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Acta Materialia 56 (2008) 1075–1083

Acta MATERIALIA

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Size distribution and morphology of Cu_6Sn_5 scallops in wetting reaction between molten solder and copper

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Received 21 May 2007; received in revised form 2 November 2007; accepted 3 November 2007
Available online 18 January 2008

Abstract

During the reaction between molten solder and copper, ripening and growth of Cu_6Sn_5 scallops take place at the solder/metal interface. An experimental study on the morphology, size distribution and growth rate of Cu_6Sn_5 scallops was conducted. The measured size distributions of Cu_6Sn_5 as a function of time from top-view and cross-sectional view scanning electron microscopy images were in good agreement with the flux-driven ripening (FDR) theory. The FDR theory assumes a non-conservative ripening under a constant total interfacial area between the scallops and the solder, while the total volume of scallops increases with reaction time. The measured average radius of the scallops was proportional to the cube root of time. Comparing the experimental results and the theoretical model, the width of the liquid channel between scallops was calculated to be ~2.5 nm. Morphology of the scallop-type Cu_6Sn_5 was dependent to the composition of the solder. The scallop morphology became more faceted when the composition was further away from the eutectic composition. The Cu_6Sn_5 scallops with a shape close to hemispheric gave better agreement with FDR theory. The small difference between the experimental data and theory was explained by taking the noise factor into account. The modified FDR model showed even better agreement with the experimental data.

Keywords: Cu_6Sn_5; Solder wetting; Ripening

1. Introduction

The growth and ripening of scallop-type Cu_6Sn_5 in the wetting reaction between molten solder and Cu is a unique phenomenon of phase change. It was found that both growth and ripening of the scallops take place at the solder/metal interface at the same time [1]. Hence the ripening is a non-conservative ripening. Copper is constantly supplied through channels between the scallops to grow the scallops. The classic theory of the conservative ripening of precipitates by Lifshitz and Slyozov [2] and Wagner [3] (LSW theory) is not suitable for non-conservative ripening of scallops in solder joint formation. When molten solder wets a metal, the metal constantly diffuses through the narrow channels between intermetallic compound scallops to react with the tin in the molten solder and grows intermetallic compounds. Therefore, the system is an open system. This is the first major difference from classic LSW ripening, which assumes a closed system. Another major difference between the classic ripening and the current case of ripening of scallops in molten solder wetting reaction is distance among particles. The LSW theory assumes an infinitely dilute solution, which means the distance between precipitates is very large compared with the size of the particles. However, as in the top-view image of Cu_6Sn_5 scallops shown in Fig. 1, the scallops are almost in contact with each other, and their base is confined two-dimensionally at the interface between the solder and the metal. To have better physical model on formation and growth of intermetallic compound in reaction between molten solder and metal, an alternative kinetic model (flux-driven ripening (FDR) theory) was proposed [4].

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doi:10.1016/j.actamat.2007.11.009

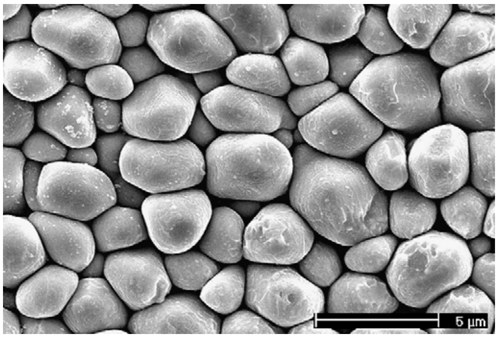

Fig. 1. Top-view image of Cu_6Sn_5 scallops formed by reaction between 50Sn50Pb solder and copper at 183.5 °C for 3 min.

The FDR model assumes, that the interfacial area between the intermetallic compound (IMC) and the molten solder is constant and that the shape of the scallops is hemispherical. As a result, the total interfacial area between the scallops and the molten solder becomes a constant, equal to twice the total interfacial area. However, the total volume of scallops increases with growth. In short, the ripening of the Cu_6Sn_5 in the FDR theory was assumed to be non-conservative ripening under a constant total surface area. The FDR theory was able to predict the scallop size distribution and rate of average size change according to the wetting reaction time. The size distribution curve is shown in Fig. 2, and the average radiu of the scallops $\langle r\rangle$ depends on time t, obeying the equation

$$\langle r\rangle = 0.913(kt)^{1/3} \tag{1}$$

The constant k in Eq. (1) is composed of several thermodynamic parameters. It is given as

$$k = \frac{9}{2}\frac{n}{n_i}\frac{D(C^b - C^e)\delta}{C_i} \tag{2}$$

where C_i is the Cu concentration in the scallop, C^e is the Cu concentration in the solder melt in stable equilibrium with a planar interface of Cu_6Sn_5, C^b is the quasi-equilibrium concentration of Cu in the vicinity of the Cu substrate, n is the atomic density in the molten solder, n_i is the atomic density in the scallop, D is the diffusivity of the Cu in the molten solder, and δ is the width of the channel between scallops.

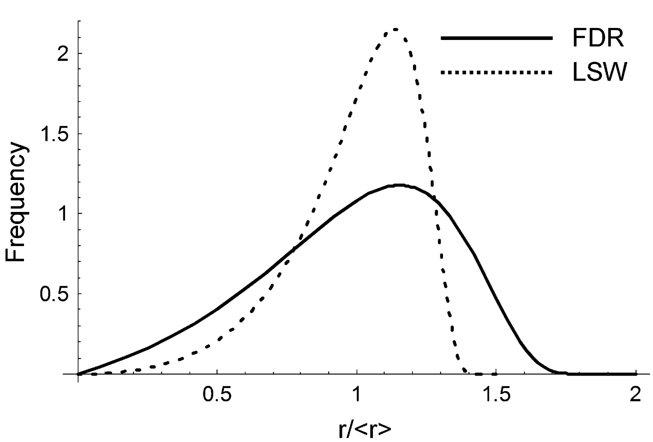

Fig. 2. Size distribution curve of FDR model, along with the curve of the LSW model.

This paper reports the experimentally measured size distribution of a large number of scallops as a function of wetting reaction time. A comparison with theoretical analysis is given. Furthermore, the morphology change of the scallops as a function of solder composition is presented.

2. Experimental

The effect of solder composition on the morphology of Cu_6Sn_5 scallops has been briefly mentioned in the literature [5]. The morphology of Cu_6Sn_5 scallops was found to be highly faceted when the solder was pure tin, and round when the solder was of eutectic composition. The morphology of the scallops may affect the kinetic path of their ripening, and the FDR theory assumes that the scallop shape is hemispherical. So the dependence of scallop morphology on solder composition and reaction temperature must be investigated systematically prior to the measurement of the size distribution and growth rate as functions of the reaction time.

To investigate the morphology of scallops in the SnPb/Cu reaction, samples with different solder compositions were prepared: pure Sn, 90Sn10Pb, 80Sn20Pb, 70Sn30Pb, 63Sn37Pb, 60Sn40Pb, 55Sn45Pb, 50Sn50Pb, 40Sn60Pb, 30Sn70Pb and 20Sn80Pb, in wt.%. Solder with a Pb concentration >90 wt.% Pb was not investigated, as Cu_3Sn will form instead of Cu_6Sn_5. Each alloy was prepared by mixing pure Sn (99.999%) and pure Pb (99.998%) in a quartz ampoule in a vacuum, and melting at 1150 °C for 1 h followed by quenching into ice water. To obtain a quenching rate high enough to produce homogenous alloys, only a small amount of alloy (~3 g) was prepared each time. The solder alloys were cut into small pieces (0.5 ± 0.1 mg) and melted in mildly activated flux (197 RMA) to form a spherical bead. Copper foil (99.999%) was cut into 1×1 cm square pieces 1 mm thick. Each Cu piece was mechanically polished down to colloidal silica to reduce the surface roughness, and ultrasonically cleaned with acetone, followed by methanol and DI water rinsing to remove organic contaminants on the surface. After removing the organics, the Cu foils were etched with 5% HNO_3+95% H_2O for 15 s to remove native oxide, and rinsed with DI water followed by drying with nitrogen gas. Then the Cu pieces were quickly immersed into the hot 197 RMA flux. The flux was used to improve the wettability of the solder. The solder bead was dropped onto the Cu foil immersed in the hot flux to form a solder cap. The solder bead melted and wetted the surface of the copper foil. To study the scallop morphology, samples were prepared at temperatures 20 °C above the melting temperature of each of the alloys. The temperature control was ±3 °C, and the reaction time was 2 min. To prepare samples to measure the size distribution of the scallops, the 55Sn45Pb solder was reacted with copper at 200 °C with different reaction times of 30 s, 1 min, 2 min, 4 min and 8 min. In this study, the reaction time over 10 min was not investigated because vertical elongation of scallops is known to take place after 10 min [4], which can cause complications in data analysis. The reacted sample was taken out and quenched down to room temperature in acetone. To observe the size of the scallops, the unreacted solder covering the scallops was removed by mechanical polishing, followed by selective chemical etching. The selective etching was performed using 1 part nitric acid, 1 part acetic acid and 4 parts glycerol at 80 °C [6].

3. Results

3.1. Morphology of scallops of Cu_6Sn_5

Fig. 3 shows the change in scallop morphology as a function of different SnPb solder composition. The observed Cu_6Sn_5 scallop morphology is summarized in Table 1. When the Pb content of the SnPb solder was >70 wt.%, faceted scallops were observed all over the sample, along with some round scallops. When the Pb content of the solder was within the range from 60 wt.% to eutectic composition (34 wt.%), only round scallops were observed. When the Pb content was further decreased <30 wt.%, again faceted scallops were observed together with some round scallops. Finally, when the solder became pure tin, only faceted scallops were observed.

For the eutectic SnPb solder, some samples showed only round scallops. However, in other samples, large clusters of faceted scallops were observed at the center of the solder cap. This also took place when the solder composition was 60Sn40Pb. The authors postulate that the composition where the transition of scallop morphology takes place is close to the 63Sn37Pb and, when a small piece (0.5 mg) is taken out from a solder chunk (~3 g), inhomogeneity of the solder chunk may cause a change in the composition in the small piece. To determine the accurate scallop morphology of the eutectic SnPb solder, solders with 80Sn20Pb, 50Sn50Pb, 30Sn70Pb and eutectic (63Sn37Pb) composition were reacted with copper at 0.5 °C above eutectic temperature (183.5 °C). The temperature control was within ±1 °C. In this way, the solders underwent partial melting, and the composition of the liquidus phase became very close to the eutectic composition. At 183.5 °C, the morphology of the scallops had a round shape, regardless of solder composition. Thus the true morphology of Cu_6Sn_5 scallops when the SnPb solder composition is eutectic was obtained: it is smooth round scallop morphology.

Classical theories on the formation of a faceted or rounded liquid–solid interface cannot be directly applied to the current case of IMC/liquid solder interface, because the classical models assume a solid–liquid interface during solidification at equilibrium temperature [7,8], whereas in soldering a reaction takes place. However, the general idea in classic theories is that, if the interface is faceted, the adatoms at the surface of the solid phase tend to fill nearly all the available surface sites before advancing to the next atomic layer, resulting in an atomically flat interface with a small number of kink sites. If the crystal surface is round, the interface is more or less atomically rough, possessing a large number of kink sites for surface adatoms. To have round-shaped scallops, scallops should have many atomic steps and kinks at the surface. Since steps and kinks have many broken bonds, scallops can afford more kinks and steps at the surface when the broken bond energy is low. The broken bond energy is low when the IMC/solder interfacial energy is low. The IMC/solder interfacial energy is related to the wetting angle between the solder and the copper. When the molten solder wets the copper, the copper surface is replaced by the IMC/solder interface. Thus the IMC/solder interfacial energy is low when the solder/copper wetting angle is low, because the molten solder will prefer to spread out to increase the IMC/solder interfacial area. Liu [9] investigated the effect of SnPb solder composition on the wetting angle of molten SnPb on Cu and found the lowest wetting angle when solder composition was slightly higher in Pb than the eutectic composition (~55 wt.% Pb). This is in agreement with the finding shown in Table 1 that scallops had a round shape near the eutectic composition.

3.2. Size distribution and growth kinetics of Cu_6Sn_5

As the scallop morphology showed a dependence on solder composition, the solder with 55Sn45Pb composition was selected to ensure round morphology of the scallops for size distribution analysis. Fig. 4 is a log–log data plot of average radius vs time, to check the consistency with Eq. (1). The linear fitting was done by the linear regression method, and the growth exponent was obtained from the slope. Originally, the measured growth exponent was 0.35. The standard deviations of normalized particle size $r/\langle r\rangle$, where r is the radius of individual scallops, and $\langle r\rangle$ is the average radius of the scallops, showed a very small amount of variation with reaction time (~0.4). However, there was one data point with an exceptionally large value (0.670). This point was eliminated because it was considered to be unreliable. After removing the unreliable data point, the measured growth exponent became 0.33, and the measured value of k was $2.10 \times 10^{-14}\ \mathrm{cm^3\ s^{-1}}$. The average standard deviation was 0.423, which was larger than the theoretical value (0.331). This resembles the typical situation when the LSW theory is compared with experiments (LSW predicts standard deviations of 0.215, while experiment usually gives values ~0.3).

The average scallop height was also measured from cross-sectional SEM images, as shown in Fig. 5. The growth exponent was 0.35, and k was $2.40 \times 10^{-2}\ \mathrm{\mu m^3\ s^{-1}}$. The particle size distributions (PSD) are shown in Fig. 6. The theoretical distributions $f(r/\langle r\rangle)$ are normalized to $\int f(y)\mathrm{d}y = 1$, where $\langle r\rangle$ is the average radius. The heights of the histogram bars were also normalized for comparison

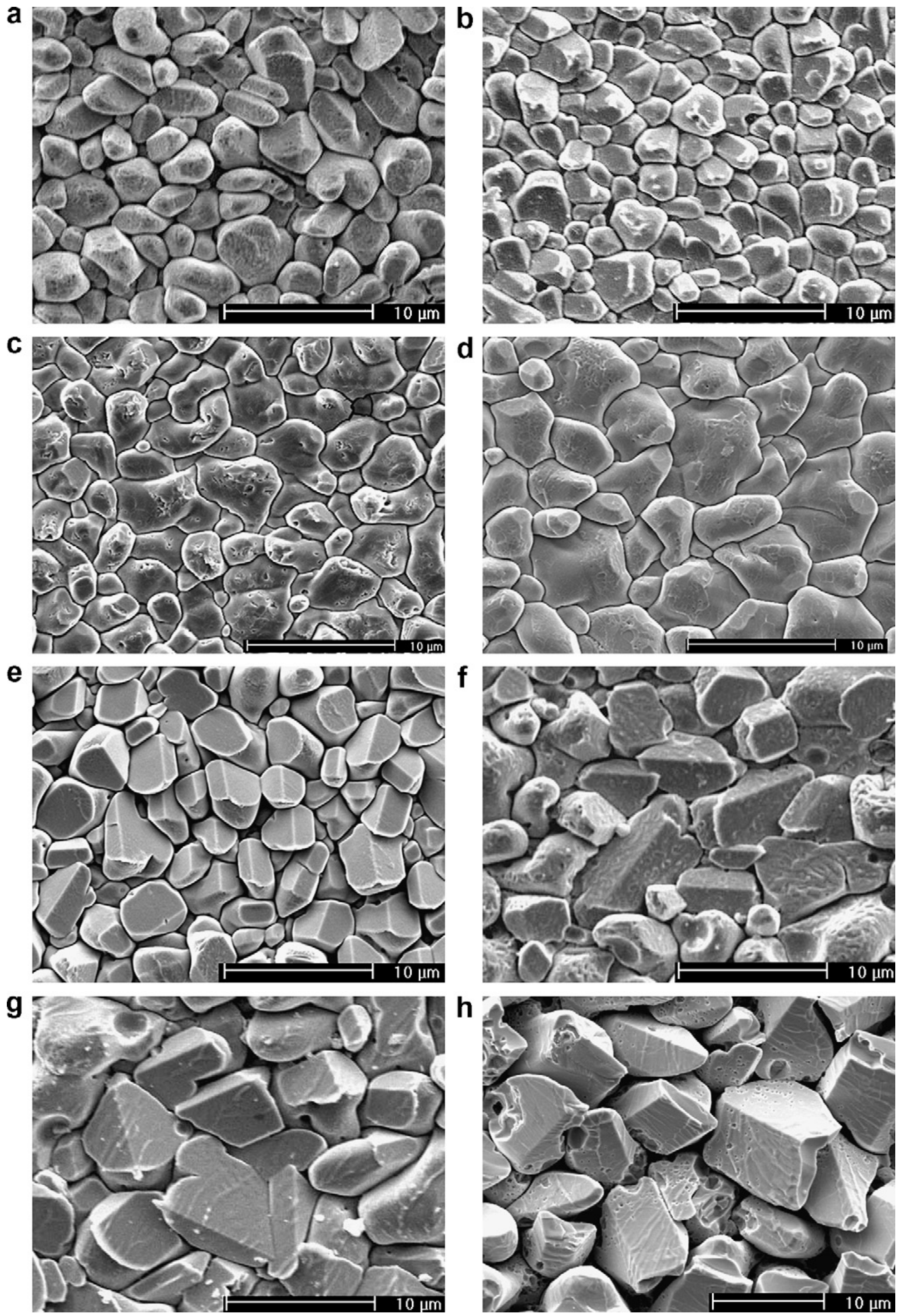

Fig. 3. SEM images of Cu_6Sn_5 IMC formed by wetting reaction with copper with solders: (a) 20Sn80Pb, (b) 30Sn70Pb, (c) 40Sn60Pb, (d) 50Sn50Pb, (e) 70Sn30Pb, (f) 80Sn20Pb, (g) 90Sn10Pb and (h) 100Sn.

Table 1
Summary of observed scallop morphology

Solder composition	20Sn80Pb	30Sn70Pb	40Sn60Pb	50Sn50Pb	55Sn45Pb	60Sn40Pb	63Sn37Pb	70Sn30Pb	80Sn20Pb	90Sn10Pb	100 Sn
Reaction temperature (°C)	295	275	255	235	200	200	200	210	225	240	250
Morphology	Facet	Facet	Round	Round	Round	Round	Round	Facet	Facet	Facet	Facet

Solders have reacted with copper for 2 min at 20 °C above their melting temperature.