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# Impact of temperature on the corrosion of lead-free solder alloy during salt spray test

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## Abstract

This paper presents the impact of temperature on the corrosion behaviour of lead-free solder alloy during neutral salt spray (NSS) test. The focus is made on the Sn-Ag-Cu (SAC305) solder alloy Ball Grid Array components. Components were aged during 24, 48, 72, and 96 hours in a salt spray chamber Ascott at 35°C with 5% sodium chloride (NaCl) solution at temperatures ranging from 25°C to 45°C to investigate the effect of temperature on the corrosion. Two observables corrosion criteria were defined for this analysis. Solder balls deterioration is visible after 72, 48, and 24 hours, respectively, at 25°C, 35°C, and 45°C. This shows that the temperature has a significant effect on the corrosion behaviour of lead-free solder balls. An increase in temperature from 25°C to 35°C and 45°C led to an earlier onset of corrosion. Tin (Sn), oxygen (O), and chloride ion (Cl) are found on solder balls. Finally, thermal “Arrhenius Law” is used to estimate an acceleration factor (AF) and an indicative value of the activation energy (Ea) after 96 hours of exposure. The kinetic of the corrosion failure mechanisms is being investigated in order to predict lead-free solder balls lifetime.

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## 1. Introduction

Electronic assemblies of some equipment are exposed to a salt environment. However, few data have been published on the impact of temperature on the corrosion of Sn-Ag-Cu (tin-silver-copper) solder, solder joint materials, and microelectronic assemblies under these conditions [1]. During electronic devices' operations, heat and corrosive agents can affect the solder and decrease the expected lifetimes. As an example, harsh marine environment can seriously affect the properties of the solder alloys during operations [2].

The reliability of the solder is important to determine the performance and lifetime of electronic assemblies when subjected to temperature and corrosive environments [3-4]. Thus, knowledge of the effect of temperature on the corrosion behaviour of the solder alloy in a salt environment is essential to prevent failure and malfunction of an electronic device [5].

Many studies have been conducted to investigate the effect of corrosion and study the physical process mechanism on the Sn96.5-Ag3.0-Cu0.5 (SAC305) solder alloy. Most studies have applied the potentiodynamic polarization and electrochemical impedance spectroscopy [5-12] to determine the corrosion resistance and assess the corrosion behaviour of a solid-state device. Fewer studies have applied the salt spray test to study corrosion behaviour and propose corrosion models [1, 13-15]. However, acceleration factors, physical mechanisms, and a corrosion model based on experimental data are still unknown. Furthermore, none of these studies investigated the impact of temperature on the corrosion of lead-free solder during salt spray test.

The purpose of this study is to investigate the evolution of corrosion kinetics on the SAC305 solder and then to calculate the acceleration factor (AF) in the salt spray test by changing the

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temperature. The ageing tests were performed on BGA (Ball Grid Array) components in an Ascott salt spray chamber.

## 2. Experimental setup

### 2.1. Materials

Experiments were carried out on the Sn96.5-Ag3.0-Cu0.5 (SAC305) solder balls of commercial BGAs components provided by Amkor. They contain 128 balls per BGA, and measure 12x12 mm<sup>2</sup>. The circuits were aged to examine the impact of temperature on the corrosion of the alloy. The non-aged BGAs are referred to as "as-received sample" (ARS) hereafter.

### 2.2. Methods

To investigate the influence of temperature on corrosion, ARSs were aged during 24, 48, 72, and 96 hours in a salt spray chamber (Fig.1) according to ASTM B117 standard (5% NaCl at T=35°C), and at 25°C and 45°C with the standard salinity.

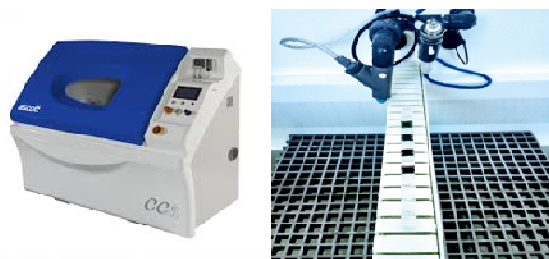


Fig. 1. Salt spray chamber

The advantages of the salt spray chamber are its temperature homogeneity ( $T \pm 2^\circ\text{C}$ ) and the possibility to study the corrosion of various metals and surfaces without interference in chemical reactions. So, the test conditions are reproducible. Moreover, this equipment is the most used for industrial tests. The chosen temperature range may seem very narrow.

However, this kind of equipment is designed to perform a standard robustness test at 35°C and does not permit tests at higher temperatures.

Nevertheless, the effect of temperature in accelerating saline corrosion phenomena on SAC is evaluated for the first time in the present study.

After being removed from the chamber, samples were washed in deionized water and dried with a stream of clean, compressed air. They were then mounted in resin, grounded using SIC papers (P1000-P1200), and finely polished using diamond liquids (9 $\mu\text{m}$ -6 $\mu\text{m}$ -3 $\mu\text{m}$ -1 $\mu\text{m}$ ). A cross-section of the treated samples was examined by optical microscopy (OM), scanning electron microscopy (SEM).

For each testing condition, 18 solder balls were observed and, statistical information on the percentage of corroded solder was obtained for each exposure time. Two observable corrosion criteria were defined for the OM and SEM analyses. The percentage of corroded solder balls was defined as the ratio of the number of solder balls corroded after the salt spray test to the total number of solder balls. The chemical composition and distribution of elements in the corroded area were determined by energy dispersive X-ray (EDX) analyses.

## 3. Results and discussion

### 3.1. Definition of corrosion criteria

Fig. 2 shows the cross-section of solder balls before and after the test. Compared to the solder ball at the initial state, the corrosion is measured by evaluating the eroded area. Image J analysis software is used to evaluate the percentage of the eroded area. For instance, in the picture (Fig.2b), the corroded area is about 22.5% of the total solder surface. A ball is considered as corroded if at least 2.5 % of the material has disappeared.

Corrosion is also detectable by a change in color. The color changing (silver gray) of a part of the ball from its initial state (Fig.2a) to dark gray allows us to highlight the corroded state of that ball (Fig. 2b). Song and Lee observed similar corrosion behaviour [16].

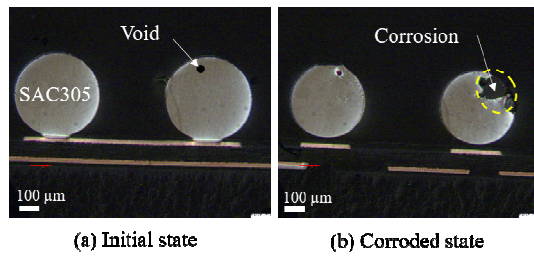


Fig. 2. Cross-section of (a) initial state and (b) corroded state of the BGA as-received samples

### 3.2. Analyses and observations

Fig.3 shows the corrosion morphology observation and the corroded area behaviour for OM analyses of the ARS solder balls exposed to a 5% NaCl salt spray at 25°C (Fig. 3a), 35°C (Fig. 3b), and 45°C (Fig. 3c) as a function of exposure time (0, 24, 48, 72 and 96 hours). Corroded areas are visible on the lead-free solder balls after 72h at 25°C, 48h at 35°C, and only 24 h, at 45°C.

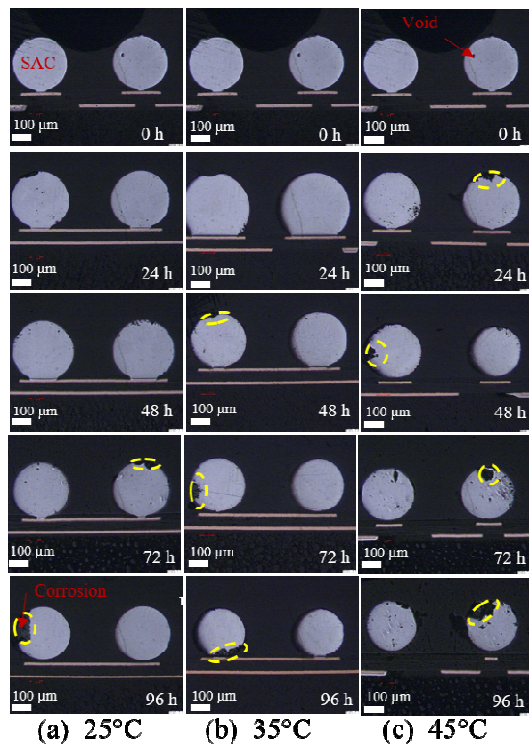


Fig. 3. Corrosion morphology observation change of the as-received SAC305 solder balls

At 25°C, after 72 h of ageing, samples have some corroded areas. These areas become larger

after 96 h.

At 35°C, after 48 h, samples have some corroded areas. These areas become larger after 72 h. After 96 h, 67% of the observed surface is corroded. Song and Lee [16] have observed a similar evolution of the corrosion on Sn-Ag-Cu solder balls in the same condition (5% NaCl at 35°C).

At 45°C, after 24 h, samples have some corroded areas. These areas become larger after 48 h and 72 h. After 96 h, 78 % of the observed surface is corroded.

An increase in temperature leads to an earlier onset of corrosion. So, these experiments clearly demonstrate that temperature has a significant effect on the corrosion behaviour of lead-free solder balls.

Another observed phenomenon concerns the corrosion location. The ball surface is not uniformly attacked. There is only one corrosion product site per ball. The corrosion site is different from one ball to another.

Fig. 4 shows EDX results of the corroded area sample after 48 hours of exposure in salt spray following the ASTM B117 standard condition (5% NaCl at T=35°C). According to the EDX analysis, the corrosion product mainly contains Sn, O, and Cl.

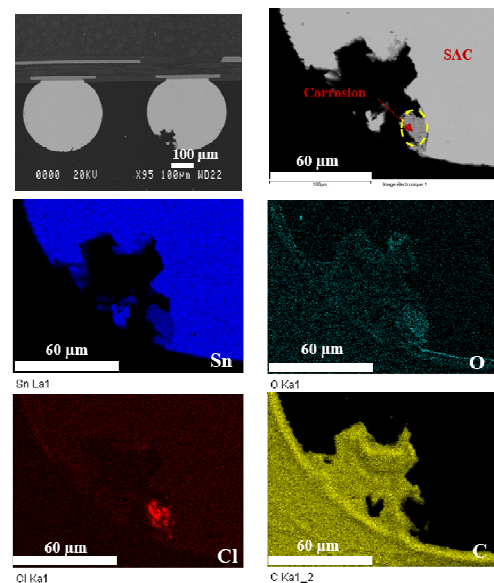


Fig. 4. EDX of as-received BGA sample solder ball (5% NaCl at 35°C) after 48h in salt spray chamber

### 3.3 Acceleration factor estimation

Even if our results are only obtained by sampling at regular times and not by real-time evolution measurement, they allow us to have a first estimation of the accelerating factor. The relatively large number of observed solder balls (18 by measurement) allows, however, to have some confidence in the results.

The acceleration factor (AF) model that links the failure time (TTF) to temperature is based on the Arrhenius equation:

$$TTF = A.exp(Ea/kT) \quad (1)$$

Despite the fact that corroded surfaces may be from 2.5% to 48% and despite the small amount of sampling times, a first estimation of the activation energy is proposed.

Fig.5 shows the percentage  $P_c$  of corroded solder balls as a function of temperature and the different exposure times defined as:

$$P_c = N_c/N_t \quad (2)$$

$N_c$  is the number of corroded solder balls after the test.  $N_t$  is the total number of solder balls.

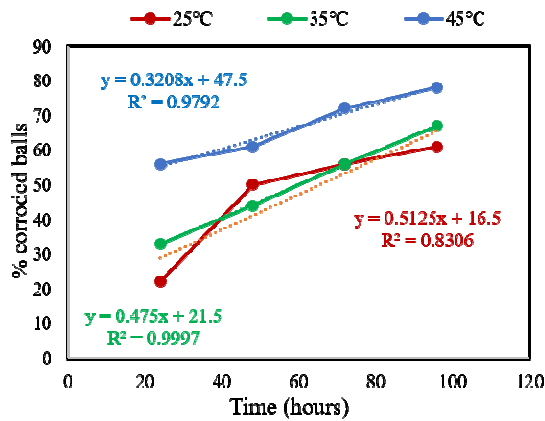


Fig. 5. Percentage of corroded balls as a function of the exposure time of the BGAs as-received samples

The data obtained at 25°C shows non-linearity, which can be explained either by the difficulty to actually assess the exact percentage of corroded areas, as at this temperature the corrosion is less severe. Or it is due to a different chemical corrosion mechanism. As a

first approximation, we select the first hypothesis and linearize all the graphs according to the dashed lines in figure 5. Then we calculated the AF and Ea, using the following equation:

$$t_{50} = A.exp(Ea/kT) \quad (3)$$

where  $t_{50}$  is the time after fifty percent of the sample are corroded.

So now we can use it to calculate the Ea by plotting  $\ln t_{50}$  versus  $1/(T^{\circ}C + 273.16)$ .

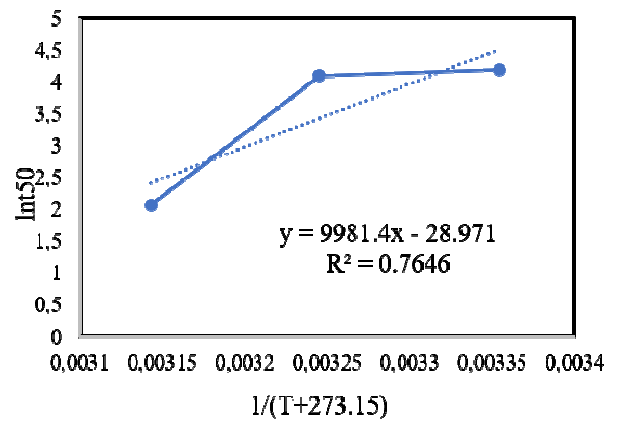


Fig. 6.  $\ln t_{50}$  as a function of the  $1/(T^{\circ}C + 273.16)$

This will yield an Ea estimate of 0.86 eV. The regression parameter  $R^2$  is low, due to the imprecision previously described. This value is obviously the first estimate. However, according to the corrosion mechanism orders of magnitude for Ea (0.3 eV to 1.1 eV) [17], this Ea value is promising. The kinetic of the corrosion failure mechanisms is being investigated to predict the lifetime of the lead-free solder balls.

### 3.4 Discussion

The discussion hereafter focuses on the influence of temperature on the corrosion behaviour of Sn-Ag-Cu (SAC305) solder alloy of ball grid array components during salt spray test. Based on results of [12], a descriptive mechanism is proposed to explain the role played by temperature.

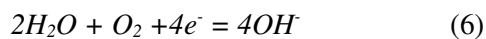
Just after assembly, SAC305 solder exposure



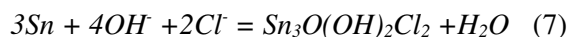
to indoor or outdoor environment are gradually oxidized by oxygen to form a protective  $\text{SnO}_2$  film on the solder surface. It is believed to be a result of direct chemical reaction between Sn and  $\text{O}_2$  see equation (4):



This protected film degrades in a short period once in contact with NaCl solution. The anodic and cathodic processes are described, respectively with the following equations:



The hydrolysis of dissolved  $\text{Sn}^{2+}$  under the effect of concentrated  $\text{Cl}^-$  forms the corrosion product,  $\text{Sn}_3\text{O}(\text{OH})_2\text{Cl}_2$ , which is a complex oxide chloride hydroxide of tin according to the following reaction [6, 12]:



Most of the defect-related failures and wear-out mechanisms can be accelerated by using temperatures higher than the temperature in operation. The induced failure usually involves some chemical or physical reactions [18]. Our study shows similar accelerated ageing processes on the solder balls when the temperature is increased from  $25^\circ\text{C}$  to  $45^\circ\text{C}$  during the NSS test.

#### 4. Conclusion

We have presented an experimental study of the impact of temperature on the corrosion behaviour of BGA samples in a NaCl humid atmosphere. Observable corrosion criteria were defined. From our test results, the following conclusions are drawn:

- The ball surface is not uniformly attacked.
- There is only one corrosion product site per ball, which varies from ball to ball.
- The corroded area observed in the BGAs solder balls mainly contain Sn, O, and Cl.

Moreover, the temperature has a significant effect on the corrosion behaviour of lead-free solder balls. An increase in temperature from  $25^\circ\text{C}$ ,  $35^\circ\text{C}$  to  $45^\circ\text{C}$  results in an earlier onset of corrosion. A first estimation of the activation energy was calculated.

Raman and XRD characterization and X-ray inspections will be performed before and after the spray test to determine the corrosion product composition and examine the presence and evolution of voids or porosities of micro-shrinkage on the surface of solder joint balls.

In addition, other investigations are currently being carried out on the solder joint of other components in order to:

- compare and confirm BGAs results
- investigate more precisely the corrosion kinetics to finally predict the lifetime of lead-free assemblies in saline corrosive environments
- develop a model of the corrosion phenomena for simulation.

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