experiments, and Fig. 2 shows the equipment for the experiments. Specimens of each type of solder material were cut into 1 cm squares, the surfaces were then prepared with water-resistant sandpaper and then buffed. A circular working electrode^{*5} 0.6 cm in diameter (0.28 cm²) was exposed from the specimen.

Platinum-plated titanium net was used for counter electrodes,^{*6} and saturated calomel electrodes (SCE) were used as reference electrodes.^{*7} An aqueous solution of 0.1 mole of sodium sulfate (Na₂SO₄, pH 6) was used for the electrolytic solution.

Measuring equipment consisted of a function generator and a potentiostat, and rest potential^{*8} and anodic dissolution characteristics were measured at room temperature.

Measurements of rest potential were made after immersion in the electrolytic solution. Measurements of anodic dissolution characteristics were made for current density and potential during the sweep from rest potential to high potential.

Table 1 Materials and measurement conditions for dissolution characteristics experiments

Experiment materials	Single metals (99.9% purity)	Sn, Ag, Zn, Cu, Pb
	Solder composition (mass%)	Sn-3.5Ag, Sn-0.8Cu, Sn-58Bi, Sn-9Zn, Sn-37Pb
Electrode materials	Reference electrodes	Saturated calomel electrodes (SCE)
	Counter electrodes	Platinum-plated titanium net
Electrolytic solution		0.1 mole aqueous solution of sodium sulfate
Measurement conditions		+25°C, potential scan speed = 10 mV/s

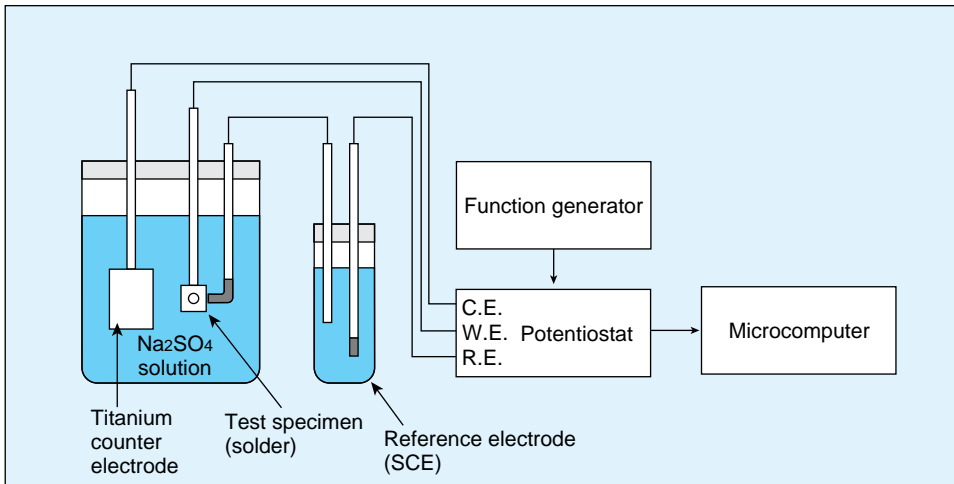


Fig. 2 Layout of equipment for experiments

3-2 Experiment results and considerations

Fig. 3 shows the rest potential for each type of solder material, and Fig. 4 shows the current–potential curves. From these results we can see that for base metals (which have low rest potential), the lower the rest potential, the greater the tendency for dissolution, while for noble metals (which have high rest potential), the higher the rest potential, the less tendency there is to form metal ions. In regard to anodic dissolution characteristics, these results also show that an abrupt rise in current density during the sweep from low potential to high potential promotes the dissolution reaction.

(1) Sn-Ag and Sn-Cu

When comparing the rest potentials of Sn-3.5Ag and Sn-0.8Cu, we find roughly the same potential (–500 to –400 mV in Fig. 3), indicating that these solder materials are dominated by the rest potential of Sn.

When comparing the initial dissolution potentials of Sn-3.5Ag (Fig. 4 (d)) and Sn (Fig. 4 (a)), dissolution showed similar progression in all materials at approximately –390 mV vs. SCE. On the other hand, when comparing Sn-3.5Ag and Ag (Fig. 4 (b)), we find that Sn-3.5 Ag is not affected by Ag. Therefore, we can assume that with this solder, the Sn composition within the solder material takes priority in dissolution. Just like Sn-3.5Ag, Sn-0.8Cu has also been reported to exhibit the same dissolution characteristics as Sn.⁸⁾

The above evidence indicates that the binary composition of Ag and Cu components in lead-free

solder materials form stable compounds with the Sn component (Ag_3Sn and Cu_xSn_x), and exhibit no progression of the dissolution reaction in solution. Only the Sn component dissolves.

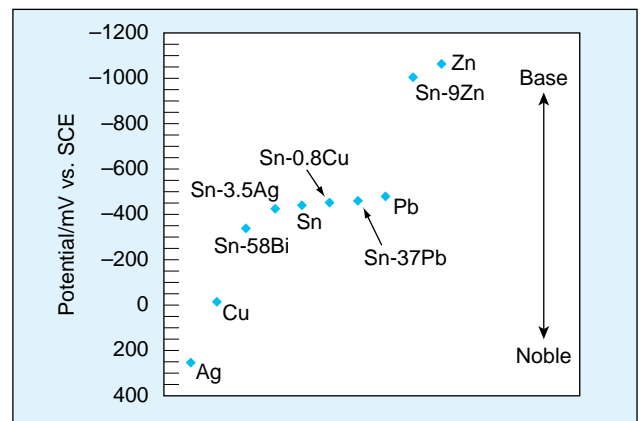


Fig. 3 Rest potential of each type of solder (in 0.1 mole sodium sulfate solution)

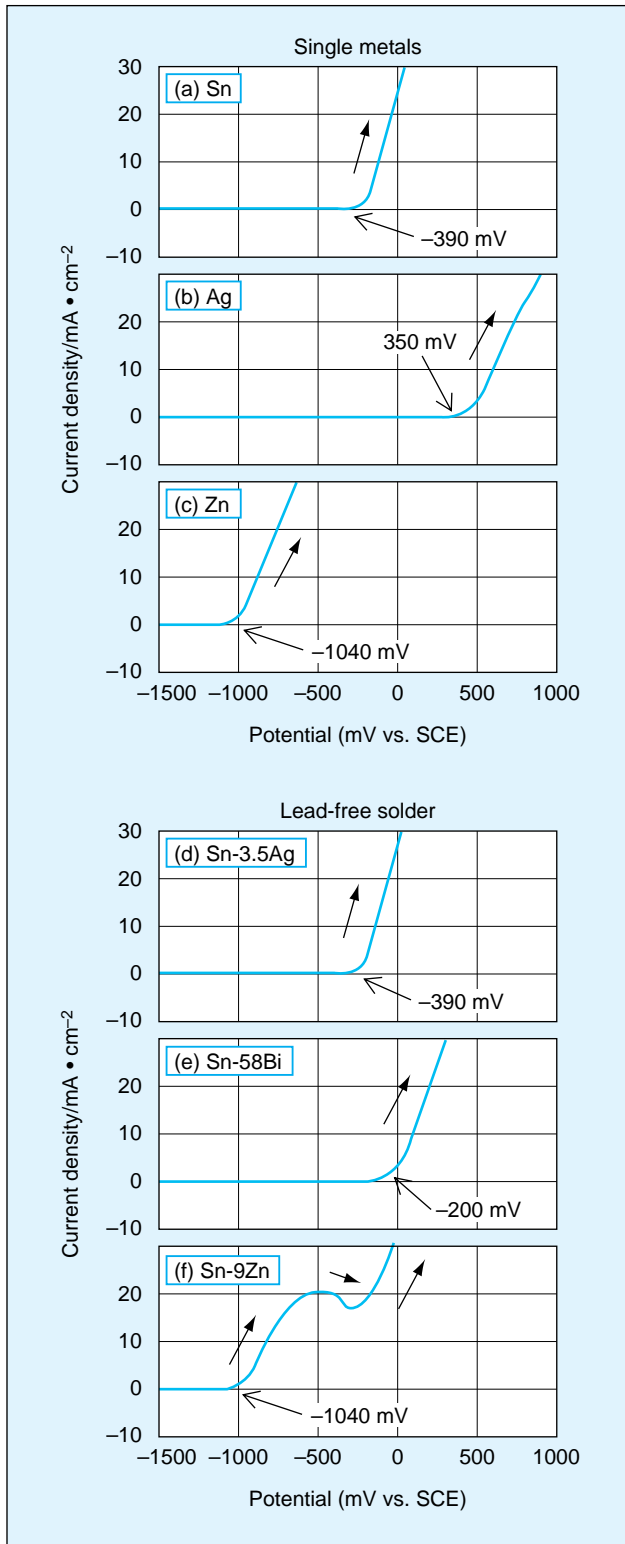


Fig. 4 Current-potential curves of single metals and lead-free solder (in 0.1 mole solution of sodium sulfate)

(2) Sn-Bi

Sn-58Bi exhibits higher electrode and dissolution potentials (approximately -200 mV vs. SCE) than Sn, and the dissolution reaction is suppressed more than in materials such as Sn and Sn-3.5Ag. Moreover, observation of the anode surface (Photo 3) following the Sn-58Bi migration test revealed sections of segregated Bi surface remaining and selective dissolution of Sn.

These results indicate that Bi does not dissolve in

solution, and the Bi electrode potential ($E = + 215$ mV vs. SHE) exhibits a hybridization potential*⁹ with Sn since the quantity of Sn in Sn-58Bi (42 mass%) is less than the quantity of Sn in materials such as Sn-3.5Ag (Sn quantity: 96.5 mass%). Thus, Sn-Bi can be assumed to suppress dissolution characteristics more than such materials as Sn alone or Sn-3.5Ag.

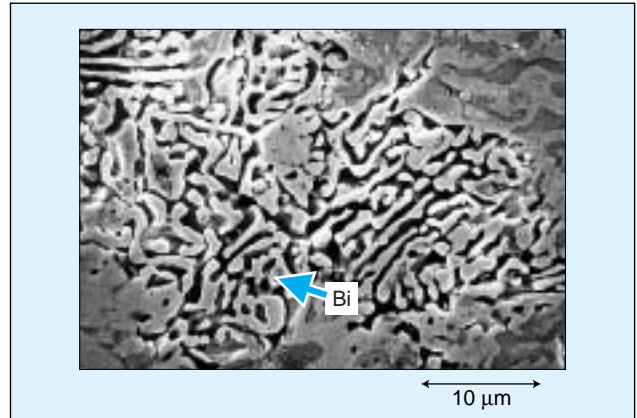


Photo 3 Anode dissolution status after migration test

(3) Sn-Zn

A comparison of the electrode potential of Sn-9Zn with Zn reveals approximately the same potential, and so we can assume that the electrode potential of this solder material is dominated by Zn.

The dissolution characteristics of Zn (Fig. 4(c)) show a sharp progression of the dissolution reaction at around -1000 mV vs. SCE, and Sn-9Zn (Fig. 4(f)) here too shows approximately the same response as Zn, exhibiting a dissolution reaction at around -1000 mV vs. SCE. Following that, a period of inaction of the dissolution reaction was seen at around -400 mV vs. SCE, which is the Sn dissolution potential, and this was followed by a subsequent resumption of dissolution.

The origin of this period of inaction of the dissolution reaction is thought to be a passivity film from Sn and Zn. Alloying the Zn component in the Sn metal is believed to produce a passive effect that inhibits an excessive dissolution reaction. As a result, Sn characteristics are assumed to dominate the Sn-9Zn migration process, because Zn and Sn form a passivity film that suppresses the dissolution characteristics of the base metal Zn.

4. Analysis of cathodic deposition characteristics

4-1 Experiment method

Table 2 shows the solder composition, electrode materials, and test conditions used in the experiments. Electrode materials consisted of JIS type-2 comb-shaped electrodes specified in JIS-Z-3197 (electrode gap: 0.318 mm) formed on glass fabric epoxy boards. These electrodes were given a plating bath using electrolytic solder plating (solder plating thickness: min. 10 μm), and

then underwent ultrasonic cleaning with isopropyl alcohol and a water bath to remove impurities for use as experiment materials.

Table 2 Solder composition and conditions used in experiments

Solder composition (mass%)	Sn-3.5Ag
	Sn-9Zn
	Sn-37Pb
Electrode materials	Substrate: glass fabric epoxy (FR-4 equivalent items)
	Electrode base: copper
	Conductor gap: 0.318 mm (JIS type-2 equivalent)
Experiment conditions	Measurement range: room temperature
	Water drip quantity: 1 μ L ion exchange water
	Impressed voltage: 5 V/DC

Fig. 5 shows the layout of experiment equipment. A micro syringe was used to drip 1 μ L of ion exchange water on each interval between a pair of comb-shaped electrodes, and a direct current power source (PMC-18-3, manufactured by Kikusui Electronics Corp.) was used to impress 5.0 V of direct current, inducing migration at room temperature. At this time, changes in the direct current levels were automatically measured and recorded at one-second intervals using a digital multimeter connected to a microcomputer. Continuous images of the migration process were also recorded using a CCD camera and a digital video camera. The surfaces of electrodes that experienced migration were observed visually using a scanning electron microscope (SEM) and these electrodes underwent compositional analysis with an energy dispersive X-ray analysis unit (EDX).

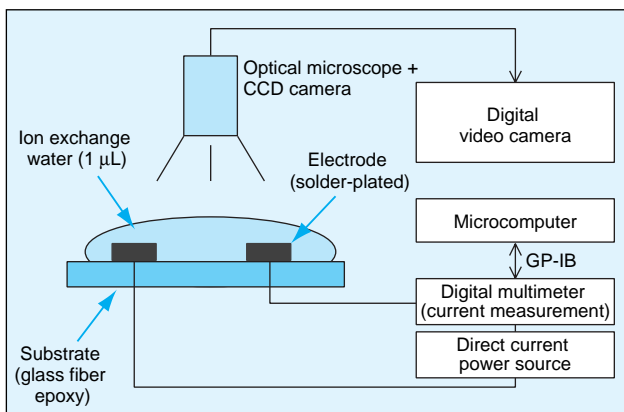


Fig. 5 Layout of equipment for experiments

4-2 Experiment results and considerations

Fig. 6 shows images of the process of migration deposition and the changes in current occurring in the processes of migration in Sn-3.5Ag, Sn-9Zn, and Sn-37Pb.

Shorting between electrodes caused by migration occurred at the following times: Sn-37Pb at about 10 seconds, Sn-3.5Ag at about 120 seconds, and Sn-9Zn at about 330 seconds. Lead-free solder showed an overall

tendency toward comparatively longer times before the occurrence of migration than conventional leaded solder (Sn-37Pb).

A comparison of the migration deposition images for Sn-3.5Ag reveals dissolved black blemishes consisting of dissolved anodic metals at approximately 20 seconds after the experiment began, corresponding to a sharp rise in current. At 90 seconds into the experiment, a single thread of needle-shaped migration appeared on the cathode, and conditions promoting migration were confirmed at the anode. Then, at the 123 second mark, the gap between the electrodes was completely short-circuited. The level of current at this time was 0.03 mA, and the current continued to rise gradually thereafter in conjunction with continued migration growth.

With Sn-9Zn, a change in color resulting from metal dissolution was seen at the anode 250 seconds into the experiment. At this time, deposition was seen at the cathode, but almost no change in current was confirmed. Then, at the 332 second mark, short-circuiting began, and at 350 seconds, migration growth again appeared, followed by a period of inactivity for migration growth. The level of current at this time was 0.3 mA.

On the other hand, Sn-37Pb experienced migration from all electrodes immediately following the initiation of the experiment. At 10 seconds, one strand of migration short-circuited the electrode gap, and within 30 seconds, multiple strands of migration had short-circuited the electrode gap. The level of current at this time was about 11 mA, a current level far higher than that seen with Sn-3.5Ag or Sn-9Zn.

The level of current during short-circuiting differed according to such factors as the shape of the migration growth and the number of migration strands, but overall lead-free solder had much lower levels of current at the time of short-circuiting than did conventional leaded solder. In other words, lead-free solder showed superior insulation characteristics at the time of short-circuiting.

Next, let's look at Fig. 7 for the post-experiment results of observing the shape of migration deposits with an SEM, and the results of compositional analysis of the deposits with an EDX.

Sn-3.5Ag exhibited needle-shaped migration extending from the cathode toward the anode. The deposits were composed of Sn.

Sn-9Zn exhibited dendritic migration, widely branched, growing from the cathode toward the anode. The migration was composed of Sn and Zn. In this experiment (electrolytic plated materials), Sn-9Zn migration was composed mainly of Sn, but Zn has been reported to be the main component with molten solder materials.⁹⁾ It is surmised that the composition of the migration deposits differs according to the surface texture of the solder materials used in the experiment.

On the other hand, Sn-37Pb experienced multiple-branching migration composed of Sn and Pb and covering the electrode gaps. This migration material is thought to come from Sn and Pb dissolving and being deposited. The primary factor is thought to be the preferential destruction of the Pb passivity film due to the relative instability of this Pb passivity film (e.g., PbO) compared to the Sn passivity film (e.g., SnO₂). Thus, the destruction of the Pb

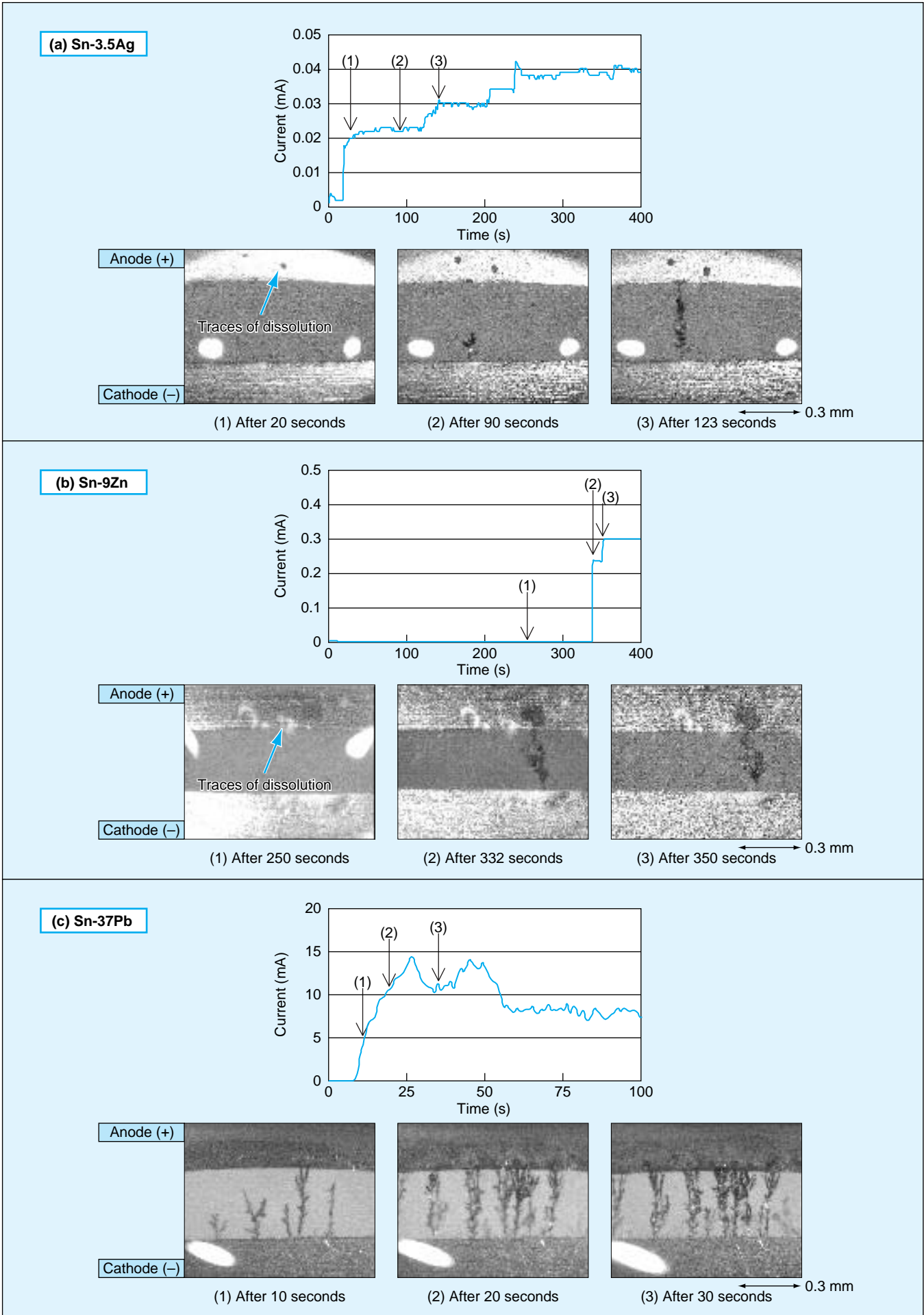


Fig. 6 Changes in current and the process of migration deposits in the migration process

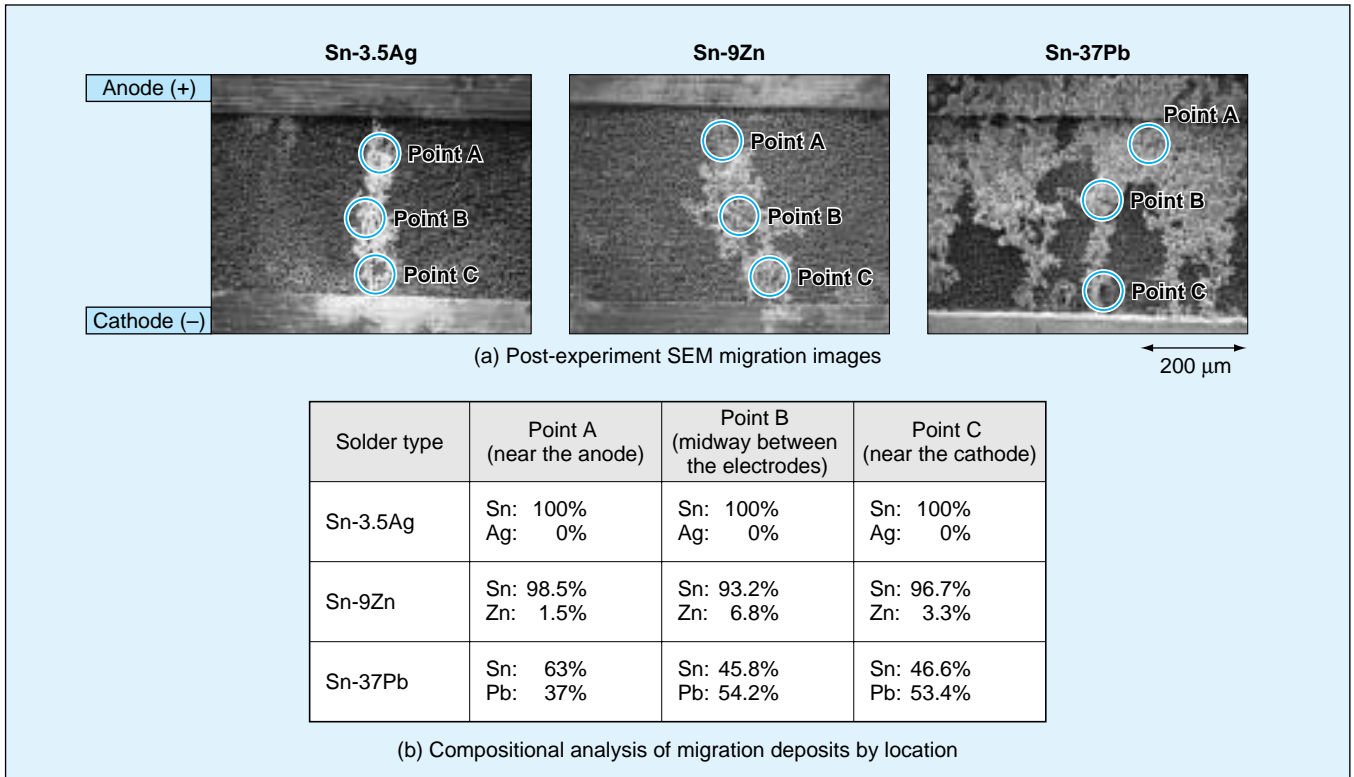


Fig. 7 Results of SEM observation and compositional analysis of deposits

passivity film provides the source for the progressive dissolution of metal ions.

From the results presented above, we can see that migration in lead-free solder comes primarily from Sn. Since the passivity film is more stable during migration than that of conventional Sn-37Pb, migration tends to take longer, and so lead-free solder is more resistant to migration.

5. Conclusions

This report studied the causes of migration occurrence from the aspects of surface texture, anodic dissolution characteristics, and cathodic deposition characteristics. The main conclusions we have drawn are as follows.

- (1) Ag and Cu, which have previously been shown to quickly lead to migration, both combine with Sn to form stable compounds that do not dissolve, and so the migration-resistant characteristics of Sn-3.5Ag and Sn-0.8Cu are related to the dissolution characteristics of Sn.
- (2) With Sn-9Zn, the base metal Zn dissolves, but then forms a passivity film with Sn, which is thought to play a role in preventing the dissolution of Zn, and thus relatively suppressing anodic dissolution.

- (3) Electrode short-circuiting caused by migration shows a tendency to take much longer to occur with lead-free solder than with conventional leaded solder (Sn-37Pb).
- (4) Migration deposits are composed of Sn when using Sn-3.5Ag, of Sn and Zn when using Sn-9Zn, and of Sn and Pb when using Sn-37Pb. The cathodic deposition reaction is greatly affected by anodic dissolution characteristics and by the composition of the dissolved metal ions.
- (5) Lead-free solder is believed to have higher resistance to migration than conventional leaded solder because Sn forms a more stable passivity film than Pb. However, the passivity film of Sn can lose its stability due to environmental conditions.

Summarizing the above conclusions, Table 3 shows the surface texture of lead-free solder compared to its migration characteristics.

For future topics, we are planning to investigate the prediction of migration occurrence and the development of evaluation techniques.

Table 3 Lead-free solder surface texture and migration characteristics

Solder type	Surface texture	Passivity film	Anodic dissolution elements	Cathodic deposition elements
Sn-3.5Ag	Sn phase, Ag ₃ Sn phase	SnO ₂	Sn	Sn
*Sn-0.8Cu	Sn phase, Cu ₆ Sn ₅ phase	SnO ₂	Sn	Sn
*Sn-58Bi	Sn phase, Bi phase	SnO ₂	Sn	Sn
Sn-9Zn	Sn phase, Zn phase	SnO ₂ , ZnO, Zn(OH) ₂ , Zn _x Sn _x O _x	Sn, Zn	Sn, Zn
Sn-37Pb	Sn phase, Pb phase	SnO ₂ , Pb _x O _x	Pb, Sn	Pb, Sn

* These results cited from bibliography 9).

6. Acknowledgements

We would like to take this opportunity to express our gratitude to everyone on the Muki Kougyo Kagaku Lab at the Utsunomiya University Faculty of Engineering for their cooperation in the experiments for this research.

Terminology

*1 Passivity film

When a metal is exposed to a corrosive environment, a passivity film forms providing resistance to corrosion. Examples include oxidative films that form on the surface of metals.

*2 Water drop test

This test serves as a simple test method for migration. This method makes it possible to quickly evaluate how easily migration can occur due to differences in electrode metals and insulation materials, and so the test is used to compare relative migration characteristics. The test method relies on conditions that are much more severe than actual environmental conditions, and so in some cases the migration resistance of the materials tested may be underestimated. Test standards include such standards as IPC-TM-650-2.6.13.

*3 Anode

When using paired electrodes in an electrolytic system, the anode is the electrode from which the positive electric charge flows into the solution.

*4 Cathode

When using paired electrodes in an electrolytic system, the cathode is the electrode into which the positive electric charge flows from the solution.

*5 Working electrode

An electrode used to examine characteristics of a component.

*6 Counter electrode

An electrode through which current flows more easily than through the working electrode. These are generally composed of materials such as titanium or carbon.

*7 Reference electrode

An electrode that serves as a standard for voltage. Examples include calomel electrodes and silver-silver chloride electrodes

*8 Rest potential

The equilibrium potential at which current is flowing neither through the anode nor through the cathode.

*9 Hybridization potential

An electric potential at which current flow is inhibited between two originating potentials.

[Bibliography]

- 1) Japan Environmental Management Association for Industry, "R&D of Lead-free solders toward Practical solution Standardization", NEDO report, 2000
- 2) Saburo Shimodaira, "Husyoku, Bousyoku no zairyo kagaku", Agne Gijutsu Center, 1995
- 3) Takeshi Yanagisawa, "History of Ionic Migration and Factor for its growth", The Journal of the Surface Finishing Society of Japan, Vol.5, No.5, p.479-483, 2000
- 4) G.T.Kohman, H.W.Hermance and G.H. Downes, Bell Sys. Tech. Journal, Vol.6, p.1115-1147, 1955
- 5) Hiroko Inoki, Hirokazu Tanaka, Yuichi Aoki, Shigeharu Yamamoto, "The affects of absorbed water on printed circuit boards, and process of ionic migration", Espec technology report , No9, p.15-20, 2000
- 6) M. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions", NACE, 1966
- 7) Kaichi Tsuruta, Sachio Yoshihara, Takashi Shirakashi, "Investigation of migration in printed circuit boards", The Journal of the surface Finishing Society of Japan, Vol.48, No.3, p.84-88, 1997
- 8) Hirokazu TANAKA, Fumitaka UETA, Sachio YOSHIHARA, Takashi SHIRAKASHI, "Effects of Reflow Processing and Flux Residue on Ionic Migration of Lead-Free Solder Plating Using the Quartz Crystal Microbalance Method", Materials Transactions, Vol.42, No.9, p.3401-3406, 2001
- 9) Hirokazu TANAKA, Mika YAMASHITA, Hiroaki HIRAMATSU, Makoto NAKAMURA, Fumitaka UETA, Sachio YOSHIHARA, Takashi SHIRAKASHI, "Investigation on Ionic Migration Phenomenon of Hot Dipped Lead-free Solders Using QCM method", The Journal of Japan Institute of Electronics Packaging, Vol.5, No.2, p.135-139, 2002