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Oxidation and Topography of Powder in Pb-free Solder Paste

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Introduction

There are compelling reasons to study the relationship between oxidation and the topography of solder powder; these include the following:

❑ Customer requirements to reflow SAC-based (SnAgCu) lead-free solder paste with profiles that are considerably longer than those used for lead-bearing products. The ultimate challenge in this requirement is to reflow using these longer profiles without a nitrogen blanket;

❑ Early developments with more reactive lead-free products such as Sn/Zn solder paste revealed the fact that some of these materials not only showed a lower wetting potential but also an inferior mobility when compared to traditional solder paste;

❑ As an ISO-TS-16949 certified company, one of our main goals is the continuing quest for further reduction in the variation of our products.

Qualification studies and field experience by major end users of Pb-free solder paste have uncovered significant issues with the material; these include surprisingly short shelf life of several types of Pb-free solder paste and significantly variable results regarding voiding. We are of the opinion that both phenomena have a potentially common root, and that is oxidation of the solder powder during production. It is common knowledge that oxidation appears to be self-propagating. So, when solder paste is manufactured with powder that is relatively oxidized, it will further deteriorate once it is in suspension with specific flux systems. Thus, shelf life may become surprisingly short, evidenced by a solder paste that, for example, has unexpectedly become as hard as concrete.

Through a considerable amount of pre-investigations incorporating a large number of process and formulation designs of experiment with regard to flux formulations, we arrived at the need for further observations of the other main constituent of solder paste, i.e., the powder.

By now, the particle size range and the spherical shape of the powder have become trivial and no more than minimal acceptance criteria.
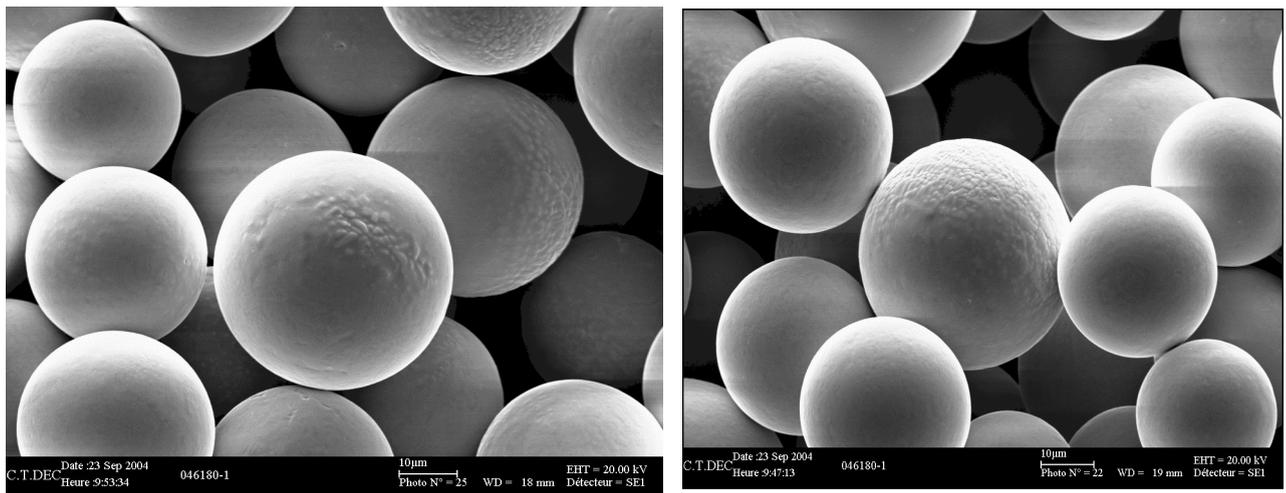

Fig. 1a and 1b: SEM-images of Class 3 powder produced from the same batch of SAC-alloy. The production of the powder, however, took place under different conditions. Depending on the resolution of the illustration, qualitative differences on the surface are clearly visible.

In order to ensure continued improvement of this main parameter of a solder paste, the powder needs to receive more attention with regard to the surface state of its particles.

Although it is evident that the state of oxidation and the purity of the alloy have an impact on wetting performance during reflow, the impact of oxidation on the topography of the solder particles has thus far escaped scrutiny, or at least has been underestimated. This factor may have been of negligible concern in the era of

lead-containing powder, since lead in the alloy made life a lot easier to the solder paste formulator. The presence of lead ensured minimum oxidation of the particles when compared to lead-free equivalents. The absence of lead in the solder paste generally requires more heat and longer profiles, impacting the thermal breakdown of the organic material in the paste flux system. The flux systems for lead-free paste thus tend to have materials of longer molecular chain length. The latter also has an impact on the mobility of solder paste. Bringing a more elastic paste-flux in dispersion with a powder of uncontrolled topography may force the user into an unacceptably small process window. The relationship between oxidation and topography as a quality function deployment of wetting and printability of solder paste is defined in **Figure 2.**

A number of interactions that impact the performance of Pb-free soldering materials are shown. Heat (on the left in the top of the map) is the independent parameter. Obviously, it has a major impact on the wetting of the metallic elements. When one takes the lead out of a solder alloy, even at ambient temperatures, the Pb-free material will oxidize at a significantly more rapid rate. When the temperature goes up, the oxidation process accelerates. In its turn, oxidation impacts both the topography of the solder particles as well as the surface tension of the solder. The topography of the particles is a parameter in the rheologic system and therefore also in the printing properties of the solder paste.[2] Changes in surface tension affect the wetting of the surfaces to be joined, ultimately impacting soldering performance.[3]

Since it is generally considered common knowledge that the majority of defects in a surface mount assembly process have their roots in the printing process, the printing properties of a solder paste are of paramount importance.
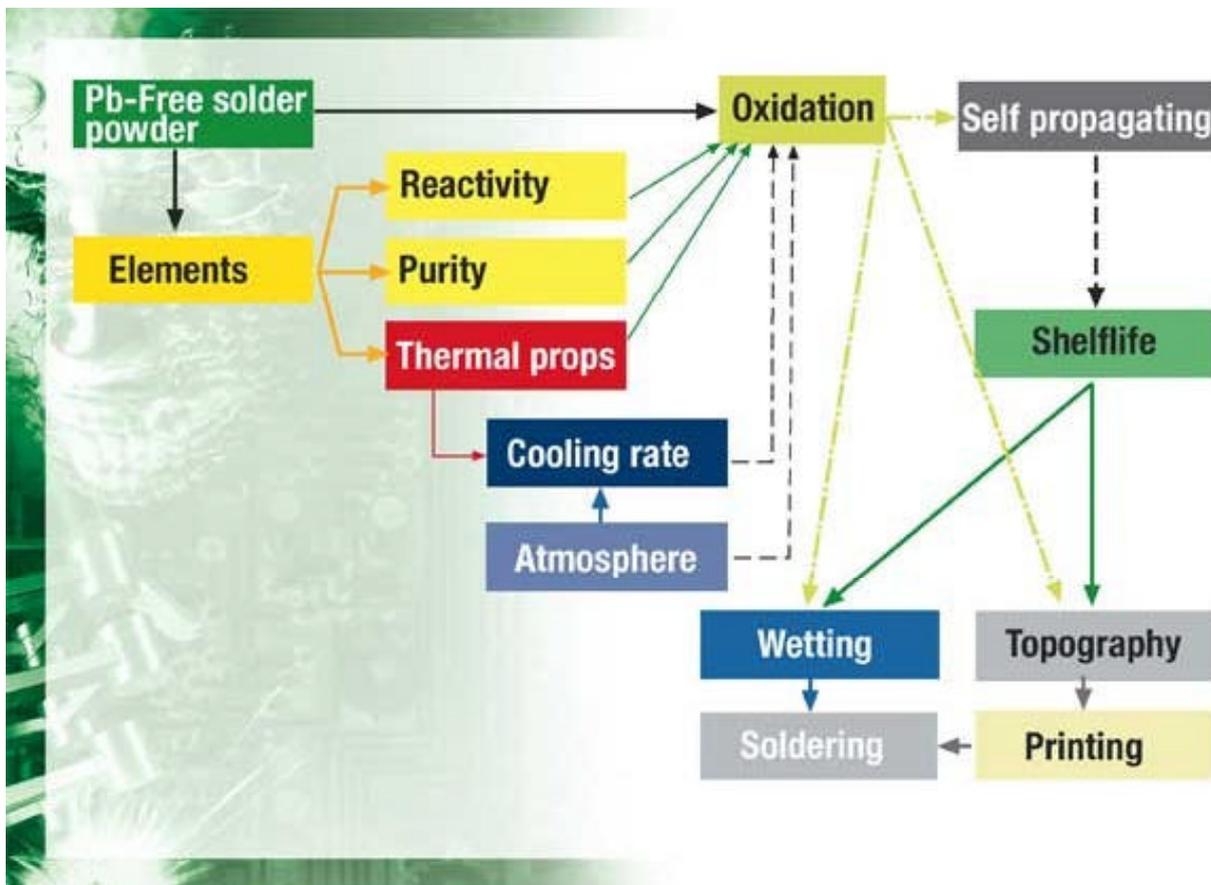

Fig. 2 : *A mind map approach to the interactions that should be addressed when designing for the production of Pb-free soldering paste.*

Our goal is to determine if there could be a possible correlation between oxide level, oxygen content and topography; and, if so, to ascertain how we can control and reduce the oxide level to achieve a smoother particle surface.

In order reach an understanding of the complex interactions taking place during the atomization process of solder powder, it might be helpful to visualize this process in a macroscopic perspective. Imagine the liquid solder droplets as hot liquid masses catapulted with high energy from their solar main mass (the nozzle) into a cosmic space, filled with a gas atmosphere. On their way through their, universe the hot liquid masses cool down while

traveling with linear and axial speed, both of which might vary. Other parameters - more or less significant - are the different mass ratios between the gases and the metals, thus impacting cooling rate, velocity, axial speed, and others. The gas may have a degree of purity, but it is never truly pure, nor is the metal. Thus, all of the aforementioned parameters can change due to coincidental impurities or due to intentional additions. The temperature variations in both the gas and the metal (the latter due to differences in thermal conductivity) may cause similar variations in the interplay between all parameters.

If we step back into the micro-world of solder particles, we might realize that there is a significant difference in impact of the various parameters that have been shown herein, of both the oxidation and topography of solder particles. However, it is worthwhile to initially explore the influence of the following factors:

1. Variation in the alloy; e.g., a slightly over-eutectic alloy has the tendency to build non-homogenous sections. Assuming a normal distribution of these sections, this will also include surface areas;

2. Small traces of impurities or additions can cause sections with a different grain formation, yielding a more homogenous and smoother surface;

3. The solidification time and method can cause differences in grain-size and thereby differences in surface topography;

4. Passive films such as oxides.

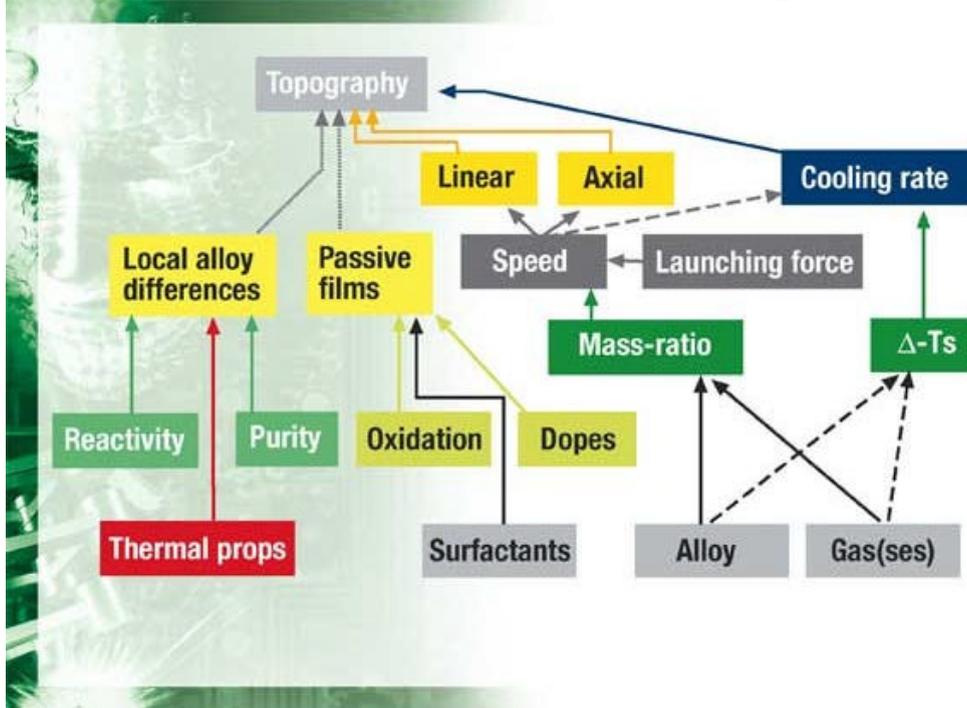Some of the parameters and their interactions have been illustrated in **Fig. 3**.

Fig. 3. *A map of some of the parameters impacting the topography of solder particles. DOEs may demonstrate which are the most significant*

When we began to further characterize and consequently control the topography of solder paste, the first step was to establish those factors that might be significant with regard to topography. We listed items such as alloy-purity, particle shape, particle size, surface state in terms of oxidation, and distribution of the atomic elements on the surface. The root/cause relationship of these factors with powder production process conditions such as melting temperature, gas atmosphere and cooling rates had to be determined.

Anticipating that oxidation and/or surface topography might become special product characteristics of solder paste in the Pb-Free future, we had to consider incorporating these phenomena into a more defined and explicit manner in our control plans. The latter implied a survey of the most accurate and quantitative, yet cost-effective ways to detect the variation of these characteristics, enabling us to perform reliable DOEs that would help us improve the process.

The current method is to reflow a defined quantity of solder powder in oil, remove the oil and determine the weight difference, which indicates the oxide content. Bearing in mind that the repeatability and reproducibility of current detection methods for the oxidation of solder powder have been questioned on a number of occasions, we

needed to review the statistical validity of this procedure. We also considered the option to run a full measurement system analysis on this method[4]. The next step would be to compare the oxide level with the oxygen content. The latter was established by means of a high-temperature fusion furnace.

After some improvements in the fusion-in-oil oxide content test, we carried out a statistical analysis. The standard deviation computed on the samples was 33. Using a probability test, we found that at an oxide level of 700 ppm there is a 95% of chance of the oxide level being between the 630 and 770 ppm.

Oxygen analysis with the fusion in a high temperature furnace method with 2 different batches of SAC-powder, IPC-class 3, provided the following averages:
- Batch A: 112 ppm
- Batch B: 119 ppm
A statistically meaningful statement that there is a significant difference in oxygen content between the two batches could not be supported by solid evidence.

In order to arrive at a better understanding of the significance of the contribution of the oxygen determination, we have also have run tests with the SAC-alloy in different particle size ranges. All cuts, however, had been classified from the same batch of powder:

Particle size (μ)	Surface (m^2/g)	Oxides (ppm)	Oxides (index)	Oxygen (ppm)
45 - 75	0.102	320	100	100
20 - 38	0.179	510	159	120
15 - 25	0.249	960	300	140

Fig 4; The surface area, oxide and oxygen content of 3 different cuts of the same batch of SAC-powder.

The results confirm assumptions and results from the past: the smaller the average particle size, the larger the specific surface area. By implication, this yields both a higher oxygen content and a higher oxide level.

However; the oxide level measurement appears to provide the highest resolution: when the surface area increases by a factor 2.5, the oxide level is increases by 3 while the oxygen content appears to increase by only a factor 1.4.

So, even if the oxide level detection may appear to be cumbersome, it seems to be more discriminating than an oxygen content analysis.

We have also made a comparative study on the SAC-powder on the possible influence of dopes and surfactants on oxide level. We found differences in surface aspect but insignificant differences with regard to the oxide level.

We also explored the influence of aging of the powder under various conditions. The solder balling results were all in accordance with IPC test rating class 1 for all of the non-aged materials as well as the test samples aged for three days under dry conditions.

Aging	None	3 days • 85° C 0% RH	3 days • 85° C 85% RH
Process 1	100	142	245
Process 2	70	177	251
Process 3	67	75	347
Process 4	70	216	NE
Process 5	88	158	NE

Fig 5; The indexed oxide levels of 5 different processes of SAC-powder production. Process 1 is the standard thus far. Processes 2 & 3 have different gas atmospheres. Process 4 was run with a different melt temperature and process 5 with a different cooling rate.

The solder ball test aged for 3 days at 85C and 85% relative humidity; for all graded class 5 or higher, the oxide results went up so astronomically that some of the samples could not even be determined. They have been marked as 'NE'.

The overall observation is that aging of the powder at high temperatures and high moisture deteriorates the powder so severely that there is no chance to produce an adequate solder paste with this material. So, a procedure to pack the powder under controlled conditions, immediately preceding the production, into inert packaging systems is a prerequisite. Instant immersion of the powder into the flux within the mixing vessels after opening the packaging, followed by a mixing operation in a closed vessel, might be an area of interest to quality auditors.

The oxide level growth seems interesting after an aging at 85°C under dry air conditions. In this regard, process # 3 seems to be better than the current standard process (#1).

We wanted to find a routine that would provide an all-in-one accurate determination of both the oxide content as well the roughness of the solder particles; thus we chose Atomic Force Microscopy (AFM).
The general idea that supported our interest in AFM is that a rougher surface may be an indication for differences in oxide levels, but also a cause of less particle mobility, which impacts the printing properties of the solder paste.
The situation worsens when it appears that these properties change from batch to batch, resulting in batch-to-batch performance differences.

Thus, in the beginning of the project, one of the assumptions made was that the oxide layer is one of the most influential parameters for the formation of the topography of solder powder. Therefore we performed a first analysis by SEM, AFM and EDX and found the following results:
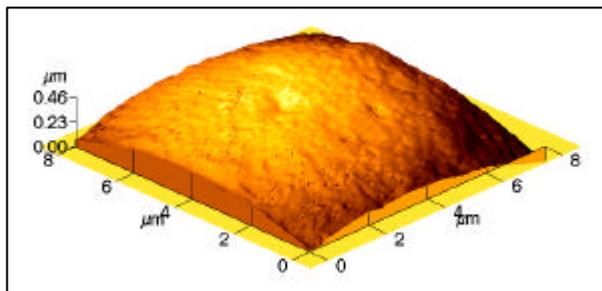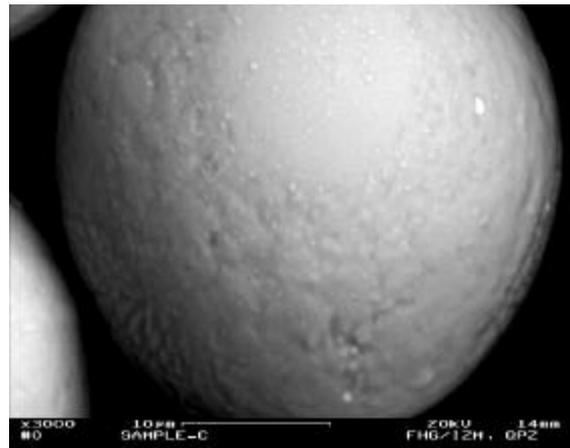

Fig. 6: *A 3D-image of a surface of 64 μm^2 of an Sn95.5/Ag4.0/Cu0.5 solder particle generated by Atomic Force Microscopy (AFM). The average nano-surface roughness (R_a) is 9.2 nm.*

Powder A 25-45 micron				
	Alloy	Surface	Dev (%)	Ra
Sn	62	44,8	27,74	10
Pb	36	53,7	149,17	
Ag	2	1,5	25,00	
Powder B 25-45 micron				
	Alloy	Surface	Dev (%)	Ra
Sn	63	56,4	10,48	12,8
Pb	37	43,6	117,84	
Powder C 25-45 micron				
	Alloy	Surface	Dev (%)	Ra
Sn	95,5	94,6	0,94	7,2
Ag	4	4,4	110,00	
Cu	0,5	1	200,00	
Powder D 25-45 micron				
	Alloy	Surface	Dev (%)	Ra
Sn	91	89,7	1,43	18,7
Zn	9	10,3	114,44	

Fig. 7a *(top): EDX-Image of a SAC-solder particle with Sn95.5/Ag4.0/Cu0.5. The analysis (Fig 7b) however results in a percentage [w/w] distribution on the surface of Sn94.6/Ag4.4/Cu1.0*

Fig. 8 *(left). A table showing the nominal alloy size, the distribution of alloying elements on the surface as determined by EDX, its deviation in % compared with the nominal value and the average surface roughness in as detected by AFM*
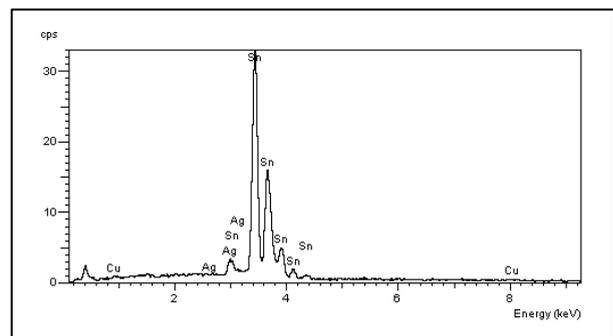
After this first exploration we wanted to get an idea of the repeatability of the AFM results and therefore ordered an AFM scan on 10 particles of 2 different batches of SAC-powder, processed with the same settings. The square surface measured was 8 by 8 microns each time.

Batch	Ra	Rp-v	Rms	O_2 [ppm]
A	14,98	200,60	20,02	112
B	11,39	138,90	14,71	119

Ra and Rms are the average surface roughness calculated over the surface area measured. The difference between both can be explained as line and surface area averages. They are the most interesting to look at. Rp-v is average of the maximum surface roughness found in the areas measured. The results are in nm. They clearly show that batch A has a rougher surface.

The fact that the statistical variation of the AFM results were not adequate as such to qualify this procedure in an environment requiring compliance with ISO-TS-16949 standards was disappointing.

The oxygen content [O_2] was determined on these batches as a parallel to this investigation. The oxygen level results could not confirm the thesis that a rougher oxide would generally also be more oxidized. The results with the oxide and oxygen test demonstrate that the relationship between oxide content and surface roughness is considerably more complex than a simple and straightforward direct relationship. Consequently, the EDX-results showed that the distribution of the elements on the surface probably had more impact on the surface roughness than the oxide content.

We felt that the research with AFM and EDX thus far had to be improved; we wanted to arrive at a level of variation by which we could meaningfully correlate the data of these analyses. Therefore, we had to develop a solution that would enable us to locate and scan the same 8 by 8 micron square surface with SEM, AFM and EDX of 10 randomly selected solder particles from different types of powder. In a number of cases, we selected 3 batches per type in order to determine the process variation in this respect. We found a way to fix 10 particles on a grid mounted on a silicon coupon. The grid enabled us to identify each particle with x-y coordinates. In this way, we were able scan the same surface on each particle by the different techniques and thus we could correlate the research data.

AFM – SEM - EDX

AFM Ra = Avg Surface Roughness

EDX Avg Alloying Elements on the Surface

SEM Avg particle size and qualitative image

Oxide-level - Application

Oil-fusion = Avg Oxide-content

Production of Paste:

• Rheological characterization
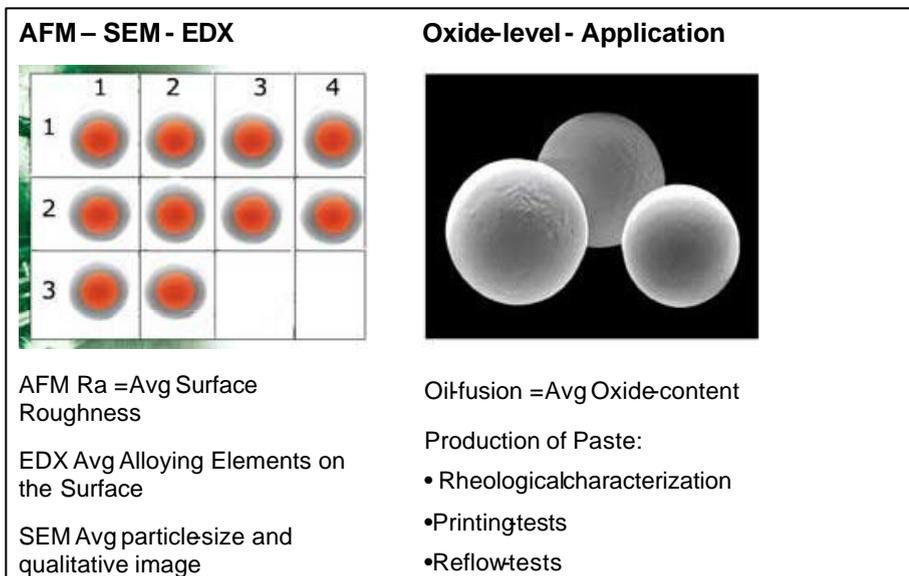
• Printing tests

• Reflow tests

Fig. 9. This shows the different tests used in phase 2 of this project. They will result in MSA compliant detection methods and finally will lay the foundation for further process enhancements that will yield a fully ISO-TS-16949 certifiable and process capable Pb-Free solder paste manufacturing process with minimal variation.

The project continued with a more synchronized program of SEM, AFM and EDX, linked with oxide level measurements of the powder samples as well as a rheological characterization and printing and reflow tests of the solder paste produced with these samples. A program of shelf life aging with different conditions will be needed to find the answers to questions about the product stability of this new generation of materials. The different types of paste include variations of the same SAC-alloy with different particle ranges. Samples processed with additives such as dopes and surfactants are also included.

For the next phase in the program, we developed some theses:

1. The oxide content is just one of the many parameters that cause variations in surface roughness of powder particles;

2. AFM data may only become meaningful when supported by EDX results obtained from exactly the same surface areas.

We need to obtain a more fundamental verification that generally there is no significant variation of oxide level within one and the same batch of powder. In fact, the common variation in our SPC files supports this thesis. Oxide level variation can change the paste parameters. This is due to different activity requirements to the flux system, resulting in a more elastic flux vehicle, impacting the mobility of the solder paste.
Moreover, the surface roughness is an important parameter at the interface between the solder powder and the flux system, resulting in stronger physical bonds, thereby also affecting the rheology of the solder paste. The latter has been confirmed on the production floor with comments about the printing speed of many of the current Pb-free solder pastes

Conclusion
With Pb-free soldering materials 'Heat' is the most important parameter. Despite the fact that our industry has to switch to Pb-free technology, the ever increasing demands for higher quality in the final electronic product is the driving force to achieve more consistent material performance. The introduction of Pb-free technology has presented additional challenges to deliver more batch-to-batch consistency of solder paste. It is not only the consistency of the flux system with a higher thermal stability that has received more attention but also, as described in this paper, a number of surface properties of the powder, impacting the interaction with the flux system, that have recently received greater recognition as important parameters. Surface roughness and the differences in the alloy between the mass of the solder particle and its specific surface area not only impact the wetting properties of a solder paste but also its rheology and consequently its printing properties.

- We strongly believe that getting more control over the oxide content becomes a key element in the successful application of Pb-free solder paste.

- An oxygen content analysis with the high temperature fusion furnace method seems to be an insignificant procedure. Although it may claim a level of repeatability, its resolution is considerably lower than the oxide level analysis by the fusion-in-oil principle.

- The ratio of fines in a particle range has a significant impact on the oxide level.

- Air oxidation doesn't have such an influence on oxide level at ambient temperatures.

- Solidification seems to have a minor influence on oxide level and yet quite a significant one on topography of solder powder.

- Even if it would turn out that AFM would be a fundamentally correct method to establish both oxide layers (indirectly) and surface-topography, we would still require a justification of the cost per analysis versus the potential to detect process variations.

- If AFM data only become meaningful when supported by EDX results, this technique has no chance to become a feasible detection routine. However, it will still be functional in supporting and guiding process improvements.

Notes
1. *A Fast, Precise and Reproducible QC-Rheometry Routine for Solder Paste, Ineke van Tiggelen-Aarden, Proceedings APEX 2004 Conference.*
2. *A Simpler Approach to Cost-Effective Solder Paste Testing, Ineke van Tiggelen-Aarden, Proceedings APEX-2003 Conference*
3. *Chrysler, Ford & GM: "Measurement System Evaluation" in Reference Manual AIAG, Troy, Michigan 1990*