

## &lt;研究論文&gt;

# 酸性주석鍍金溶중에서의 C-Dip package 上的 Tin-bridge 形成機構와 그의 抑制法 (I)

李 完 求\* 南 宗 祐\*

Mechanism of Tin-bridge formation on C-Dip packages in acid tin bath, and its inhibition technique

Wan K. Lee and Chong W. Nam

## 요 약

酸性光澤 주석 鍍金시 C-Dip package 에 사용된 PbO-ZnO-B<sub>2</sub>O<sub>3</sub> 系 solder glass 表面上的 Tin-bridge 形成機構를 說明코져 하였다. 豫備處理用 酸溶液에 의해서 形成된 solder glass 表面의 反應生成物이 陰極還元을 하므로서 Tin-bridge 가 形成함을 알았으며 '또한 이 Tin-bridge 를 形成할수 있는 鍍金溶 條件을 변경 시키므로서 Tin-bridge 形成의 內容을 說明할수 있다. solder glass 의 特性을 검토 하므로서 과산화수소 용액에 의한 Tin-bridge 形成을 抑制 할수 있다.

## ABSTRACT

We investigate the mechanism of a tin-bridge formation on the solder glass surface during acid bright tin plating of a C-Dip package. In the PbO-ZnO-B<sub>2</sub>O<sub>3</sub> system under study, the formation is found to be primarily due to the cathodic reduction of sulfates on the glass surface. And these sulfates, mainly PbSO<sub>4</sub>, are shown to be the products of a precleaning with acids. The bath conditions are varied to see their effect on the tin-bridge formation. We find that the formation can be avoided by pretreating the glass surface with oxyful. Possible mechanisms for this are discussed.

### 1. Introduction

The purpose of this work is to find an efficient means to tinplate the leads of C-Dip for a minimum thickness 200 microinches, which is required to ensure easy soldering.

Previously the minimum was set at 100 microinches. For thicker plating, one need to increase the current density, the bath concentration, the plating time or any combination of them.

During the tin plating for an increased thickness, it happens that a tin-bridge is formed on the surface of the solder glass, causing an unwanted short circuit

among the relays. (See Fig 1.) Such packages have to be thrown away.

The solder glass, PbO-ZnO-B<sub>2</sub>O<sub>3</sub> in our case, readily reacts with the common precleaning acids, which are used to remove the oxide scales from the leads. With the nitric and then the sulfuric acids for the precleaning, we find that the glass surface is covered with insoluble white salts, mainly PbSO<sub>4</sub>.

The various conditions of plating seem to be playing complicated roles in replacing this salt layer with a tin-bridge.

To solve the tin-bridge trouble, it seems necessary to understand the characteristics of the crystal growth and its distribution in the solder glass. In coming sections, we discuss its physico-chemical properties in

\* 韓어차일드 세마이 콘닥터 (한국주석회사)

\*\* 인하대학교 화학공학과 교수



Fig. 1: Tin bridge formed on sealed glass, linking together both the right and left leads of lead frame  
 1; Lead of flame. 2; Tin-bridge (tin deposition),  
 3; Solder glass after sealing

detail in terms of the homogeneous crystal vs. the glass phases.

In a parallel development with the electronics industry, there have been many studies (1, 2, 3, 4) concerning the  $PbO-ZnO-B_2O_3$  solder glass. Sometimes the differential thermal analysis and the X-ray diffraction methods are employed (3). We think that such information is the key to the tin-bridge problem.

## 2. Experiments and Discussions

### Sealing of a C-Dip Package

In a mass production of C-Dip packages (See Fig. 2), it is usual to assemble, heat-treat (seal), and tin-plate it in a sulfuric acid bright bath to chance the solderability. The preglazed  $PbO-ZnO-B_2O_3$  solder glass has a low-melting point and thus is suitable as a sealing material for joining the metal substrate to ceramic bodies of a package.

The solder glass sealing displays needle-shaped crystals at around the crystallization temperature (Fig. 4), its depth and area depending on the heating rate. Although this crystalline phase increases the adhesion strength, it reacts readily with the precleaning solutions (10–15%  $HNO_3$  at room temperature, 50–60%



Fig. 2: Completely assembled C-Dip package prior to tin plate.

$H_2SO_4$  at 90–95°C) to form the troublesome white crystals if its coverage is not uniform.

These precleaning acids are employed to remove the oxide scales, formed in the furnace, on the leads.

### Temperature Variation

The pictures (Figs. 3-A and 3-B) show the degree of crystallization of the solder glass when the sealing

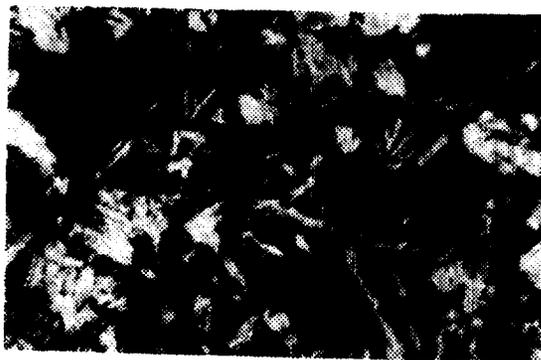


Fig. 3. 3-A: Poor crystal growth corresponding to No. 4 described in Fig. 4 (5)

proceeds at different temperatures (also see Fig. 4).

In Fig. 3-A a case when lower than the peak temperature of primary crystallization, we see rough and nonuniform crystals developed in locally. Fig. 3-B shows crystalline phases that exhibit fine and

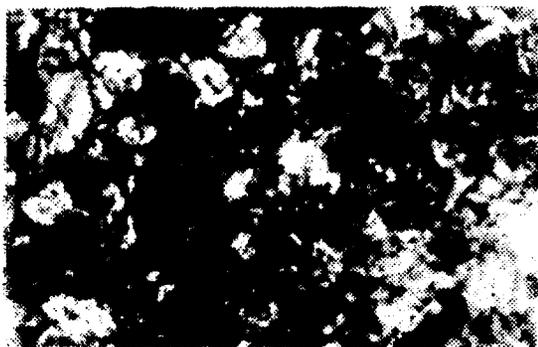


Fig. 3-B: Optimum crystal growth corresponding to No. 5. described in Fig. 4 (5).

homogeneous grain structures. It looks rigid and chemically inert layer because the components' crystal lattice is of the long range order (3).

The effect of temperature variation on the crystal growth in the solder glass (Type CV-97) can be explained by examining the DTA curve. The DTA curve (5) of Fig. 4 is characterized by the occurrence of exothermic or endothermic reactions, which we can check with the furnace sealing operations 1-portion

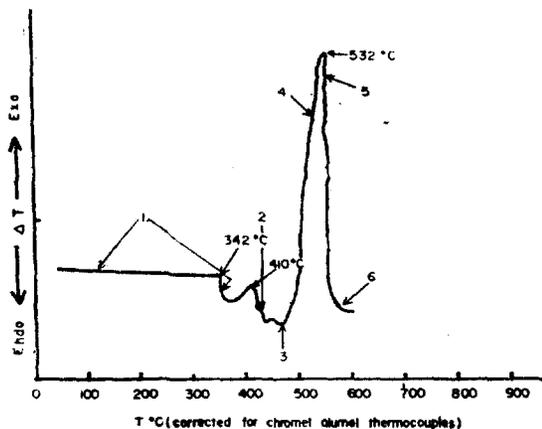


Fig4: DTA Curve of CV-97 solder glass at the heating rate of 50°C/min (5).

of this curve may be described as a transformation range. 2-portion is observed only for powdered glass ceramics (3).

Homogeneous nucleation begins at 3.

As the temperature increases, devitrification begins and the glassy phase is consumed at 6. The peak between 3,6 is the primary crystallization exotherm for this material, Its peak temperature position is a function of heating rate. If proper control of furnace tem-

perature is not maintained, sealing profiles may come into a region to cause partial remelting of crystalline phases, and besides, the crystallizing zone will pass on without completing the mature and uniform crystals throughout the sealed glass. The poor fluidity at lower temperature sealing results in heterogeneous phases on the the surface, and thus many pinholes or voids (4) which may lead to formation of lead sulfate precipitates in the process of descaling. Sharper diffraction spectra were observed by Ramsey (3) for higher temperatures which, because of the higher fluidity enabled a higher degree of crystallinity, Our work, shown in Fig. 3-B, confirms it.

### Oxygen flow variations.

Our experience at the productions line is that a change of oxygen folw rate during sealing plays an important role in controlling the crystallization. This fact is also mentioned by Kingery (6).

Experiment was conducted by varying oxygen flpw rate from zero to 30, 50 and 70 SCFH (standard cubic feet per hour) (see Fig. 5-A, 5-B). Comparing

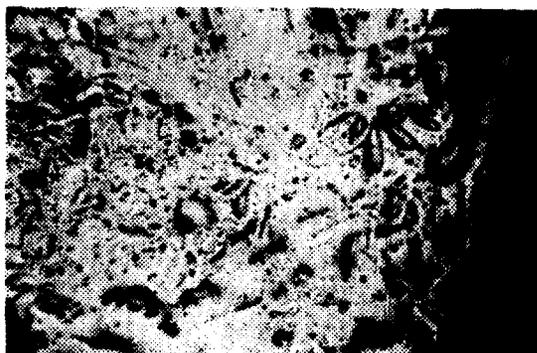


Fig 5-A: Glassy phassy of sealed glass formed at 500°C and 30 SCFH nitrogen gas flowing



Fig. 5-B: Almost complete crstallization can be see at 510°C and 70 SCFH oxygen gas flowing.

the rate of crystallization with the microscopic examination.

(Fig 5-A and 5-B), We find that the crystallization with higher oxygen flow rate lead to denser and more homogeneous surface. Increase of oxygen flow rate means increased partial pressure of oxygen and it seems to restrict the dissociation of lead oxide of solder glass to metallic lead. The lead oxide the major component of this solder glass, may be reduced to metallic lead if it is heated in the presence of carbon particles (7) contained in the ethyl cellulose vehicle flux.

Thus the necessity for increasing the oxygen flow rate Ramey's X-ray diffraction analysis indicated that the CV-97 type solder glass has a  $2PbO-ZnO-B_2O_3$  crystal structure. Thus a rigid formation of crystal lattice needs higher supply of oxygen. Manchot, Pilling and Bedvorth (7) observed that the oxygen reacts with metallic lead and lead oxides fairly quickly at  $300^{\circ}C$ , turning them into a reddish brown oxide, which is smooth and adherent to metal.

With poor oxygen flow devitrification can not be expected over all surface of sealed glass. In contrast, numerous bunches of amorphous glass are formed as shown in Fig. 5-A. Thus poor crystalline phases may be formed during a normal sealing operation,



Fig. 6: Voids contour (ground by 0.5 millimeter) of the poor sealed glass (400X)

and many voids underneath the external surface (Fig. 6) introduced in sealed glass as discussed in the previous section.

During the descaling operation, these voids and holes (their surface crystallization not being continuous) initiate and accelerate the corrosion of the external surface of sealed glass, which is possible because of the electrostatic potential difference between grain boundaries in glassy phase (8).

In addition, these holes may hold a large amount of lead sulfate precipitates, which are difficult to rinse off with tap water.

Fig. 6, shows the pinholes or voids, concentrated in glassy phases. Most of the voids under the surface (see Fig. 7) remain even after heating or sealing.

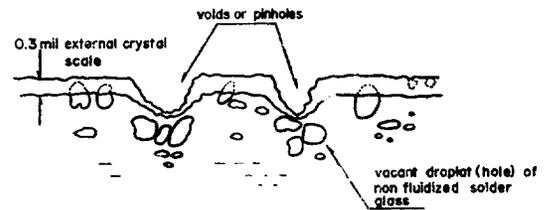


Fig. 7: Schematic picture of the cross-sectioned sealed glass.

In conclusion, the presence of the glassy phase in the sealed glass, which is due to an improper control of sealing, influences the degree of tin-bridge formation.

#### Acidic Tin Plate and Cathodic Reduction of Lead Sulphates.

To investigate the tin-bridge formation, we examined the cross-section of units with tin-bridge formation (See Fig. 8-A, 8-B).

We could observe a somewhat different film on the neighbouring layers, which looks very thin and spongy. The presence of the film suggests a mechanism for tin-bridge formation. We have conducted a series of experiments to see if the mechanism is the reduction of basic lead sulfate into the conducting metallic lead.

To study the reduction mechanism of sealed glass during the tin plating, samples were pretreated as in



Fig. 8-A: Cross section of tin-bridged unit

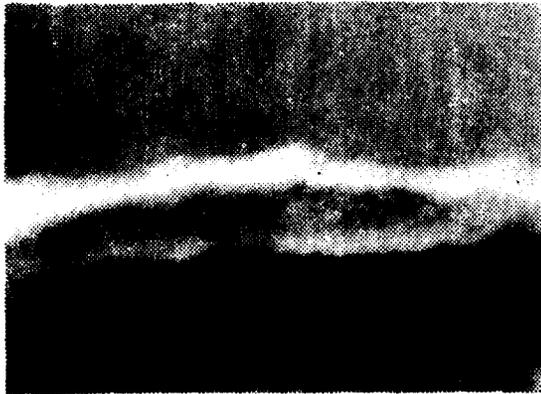


Fig. 8-B: Magnification of the above feature by.

the descaling; 60% sulfuric acid (volume %, 90-95%, 40 sec-90 sec)—Tap rinse— Deionized water rinse— Electrolysis in 10% sulfuric acid (Room temp. 5A/in<sup>2</sup>-10A/in<sup>2</sup>, 5min-10min). for which an inert carbon anode was used.

With the Current flowing into 10% sulfuric acid electrolyte, we could observe that the vigorously evolving hydrogen gas changes the white lead sulfate from a "porous" to a "rigid" layer and then to a "solid" (with the aid of a 600X microscope).

The rate of these changes was studied for different values of applied current density, temp. of electrolyte and the electrolyzing time.

Another experiment was conducted with the same sulfuric acid electrolyte but with a copper plate in place of the carbon plate. (See Fig. 9). The cathodic reduction of lead sulfates resulted in a conductive layer for new electrodeposition of copper metal. The reaction is known to be same as that in a lead storage



Fig. 9: Spongy-like copper deposition on the lead sulfate precipitate.

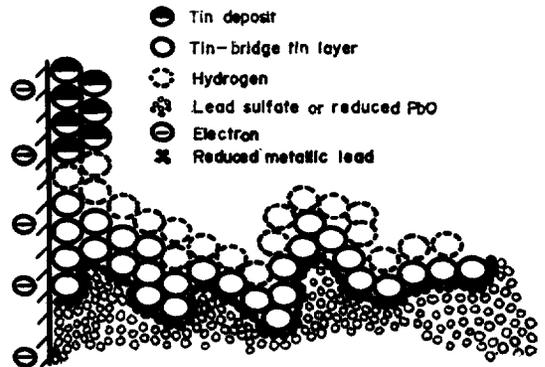
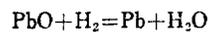
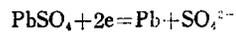
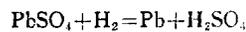
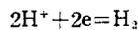


Fig. 10: Micro-faceting of tin bridge formation.

ge battery: Refer to Fig. 10



The tin-bridge failures were reported from the mass barrel production line when the bath conditions were: current density increase (from 10A/ft<sup>2</sup> to 20A/ft<sup>2</sup>), electrolyte concentration increase (H<sub>2</sub>SO<sub>4</sub> from 12 fl. OZ./gl to 18 fl. OZ./gl, SnSO<sub>4</sub> from 2 OZ./gl to 4 OZ./gl), the bath temp. (from 11°C to 19°C), and the plating time (from 12 min/14 ft<sup>2</sup> to

20 min/14 ft<sup>2</sup>).

From the results of the two related experiments in the above, one can see that the plating bath has much influence on the degree of cathodic reduction, which is now proud a basic cause of the tin-bridge formation.

**30% Hydrogen Peroxide Solution Pretreatment.**

As discussed in previous sections the poorly sealed glass is a mixture of glassy and crystalline phases, depending on the selection of descaling solution (9).

Nitric or chloric acid or their mixture reacts violently with the sealed glass whether it be a crystalline or a glassy phase.

Hydrogen peroxide has an effect of auto-oxidation that can be accelerated by dust particles and pinholes ro active spots on solid surface (10). We used it in reducing the formation of tinbridge through oxidation of the fused metallic lead to lead oxide.

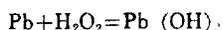
Hydrogen peroxide solution is also known as a oxidizing inhibitor (11).

When the glassy surface (Fig. 5-A) was pretreated with hydrogen peroxide solution, we could get better uniformity in the surface (See Fig. 11).



**Fig. 11:** Sealed glass surface (of Fig. 5-A) treated in not hydrogen peroxide (80°C, 40 Sec)

Those metallic lead in glassy phase reacts with hydrogen peroxide solution (30%):



This lead hydroxide is converted into lead oxide or

higher oxides as more hydrogen peroxide is applied (12).



Hydrogen peroxide pretreatment was carried out as follows; Hydrogen peroxide solution (30%, 30°-80°C, dipping time 20 sec to 60 sec.) (See Fig. 11)-Hot sulfuric acid (60%, 90-95°C, 40 sec-90 sec)-Tap rinse (Room temp., 10 sec)-Electrolysis(10% sulfuric acid, 20°C, 7A/in<sup>2</sup>, 1 min to 20 min) (See Fig.12).



**Fig. 12:** Sealed glass surface (of Fig. 14) implemented by dummy-charge process at 10% H<sub>2</sub>SO<sub>4</sub>, 20°C, 7A/in<sup>2</sup>, 15 min.

This experiment indicates the two important roles of Hydrogen peroxide pretreatment enhancing the uniformity in the sealed glass surface with pinholes and pots, and oxidizing metallic lead.

**3. Conclusions**

The lead sulfatte precipitate on the surface is reduced by the electrolysis of tin plating to form the tin-bridge (Fig. 1).

The distribution of the glassy phase on the sealed glass surface controls the corrosion rate of sealed glass in the sulfuric acid descaling. It is shown that the glassy phase causes the tin-bridge formation during the acid tin plating of C-Dip package.

Higher crystallinity or more uniform devitrification, achieved by means of high temperature sealing and sufficient oxygen flow, ensure better tin plate with-

few voids and pinholes Figs. 6.7).

Controlling factors for the tin-bridge formation such as current density electrolyte concentration and plating time must be considered in solving the problem.

Hydrogen peroxide pretreatment before descaling prevents and inhibits the formation of lead sulfate precipitates.

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