Investigation of Characteristics of Lead-Free Powders for Solder Paste Application

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Abstract

Solder paste has been used in the surface mount technology for many years. However, a complete understanding of the effect of key powder characteristics on the paste properties is still not achieved. This understanding becomes much more important when new solder pastes with finer powder size are developed for advanced applications. In addition, the effect of other parameters such as time, humidity and temperature may also influence the performance of pastes made with fine and ultra-fine powders. In this work, the influence of key powder characteristics on the reflow property of paste made with powders produced with a proprietary atomising technology, particularly effective in producing solder powder ranging from 1 to 25 µm, is presented and discussed. Powder characteristics considered are particle size distribution and oxygen content. SAC305 powder were aged at various humidity/temperature conditions. The reflow performance of the pastes made with aged powder was evaluated. Moreover, the oxide layer formed at the powder surface was characterized using Auger Electron Spectroscopy and Transmission Electron Microscopy. The influence of external parameters such as humidity and temperature on the powder is discussed.

Keywords: Lead-free solder, powder, humidity, surface oxide.

Introduction

Surface Mount Technology (SMT) has become popular as an assembly technology in the late 1980s. As electronic components are mounted and placed directly on the surface of printed circuit boards (PCBs) instead of having connections that go through the holes (Through-Hole Technology, THT), the assembly technology has been named Surface Mount Technology. SMT enabled the electronic industry to increase the level of automation in the production line, to increase the capacity of production and consequently significantly lower manufacturing costs. It also enabled to manufacture more complex and compact electronic packaging. Solder paste is the main solder material which is used in the SMT lines. The paste is made of mixture of solder powder and tacky (creamy) flux, the mixing ratio of which mainly depends on the application, powder size, and chemical compositions of powder and flux.

The continuing demand for smaller and lighter electronic products has driven the use of miniature PCBs as well as miniature components. Very tiny components such as 01005 size (0.4 mm x 0.2 mm) and 008004 size (0.25 mm x 0.125 mm) capacitors [1] are being recently developed and used in portable electronic devices. Figure 1 shows some of available component sizes with metric and imperial codes. As the size of the components decreases, some problems can be observed during printing of conventional solder pastes such as insufficient deposit, deposit size variation and stencil clogging. For assembly of fine components such as 0201, 01005 and 008004, developing advanced solder paste becomes more important. In fact, the assembly of these miniature components requires fine solder joints; and, fine solder joints require advanced solder paste with finer particle sizes.

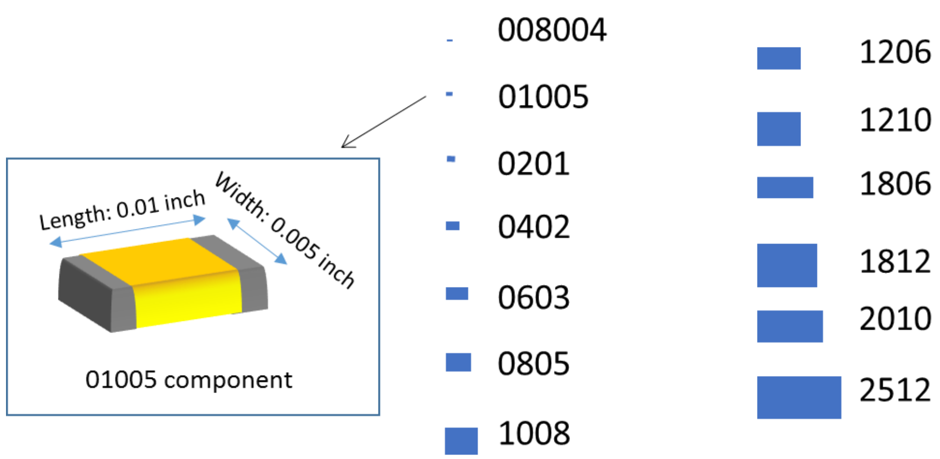


Figure 1: Example of component sizes and imperial codes.

As the size of solder powder decreases, the total powder surface per unit volume of the paste increases. Therefore, the understanding of paste properties related to the powder surface becomes more important. One of the key surface characteristics of the powder is the surface oxide layer. Using thermodynamic calculations, it has been shown that formation of tin oxide is possible with the presence of oxygen even as low as ~10^{-90} ppm [2]. It is almost impossible to completely prevent oxide formation at the powder surface even with most advanced vacuum equipment. Therefore, it is critical to have knowledge on characteristics of the tin oxide layer formed at the surface of the powder particles. At the company, a comprehensive and systematic study was launched to investigate surface oxide and its effect on the solder paste properties. The objective of the current paper is to understand the link between surface oxide and the reflow performance of pastes. Moreover, the effect of powder aging condition on the powder oxidation is also discussed.

Experimental methodology

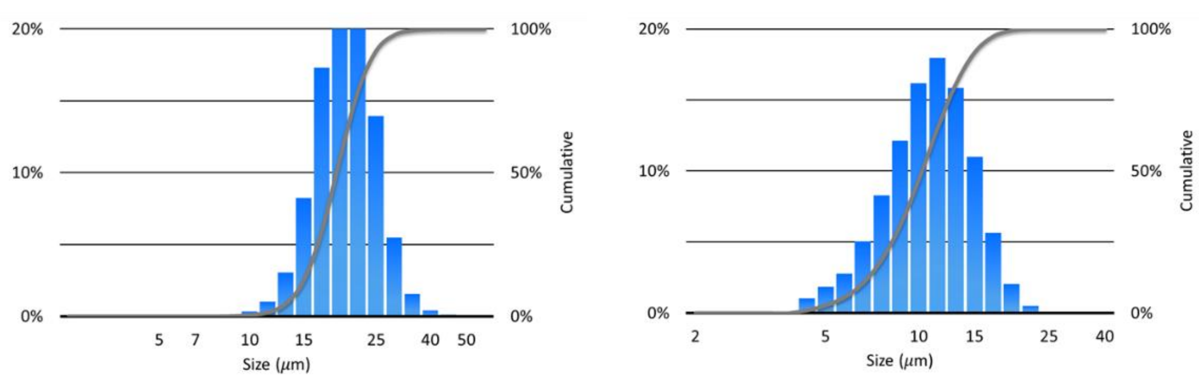
Lead-free SAC305 (Sn-3Ag-0.5Cu) powders of Type 5 and Type 6 were chosen for this study. Powders were produced with a proprietary atomising technology particularly effective in producing solder powder ranging from 1 to 25 µm. Figure 2 shows the particle size distribution of the powder tested in this study [3]. In order to study the effects of temperature and relative humidity on the oxidation and reflow performance, powders were aged in various conditions according to Table 1. The powders were aged in air for 0, 1, 7, and 15 days.

Table 1: Conditions of SAC305 powder aging in air

Aging Condition	Temperature, °C	Relative Humidity
AC1	23	0%
AC2	23	30%
AC3	23	80%
AC4	5	30%
AC5	40	30%

Solder ball tests were performed according to IPC-TM-650 2.4.43. Two no-clean ROL0 fluxes were used to make pastes. Frosted glass microscope slides were used as the substrates. For all powders, a stencil of 76 mm x 25 mm x 0.1 mm with holes of 1.5 mm diameter was used. Reflow was performed 15 minutes after printing on a hot plate. Reflow temperature was set to 245°C. An index called Solder Ball Test Index (STI) was internally developed to qualitatively evaluate and score reflow performance of the pastes. The STI score varies between 0 to 5. Lower STI means less small particles observed around the main solder ball and; therefore, better reflow. An average of 18 measurements and relevant standard deviation were reported for each test.

In order to measure the oxygen content in the powder, Instrumental Gas Analysis (IGA) was used. The powder is heated up to above 2500°C in the presence of an inert gas and then oxygen content is measured using a detector for analyzing the gas stream. In order to measure the thickness of oxide layer, Auger spectroscopy and Transmission Electron Microscopy (TEM) were employed.



(a) (b)

Figure 2: Particle size distribution of powders: (a) Type 5, (b) Type 6.

Results and Discussion

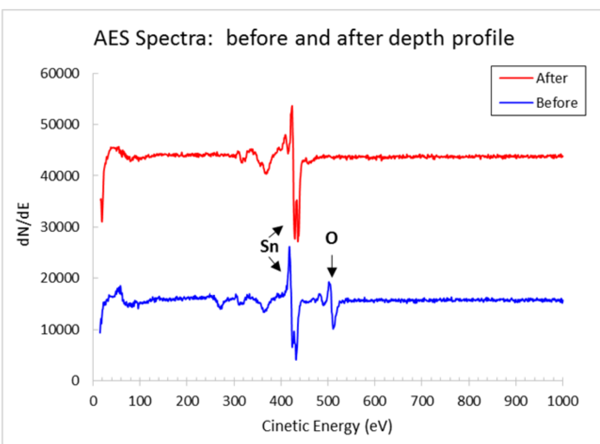
It is vital to have a well oxygen-controlled powder production process to have satisfactory reflow performance. In fact, since the melting temperature of oxides is so high compared to the melting point of the tin alloys, oxides have tremendous negative effect on the reflow performance. It is believed that the thickness and the nature of the oxide present at the surface of particles are two key parameters that impact the reflow of powder [4].

In order to measure the thickness of the oxide, Auger Electron Spectroscopy (AES) was applied. AES combined with an ion sputter etching system was used to show the composition of the elements as the layer of the tin oxide is etched. Figure 3 shows the analysis of the depth profile of elements. Figure 3a shows two AES spectra. The blue spectrum is captured at the powder surface before etching starts. The two main peaks in the blue spectrum are related to the formation of SnO_x. As ion sputtering is applied, the oxide is being etched and removed. The red spectrum was captured when the whole oxide layer was fully removed. As seen, the peak of oxygen has disappeared, confirming that the oxide is not present anymore.

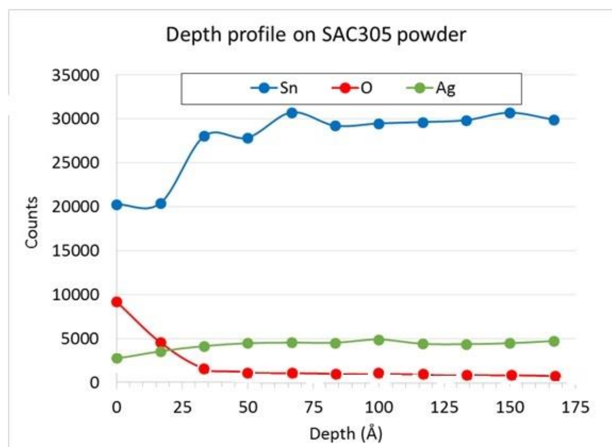
Figure 3b shows the depth profile of the elements. The elemental analysis shows that oxygen is present in the first ~3 nm depth and Sn content increases in this layer, after which it remains constant. The trends of Sn and O curves confirm the formation of surface tin oxide with a thickness of ~3 nm at the surface.

In order to validate the oxide thickness values obtained by AES, microstructure characterization of the SAC305 powder was performed (Figure 4). Figure 4a shows a TEM picture on a cross section of the SAC305 powder. A thin bright layer is formed at the surface of the powder. EDS analysis on this layer (Figure 4b) shows the presence of the oxygen and tin and consequently confirms the layer is tin oxide. Moreover, the thickness value measured by TEM is in agreement with the measurements done by AES.

We recently showed that oxide layer thickness is the same for particles with different sizes produced with the same process conditions [4]. This was found by performing surface characterization techniques on particles having different sizes from 3 to 40µm.

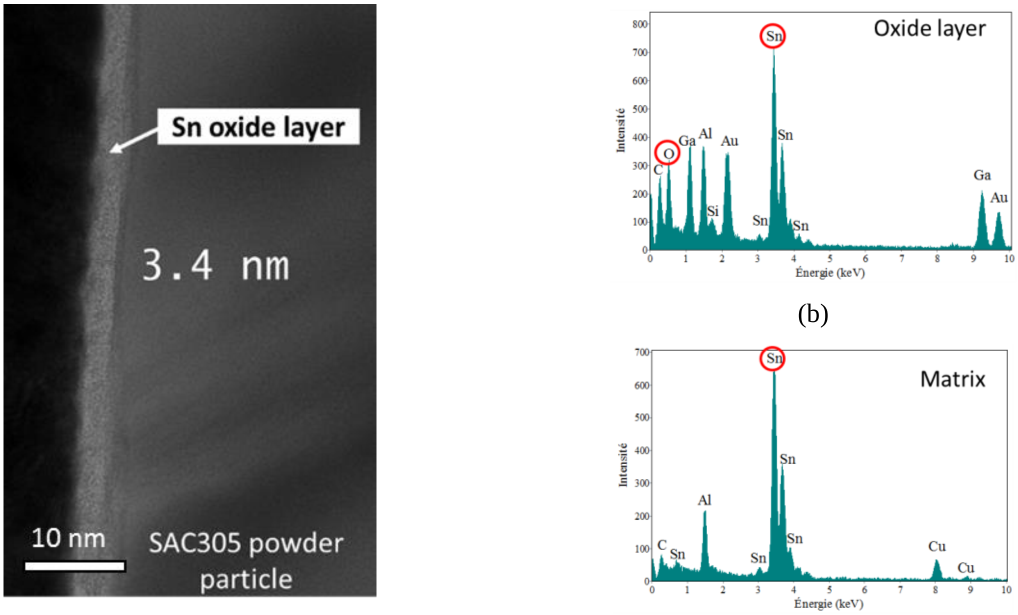


(a)



(b)

Figure 3: Auger Electron Spectroscopy (AES) technique is used to characterize the surface oxide layer: (a) Auger spectra, (b) peak-to-peak height vs. depth which shows depth profile of elements. Depth=0 is the position at the surface of powder.



(a) (c)

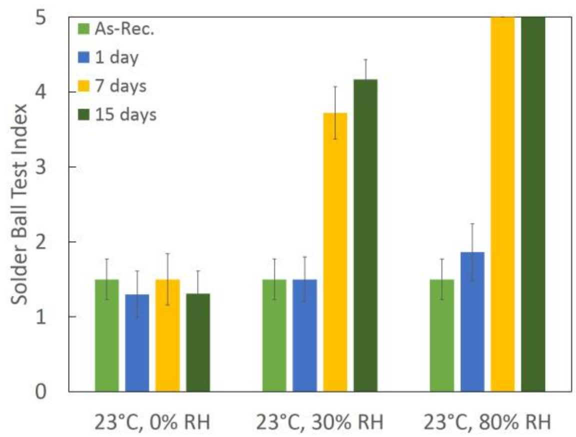
Figure 4: TEM and EDS on the cross section of SAC305 powder, (a) the picture shows the oxide layer formed at the surface of powder, (b) EDS on the oxide layer, (c) EDS on the powder matrix. Presence of some elements are related to the sample prepration.

Effect of powder aging on the reflow performance:

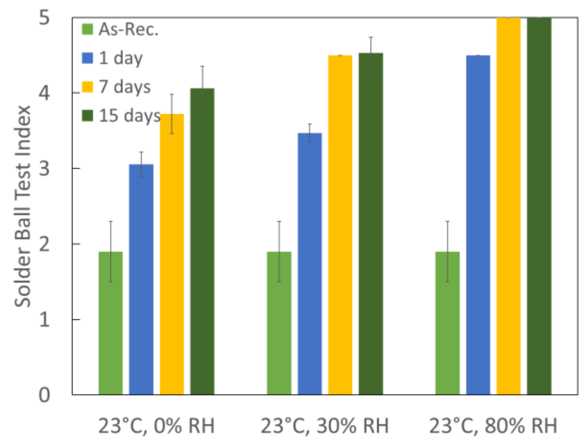
Figure 5 shows the variation of the reflow performance for pastes made from powders aged at various humidity conditions (0, 30 and 80 % RH). Error bars show the standard deviation of 18 measurements for each test. For Type 5 powder, the results show that when the environment in which the powder was aged is completely dry (~0% RH), the powder aging does not affect the reflow performance. However, as the level of humidity during powder aging increases, STI significantly increases after 7-day aging. These results show that the level of humidity during powder aging has an important effect on the reflow performance of the paste. For Type 6 powder, the increase of STI happens earlier (after only 1 day). Moreover, the increase of the STI is even seen for 0% RH (dry condition). This clearly shows that fine powders, like Type 6 powder, are more sensitive to the oxidation than coarser ones like Type 5. Therefore, having a well oxygen/humidity controlled condition during the powder process and packaging is more critical for fine powders.

Figure 6 shows the sensitivity of the Type 6 powder to the aging temperature (5-40°C). For the powders kept at room temperature or at a higher temperature, the deterioration of the powder is visible after only 1 day. However, for the powder that has been aged at 5°C, the significant deterioration will be delayed (1 week instead of 1 day).

To check the sensitivity of the powder to aging conditions, some solder ball tests were also performed with a second NC ROL0 flux (flux B). Type 6 powder was aged at 23°C with 30% RH and then two pastes were prepared using these two fluxes (flux A and flux B). Figure 7 shows the variation of STI. The paste made with flux B shows stable reflow performance in spite of the fact that the powder was aged in air, at room temperature, and in 30% RH. The results show that the influence of flux is very significant.



(a)



(b)

Figure 5: Effect of powder aging humidity on the reflow performance of the paste, Flux A; (a) Type 5, (b) Type 6.

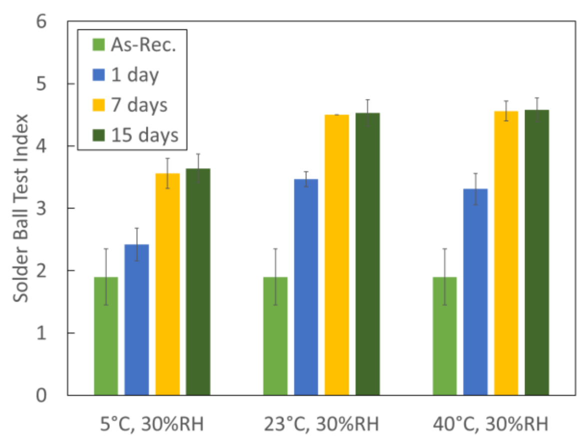


Figure 6: Effect of powder aging temperature on the reflow performance of the paste, Type 6, Flux A.

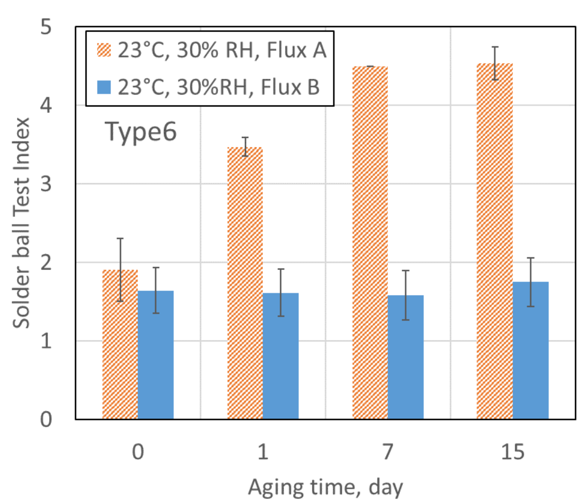
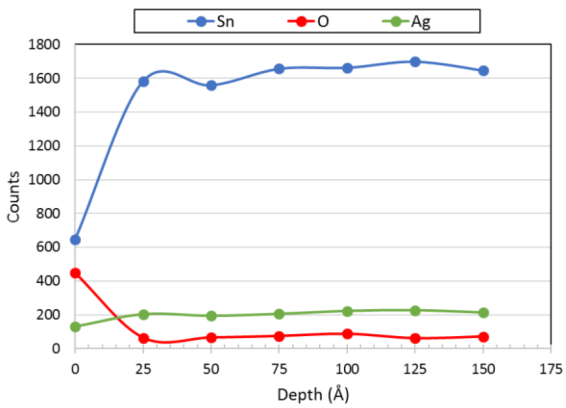


Figure 7: Solder Ball Test Index; SAC305 Type 6 powder with NC ROL0 fluxes: Flux A and Flux B.

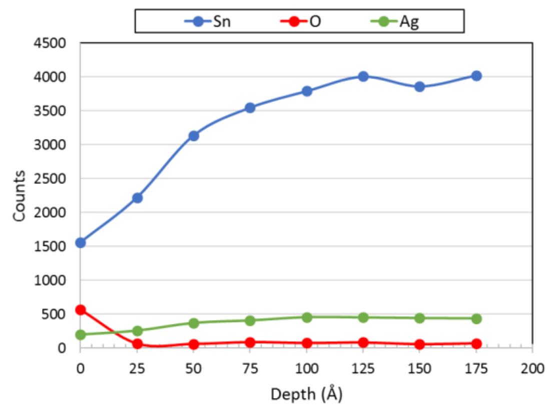
Effect of powder aging on the surface oxide:

In order to understand the effect of aging on the reflow performance, the surface oxide layers for powders were characterized via Auger Spectroscopy. Figure 8 shows depth profile of elements inside SAC305 particles with 12 µm diameter (Type 6). The elemental analysis of the powder before aging (Figure 8a) shows that oxygen is present in the first ~2.5-3 nm depth and Sn content increases in this distance, after which it remains constant. These observations indicate the formation of surface tin oxide with thickness of ~3 nm.

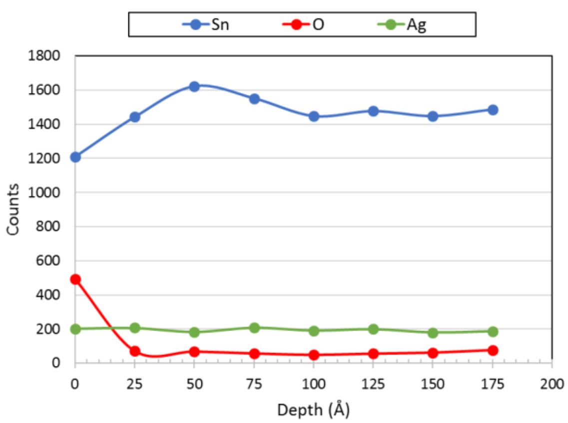
Auger Spectroscopy was also performed on the powders aged at different humidity levels (Figure 8b,c,d). The analyses reveal that oxide thickness does not change when relative humidity is 0% and 30%. In fact, the oxidation rate is not significant at room temperature and low humidity level. However, when the humidity increases to 80% RH, the thickness of the oxide layer reaches up to 10 nm after 7 days. This confirms that oxidation rate is highly increased in high humidity conditions even at room temperature. Similar testing was conducted on Type 5 powder and the same conclusion was made on the effect of humidity on oxidation rate. Moreover, AES on several particles of Type 5 and Type 6 powders aged in AC3 (23C, 80% RH) shows that the oxide thickness is not uniform. In fact, the oxide layer become more non-uniform as the powder becomes oxidized.



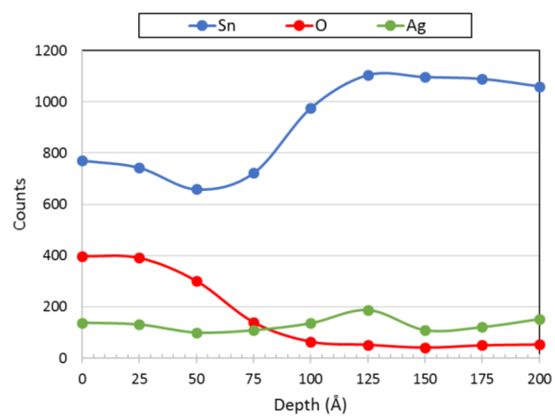
(a) As-received



(b) Aged: 23°C, 0% RH, 15 days



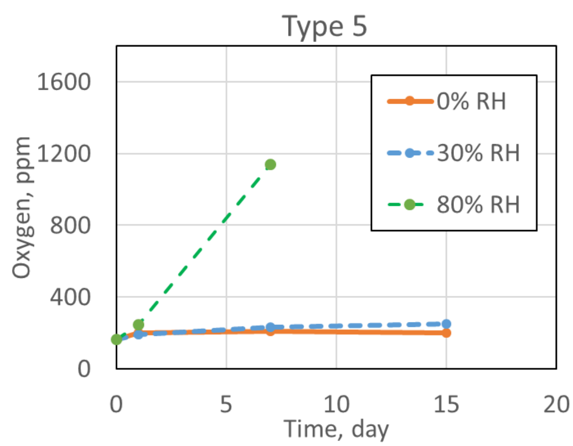
(c) Aged: 23°C, 30% RH, 15 days



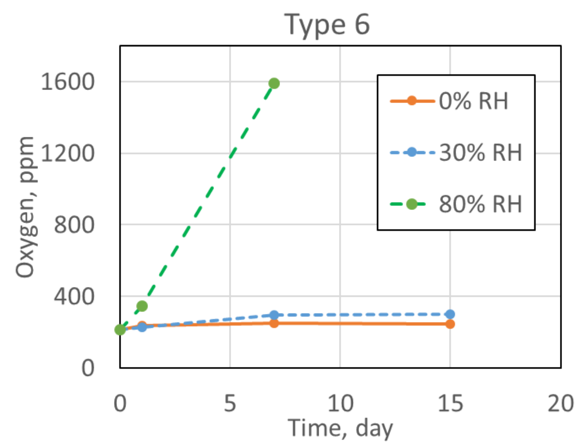
(d) Aged: 23°C, 80% RH, 7 days

Figure 8: Depth profile of elements by Auger Spectroscopy, oxygen curve is indicative of the oxide layer thickness at SAC305 T6 powder. (a) as-received, (b) Aged: 23°C, 0% RH, 15 days, (c) Aged: 23°C, 30% RH, 15 days, (d) Aged: 23°C, 80% RH, 7 days.

Oxygen content of the aged powders at different humidity levels was measured using Instrumental Gas Analysis (IGA). Oxygen content of Type 5 powder increases to ~1100 ppm after the powder is aged in the high humidity condition (80% RH) for 7 days (Figure 9). For Type 6 powder, which has higher surface per unit mass than Type 5 powder, oxygen content increases to ~1600ppm at the same aging condition. The increase in the oxygen content, when the relative humidity was set at 0% or 30%, was not significant even for 15-day aging.



(a)



(b)

Figure 9: Oxygen content of SAC305 powder aged at room temperature, (a) Type 5, (b) Type 6.

Solder powders exposed to air form an oxide layer at the powder surface. SnO and SnO_2 are the main oxides of tin. Metastable oxide species like Sn_2O_3 and Sn_3O_4 are extremely unstable [5]. Oxidation reactions for formation of SnO and SnO_2 and the standard Gibbs free energy of formation are as follows [6]:

$Sn + ½ O_2 = SnO$ $\Delta G°_f = -251.9$ kJ/mol

$Sn + O_2 = SnO_2$ $\Delta G°_f = -515.8$ kJ/mol

SnO_2 has a lower Gibbs free energy of formation, it is therefore, thermodynamically more stable than SnO. In order to determine the nature of the oxide (SnO or SnO_2) which is formed at the SAC305 powder surface, AES analysis was carried out on SAC305 powder, pure SnO (97% purity) powder and pure SnO_2 (99.9% purity) powder. The peak-to-peak intensity ratios between Sn and O at the surface of pure oxide powders as well as SAC305 powder were measured. Figure 10 shows the peak-to-peak count intensity ratio. According to this figure, the oxygen intensity ratio for SAC305 powder (30%) are closer to that for pure SnO powder (35%). In fact, it is within the range of the standard deviation of measurements. However, oxygen intensity ratio for pure SnO_2 powder (44%) is much higher than the oxygen intensity ratio of SAC305. This indicates that the type of oxide that formed on SAC305 powder is mainly SnO.

Our AES results also show that even when the oxide layer becomes thicker after aging at room temperature, the type of oxide present at the surface of particles still mainly remains SnO. Previously, Harburn [7] studied the oxidation of the bulk of some tin alloys at the elevated temperatures. A very thin SnO_2 layer may grow on the top of the SnO at the elevated temperature (~180°C). However, even at high temperatures, SnO is still present in much higher proportion that SnO_2. Our findings are in agreement with the results presented in reference 7. However, further studies are recommended to confirm this finding in a more quantitative approach with other characterization techniques. Moreover, it is worth to investigate the possibility of hydroxide formation when the humidity level is very high.

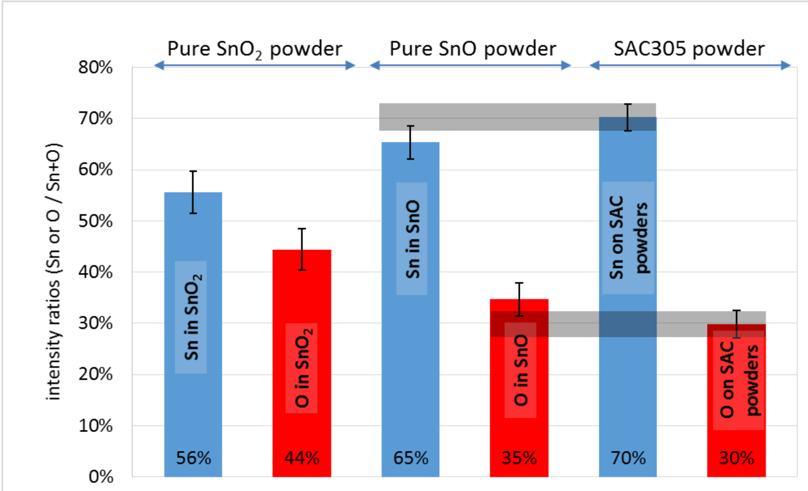


Figure 10: Chemical composition of oxide measured using AES spectrum; the vertical bars show Sn and O concentrations estimated by peak-to-peak height in the AES spectrum. The first four bars show Sn and O concentrations in pure SnO_2 and pure SnO powders; the last two bars show Sn and O concentrations at the surface of SAC305 powder. SAC305 powder data are the average of measurements performed on powders aged under various aging conditions.

Conclusions

SAC305 solder powder was aged in air under various conditions. Surface characterization of the powder was performed and the effect of powder aging condition (humidity and temperature of the environment) on the powder oxidation and reflow performance was studied. The following conclusions were obtained:

- Finer powder is more sensitive than coarser power to oxidation, i.e. reflow performance is more affected by a higher level of oxidation for fine powder. Moreover, this sensitivity significantly increases when the powder is placed in a high humidity environment.
- AES results confirmed that humidity has a significant effect on oxidation rate of the SAC305 powder. Thickness of oxide layer does not increase at medium or low humidity when the powder is aged at room temperature for 15 days. However, at a high humidity condition and room temperature, the oxide layer thickness increases from around 3 nm to around 10 nm in 7 days.
- The oxide layer at the surface of the powder mainly consists of SnO. This was found by comparing AES results on SAC305 powder with AES results on pure SnO and SnO_2 oxide samples.
- The type of flux can change the reflow performance of the aged powders. Fine powders should be mixed with appropriate fluxes to maintain the robustness of solder pastes for a long time.

Acknowledgements

The authors acknowledge Mr. Arslane Bouchemit and Prof. Gilles L'Espérance at Center for Characterization and Microscopy of Materials, $(CM)^2$, École Polytechnique de Montréal for their kind collaborations and providing powder characterization results. The authors would also thank Ms. Vicki Maheux for her contribution on the experimental work of this study.

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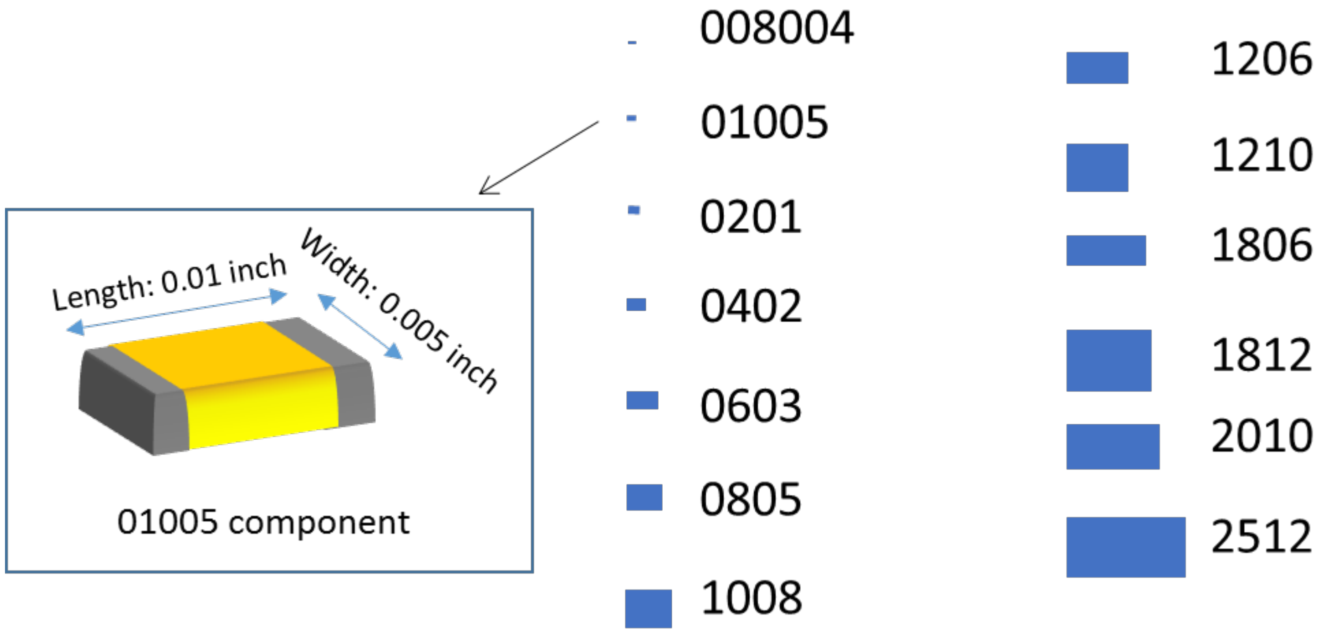
Outline:

- Introduction
- Experimental methodology
- Results and Discussion
  - *Effect of powder aging on the reflow performance*
  - *Effect of powder aging on the surface oxide*
- Conclusions
- Q & A

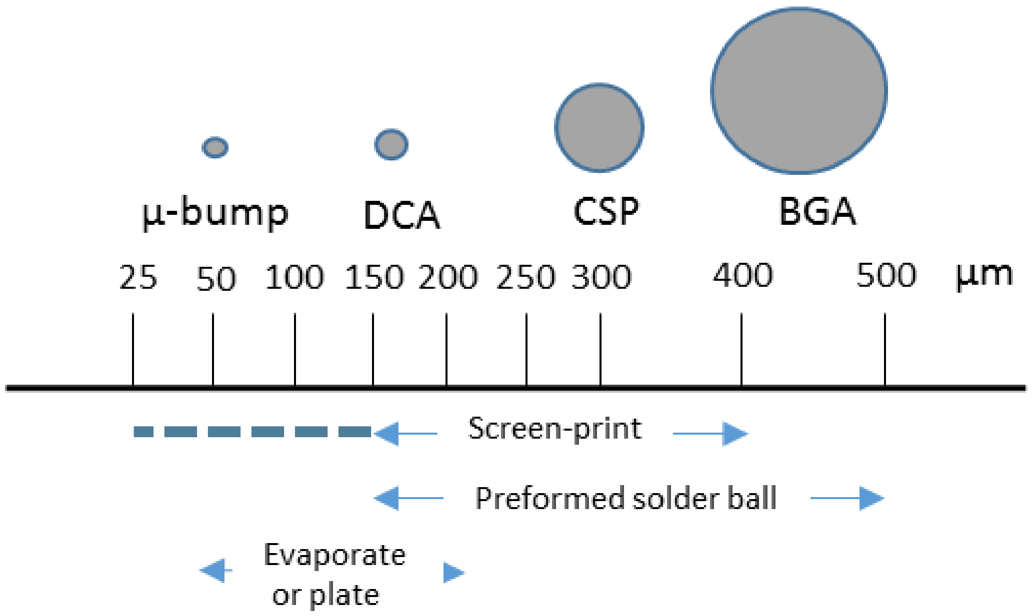
Continuing demand for smaller and lighter electronic packaging



Component sizes and imperial codes

Continuing demand for smaller and lighter electronic packaging

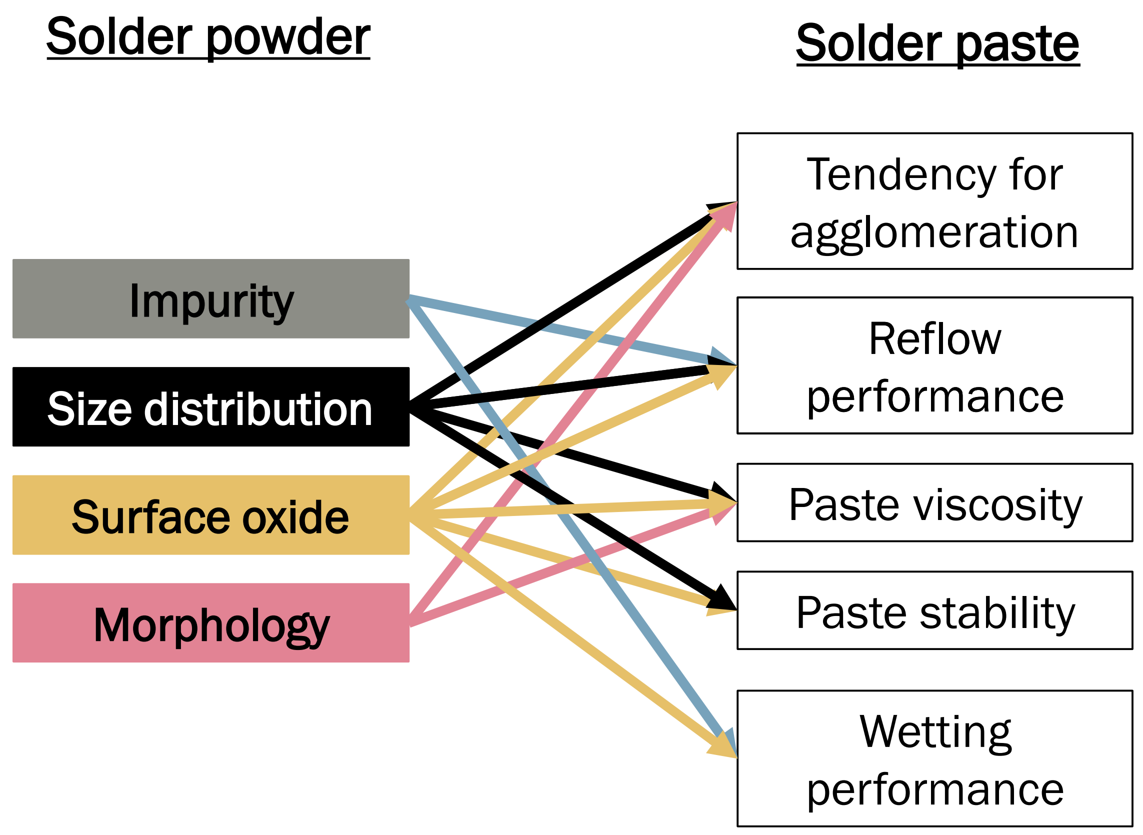
Bumping technologies in accordance with bumping pitch sizes



(Adapted from Son et al. , ETRI Journal, 2015, 37, 523)

- Printing technology for wafer bumping process:
  - *Economical technique because of simplicity for high-volume production*
  - *Compatibility with pre-existing printing equipment in a SMT line*
  - *Capability to use various lead-free solder alloys*
- In order to extend the capability of this technique for fine bumps, producing fine solder powders with superior quality is vital.

Solder powder characteristics → solder paste performance

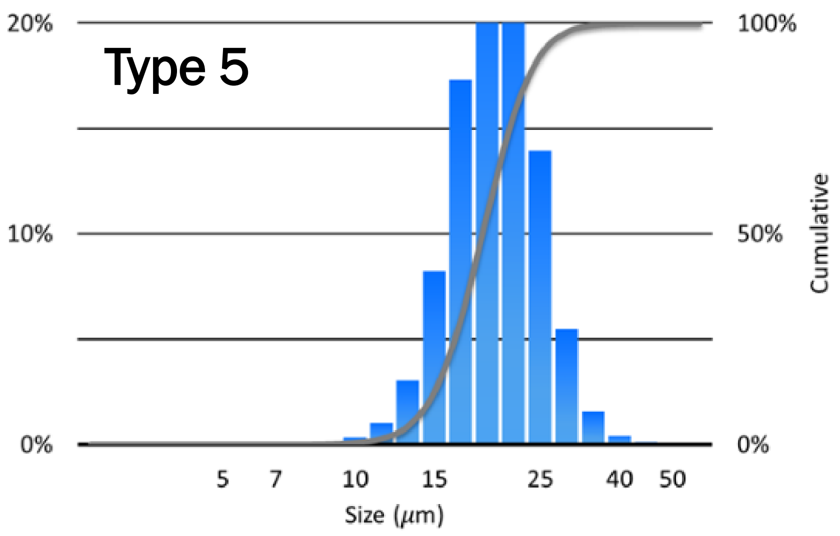


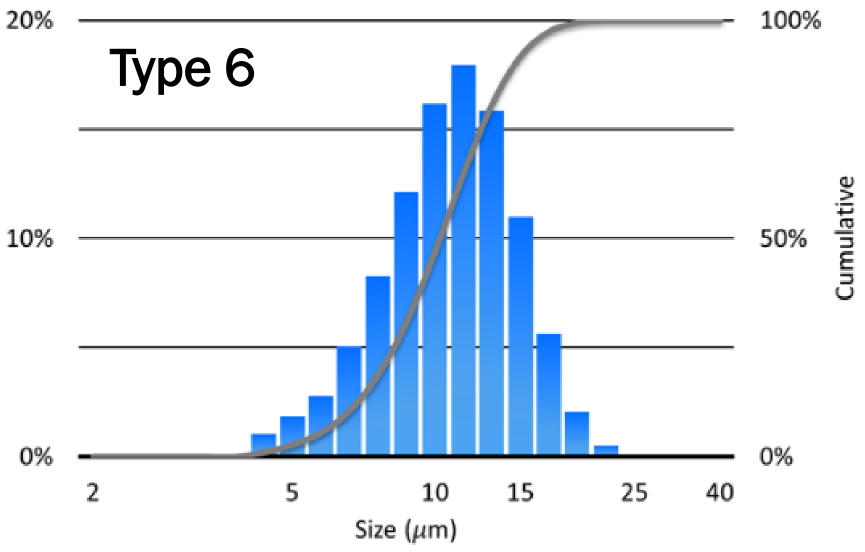
Objective

- Among different powder characteristics, powder size and oxide content are studied in the present paper.
- The effect of powder aging on the oxide content and reflow performance of solder pastes is investigated:
  - *Effect of humidity*
  - *Effect of temperature*

Experimental methodology - Materials

- Powders were produced with a proprietary atomising technology particularly effective in producing solder powder ranging from 1 to 25 µm.
- SAC305 powders: Type 5 and Type 6





Experimental methodology – Powder aging

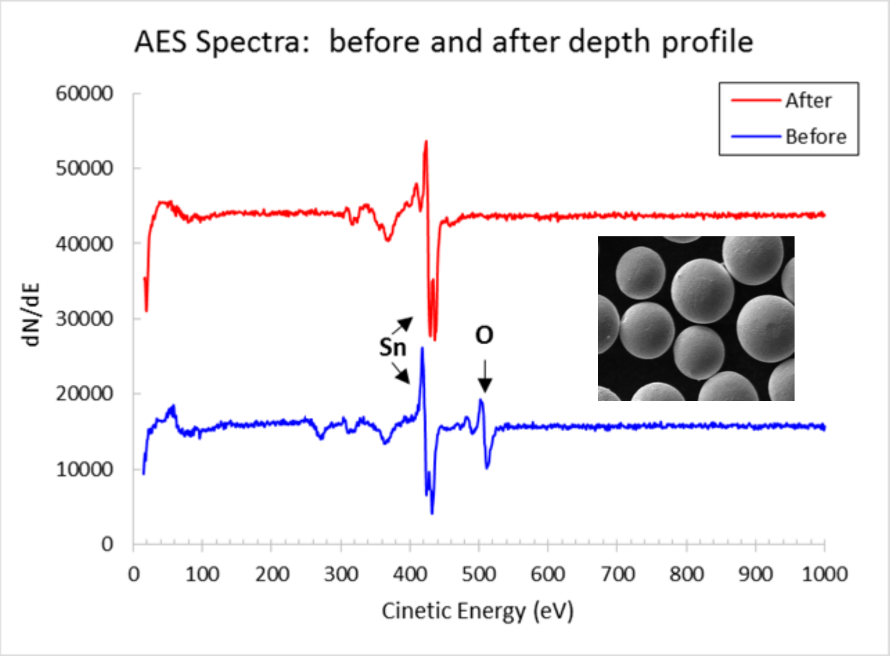
Aging Condition	Temperature, °C	Relative Humidity
AC1	23	0%
AC2	23	30%
AC3	23	80%
AC4	5	30%
AC5	40	30%

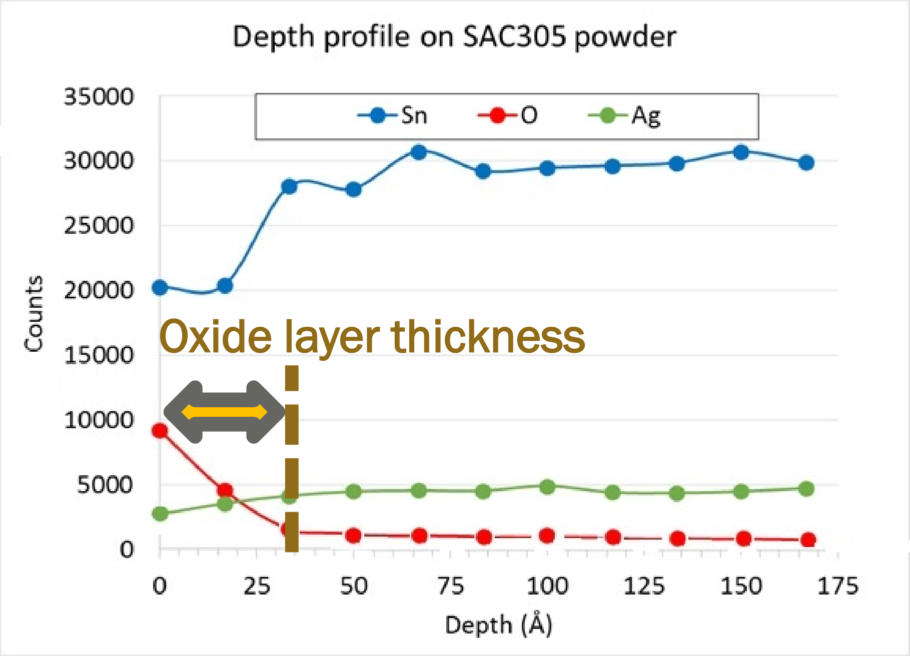
- Powders were aged in air for 0, 1, 7, and 15 days before mixing with flux.

Experimental methodology – Reflow and powder characterization analyses

- Solder ball test (IPC-TM-650 2.4.43)
  - *Flux: No clean ROL0*
  - *Reflow temperature: 245°C*
  - *Scoring method: Solder Ball Test Index (0 – 5)*
- Oxygen content measurement
  - *Instrumental Gas Analysis (IGA)*
- Microstructure and surface characterization
  - *Auger Spectroscopy*
  - *Focus Ion Beam (FIB)*
  - *Transmission Electron Microscopy (TEM)*

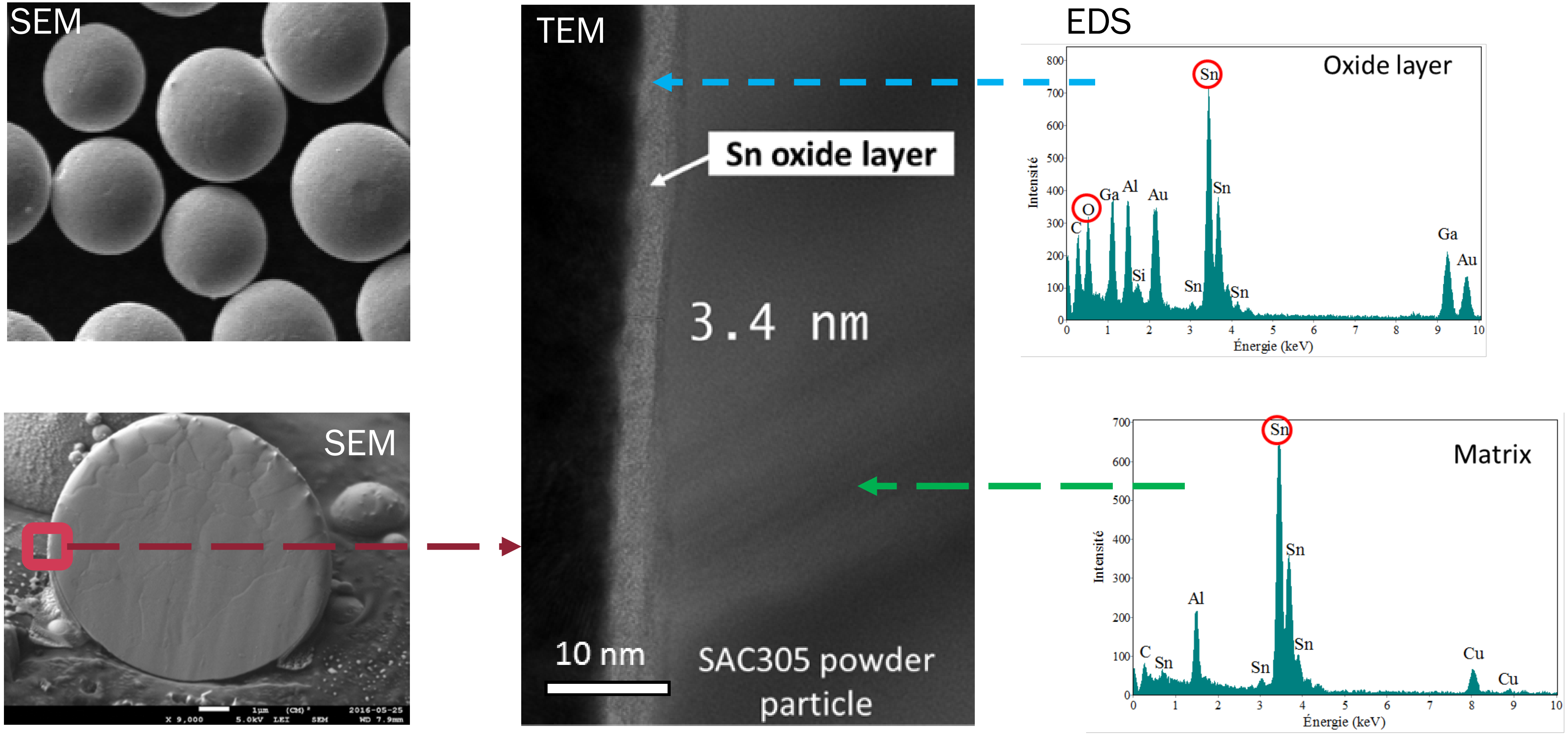
Oxide layer thickness – Auger Spectroscopy technique





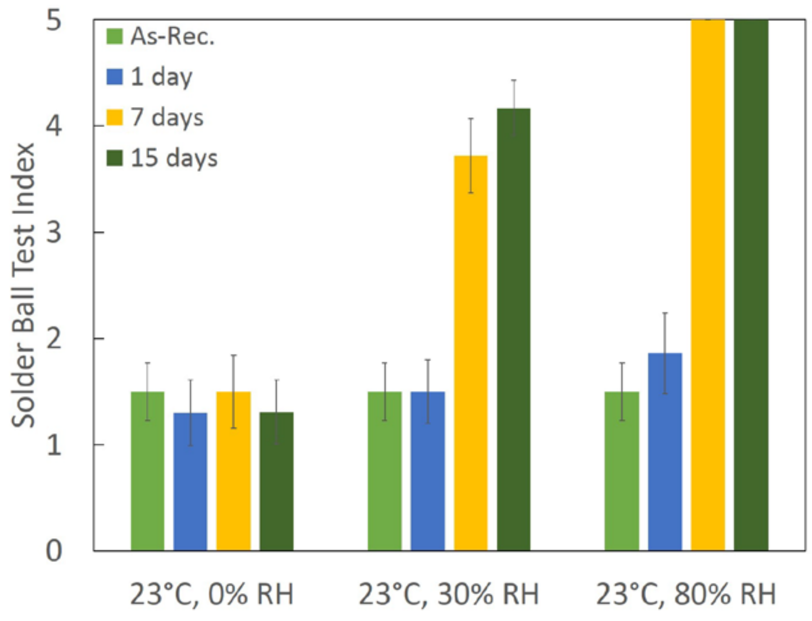
- The trends of Sn and O curves confirm the formation of surface tin oxide with a thickness of ~3 nm at the surface.

SEM, TEM and EDS on the cross section of SAC305 powder

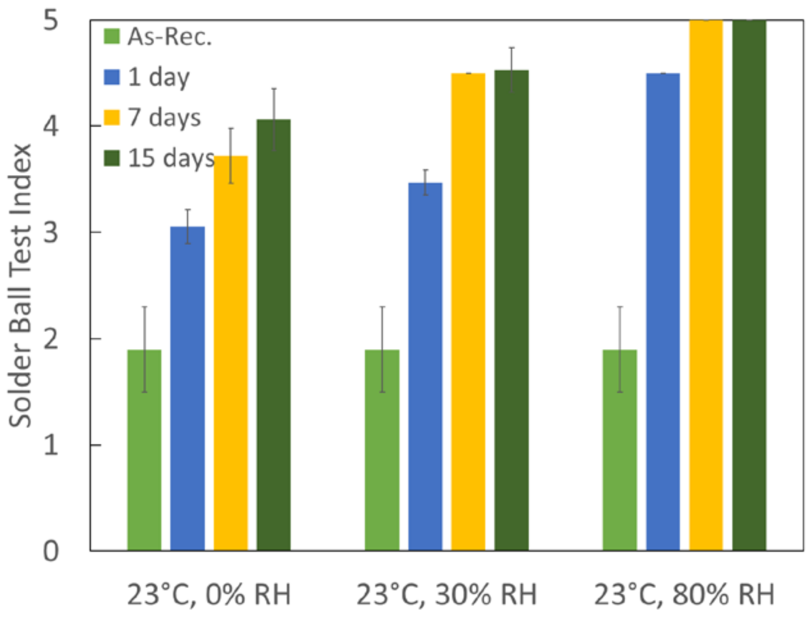


Reflow performance of aged powder – effect of humidity

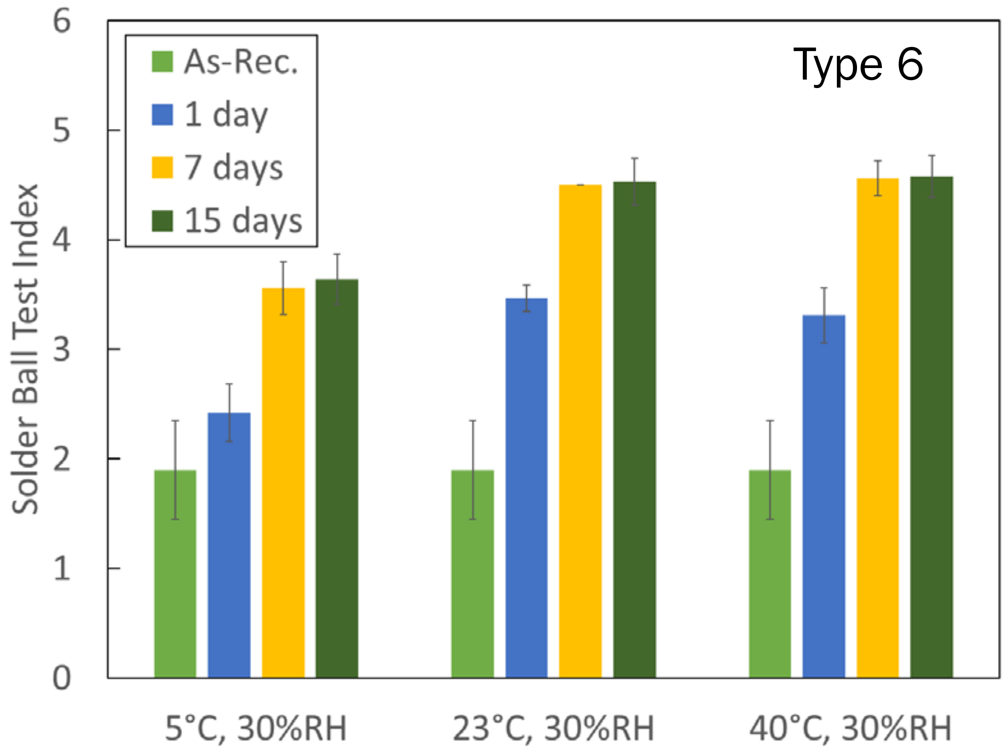
Type 5



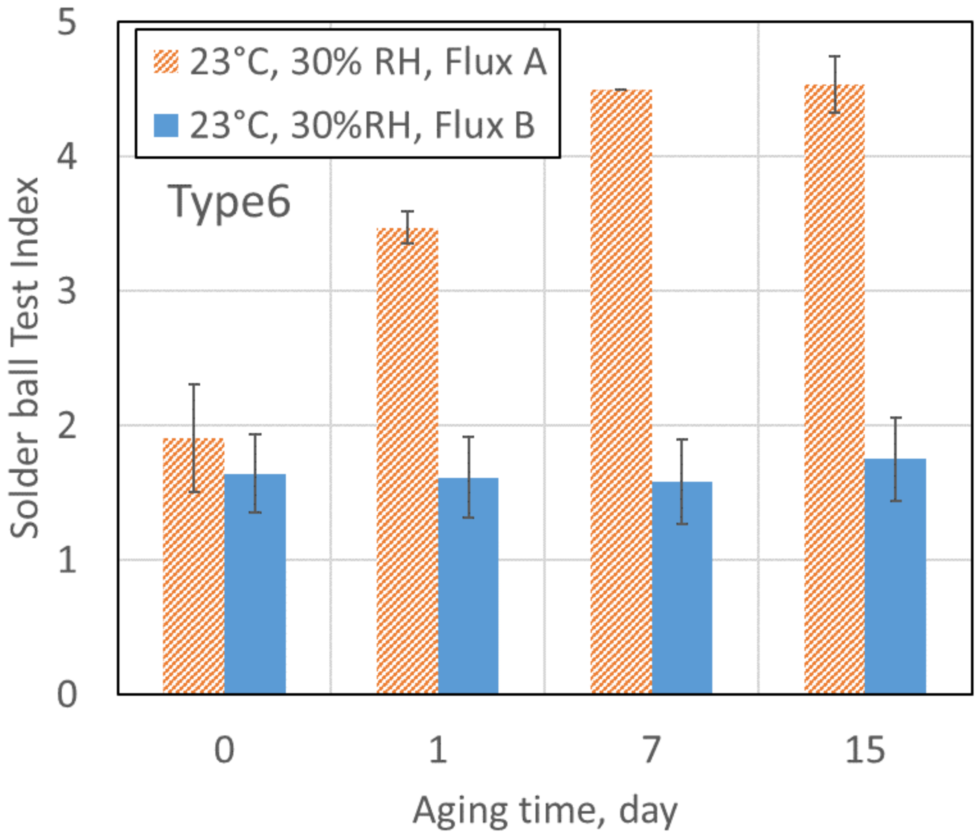
Type 6



Reflow performance of aged powder – effect of temperature



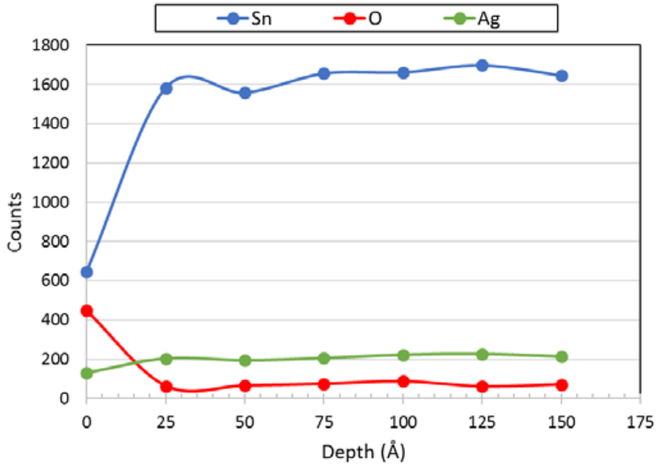
Reflow performance of aged powder – influence of flux

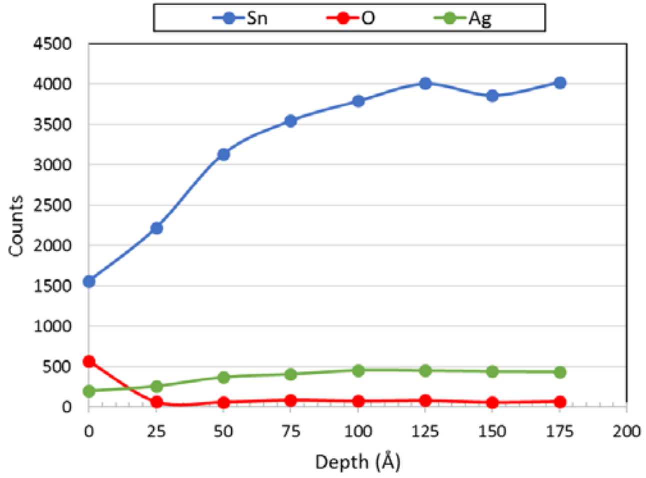


Effect of aging condition on the oxide thickness

SAC305 Type 6

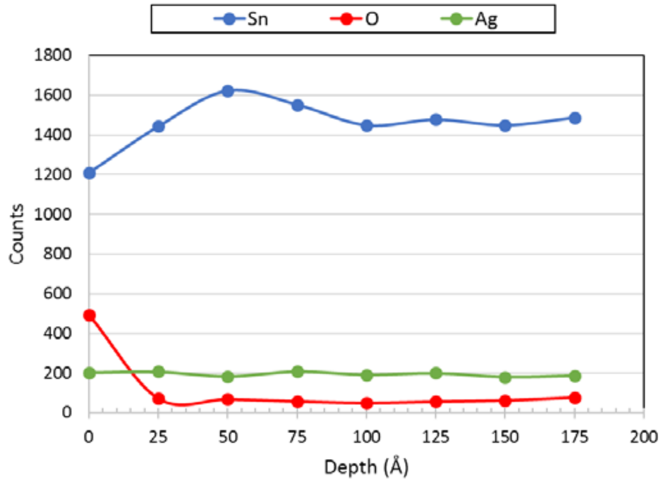
As-received

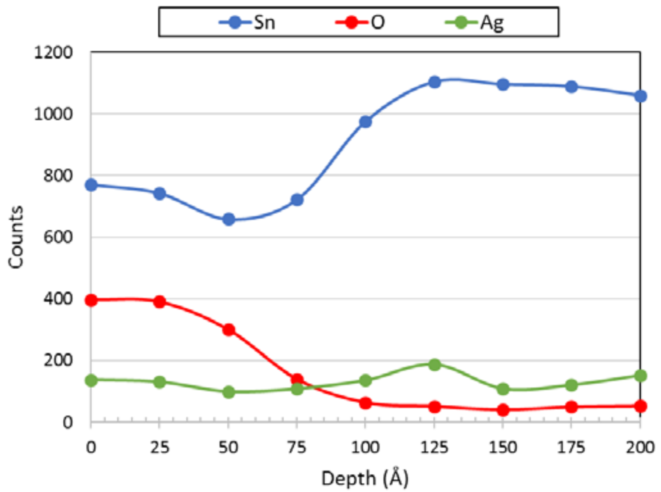




Aged: 23°C, 0% RH, 15 days

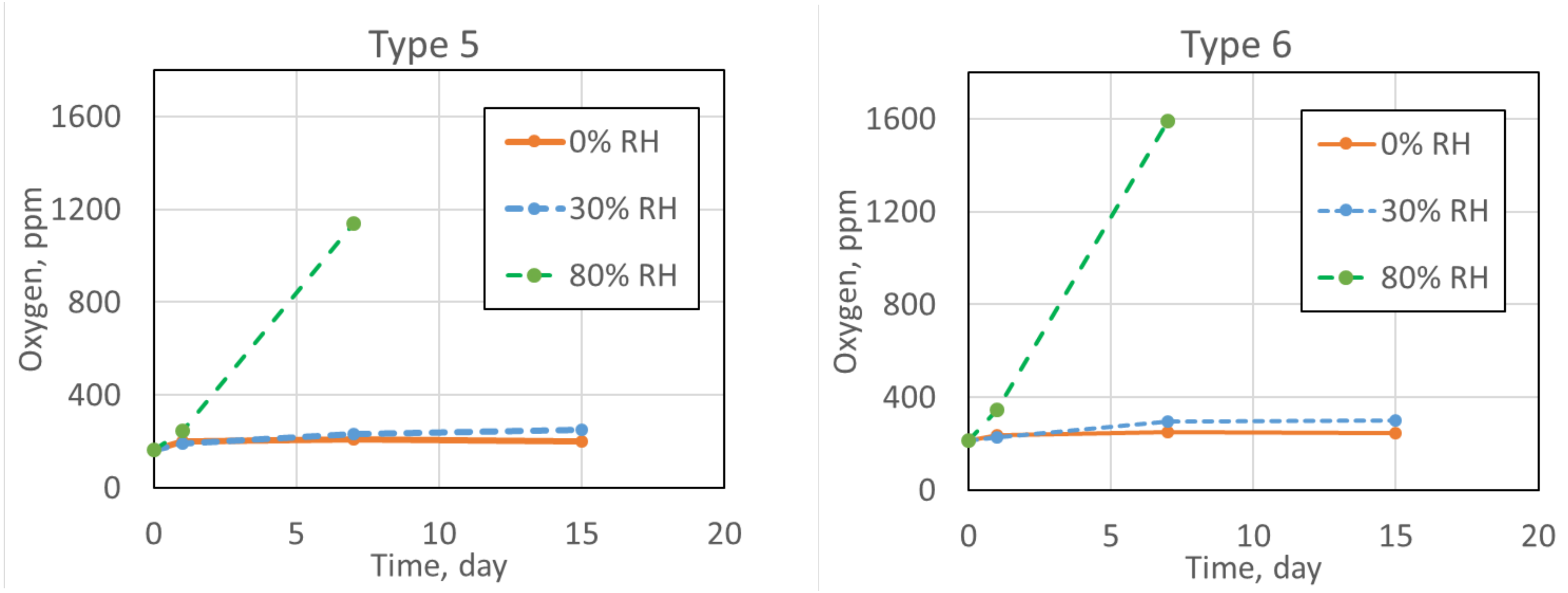
Aged: 23°C, 30% RH, 15 days



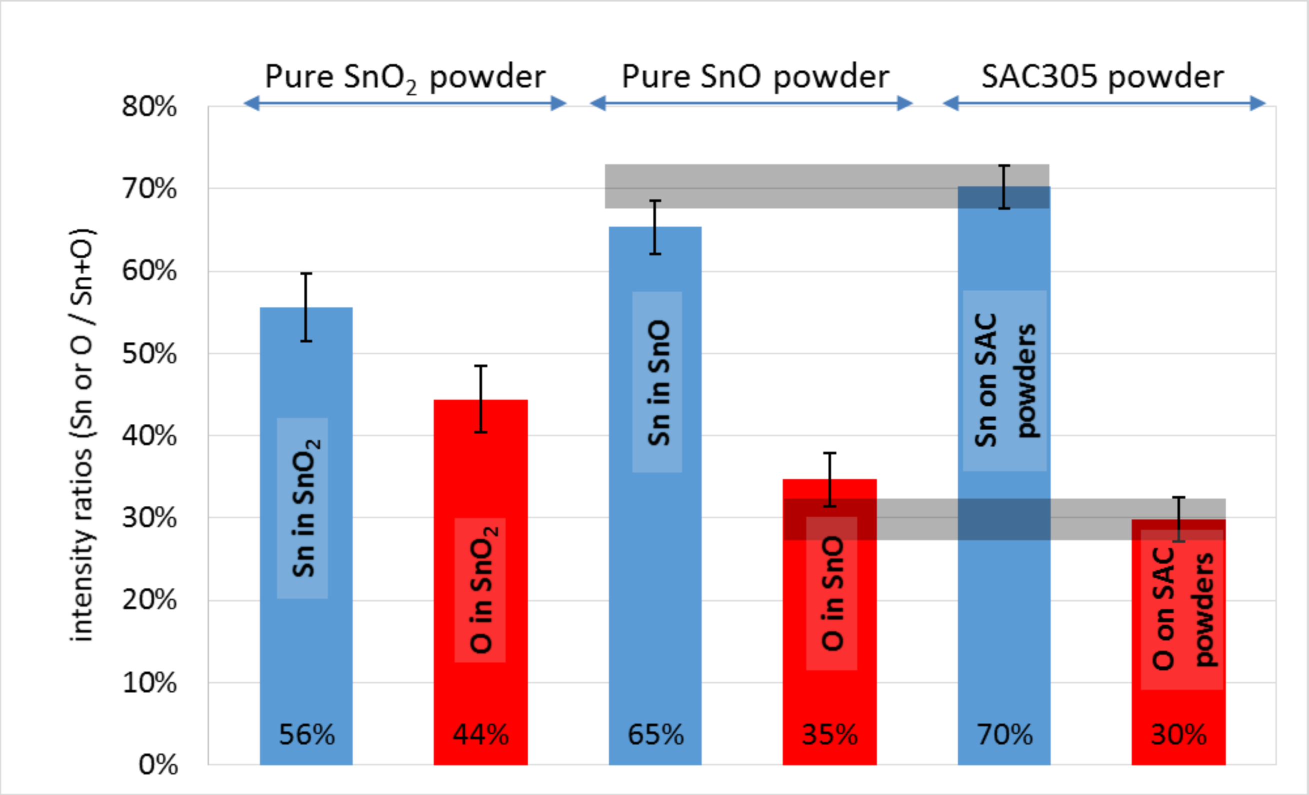


Aged: 23°C, 80% RH, 7 days

Oxygen content of SAC305 powder aged at room temperature



Type of oxide: SnO or SnO_2 ?



- AES analysis was carried out on
  - *pure SnO_2 (99.9% purity) powder*
  - *pure SnO (97% purity) powder*
  - *SAC305 powder*
- The peak-to-peak intensity ratios between Sn and O at the surface of each sample were measured.
- Results indicate that the type of oxide formed on SAC305 powder is mainly SnO.

Conclusions (1/2)

- Finer powder is more sensitive than coarser powder to oxidation, i.e. reflow performance is more affected by a higher level of oxidation for fine powder. Moreover, this sensitivity significantly increases when the powder is placed in a high humidity environment.

- AES results confirmed that humidity has a significant effect on oxidation rate of the SAC305 powder. Thickness of oxide layer does not increase at medium or low humidity when the powder is aged at room temperature for 15 days. However, at a high humidity condition and room temperature, the oxide layer thickness increases from around 3 nm to around 10 nm in 7 days.

Conclusions (2/2)

- The oxide layer at the surface of the powder mainly consists of SnO. This was found by comparing AES results on SAC305 powder with AES results on pure SnO and SnO_2 oxide samples.

- The type of flux can change the reflow performance of the aged powders. Fine powders should be mixed with appropriate fluxes to maintain the robustness of solder pastes for a long time.

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Q&A

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