Report 3

Evaluating lead-free plating using gas corrosion tests

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Gas corrosion constitutes one aspect of environmental stress on electronic parts. The gas corrosion tests carried out for evaluations in this report can be seen as one weapon in the effort to increase reliability. The corrosiveness of gas varies according to the temperature and humidity of the ambient environment, and testing involves other factors as well, such as gas concentration, reproducibility of field conditions, and accelerated investigation. A variety of public standards address test methods for gas corrosiveness.

For this report, we have studied the plating of lead-free solder that industry has been trying to incorporate. We have carried out gas corrosion tests, and we present our findings on visible changes (discoloration), wettability and surface analysis.

1. Introduction

Electronic parts are subjected to a wide range of environmental conditions resulting from their use in such varied equipment as automobiles, household appliances, and IT equipment. The usage environments contain various types of stress such as temperature, humidity, vibration, pressure, and corrosive gas.

The problem with corrosive gas is particularly acute in such environments as seaside industrial belts, paper and pulp factories, and in hot springs regions. Relocation of manufacturing to overseas bases can also result in severe environmental conditions, and require special consideration for such factors as the effect of outgas originating from cardboard containers during transportation.

Corrosion is considered to be wear generated in response to the environments to which materials are exposed. Considerable economic loss can be traced to corrosion, and preventing corrosion is also one aspect of improving reliability. Furthermore, the lead eluting from discarded products introduces toxic health effects into the environment, and so we are now approaching the stage of global employment of lead-free solder. In past reports, we have pointed out the reliability problems encountered in combining lead-free solder with conventional Sn-Pb plating, and we are also calling for the use of totally lead-free solder. Several types of alternative plating are under consideration, such as Sn-Ag, Sn-Bi, Sn-Cu, and Sn-Zn.

The metal additives in these alternatives include traces of metals such as silver and copper, leading to apprehension of gas corrosion. The gas corrosiveness of individual metals is well-documented, but few available reports evaluate the alloy gas corrosiveness stemming from binary compounds such as those used in lead-free solder. Because of this, we decided to study and compare Sn-Ag and Sn-Cu used in lead-free plating, as well as Sn and Sn-Pb used in conventional plating, in order to examine the corrosion resistance exhibited by lead-free plating.

2. Test methods and standards for gas corrosion testing

2-1 The relationship between environmental factors and corrosion

Gas corrosion appears as a variety of phenomena in various forms, such as localized metal corrosion, or gas entering solution in moisture-related humidity and affecting the pH. Possible evaluation methods for this type of complex contact area corrosion include tests comparing such factors as the metals used and the environmental conditions, as well as tests using electrical resistance to make a quantitative comparison of the level of corrosion. Up to now, the principle source of corrosive gas has been free atmospheric gas (e.g., the SO_X and NH_3 produced in industrial areas, and the H_2S emanating from hot springs areas), but recently parts such as switches, connectors, and sockets are experiencing contact reliability problems induced by gases originating from packaging materials and materials used in the products themselves. In addition, miniaturization of electronic parts has contributed to situations in which sealed construction traps corrosive gas, which then reacts with dew condensation to produce corrosion.

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Corrosion occurs when gas enters into solution in moisture adsorbed onto the surface of metals, changing the pH and causing localized corrosion. This means that the quantity of adsorbed moisture affects the level of corrosion, and so atmospheric humidity affects both reproducibility and acceleration in testing.[1] In particular, since the moisture adsorption quantity rises abruptly in the range from 60 to 70% RH, this range is generally considered the corrosion enhancement range, and more effective results in corrosion testing can be obtained using humidity conditions above this range.

2-2 Test standards and test methods for gas corrosion tests

Contact area corrosion leads to contact failure of electronic circuits in electronic equipment parts such as switches, connectors, and terminals. Various gas corrosion tests have been devised and standardized concerning the corrosion of electronic parts being generated from the presence of the following three combined factors: dust particles, dew condensation, and corrosive gas. The four most typical corrosive gases are H_2S (hydrogen sulfide), SO_2 (sulfur dioxide), NO_2 (nitrogen dioxide), and Cl_2 (chlorine). Test conditions have been standardized not only for individual gas corrosion tests, but also for mixed gas corrosion forms as well. For items such as electronic parts, there is an increasing tendency to employ mixed gas tests at low concentration ppb (parts per billion) levels that have higher field reproducibility. Table 1 shows the principal test methods.

Table 1 Gas corrosion test standards

<table>
<tr><th colspan="2">Test standard</th><th>Gas type</th><th>Gas concentration (ppm)</th><th>Temperature (°C)</th><th>Humidity (% RH)</th><th>Test time (days)</th><th>Comments</th></tr>
<tr><td>IEC 60068-2-42 (JIS C 0090)</td><td></td><td rowspan="4">SO_2</td><td>25 ±5</td><td>25 ±2</td><td>75 ±5</td><td>4, 10, 21</td><td>JIS also includes Temperature 40 ±2°C, Humidity 80 ±5% RH</td></tr>
<tr><td>ISO 10062</td><td>Method A</td><td>0.5 ±0.1</td><td>25 ±1</td><td>75 ±3</td><td>1, 2, 4, 10, 20, 30, 90</td><td></td></tr>
<tr><td rowspan="2">JIS H 8502</td><td rowspan="2"></td><td>25 ±5</td><td rowspan="2">40 ±1</td><td rowspan="2">90 ±5</td><td rowspan="2">1, 2, 4, 10</td><td rowspan="2">Additional test times are 4 and 8 hours</td></tr>
<tr><td>1000 ±50</td></tr>
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<table>
<tr><th colspan="2">Test standard</th><th>Gas type</th><th>Gas concentration (ppm)</th><th>Temperature (°C)</th><th>Humidity (% RH)</th><th>Test time (days)</th><th>Comments</th></tr>
<tr><td>IEC 60068-2-43 (JIS C 0090)</td><td></td><td rowspan="4">H_2S</td><td>10 to 15</td><td>25 ±2</td><td>75 ±5</td><td>4, 10, 21</td><td>JIS also includes Temperature 40 ±2°C, Humidity 80 ±5% RH</td></tr>
<tr><td>ISO 10062</td><td>Method B</td><td>0.1 ±0.02</td><td>25 ±1</td><td>75 ±3</td><td>1, 2, 4, 10, 20, 30, 90</td><td></td></tr>
<tr><td rowspan="2">JIS H 8620</td><td rowspan="2"></td><td>3 ±1</td><td rowspan="2">40 ±1</td><td rowspan="2">90 ±5</td><td rowspan="2">4, 10, 21</td><td rowspan="2">Additional test times are 4 and 8 hours</td></tr>
<tr><td>10 ±2</td></tr>
</table>

<table>
<tr><th colspan="2" rowspan="2">Test standard</th><th colspan="4">Gas type and concentration (ppb)</th><th rowspan="2">Temperature (°C)</th><th rowspan="2">Humidity (% RH)</th><th rowspan="2">Test time (days)</th></tr>
<tr><th>H_2S</th><th>SO_2</th><th>NO_2</th><th>Cl_2</th></tr>
<tr><td rowspan="4">IEC 60068-2-60 (JIS C 0048)</td><td>Method 1</td><td>100 ±20</td><td>500 ±100</td><td>—</td><td>—</td><td>25 ±1</td><td>75 ±3</td><td rowspan="4">4, 7, 10, 14, 20</td></tr>
<tr><td>Method 2</td><td>10 ±5</td><td>—</td><td rowspan="2">200 ±50</td><td>10 ±5</td><td rowspan="2">30 ±1</td><td>70 ±3</td></tr>
<tr><td>Method 3</td><td>100 ±20</td><td>—</td><td>20 ±5</td><td rowspan="4">75 ±3</td></tr>
<tr><td>Method 4</td><td>10 ±5</td><td>200 ±20</td><td>200 ±20</td><td>10 ±5</td><td rowspan="3">25 ±1</td></tr>
<tr><td rowspan="2">ISO 10062</td><td>Method C</td><td rowspan="2">100 ±20</td><td>500 ±100</td><td>—</td><td>—</td><td rowspan="2">1, 2, 4, 10, 20, 30, 90</td></tr>
<tr><td>Method D</td><td>200 ±50</td><td>—</td><td>20 ±5</td></tr>
<tr><td rowspan="6">EIA-364-65A-1998</td><td>Class I</td><td colspan="7">Class I only abolished</td></tr>
<tr><td>Class II</td><td rowspan="2">10 ±5</td><td>—</td><td rowspan="5">200 ±50</td><td rowspan="2">10 ±3</td><td>30 ±2</td><td rowspan="2">70 ±2</td><td rowspan="5">20</td></tr>
<tr><td>Class IIA</td><td>100 ±20</td><td>30 ±1</td></tr>
<tr><td>Class III</td><td rowspan="2">100 ±20</td><td>—</td><td rowspan="2">20 ±5</td><td>30 ±2</td><td>75 ±2</td></tr>
<tr><td>Class IIIA</td><td>200 ±50</td><td>30 ±1</td><td>70 ±2</td></tr>
<tr><td>Class IV</td><td>200 ±20</td><td>—</td><td>30 ±5</td><td>40 ±2</td><td>75 ±2</td></tr>
</table>

3. Test methods

Table 2 shows plating conditions, Fig. 1 shows test specimen shape, and Table 3 shows test conditions. To compare corrosiveness, Sn and Sn-Pb plating were exposed to identical environments, and evaluated using gas corrosion tests.

Table 2 Plating conditions

Plating composition (wt %)	Gloss	Plating thickness	Foundation plating
Sn-3Ag	Semi-gloss	4 µm	Nickel 1 to 2 µm
Sn-1Cu	Semi-gloss		
Sn	Gloss		
Sn-20Pb (Ref.)	Gloss		
Material	Phosphor bronze		
Dimensions	15 × 32 × 0.25 (mm)		

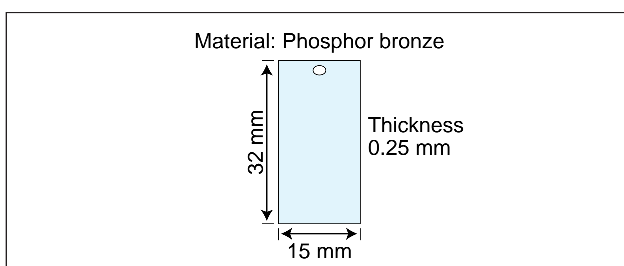

Fig. 1 Test specimen shape

Table 3 Test conditions

Temperature and humidity	40°C, 80% RH
Gas type (concentration)	H_2S (1 ppm, 5 ppm) SO_2 (1 ppm, 5 ppm)
Test time	100, 200, 300 h

When setting test conditions, the high-temperature, high-humidity Asian environment was assumed, and gas that could be used for evaluating the corrosiveness of silver and copper was selected. For evaluation, a scanner was used to read the level of corrosiveness as determined by external discoloration based on uniform conditions, and corrosion was confirmed by visual observation. Furthermore, to provide numerical values for corrosion levels, the image was digitized in two gradations, and the discoloration distribution ratio was calculated using the initial black and white ratio as the standard. In addition, using a uniform load (load 0.1N) the surface changes due to corrosion film were confirmed using contact resistance measurements, and the solder wettability was evaluated using the meniscograph method.[*1] In addition, changes in granulation were confirmed using SEM (scanning electron microscope) images, and elemental analysis was used to identify the corrosive elements.

4. Discussion of results

4-1 Externally observable results

Fig. 2 and 3 shows discoloration distribution ratios for image processing and the discoloration process for Sn-Ag and Sn-Cu. The discoloration distribution ratio was rated numerically according to visual observation and scanner images and showed trends that displayed correlation. In this case, the quantification achieved through image processing can be seen as a rough measure of corrosion. In trends of change in plating, the Sn-Ag plating showed heavy discoloration, and the higher the concentration, the greater the discoloration. Among the gases, the H_2S showed the strongest tendency to cause discoloration. The Sn and Sn-Pb platings showed very little change in response to any of the gases.

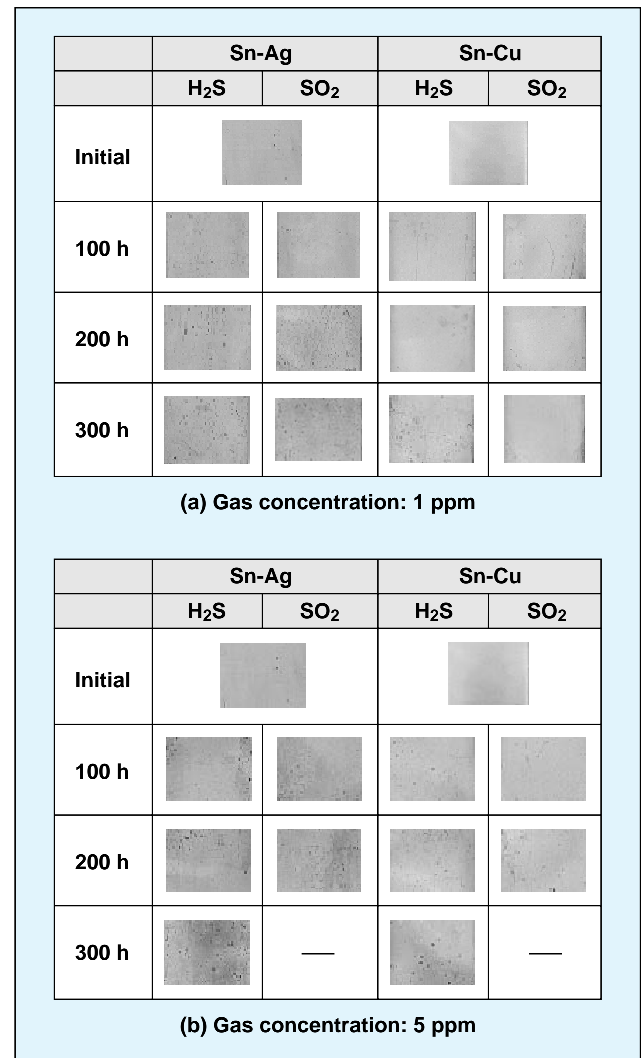

Fig. 2 Discoloration process of plating surface caused by corrosive gas

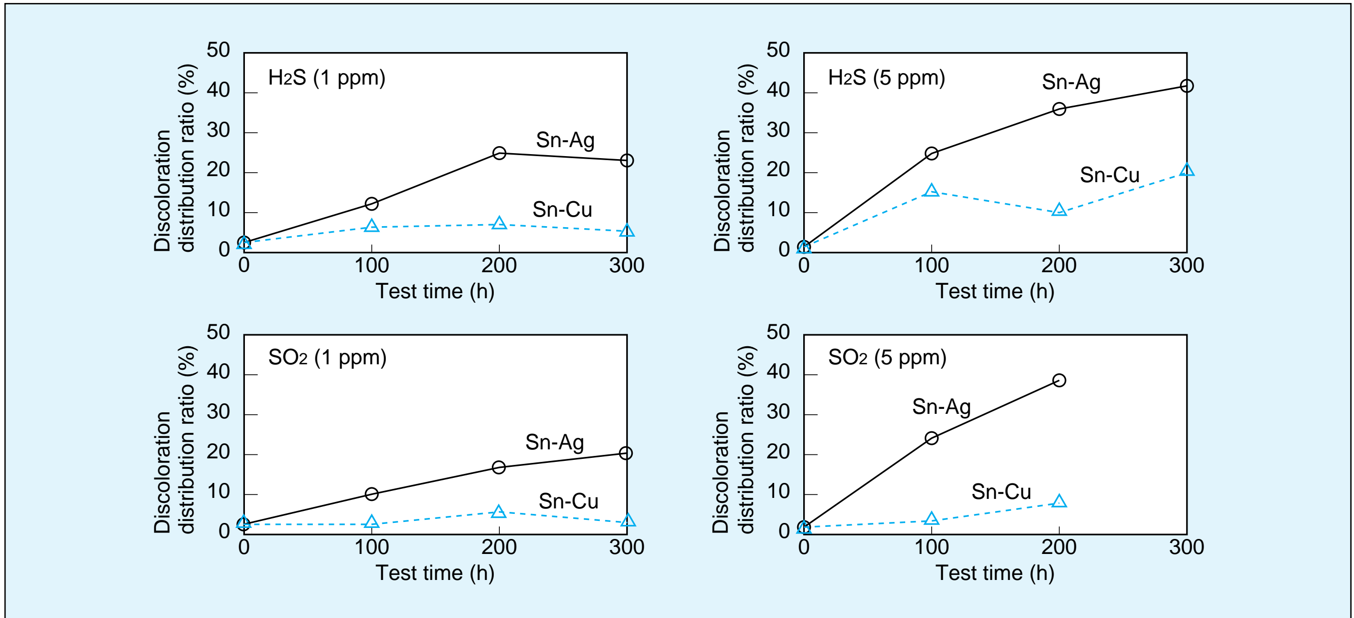

Fig. 3 Changes in discoloration distribution ratio caused by corrosive gas

4-2 Contact resistance measurements

Areas such as the silver contact points of electronic parts often have performance problems due to increased contact resistance caused by corrosion. Fig. 4 shows measurement values for contact resistance. The results showed marked discoloration, but almost no change is seen in the contact resistance values. The lack of increase in resistance values is thought to result from an extremely thin corrosion film that does not reach beyond the surface, and is broken by contact surface pressure.

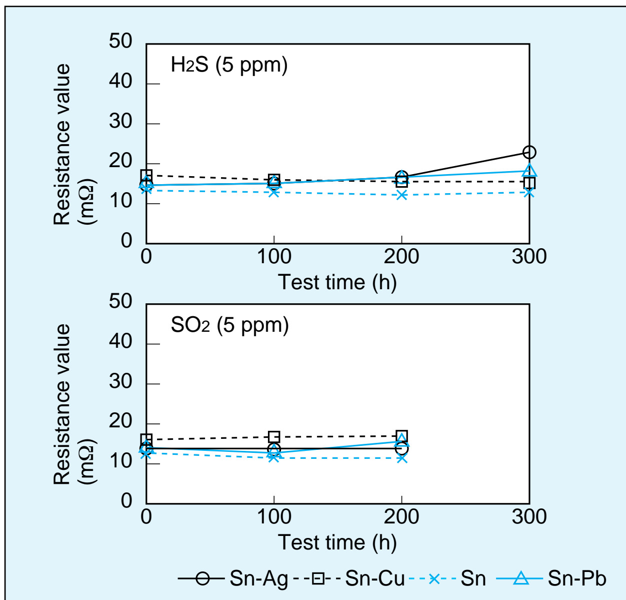

Fig. 4 Changes in contact resistance values due to gas corrosion

4-3 Wettability test results

Fig. 4 shows wettability test conditions and Fig. 5 shows test results using the meniscograph method. In an H_2S environment, the Sn-Cu showed worse deterioration than the Sn-Ag, quite unlike the discoloration results. This is thought to result from the affect of additives to the Cu and Ag, and perhaps from differences in the form of plating deposition.

Both discoloration and wettability changes were minimal at over 200 hours. This is said to be due to the barrier formed by the oxidation film and sulfuration film, but in the case of the Sn-Ag and Sn-Cu, the possibility can be considered that since the combined gases function as oxidants, they accelerate the formation of oxidation film, and so change is linear.

Zero cross time indicates the base line for the existence of repellence between the test piece and the solder bath. Therefore, we can judge that the longer the zero cross time, the worse the wettability.

Table 4 Wettability test conditions using the meniscograph method

Dip speed	10 mm/sec
Dip depth	5.0 mm
Dip time	10 sec
Solder bath temperature	245°C
Solder	Sn-2.5Ag-1Bi-0.5Cu
Flux	Rosin 30%

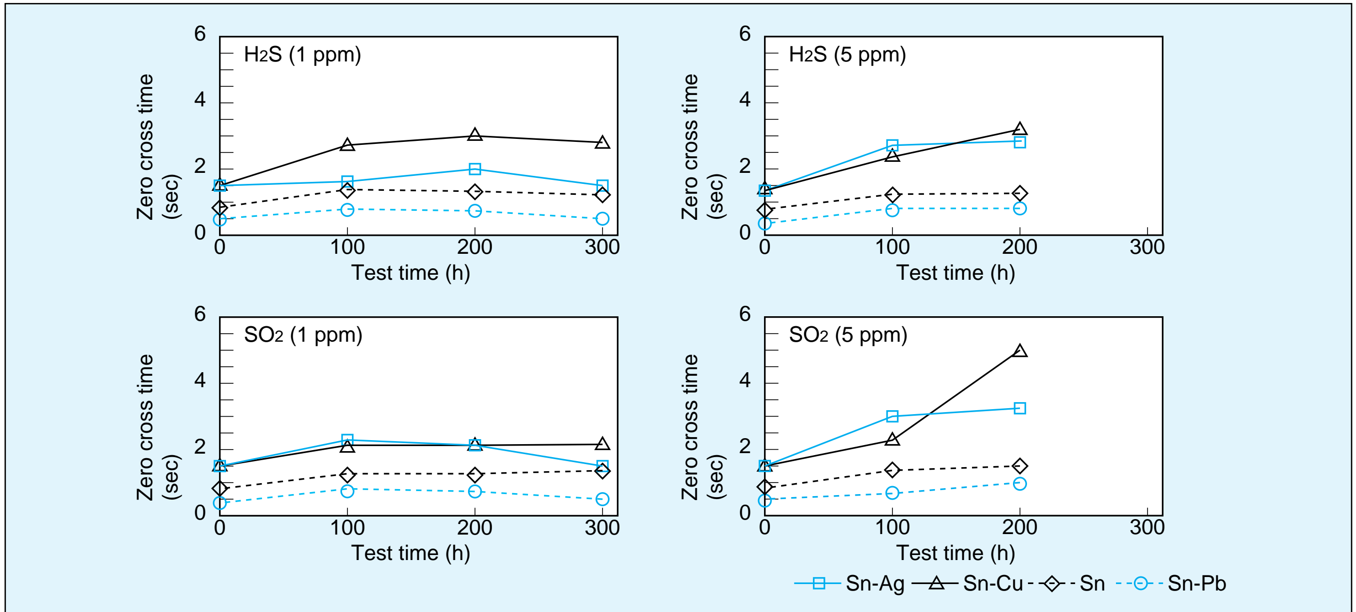

Fig. 5 Effects of corrosive gas on wettability

4-4 Results of surface analysis

As seen in Fig. 6, a corrosion film forms over all the plating granules. A plating corrosion film of 1 nm to 1μm due to gas corrosion is often reported, and the granular diameter is roughly equivalent to the film thickness. The factors affecting discoloration and wettability are thought to result from this corrosion film.[1), 2), 3)]

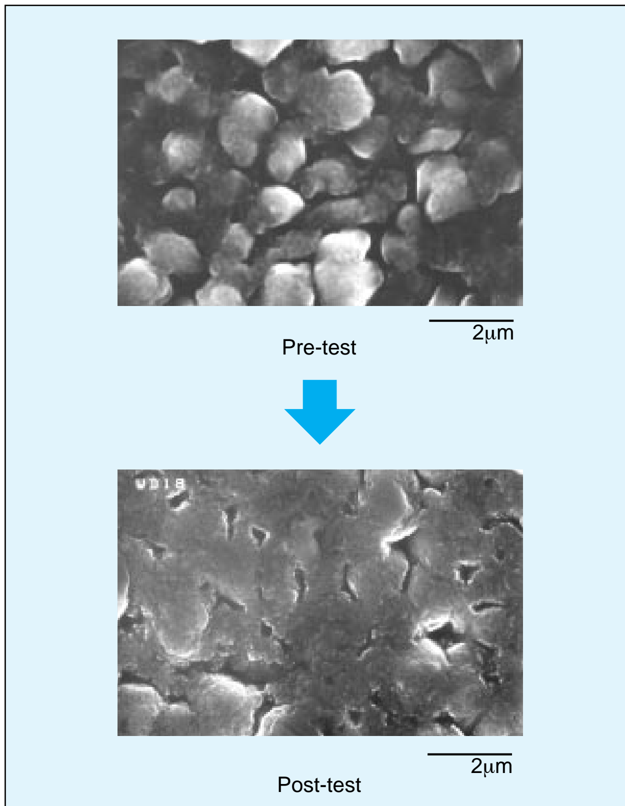

Fig. 6 SEM images of Sn-Cu plating surface

Fig. 7 shows the results of elemental analysis of corrosion surfaces using GDS (Glow Discharge Optical Emission Spectroscopy[*2]). Sulfur (S), which was not seen on the initial surface, is seen on the surface layer only, and is thought to lead to corrosion due to sulfuration.

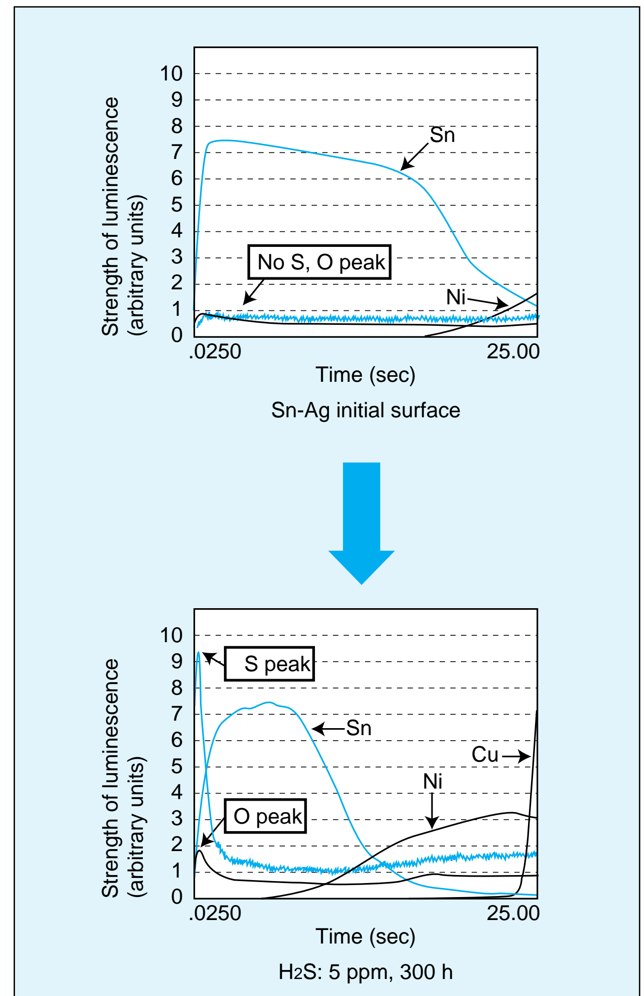

Fig. 7 GDS (Glow Discharge Optical Emission Spectroscopy) analysis results

5. *Summary*

The results of analyzing the resistance of lead-free solder to gas corrosiveness showed discoloration due to corrosion in Sn-Ag and Sn-Cu plating in single gas environments of H_2S and SO_2. However, the wettability is inferior to conventional Sn-37Pb plating, though at present, the results have not shown an extreme loss of wettability. In the future, it will also be necessary to evaluate the Cl_2 and NO_2 gases that function as accelerating factors, from the standpoint of the presumed field environment.

6. *Acknowledgement*

We would like to express our sincere gratitude to Mr. Hiroyuki Moriuchi and Mr. Yoshiichi Nakano of the Research and Development Department of the Dai-ichi Denshi Kogyo K.K. for their opinions and cooperation that played a valuable role in carrying out these tests.

Terminology

***1. Meniscograph method**

When dipping the specimen in the molten solder bath, this method detects the upward and downward forces of the surface tension of the solder received by the specimen, and by recording this over time, is able to discover time-related changes in wettability. The method is JIS C 0053, Environmental testing. Part 2: Tests. Test ta; Soldering. Solderability testing by the wetting balance method.

***2. Glow Discharge Optical Emission Spectroscopy (GDS)**

Glow discharge spattering is used to illuminate the target for qualitative and quantitative analysis using spectroscopy. The steel industry uses this method of analysis because it is possible to measure the elemental concentration in the direction of depth by correlating basic properties of the materials.

[Bibliography]

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