A study on the degassing mechanism of Pb-based alloy under ultrasonic treatment

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Abstract-In recent years, the ultrasonic technique is being developed at a pretty faster speed, whose assisting tactic has been applied in the electronic packaging field. What we need is to determine the mechanisms of ultrasonic treatments on electronic packaging fillers. In this paper, Pb-based alloy is typically chosen as the filler metal, in this paper, it is found that the flowability of which can be improved under ultrasonic vibration. Also, ultrasonic degassing efficiency is greatly promoted, with the best parameter for degassing that ultrasonic power and duration time of 1000W and 60s, a molten alloy’s treating temperature of 340℃. The assistance of ultrasonic is deeply explained from the thermodynamic aspect. Understanding of the atomic level interactions of liquid Pb atoms and vacuum is crucial, so we make an ultrasonic-assisted molecular dynamic simulation of melting Pb to room temperature to 330℃ in 10ps, and the diffusion behavior of Pb atom under periodic vibration is revealed.

1. Introduction
Ultrasonic technology is becoming more and more reliable in packaging usage. Little chip pads are soldered inside circuits by molten Pb at relatively lower temperatures. Degassing is the first step to treat solder materials when they are in liquid states. Generally, degassing efficiency is the degree of tracing molten Pb materials, which elevates the number of gases having migrated and partitioned out of the liquid phase, as a function of their affinity diffusion rate[1]. However, how to manipulate the degassing process of Pb-based solder by using ultrasonic vibrations is deeply introduced. In this paper, we manage to predict the mass transmission of gas by ultrasonic degassing technology. Till now, we are unknown about either the mechanism of ultrasonic driving energy or how ultrasonic degassing works.

Traditionally, we used a degasifier for gas removal, however, the efficiency was quite unsatisfied. After being assisted by ultrasonics, Li[2] found that efficiency values were promoted about 2.7 to 3.6 times. According to other researchers[3-4], the main influence of ultrasonic waves in the melt was the cavitation behavior. The cavitation bubbles disserved the continuously flowing liquid, holes gathered up gases, which had previously dissolved in liquid metals. The core of crystallization was formed when facing elastic ultrasonic oscillation, and the size of the core became bigger. That ensured the evolved gas dissolves out[5]. Finally, it succeeded in moving away gases from liquid filler metals.
2. Methods

Pb₉₀Sn₁₀ is chosen as filler materials during degassing, and the further flowing experiments. As is shown in Fig.1, those raw materials are (a): Pb and (b): Sn metals, both are in the purity of 99.99%, the liquidus and solidus temperatures of the two pure metals are 302°C and 275°C, they are alloyed in a weight percentage of 9:1. The intensity of Pb₉₀Sn₁₀ is 10.6g/cm³.

![Fig.1 Specimens of raw materials.](image)

Two parts of the experimental apparatus are designed, according to two different functions of the ultrasonic generator, illustrations of both are drawn with diagrams: Fig. 2(a) and (b).

![Fig.2 Experimental apparatus.](image)

Except for experiments, we have carried out numerical simulations on the melting process of Pb metal materials under atomistic level. Based on the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)[6-8], we investigate the hole vanishment in the melt structure, which is performed under the different states of a sinusoidal wave. The cubic Pb structure contains 128,833 Pb atoms, the whole model is a polycrystal one before melting, it contains 12 grains inside each box with three-dimensional sizes of 25.0117×25.0117×25.0117nm. During the simulation process, the cutoff radius of interatomic potential is 8.5Å. The timestep is set to 1fs, and each dynamic melting system runs for 200ps in an NPT ensemble, the processive temperature raises from 1K to 600K, and as the process is accompanied by ultrasonics, we have simulated the vibration of ultrasonic on Pb, whose frequency and amplitude are 250GHz and 5.0Å.
In order to evaluate the degassing efficiency, here is the definition of melt’s relative density $\eta(\rho)$. First, the differences $\Delta \rho$ used in equation (1), is a constant evaluation [9-10]. And we need to refer to the Archimedes principle, so the drainage method is a direct way for the measurement of density $\rho$. Suppose that the density of purified water is $\rho_{\text{water}}$, the theoretical density is $\rho_t$, when $W_{\text{dry}}, W_{\text{wet}}$ represent the weight of the same sample when separately placed in dry air and pure water, $\rho = (W_{\text{dry}}/W_{\text{wet}})\rho_{\text{water}}$, so the percentages of gas in a liquid is calculated by $\Delta \rho$ using a percentage value. Calculations of degassing efficiency are defined in (2), after evaluating $\eta$ by dividing $\rho_{\text{measured}}$ and $\rho_t$.

$$
\Delta \rho = (\rho_t - \rho)/\rho_t \times 100\% 
$$

$$
\eta(\rho) = (\rho_{\text{measured}} - \rho)/(\rho_t - \rho)
$$

3. Test Results and Discussions

The degassing experiments were carried out and the results were listed in Table 1. Here, we can judge from the degassing results that temperature is obviously a crucial factor, liquid Pb-Sn alloys have higher degassing efficiencies when at the temperature of 340 Centigrade. At 320℃, the degree of ultrasonic degassing efficiency won’t be firing, since the diffusion rate of gas in the melt is relatively lower. By reaching the low-temperature threshold, the diffusion of each gas atom is fully activated, as a result, the efficiencies are elevated from 22.65~36.4 to 49.89~55.97. When the temperature of the melt becomes excessively high, the saturation of gas decreases, which brings less motivation for the gas atoms to separate out.

During the gas moving toward the vapor/liquid surface, there is a balanced equation as (3), according to which, the surficial volume of gas bubble $C_f$, reaction equilibrium constant $K$, and the pressure inside the bubble $P_g(t)$, togetherly meet the relationship.

$$
P_g(t) = \left(C_fK\right)^{1/2}
$$

At different times, the average diffusion flux $J$ expresses as equation (4):

$$
J = (C_t - C_f)K
$$

$C_f$ symbolizes the gas content, and at the same time, $K$ is higher when under ultrasonic treatment. As is calculated by the Machin model [11],

$$
K = 2\left(2DR_g/\pi R_g\right)^{1/2}
$$

$D$ is the transport coefficient of gas atoms, $R_g$, $R_g$ is the velocity and radius of the bubbles. Referred to the Arrhenius equation, $D = D_0 \exp(-Q/RT)$ where $D_0$ is atomic diffusion coefficient in normal pressure at thermal temperature $T$, $Q$ is the activation energy of diffusion, $R$ is the constant of gas. As bubbles are moving with ultrasonic vibrations, the actual transport coefficient is written as (5). Therefore, with a high-power ultrasound and an appropriate temperature, the efficiency of degassing will be promoted. With the aid of ultrasonic vibration, degassing degree is up to the highest level, the chosen parameter for degassing is the 1000W power ultrasonic excitation matched with 340℃ temperatures. When we change the time of ultrasonic treatment: 60, 120, and 180 seconds, the effect of prolonging ultrasonic time is not significant. As is seen from Fig. 3(c), the main attribution of ultrasonic is concentrated on the first 60 seconds.

![Graph](image-url) (a) Temperature’s effect on efficiency  (b) Power’s effect on efficiency  (c) Time’s effect on efficiency

Fig.3 The influences of different ultrasonic degassing valubles on the measured efficiencies.
Table 1. Results of efficiency (abbreviated as $E$, unit: %) with different experimental variables, ultrasonic power, unit: W; ultrasonic time, unit: second; and temperature, unit: °C.

| Items | Parameters ($W$, $s$, °C) | $E$ (per.) | Parameters ($W$, $s$, °C) | $E$ (per.) | Parameters ($W$, $s$, °C) | $E$ (per.) |
|-------|--------------------------|------------|--------------------------|------------|--------------------------|------------|
| 1–3   | 600, 60, 320             | 22.65      | 800,120,320              | 36.40      | 1000,180,320             | 33.70      |
| 4–6   | 600,120,340              | 49.89      | 800,180,340              | 57.01      | 1000,60,340              | 55.97      |
| 7–9   | 600,180,360              | 41.33      | 800,60,360               | 20.27      | 1000,120,360             | 30.79      |

With ultrasonic vibration, inter-facial reaction proceeds more quickly, so Pb-Sn filler is in a continuous distribution of better flowabilities, as can been seen from Fig. 4(b). The cavitation effect of the ultrasonic wave in the melt is related to the ultrasonic frequency and intensity. When the ultrasonic frequency is constant, the cavitation effect is not completely correlated with the ultrasonic intensity $P_0$, which is related to the growth and collapse time of the cavitation bubble. In the melt, the maximum radius of the cavitation bubble is related to the amplitude of the ultrasonic wave as follows\[11\].

$$\frac{P}{P_0} = 1 + \left( \frac{R}{3R_{\text{max}}} \right)^3 - 4 \left( \frac{R}{3R_{\text{max}}} \right)^2 + \left( \frac{R}{3R_{\text{max}}} \right) - 1$$

(6)

Where $P$ is the pressure amplitude of the ultrasonic wave. $R_{\text{max}}$ or $R$ is the maximum or ordinary radius of the cavitation bubble generated from the melt. The maximum radius of the cavitation bubble increases with the ultrasonic pressure amplitude when the cavitation bubble expands in the half-cycle of the ultrasonic wave, and the collapse time of the cavitation bubble also increases with the ultrasonic pressure. Besides the maximum radius of the cavitation bubble increases.

![Fig.4 Samples after ultrasonic degassing and the micrograph of which flowing into Si substrate gaps.](image)

(a) Pb$_{90}$Sn$_{10}$ samples, the upper ingot is treated badly whose $E$ equals 22.65%, the other is with the best experimental variables (b) A side view SEM of Pb$_{90}$Sn$_{10}$ inside substrate plates, flowing under ultrasonic vibration

After promoting the flowability of Pb-Sn alloy, it utilizes flowing to wet the solid gap well but remains a non-wetting state to the substrate. The obtuse angle, as is seen from Fig. 4(b), is higher than 90°, that is because of oxide films that hinder the wetting degree during filling. Studies also found that Al, Mg oxide films can be both removed by ultrasonic cavitation\[12\]. The structure and distribution of cavitation will directly affect cavitation intensity, thus affecting the removal of the oxide film on the base metal surface. After ultrasonic degassing, the molten Pb$_{90}$Sn$_{10}$ is well treated and can well be used. In the newly done experiments, the flowability of ultrasonically treated filler alloy is moving inside Si intervals at a faster speed; the texture filling rate is higher than 99.9\%\[13\]. Meanwhile, the flowing speed of Pb-Sn when with ultrasonic excitation is more even swift, we have observed that all the pastes can be well soldered within 10 seconds.

By the method of anodizing a layer of oxide film on surfaces of the silicon wafer, we studied the structure and distribution of ultrasonic cavitation within a narrow gap. It is found that in a thin layer of
liquid Pb-Sn metal, the cavitation structure is composed of a large number of single cavitation bubbles and small size of cavitation clusters. The rule seems like this, the greater the ultrasonic amplitude is, the smaller the gap and the solder viscosity are. Due to all of these elements, Pb-based filler after degassing flows into the thin gap clearance of Si plates, although the intrinsic wettability still has never been promoted, and the contact angle is kept to 165°.

Fig.5 Molecular dynamic simulation results: on the right is a Pb polycrystal (containing 128,833 atoms and 12 grains); on the left, the dynamic process of degassing at four vibration steps.

Molecular dynamic simulations of polycrystal are performed for a cubic Pb atomic structure shown on the right of Fig. 5. When simulation temperatures are elevated to 323℃, as is shown at step 1 on the left of Fig. 5, there are almost ten atomic districts where the nucleation cores of gas massively exist. At step No.2, there is the acceleration of atomic diffusion, that is because the ultrasonic oscillation shows the biggest amplitude. We define the two steps as under-saturation degassing and over-saturation. At step No.3, the gas districts are filled, inside the Pb grains, liquid atoms rearrange quickly, that step is called the heterogeneous nucleation period. The final step is No.4, before which a positive sinusoidal period finishes, and it is found that the degassing process has already been accomplished. So the molecular dynamics reveal how gas bubbles vanish under the assistance of ultrasonic waves.

4. Conclusion

Based on the results and discussions presented above, the conclusions are obtained as below:

(1) It is shown that ultrasonic power has an optimal value when Pb-based alloys are being degassed with ultrasonic-assisted. The best power is 1000W. Temperature for degassing needs to be moderate, if too large, the cavitation bubbles in the melt can grow larger, while collapse time will be insufficient, which is disadvantageous for degassing, the best temperature is 340℃.

(2) Ultrasonic promotes the chemical reaction between filler metals and substrates. It strongly depends on the ultrasonic cavitation effect. After ultrasonic treatment, the porosity of the solid-liquid region is reduced, thus the flowability is quite satisfied.

(3) Molecular dynamic simulation results show that ultrasonic affect the grain boundary area inside the molten Pb. During a single oscillation of 250GHz wave, the core of gas has vanished inside the liquid Pb structure.

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