EFFECT OF FINE AND ULTRA-FINE LEAD-FREE SOLDER POWDER CHARACTERISTICS ON THE REFLOW PROPERTY OF PASTES

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ABSTRACT

The recent movement of electronic market toward miniaturization of components and printed circuit boards (PCB) has increased demand for finer pitches both on PCBs and on chip level. In order to meet this demand, more advanced solder pastes with finer particle sizes are needed. However, determination of the real effect of particle size distribution on oxidation, reflow performance and paste properties is still required. It is the object of this paper to evaluate the effect of particle size distribution and oxidation on the reflow performance of solder paste. The powder investigated here was produced with a proprietary atomising technology particularly effective in producing powder ranging from 1 to 25 µm. Solder powder was classified into the different size categories. Powders were then admixed with fluxes and reflow characteristics were evaluated. The reflow property of pastes is then discussed as a function of the particle size, and oxidation level.

Key words: Solder powder, miniaturization, reflow, oxide layer

INTRODUCTION

Solder paste is the main solder material which is used in the surface mount assembly lines. The creamy characteristic of the solder paste enables it to be applied in automated precision-deposition technology, such as stencil printing, jet printing, and dispensing [1]. The paste is made of mixture of solder powder and tacky (creamy) flux, the ratio of which mainly depends on the application, powder size, and powder and flux chemical composition.

In the past decade, two events have been observed in terms of market change in the surface mount technology: (i) elimination of lead from solder alloys and (ii) miniaturization in electronic assembly. Both of which are discussed in more details in the following.

(i) Solder alloys containing lead were used for many years in the electronic packaging industry. However, the RoHS (Restriction of Hazardous Substances) has placed a restriction on the use of certain hazardous substances (such as lead, mercury, cadmium, etc.) in electrical and electronics devices sold or used in the European Union as of July 1, 2006. This promoted a fast transition from tin/lead solders towards lead free solder alloys in the past decade. Figure 1 shows the historical trend in proportion of lead-free versus tin/lead solder shipments worldwide [2]. Although several lead-free alloys have been developed, there is only a limited number of adequate solder alloys for solder paste application. The most acceptable family of the alloys is Sn-Ag-Cu system. Japanese Electronic Industry Association (JEIDA) has chosen Sn-3Ag-0.5Cu (SAC305) alloy as the first choice. International Electronic Manufacturing Initiative (iNEMI) recommends Sn-3.9Ag-0.6Cu and Sn-3.5Ag for reflow soldering [1]. More advanced alloys by adding other elements such as Zn, Bi, Sb, Ni, and In to Sn-based solder alloys have been investigated. However, some concerns always exist regarding corrosion, wetting performance and/or powder-flux compatibility as the number of elements in an alloy increases.

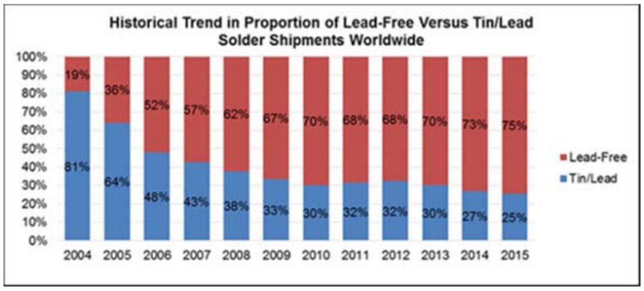


Figure 1. Historical trend in proportion of lead-free versus tin/lead solder shipments worldwide. Reprinted from [2].

(ii) The continuing demand for smaller and lighter electronic products has driven the use of miniature PCB as well as miniature components. Very tiny components such as 01005 size (0.4 mm x 0.2 mm) capacitors are being used in various portable electronic devices. More recently, even smaller components have been introduced to the market. For instance, a multilayer ceramic capacitor with 008004 size (0.25 mm x 0.125 mm) has been developed to be used in advanced and light electronic devices [3]. As the size of the components decreases, developing advanced solder paste is becoming more important. In fact, the assembly of these miniature components requires advanced solder paste with finer particles size.

In addition, the bump pitch on substrates and devices is decreasing and different types of solder bumping technologies have been developed, such as electro-plating, evaporation, micro-ball placement, solder jetting, and printing. Figure 2 displays different bumping methods in accordance with bumping pitch ranges [4]. Among different techniques, printing of solder paste containing fine powders is the most economical technique because of its simplicity for high-volume production [4]. Other advantages are its compatibility with pre-existing printing equipment in a surface mount assembly line as well as its capability to use various lead-free solder alloys. In order to extend the capability of this technique for fine bumps or using the solder jetting method, producing fine solder powders with superior quality is vital. The solder powder with size of Type 4 or Type 5 is used for coarser pitches; however, size of Type 6 or Type 7 is required for finer pitches.

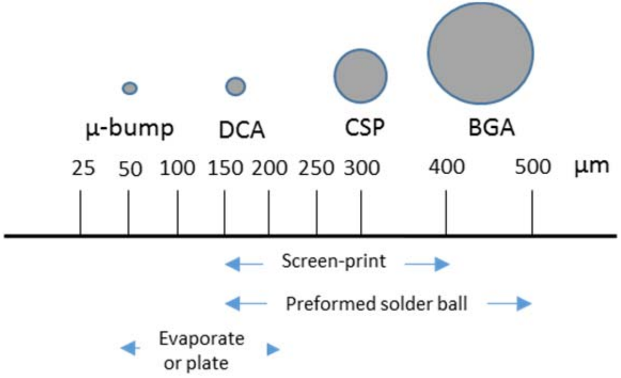


Figure 2. Bumping technologies in accordance with bumping pitch sizes. Adapted from [4].

IMPORTANT CHARACTERISTICS OF SOLDER POWDER

Properties of solder paste are originated from powder characteristics, flux characteristics, and the interaction between the powder and flux after mixing. Powder characteristics that are critical to be reviewed are impurities, particle size distribution, surface oxide, and morphology. Figure 3 shows the influence of the powder characteristics on the solder paste properties.

Impurities can change paste properties. Specifically impurities that have high tendency for oxidation (such as Zn) can have a negative effect on reflow and wetting performance.

As the size of the powder decreases, total surface area increases. This can affect the reflow performance of the paste if the flux is not capable of reducing the oxide. The effect of size distribution on viscosity and tendency for agglomeration/clogging has not been clearly understood. However, it has been reported that existence of too much fine particle may increase cohesive force [5] and therefore, it increases viscosity and tackiness of the paste.

It is important to have low oxide content of solder to have satisfactory reflow and wetting performance. In fact, since the melting temperature of oxides is very high compared to the melting point of the solder alloys, oxides have tremendous negative effect on the reflow and wetting properties. It has been reported that active flux may react with metal oxide and forms a metals salt that can significantly increases the viscosity of the flux [5]. On the other hand, oxide layer at the surface may act as protective layer to help reducing formation of cluster and agglomeration of soft alloy powders. Therefore, insight knowledge is required to discuss influence of oxide on the overall performance of a paste.

Powders with high sphericity and less satellites have higher flowability. This may decrease the viscosity of paste and reduces the risk of nozzle clogging for dispensing application. However, a systemic study on this effect has not been performed yet.

Although some studies have been done, there is still a lack of in-depth knowledge about key properties of lead-free solder powders. In fact, most of studies on solder paste property have only discussed the effect of fluxes. Therefore, more experimental data are needed to verify the role of the powder characteristics as well the interaction between the flux and powder after mixing. At 5N Plus Micro Powders, a comprehensive and systematic study has been recently lunched to investigate these two roles on the solder paste properties. Among different powder characteristics, powder size and oxide content is studied in the present paper. Effect of these characteristics on the reflow performance is also discussed.

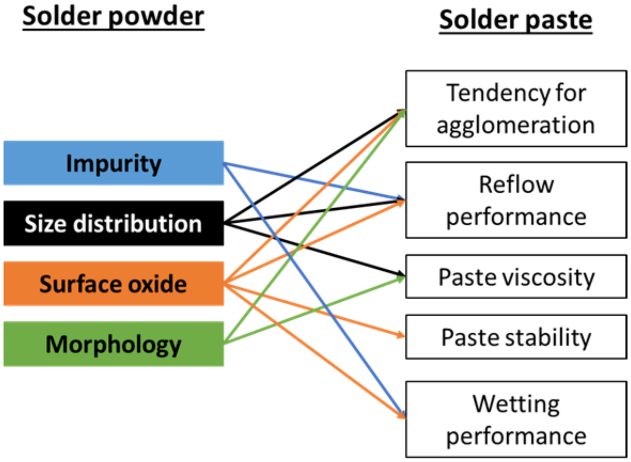


Figure 3. Effect of powder characteristics on solder paste properties.

METHODOLOGY

Lead-free SAC305 (Sn-3Ag-0.5Cu) powders of Type 4, Type 5, Type 6, and Type 7 were chosen.

Table 1 and Figure 4 show the particle size distribution according IPC J-STD-005A for different Types available in the market [6].

Table 1. IPC J-STD-005A, percent of samples by weight. Adapted from [6].

Type	Less than 0.5% larger than	Less than 10% between	More than 80% between	Less than 10% lower than
T3	60	45 – 60	25 - 45	25
T4	50	38 – 50	20 - 38	20
T5	40	25 – 40	15 - 25	15
T6	25	15 – 25	5 - 15	5
T7	15	11 – 15	2 - 11	2

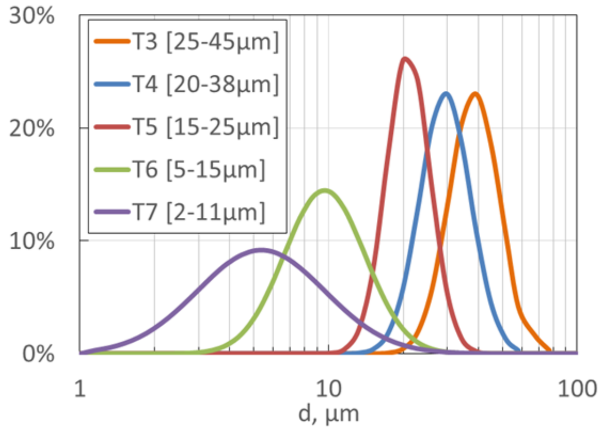


Figure 4. Typical particle size distribution according to IPC standard (Table 1).

Solder ball tests were performed according to IPC-TM-650 2.4.43. A no-clean ROL0 flux is used to make pastes. Frosted glass microscope slides were used as the substrates. For Type 4 powder, stencil 76 mm x 25 mm x 0.2 mm with holes of 6.5 mm diameter was used. For Type 5 and Type 6 powders, stencil 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 245°C. An index called Solder Ball Index (STI) was developed to qualitatively evaluate and score reflow performance of the pastes.

Instrumental Gas Analysis (IGA) was used to measure the amount of oxygen present in the powder. The device heats up the powder to around 2500°C in the presence of an inert gas and measures the oxygen content using a detector for analyzing gas stream.

The microstructure of the powder was characterized using Focus Ion Beam (FIB) technique and Scanning Electron Microscopy (SEM). In order to measure the thickness of oxide layer, Augur spectroscopy and Transmission Electron Microscopy (TEM) were employed.

OXIDE LAYER AND REFLOW PERFORMANCE

Oxide content of the powder has a significant role on the reflow performance of the solder paste. Powder with high oxide content does not perfectly melt and as a result solder balling occurs. Solder balling is the creation of small particles with various diameters that cannot coalesce with the main solder joint and form away from the solder joint. The solder balling can cause electrical circuit shorts and damage the electronic device. Moreover, it can increase the possibility of insufficient volume of the solder at the joint [5]. Thus, low oxide content is essential to achieve satisfactory performance in the surface mount assembly line.

Therefore, it is necessary to characterize the oxide layer formed at the surface of the powder particles. In particular, with decreasing the size of solder joint for new generation of electrical components, surface characterization of the powder is of great importance. 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 [7]. Oxidation reactions for formation of SnO and SnO_2 are as follow:

$$Sn + \frac{1}{2} O_2 = SnO \qquad (R1)$$

$$Sn + O_2 = SnO_2 \qquad (R2)$$

Critical oxygen partial pressure for oxide formation has been calculated and it has been shown that tin oxide formation is possible with even presence of $\sim 10^{-90}$ ppm oxygen [8]. Therefore, it is almost impossible to prevent oxide formation at the powder surface even with most advanced vacuum equipment. Table 2 shows standard free energies of oxide formation for elements present in SAC305 alloy. Among Sn, Ag, and Cu, Sn has the highest tendency to form oxides. Since SnO_2 has the lower free energy it is thermodynamically more stable than SnO. According to Table 2, the formation of oxide can happen even at the room temperature.

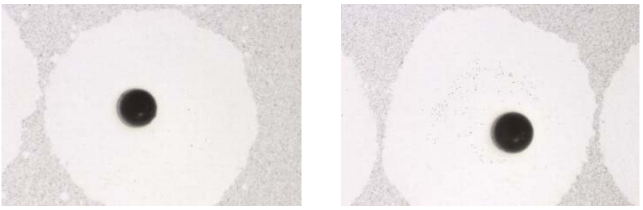
Table 2. Standard free energy of oxide formation for elements in SAC305 alloy [1]

Oxide	Standard free energy (ΔG°_f), kJ/mol
Ag_2O	-11.2
Cu_2O	-146
CuO	-157.3
SnO	-251.9
SnO_2	-515.8

One of the important functions of fluxes is to clean and to remove oxide at the surface of the solder powder. Moreover, flux should be able to protect the powder surface from re-oxidation at the elevated temperatures during reflow. There is an important challenge for finer powders; finer particles have more surface area per volume of paste. Therefore, understanding the surface characterization of the powder becomes more important.

Figure 5 shows examples for the solder ball tests on Type 4, Type 5, and Type 6 powders. According to IPC-TM-650 2.4.43, there are three scores for reflow performance: preferred, acceptable, and unacceptable. In order to score the reflow performance more accurately, a new index has been developed which is called Solder Ball Index (STI). The score is between 0 – 5. Lower Solder Ball Index means less small particles observed around the main solder ball and therefore, better reflow. STI=0 means the ideal reflow without any remaining particles.

To study the effect of oxygen on the reflow performance of paste, powders with different oxygen contents were intentionally prepared. Figure 6 shows the influence of the oxygen content on Solder Ball Index. The dash line which is the linear regression confirms that higher oxygen content generally results in worse reflow performance. As seen in Figure 5, there are some scattering in data which can be due to the uncertainty in oxygen measurement and/or in the solder ball test. Also, we hypothesize that, there might be another parameters like surface quality that also affects the solder balling.


T4: Preferred reflow T4: Unacceptable reflow


T5: Preferred reflow T5: Unacceptable reflow


T6: Preferred reflow T6: Unacceptable reflow

Figure 5. Solder ball test for SAC305 with size of Type 4, Type 5, and Type 6. Tests have been done according to IPC-TM-650 2.4.43.

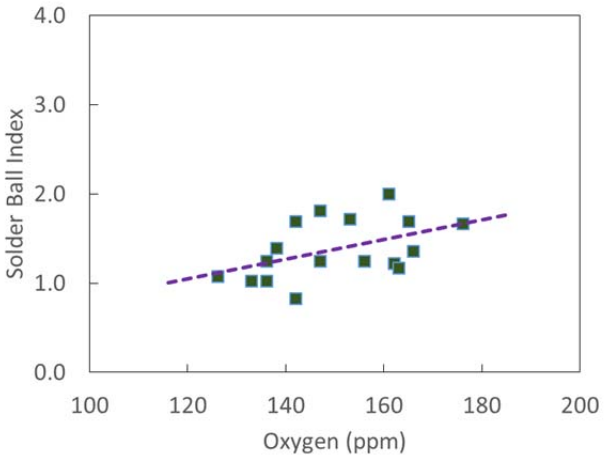


Figure 6. Solder Ball Index vs oxygen content; SAC305 Type 5.

In the surface mount technology community, it is well accepted that as particle size decreases, the probability of solder ball formation increases. This can be explained by:
(i) Fine particles have higher tin oxide content, and
(ii) There is higher probability that some particles do not coalesce because of higher number of particles.

The following paragraphs discussed the effect of particle size on oxide formation and reflow characteristics taking into consideration the two explanations given above.

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. Figure 7 shows depth profile of elements up to 170 Å inside the SAC305 particles with 13 and 40μm diameters. The measurement has been done using Augur spectroscopy. The elemental analysis of this measurement shows that oxygen is present in first 3.5 nm depth. Moreover, Sn content increases and then it remains constant after around 3.5 nm. These observations indicate the formation of tin oxide on the surface with thickness of ~3.5nm. The existence of carbon is due to the surface contamination of powder in air.

Augur spectroscopy was also performed on the different particles with sizes from 3μm to 40μm produced in one production batch. The analyses reveal that oxide thickness is between 3.5 to 4.5nm for all particles. More importantly, it is found that oxide layer thickness is the same for particles with different size and does not depend on the particles size.

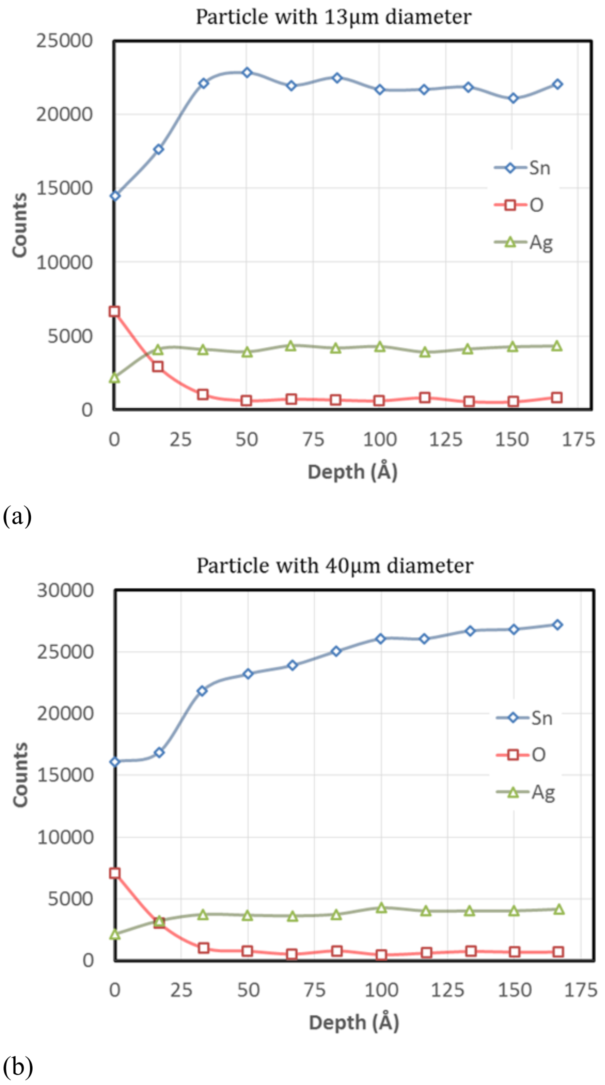


Figure 7. Depth profile of elements by Auger, oxygen curve is indication for the oxide layer thickness; (a) Particle with 13µm diameter, (b) particle with 40µm diameter.

In order to understand the powder characteristics in more details as well as to confirm the results of Augur spectroscopy, microstructure characterization of the SAC305 powder is performed. The first step was sample preparation which was cross sectioning. FIB system was used to cut the powder and make the cross section. Figure 8 shows an example of a cross section of a particle. The FIB system was used to make sure the microstructure is not damaged by severe polishing. Using the secondary electron (SE) detector, topography of the cross section is seen in Figure 8a. The intermetallic and grain boundaries are also revealed with the backscatter (BSE) detector. Surface oxide could not be observed by SEM since the thickness of oxide is too thin to be detected by SEM images.

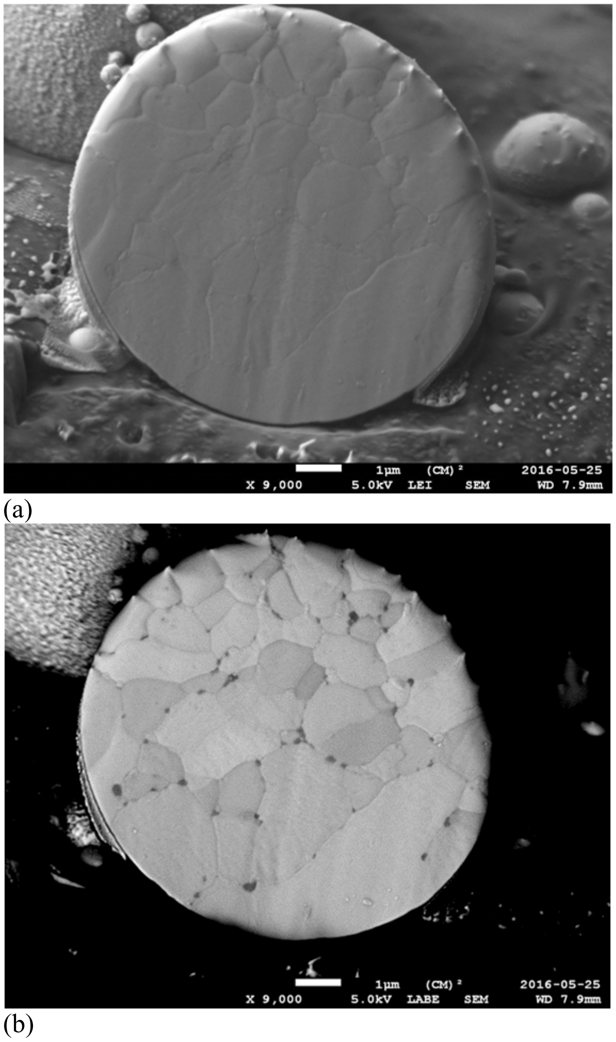


Figure 8. SEM pictures of SAC305 Type 6 powder which is cross sectioned by FIB system; (a) SE image: topography (b) BSE image: compositional contrast.

However, TEM image in Figure 9 shows the formation of a very tin oxide (bright layer) at the surface of the powder. TEM at different positions show that although there is some variation in oxide layer thickness, tin oxide is a continuous layer and covers the surface. The thickness value measured by TEM is in agreement with the measurements done by Augur spectroscopy.

In order to determine the type of tin oxide, oxygen content for different particle sizes are estimated and then, they are compared with the oxygen content measured with IGA device. For the calculation, it is assumed that D50 is the representation for the size of all particles. Also, it is assumed that the oxide thickness is the same for particles with different sizes. As seen in Figure 10, the curve that assumes SnO as the oxide layer with a thickness of 4.5 nm, matches the measured curve. Also, when we assume that oxide type is SnO_2, a curve with 2 nm oxide thickness matches. An oxide with thickness of 4.5nm matches closer to our observation in Augur and TEM studies. Therefore, we can conclude that the oxide layer formed at the powder surface may contains both oxide types; however, SnO has a higher portion.

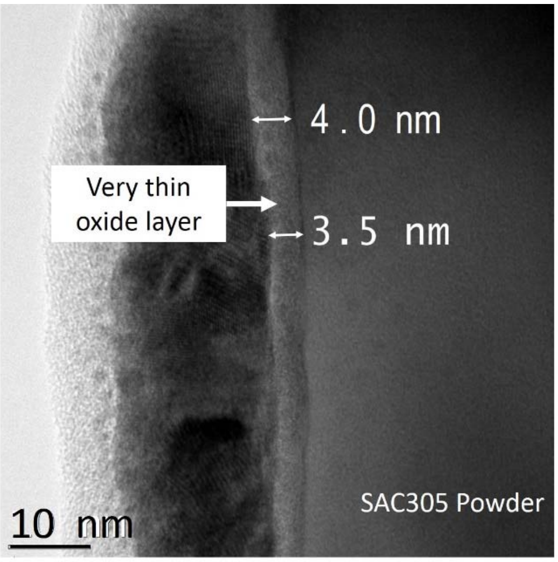


Figure 9. TEM image of oxide layer at the surface SAC305 Type 4 powder.

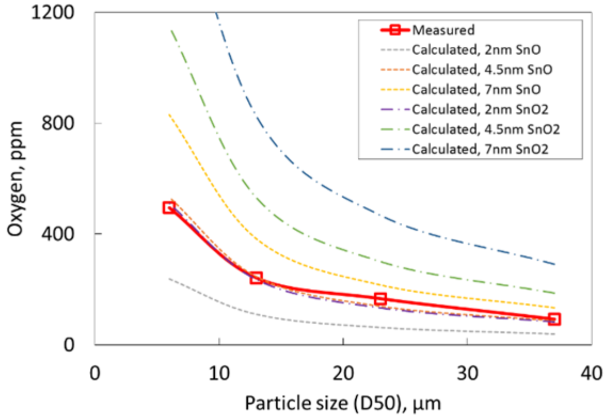


Figure 10. Plot of oxygen content vs particle size.

In order to validate the effect of i) oxide content and ii) the higher probability that some particles do not coalesce when particles are finer, solder ball test was done on powders with different size distribution (T5 and T6) and two levels of oxidation. The first series of powders were processed and stored under normal conditions (N process) while the second series of powders were intentionally oxidized after the production (OX process). Figure 11 shows solder ball test results performed on these powders with Type 5 and Type 6 sizes. Figure 11 shows that when powders are processed adequately, leading to very similar level of oxidation and thickness, the reflow characteristics of T5 and T6 powders are very similar, indicating that size had no effect on reflow performance. However, according to Figure 11, much more individual particles are seen after reflowing when oxidation is favored. In addition, the reflow performance is worst for the finer grade, indicating that particle size can affect the reflow performance of oxidation at the surface if not well controlled.

Based on the results in the present paper, it is clear that the key parameter that controls the reflow performance is the thickness of the oxide at the surface of powder, not the oxygen content, which is also function of the surface area of particles and not the higher quantity of particles found in finer powder. This paper showed that the thickness of the oxide layer is not thicker for finer particles. Moreover, when the oxide thickness of powder is thin enough, the powder with difference size exhibit the same reflow performance. However, it is also true that finer powder are more sensitive to the surface oxidation state than coarser one.

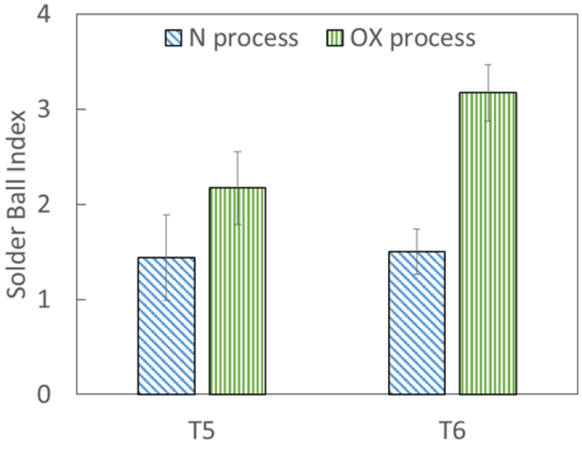


Figure 11. Solder Ball Index of Type 5 and Type 6 for N and OX processes.

In summary, fine powders can exhibit very similar reflow performance to coarser powders if oxidation is very well controlled and the oxide thickness remains very thin. This clearly emphasizes the importance of controlling and maintaining very thin oxide layer to have good reflow performance. It is crucial to maintain this constant during powder production in order to have very consistent paste performance. However, it should also be stated that the flux, that was not the object of this paper, also plays a key role in the paste performance.

CONCLUSIONS

Surface characterization of SAC305 solder powder was performed and effect of powder oxidation on the reflow performance of solder paste was studied. The following conclusions were obtained:

(i) Oxide thickness is the main factor that affect the solder balling; however, some other powder characteristics and/or some external factors play role in reflow performance of solder pastes.

(ii) The oxide thickness formed at the powder surface is the range of 3-5 nm.

(iii) The thickness of tin oxide at the surface powder is not dependent on the particle size.

(iv) When the oxide thickness of powder is thin enough, powder with difference sizes exhibit the same reflow performance. Therefore, finer powders can have same reflow performance as coarser powders.

(v) Finer powder is more sensitive than coarser power to oxidation, i.e. reflow performance is more affected by higher level of oxidation for fine powder.

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