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The Significance of Heating Profiles and its effect on Sintered Ag Die Attach Agglomeration, Aggregation and Adhesion On a Copper Lead Frame Surfaces

Richard Q. Clemente[1], Blessie B. Basilia[1, 2] Erik Nino Tolentino
[1] *Mapúa Institute of Technology School of Graduate Studies, Muralla St. Intramuros Manila, Philippines*
[2] *Industrial Technology Development Institute, Department of Science and Technology, Bicutan Taguig City, Philippines*

Abstract:- Sintered Silver (Ag) die attach is known to be one of the options towards lead free packaging was further characterized in terms of varying heat profiles. To be able to understand the mechanisms at different heating combinations, Thermo-gravimetric (TGA) experimentation coupled with design of experiment (DOE) runs were undertaken to look into main factors (Temperature 1) T_1 and (time/duration 1) t_1 as well as (Temperature 2) T_2 and (time/duration 2) t_2. The DOE result suggests that the critical factors for sintering include the 2nd temperature plateau (T_2) and its duration (t2). T_1 and t_1 values were not significant in the experiments due to the fact that sintered Ag organic components had volatized during temperature ramp up approaching T_1. Also, the DOE suggests higher sintering temperature (T_2) and duration (t_2) results into optimal shear results which correlates to better agglomeration of silver micro and Nano-particles when examined in scanning electron microscope (SEM). Although the values for T_1 were found to be insignificant it is critical that organic burnout is achieved. This was proven in the experiments by re-characterizing a low T_1 (100°C) which results to inferior die shear, agglomeration and aggregation results. Further optimization can be achieved by decreasing the durations of T_1 and augmenting this duration to T_2 wherein actual sintering of silver particles exists.

Keywords: Die Attach, Sintered Silver (Ag), Agglomeration, Aggregation, Design of Experiments

I. INTRODUCTION

Silver Sintering has emerged as an option for lead containing alloys used in attaching the silicon die inside the semiconductor package. DA5 (Die Attach 5) is the research arm for these types of material. The main objective of this group is to look for alternative materials which have equal or better performance in comparison to high lead solder. From current findings [1], they arrived into four types of materials which can replace SnPb in response towards lead free packaging. These are Trans-liquid Phase Sintering (TLPS), conductive die attach, alternative solders and sintered silver. There have been increased research efforts over the years based from Siow [2]. In this work, silver sintering as a die attach material was examined taking into account different heating profiles. Sintering is different from conventional SnPb wherein liquification is necessary to attach the silicon die and the lead frame. Moreover, silver sintering presents a different concept wherein the silver micro and Nano-flakes are suspended in a solution called organic component [3]. The term organic component is to collectively include a dispersant, binder and a solvent [4]. The organic material is responsible for making silver Nano and micro flakes workable in terms of viscosity and rheology when applied in high volume production. During sintering process, it is necessary for the organic material to evaporate (organic burnout). This results to enhanced agglomeration and aggregation of silver micro and Nano flakes. This is the reason why the heat treatment for sintered silver die attach includes 2 heating plateaus. The first plateau is responsible to ensure solvent evaporation and the 2nd plateau is responsible for sintering process. It is necessary that no organic material (full organic burnout) is present in the 2nd plateau otherwise it will hinder effective agglomeration and aggregation.

II. EXPERIMENTAL METHOD

To be able to determine the optimal profiles for sinter Ag die attach, DOE experimentation was carried out to define the critical temperature and required durations for organic burn out and sintering of silver die attach. The heat profiles for this type of paste involve two levels wherein the first temperature plateau is necessary to evaporate the organic material (e.g. composed of a binder, solvent and dispersant). The 2nd temperature plateau activates sintering process of silver micro and Nano flakes in the die attach material. The temperature profile is in the form of figure 1. However, characterization should be carried out to determine the temperature and time otherwise full organic burn out could not be achieved. It is composed of the following variables illustrated below.

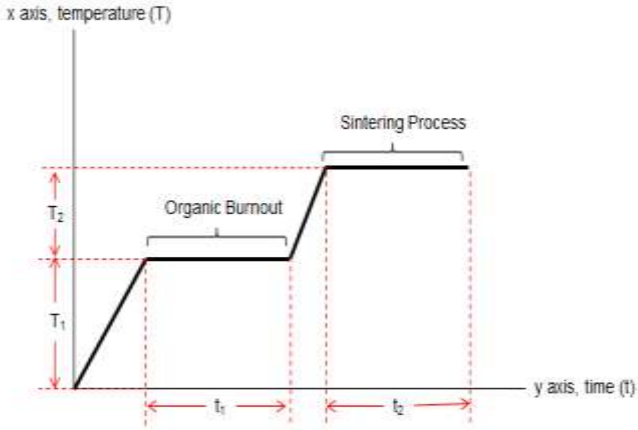

Figure 1: Two level temperature profiles for sinter Ag paste

Where T_1: Initial Temperature plateau/ Temperature 1
T_2: Secondary Temperature plateau/ Temperature 2
t_1: time/duration 1
t_2: time/duration 2

Boundary conditions were set for Temperature (T_1) at 100 - 200°C at soak times (t_1) between 10 minutes to 120 minutes. T_2 values were set at 200 to 265°C. The heating duration for T_2 has a boundary condition similar to t_1 from 10 minutes to 120 minutes. TGA experimentation was conducted to validate the sintering profile based on related literature [8]. After thawing the sintered Ag paste for 1.5 hours, it was placed in an aluminum pan illustrated in figure 3. Each sample were prepared weighting 5mg and subjected eventually subjected to thermal processing. The thermal processing steps is illustrated below

1.) Temperature ramp from 23°C to 150°C
2.) Followed by 150°C for 30 minutes
3.) Ramp from 150°C to 250°C
4.) Constant temperature of 250°C for 1.5 hours
5.) Cool down from 250°C to 27°C for 1 hour

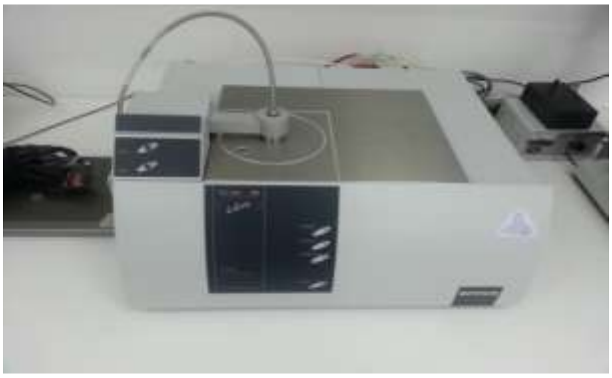

Figure 2: TGA equipment for the pre heating profiles of the die attach material


Figure 3: Aluminum Pads used for TGA; Figure 4: Sintered Ag die attach material

In order to quantify the process windows fractional factorial experiments were implemented taking into account four variables T_1, T_2, t_1 and t_2 which resulted in 17 legs. Table 1 illustrates the DOE runs for sintering profiles; the ramping process is fixed at 30 minutes due to machine capability. Experimental samples were prepared using a copper lead frame and a silicon die. The dimension of the die is $1750x966mm^2$ having a surface composition of TiNiAg. Lead frame-to-die attachment was achieved using a die attach machine.

Profile	Pattern	ramp1	T1	t1	ram2	T2	t2	N2
1	----+	30	100	10	30	200	10	200
2	---+-	30	100	10	30	200	120	0
3	--+--	30	100	10	30	265	10	0
4	--+++	30	100	10	30	265	120	200
5	-+---	30	100	120	30	200	10	0
6	-+-++	30	100	120	30	200	120	200
7	-++-+	30	100	120	30	265	10	200
8	-+++-	30	100	120	30	265	120	0
9	0	30	150	65	30	232.5	65	100
10	+----	30	200	10	30	200	10	0
11	+--++	30	200	10	30	200	120	200
12	+-+-+	30	200	10	30	265	10	200
13	+-++-	30	200	10	30	265	120	0
14	++--+	30	200	120	30	200	10	200
15	++-+-	30	200	120	30	200	120	0
16	+++--	30	200	120	30	265	10	0
17	+++++	30	200	120	30	265	120	200

Table 1: Fractional Factorial Experiments to determine optimal T_1, T_2, t_1, t_2 values for sintering

A convection oven was used to sinter these samples with a temperature profile illustrated in table 1. Die shear, SEM inspections and X-ray were also taken to understand the structure and property relationship of each runs.

Die Shear Methods

Thirty (30) samples were subjected to die shear strength measurement using Mitutoyo die shear equipment. Minimum shear strengths were collected and replotted into the prediction profiler in the JMP analysis tool.

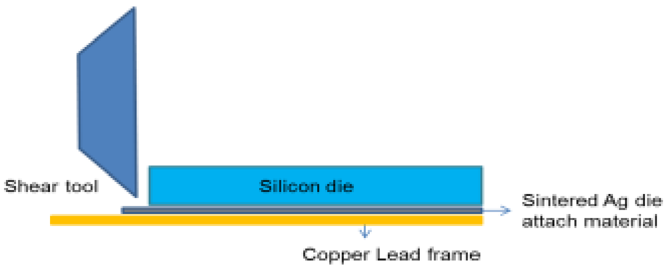

Figure 4: Die shear test setup

X-ray Inspection Methods

Samples from each batch were subjected to X-ray for the purpose of observing outgassing paths of various sinter paste. This is to determine if there is a relationship between the outgassing paths, die shear strength, agglomeration and aggregation.

Figure 5: X-ray machine to observe outgassing paths of sinter Ag die attach materials

SEM inspection methods

Samples from each batch were mounted over a polymer solution for lapping purposes in order to expose the surface of interest. These samples were eventually subjected to SEM to observe the morphological characteristics as well as the degree of agglomeration and aggregation of the silver paste.

Figure 6: (a) specimen for SEM imaging (b) polishing of specimen to expose surface of interest in SEM

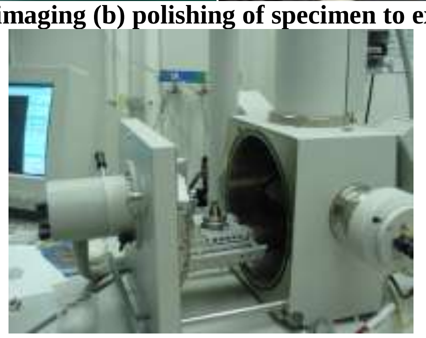

Figure 7: SEM equipment to analyze the morphology and degree of agglomeration and aggregation among sinter paste

III. RESULTS AND DISCUSSIONS

The TGA curve is shown below; the temperature profile is described in the methodology section. The heating profile illustrated in figure 6 produces two pronounced regimes on the weight behavior of the sinter paste; a sharp curve with decreasing behavior is attributed to solvent evaporation wherein the weight percentage decreases from 100% to 93%.This graph also illustrates the % weight of the organic component in relation to the sinter paste is approximately 7%.

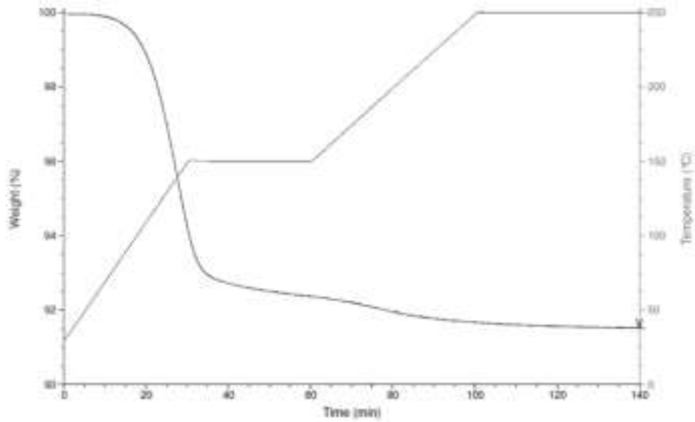

Figure 6: TGA graph of Sinter Ag Paste with heating profiles based on related literature.

In this experiment, the temperature range to volatize the organic material was initially assumed between 100°C to 150°C. Continuous heating results in further weight decrease which is attributed the un-volatized organic component. Sintering is achieved when there are no drastic changes in weight which happens between 200°C to 265°C as referred from figure 6. It is worthy to note that during the initial temperature ramp, significant amount of organic material has evaporated. The "organic material" includes a binder, dispersant/capping agent and thinner/solvent [2]. The binder enables consistency of the paste resulting to easier dispensing capability. A dispersant/capping agent is added to inhibit coalescence between Ag particles resulting in better diffusion over the sinter Ag matrix [5, 6]. The thinner/solvent enables the paste to achieve optimal viscosity [2]. With the application of temperature during sintering, these organic materials evaporate and sintering action between Ag particles is initiated. Ag particle reaction is divided into 3 phases. First is the shrinkage of the material that occurs due to the particle rearrangement by sliding across each other. This leads to necking formation between silver particles [3]. The second stage leads to densification which results to pore formation due to the interfacial surface energies. The final stage includes the collapse of the isolated pores forming grain growth by which the small grains integrates with the larger grains [5]. Table 2 illustrates the components of an organic material found in sintered Ag paste.

No	Component	Example
1	Dispersant/passivating layer/ organic shell/capping agent	Menhaden fish oils, poly(diallydimethyl ammonium chloride), polyacrylic acid, polystyrene sulfonate, triethylene glycol, methyloctylamine, dodecylamine, hexadecylamine, myristyl alcohol, 1-dodecanol, 1-decanol stearic acid, oleic acid, palmitic acid, dodecanethiol
2	Binder	Ethyl cellulose, polyvinyl alcohol, polyvinyl butyral, wax
3	Solvents/thinner	Isobornyl cyclohexanol, texanol, terpineol, butyl carbitol, toluene, xylene, ethanol, phenol

Table 2: Organic component of Ag sinter paste [2]

This experimental activity also extends to determine the effects of various temperature profiles which in turn determine the process envelope for sinter paste as applied to a clip package. The following parameters were varied.

a.) N_2 concentration

b.) 1st temperature ramp T_1 and its duration t_1 (soak 1)

c.) 2nd temperature ramp T_2 and t_2 (soak 2).

Parameters a, b and c are known as main factors. The response variables are shear and corrosion presence on the lead frame. The DOE run resulted into 17 possibilities. Each run were subjected to die shear tests wherein the numerical values were replotted in JMP software. The oxidation presence was quantified visually as illustrated in figure 8. The prediction profiler is visualized in figure 7. Based from the results; it is observed that t_1 (soak 1), and T_1 (temp 1) has no effect in terms of the desirability (die shear). However t_2 and T_2 has significant effect in the overall desirability. The insignificance of T_1 and t_1 can be explained by the rapid volatility of the organic material during the initial ramp up. This is evident in figure 6 wherein majority of the organic material has vaporized prior reaching T_1. This explains why T_1 and t_1 values were insignificant in the experiment.

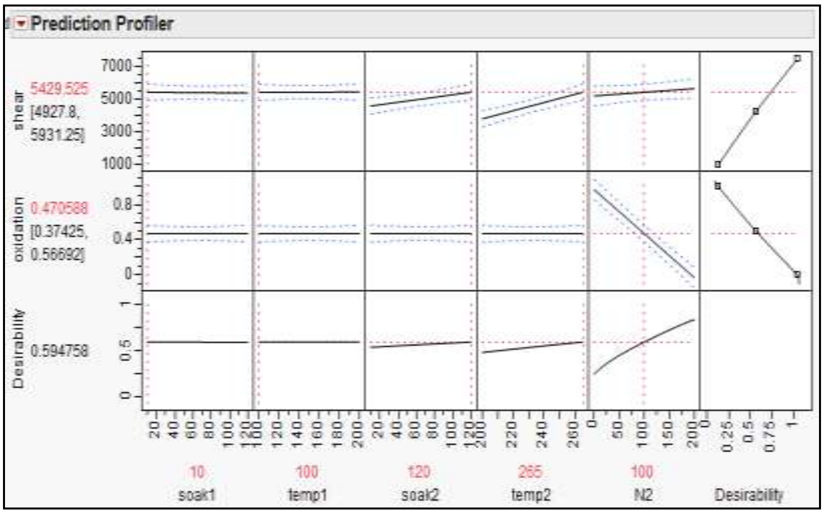

Figure 7: Predictive profiler graphs for the 17 design of experiment (DOE) runs on sinter Ag.

Variations in N_2 concentration during sintering were included in the DOE runs since N_2 level has a direct relationship on corrosion presence on the lead frame. High N_2 levels minimize corrosion on the lead frame while ordinary atmosphere accelerates corrosion. Figure 8 is an illustration of corrosion bahavior for variaous lead frame subjected to low (0 schf), mid (50-100 schf) and high (200 schf) original temperature profiles.

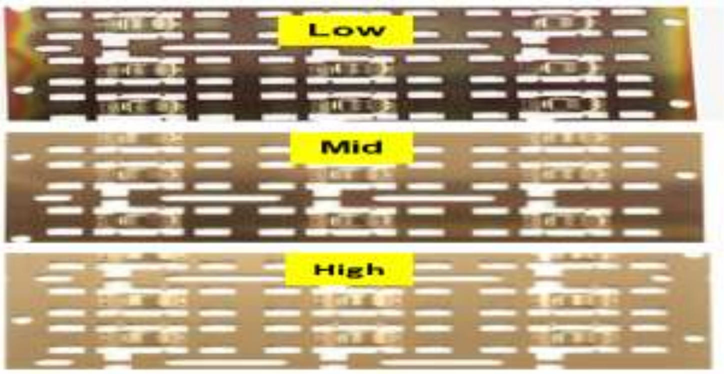

Figure 8 shows oxidation experiments with varying levels of low, mid and high N_2 concentration.

Three profiles were retained for further characterization. The original profile based on TGA experiments is compared to Profile 1 which is seen to be optimal based from experimentation. Profile 2 is similar to profile 1 with Temp 1 at 100^{o}C. The purpose is to quantify the effects of a partially evaporated organic material in a sinter paste during production runs. The parameter settings are illustrated in Figure 9.

Profile	Soak1	Temp 1	Soak 2	Temp2	N2
Original	40	150	180min	250	100
Profile 1	40	150	180min	265	100
Profile 2	40	100	180min	265	100

Figure 9: Sinter Ag pastes parameters for further characterization.

The die shear readings were collected for all the 3 runs. Both the original and profile 1 shows significant readings while profile 2 illustrates less shear strength based on JMP Tukey Kramer plots. Looking closely at Figure 6, full evaporation of organic component is achieved at temperatures around 150^{o}C. This constitutes 7% of the die attach material component. However when we have T_1 values at 100^{o}C, we observe from the TGA graphs that 99% of the sintered Ag or 6% of the total organic material is still present in the sintered Ag die attach material. Therefore, the remaining solder material hinders the sintering formation of the silver flakes. SEM inspections were collected from sample runs. The morphological formations of the original profile compared to profile 1 show similar densification rates whereas profile 2 incurred random pore formations. This explains why the die shear of the original profile compared to profile 1 are statistically significant whereas profile 2 exhibits less shear strength values. Figure 12 is an optical image of the lead frame remnants for each profile. We notice similar amounts of silver remnants for both Original and Profile 1 whereas profile 2 shows slightly less silver remnants compared to other silver profiles.

Figure 10: Tukey-Kramer Plot for statistical significance for Original, Profile 1 and Profile 2.

Figure 11: SEM micrographs (10um scale) of sinter Ag particles at three different profiles

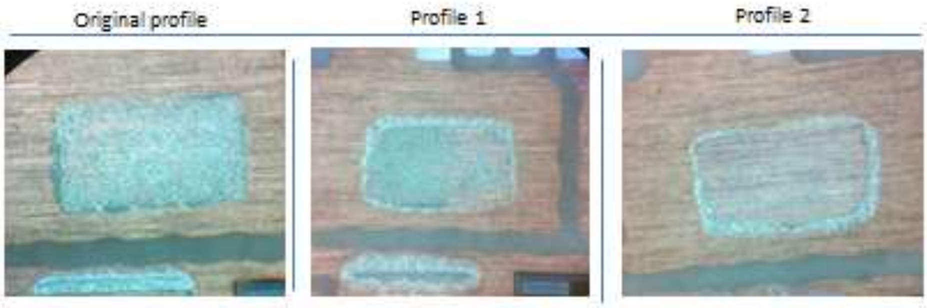

Figure 12: Optical Inspection of lead frame and sheared die indicating Less remnants of sinter Ag pastes at profile 2.

Outgas paths were also examined on the samples. The relationship of outgassing behaviors to aggregation and agglomeration were observed was proportional. This is due to the increased solvent that has evaporated in the paste. The result show similar outgassing paths for the original and profile 1 whereas profile 2 exhibits less outgassing behavior.

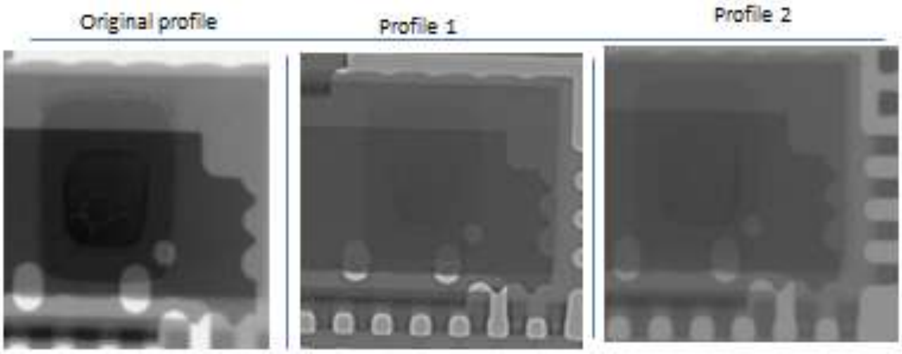

Figure 13: Outgassing behavior for the the three reruned profiles.

IV. CONCLUSION

Sintered Silver die attach is one of the candidate material closely being looked into as an alternative for lead free packaging. Sintered silver (Ag) presents a different approach in attaching silicon dies into the lead frame. One differnce in comparison to solders versus sinter paste is that melting is not necessary during the thermal process. The temperature plateaus in sinter Ag is necessary to first; stabilize and eliminate the organic material. Second is to sinter the micro and nano silver flakes remains after the organic material is fully evaporated. In the design of experiments, we observe that T_1 and t_1 were not significant factors this is due to the fact that majority of the organic material has evaporated already prior reaching T_1. This eventually results to insignificance. The T_2 and t_2 values from the experiments provided high significance wherein the higher T_2 and t_2 produced better shear strenght and more outgas paths which translates to better agglomeration and aggregation. Although T_1 and t_1 values were not seen to be significant the right values should still determined. A low value of T_1 results into inferior shear performance and less aggregation among silver particles. In this experiment, the initial ramp was an important factor since majority of the organic material volatizes prior reaching T_1. With this finding, it is possible to optimize the current profile by lessening the duration of t_1 and augmenting that to T_2 where sintering of silver micro and nanoflakes occur.

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