Materials Letters 234 (2019) 92-95

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

The wetting phenomenon and precursor film characteristics of Sn-37Pb/Cu under ultrasonic fields

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ARTICLE INFO

Article history: Received 28 June 2018 Received in revised form 29 August 2018 Accepted 2 September 2018 Available online 4 September 2018

Keywords: Ultrasonic Welding Interfaces Precursor film Wetting kinetics

ABSTRACT

The wetting phenomenon of Sn-37Pb alloy solder spreading on Cu substrate under different ultrasonic fields was investigated. Sn-37Pb/Cu wetting systems showed significant precursor film characteristics with the assist of ultrasonic energy. A short-time ultrasonic field evidently enhanced the wettability of Sn-37Pb/Cu compare to a common wetting field which had no introduced ultrasonic. At the temperature of 213 °C, spreading area of a Sn-37Pb solder drop in a 20 kHz, 1000 W ultrasonic field reached maximum at 2 s, and showed significant precursor film characteristics. Atomistic dynamic models showed the relevance between wettability and precursor film formation. The observed dynamic results agreed with the experimental results.

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1. Introduction

Flux-free solders are indispensable to the packaging of printedcircuit boards (PCB), while good wettability is a prerequisite for reliable solder connections. Methods like surface coating, or adding surface-active elements to the solder can improve wettability [1], polluted microelectronic devices. By comparison, ultrasonic-assisted soldering makes no pollution, being both effective and environmental friendly. Ultrasonic-assisted technology has been widely adopted in the field of electronic packaging industry, for manual soldering, ultrasonic soldering irons have been invented, and for dip soldering, ultrasonic energy can be concentrated into the solder/substrate region with an ultrasonic bath. The ultrasonic-assisted soldering method also achieves quick and reliable connections between Cu seed layers in flipchip packaging [2].

In metal/metal joints with ultrasonic, the contact angle (CA) of the molten solder on the substrate decreases [3], that proves the assistance of ultrasound can enhance the wettability of metal/ metal wetting systems according as a low CA wetting system has good wettability. Eutectic Sn-37Pb is commonly used for soldering copper, from previous work, Sn-37Pb/Cu reactive wetting system has the occurrence of precursor film, which is another hint of good wettability [4], Significant precursor film characteristics are found in certain systems where substrates are well wetted, a wetting sample with precursor film looks like a cap with bright "halo" around the cap tip [5]. Xian summed up several factors for precursor film formation (temperature change, extra element addition, etc). Due to the limitation of experiment apparatus, molecular dynamic simulations (MD) is replacing traditional experimental method in some studies. E.B. Webb III simulated the precursor film controlled spreading of Pb/Cu(1 1 1) through MD method, similar results were found in Pb/Ni [6] and Li/Fe systems [7].

2. Experimental

2.1. Experimental procedure

The copper sheets of 99.9 wt% purity ($20 \text{ mm} \times 20 \text{ mm} \times 2.5 \text{ mm}$) were used as substrates. Sn-37Pb solder was rubbed into ball shape weighing 0.04 ± 0.001 g each, and then dipped into dilute hydrochloric acid pickling to remove oxide film. Substrates were heated to 486 K (30 K above the melting point of solder) before placing on solder pieces, timed for the spreading in 0.5 s, 1 s, 1.5 s, 2 s, 3 s, 4 s and 6 s ultrasonic fields. Set input power to 400 W, 600 W, 8000 W and 1000 W separately, used a tool head to propagate 20 kHz ultrasonic vibration. After spreading, took samples out of the heating platform and cooled down. Used Quanta 200FEG scanning electron microscopy (SEM) in back scattering (BSE) mode to make observation, component was analyzed by energy dispersive spectroscopy (EDS). Used image processing software to measured CA, then calculated spreading area with geometrical equations for spherical crown.







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2.2. Simulation procedure

The modified embedded atom method (MEAM) was employed for Sn-Cu interatomic potential function, another EAM potential in "setfl" format by Hoyt [8] for Pb-Cu. 4000 Sn atoms composed a hemisphere model, with a radius of 3.5 nm. An atomistic model of Pb was similarly established, Set two separate Cu slabs below Sn and Pb hemispheres, each slab ($12.5 \times 12.5 \times 2.5$ nm) was cut in (1 1 1) plane and included 80,000 Cu atoms. Periodic boundaries were implemented in *x*, *y* directions, leaving *z* in open boundary condition. Time step was fixed to 2 fs. After energy minimization for all, atoms obtained random velocity in Boltzmann distribution. Each wetting model was relaxed in *NVT* isothermal ensemble at 500 K with Nose-Hoover algorithm. The simulation of wetting was observed in *VMD*, a post-processing software. Recorded $\theta(t)$, which illustrated the time-dependent variation of CA in two simulations.

3. Results and discussion

A modified Young's equation is commonly used for reactive wetting system:

$$\gamma_{\text{L-V}} \cdot \cos\theta = \gamma_{\text{S-V}} - \gamma_{\text{S-L}} - \Delta G_{\Omega} \tag{1}$$

Solid-liquid (S-L), solid-vapor (S-V), and liquid-vapor (L/V) interfacial energy are separately defined as γ_{S-V} , γ_{S-L} and γ_{L-V} , θ (CA) is the angle connecting S-V and S-L interface, ΔG_{Ω} denotes the activation energy of intermetallic compound (IMC) on S-L interface (per unit area). Suppose that β_1 characterizes the thickness of the IMC layer, marked in Fig. 1(b). So an acoustic energy term f_u changes the thermodynamic model of wetting, see Eq. (2), where the ultrasonic-assisted CA is defined as θ_u , and IMC thickness is β_2 in ultrasonic wetting, both are shown in Fig. 1(d).

$$\gamma_{\text{L-V}} \cdot \cos\theta_u = \gamma_{\text{S-V}} - \gamma_{\text{S-L}} + f_u - \Delta G_\Omega \tag{2}$$

100 um

Sn-37

Cu

100 um

(a)

(c)

From the experiments (Fig. 1(a) with no ultrasonic after 2 s and Fig. 1(c) with 2 s 1000 W ultrasonic-assisted), we know that ultrasonic energy has enhanced Sn-37Pb/Cu wettability and $\theta_u < \theta_r$, so f_u is thermodynamically positive. Ultrasonic also promotes interfacial reaction, IMC grows thicker when wetting in ultrasonic fields, $\beta_2 >> \beta_1$. Chemical reaction has taken Sn into consumption, the cooling curve in solidification shifts left from eutectic point, Fig. 1(c) shows more petal-type α -Pb phase microstructure in contrast with Fig. 1(a).

We assert that Sn-37Pb/Cu has two stages of wetting, drop spreads on homogeneous Cu, then on the mixed layer of Cu-Cu₆Sn₅. Synchrotron X-ray radiation found that Cu-Sn interfacial reaction could last for 2000 s at 250 °C [9], The equilibrium spreading of millimeter scale solders needs much time, which can be overly reduced with ultrasonic. Spreading coefficient is predicted by $S = \gamma_{S-V}-\gamma_{S-L}-\gamma_{L-V}$ (for inert systems), if S < 0, the system has a spontaneous tendency to wet, *Sultrasonic-assisted* (for ultrasonic-assisted systems) satisfies (3).

$$S_{ultrasonic-assisted} = \gamma_{S-V} - \gamma_{S-V} - \gamma_{L-V} - G_t + F$$
(3)

F is ultrasonic force, and *G*_t characterizes the change in tension from the IMC reaction's attribution, within per area in a time unit, $\bar{G}_t = \Delta G_{\Omega}/t$. Interfacial reactions happen on S-L interface, similarly, *F* acts on the interface vicinity only, so Manor [10] predicted *F* with two equations from Reynolds stress models, (4) and (5).

$$We \equiv \rho v^2 r / \gamma \tag{4}$$

$$F \approx We \cdot \frac{r}{\beta^{-1}} \gamma_{\rm LV} \cos^2 \theta_2 \tag{5}$$

In (4), v characterizes vibrational velocity, $v = w \cdot A$, and in (5), β^{-1} characterizes the vertical thickness of S-L layer suffering vibration, $\beta^{-1} = \sqrt{(2\mu/\rho w)}$, other quantities like ρ , γ , r, μ are density, surface tension, spreading radius and viscosity of solders. Power

 $4G_0$



(b)

(d)

Fig. 1. Cross-section micrographs and thermodynamic models of three-phase intersection (a), (b): no-ultrasonic 2 s, (c), (d): 1000 W ultrasonic-assisted 2 s.

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