Materials Chemistry and Physics 154 (2015) 60–65

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Solid-state reactions between Sn-20.0 wt.%In-*x* wt.%Zn solders and Ag and Ni substrates

Shih-kang Lin [a, b, c], Ru-Bo Chang [d], Sinn-wen Chen [d, *], Ming-yueh Tsai [a], Chia-ming Hsu [e]

[a] *Department of Materials Science and Engineering, National Cheng Kung University, Tainan 701, Taiwan*
[b] *Promotion Center for Global Materials Research, National Cheng Kung University, Tainan 701, Taiwan*
[c] *Center for Micro/Nano Science and Technology, National Cheng Kung University, Tainan 701, Taiwan*
[d] *Department of Chemical Engineering, National Tsing Hua University, Hsinchu 300, Taiwan*
[e] *Department of Chemical Engineering, National United University, Miaoli 360, Taiwan*

HIGHLIGHTS

- Sn–20In–xZn/Ag and Sn–20In–xZn/Ag interfacial reactions at 150 °C were investigated.
- Sn–20In–xZn/Ag reactions show strong dependence on Zn-doping levels.
- Ni_5Zn_{21} is the only product with a very slow growth rate in Sn–20In–xZn/Ni couples.
- Ni is an effective diffusion barrier for Sn–20In–xZn Pb-free solders.

ARTICLE INFO

Article history:
Received 3 January 2014
Received in revised form
14 December 2014
Accepted 14 January 2015
Available online 29 January 2015

Keywords:
A. electronic materials
A. interfaces
D. diffusion
D. phase transitions

ABSTRACT

The Sn-20 wt.%In (Sn–20In) alloy is a promising base material for low-temperature Pb-free solders. Zn is usually added in solders to reduce the extent of undercooling during reflow, while Ag and Ni are commonly seen under bump metallurgy in contact with solder in electronic products. In this study, solid-state reactions at 150 °C between Zn-doped Sn–20In solders and Ag and Ni substrates are investigated. In Sn–20In–*x*Zn/Ag couples, when the Zn-doping level is low ($x \leq 1.0$), the reaction path is γ-$InSn_4$/ζ-AgZn/ζ-(Ag,In)/ζ-AgZn/Ag, that the ζ-AgZn layer near the solder has non-uniform composition, the ζ-(Ag,In) layer has a porous microstructure, and the ζ-AgZn phase near the substrate is composed of small grains. When the Zn doping level is high ($x \geq 2.0$), the reaction path becomes γ-$InSn_4$/ε-$AgZn_3$/γ-Ag_5Zn_8/ζ-AgZn/Ag, that all intermetallic compounds (IMCs) are planar and neither Sn nor In participate in the reactions. Although the reactions are very sensitive to Zn contents, the overall thicknesses of IMCs do not vary much with different Zn-doping levels. In Sn–20In–*x*Zn/Ni couples, the planar Ni_5Zn_{21} phase is the only reaction product with a very slow growth rate. The interfacial liquation in Sn–20In/Ni contacts can be fully mitigated with a minor Zn addition of 0.5 wt.%.

1. Introduction

With the rapid developments of Pb-free solders and packaging technologies, soldering has been regarded as a critical step for forming interconnections in electronic products and has gained increasing attention [1–5]. At solder joints, intermetallic compound (IMC) formation, interfacial morphology evolution, and the growth kinetics of IMCs strongly affect the reliability of electronic products [3,6–8]. Therefore, information on interfacial reactions in various solder/substrate systems is of importance for assessing and improving joint properties. Sn–In alloys are base-materials for low melting-temperature soldering applications and their reactions with various substrates have been extensively investigated [9–28]. Among these Sn–In based solders, Sn–In–Zn solders are regarded as promising candidates [20–22], because minor addition of Zn can reduce the extent of undercooling during reflow process [29]. Ag and Ni are both commonly used substrates in under-bump metallurgy (UBM). However, only the reactions between molten Sn–In–Zn solders and Ag and Ni substrates have been reported in the literature [20]. In this study, the solid-state reactions at 150 °C between Sn-20 wt.%In-*x* wt.%Zn (Sn–20In–*x*Zn) solders and Ag and

* Corresponding author.
E-mail address: swchen@mx.nthu.edu.tw (S.-w. Chen).

http://dx.doi.org/10.1016/j.matchemphys.2015.01.045

Ni substrates were investigated. The doping effect of Zn on interfacial IMC formation, microstructural evolution, and kinetics of IMC growth are elucidated in the paper.

2. Experimental procedures

Sn–20In–xZn (x = 0.5, 1.0, 2.0, 3.0, and 5.0) alloys were prepared from pure Sn (99.98%, Showa, Japan), pure In (99.9%, Showa, Japan), and pure Zn (99.9%, Showa, Japan). Proper amounts of constituent elements were cleaned, precisely weighed, and encapsulated in quartz tubes under a 10^{-2} mbar vacuum. The capsules were annealed at 600 °C for a week to ensure homogeneity of alloys. After heat treatments, the capsules were quenched in icy water. The alloys were then sectioned into 2 g-weight ingots by a diamond saw. 500 μm-thick pure Ag foil (99.98%, Sigma-Aldrich, USA) and pure Ni foil (99.98%, Sigma-Aldrich, USA) were cut into 5 mm by 8 mm pieces and then metallographically ground and polished down to 0.3 μm Al_2O_3 powders. Each Ag or Ni substrate was coated with a thin layer of flux (water soluble, MEC-W-2326, MEC, Taiwan) and encapsulated together with the Sn–20In–xZn solder ingot in quartz tubes under a 10^{-2} mbar vacuum. The capsules were first reflowed at 230 °C for 30 s and quenched in icy water. Subsequently the samples were annealed at 150 °C for predetermined reaction times ranging from 50 h to 600 h. After reactions, the couples were also quenched and analyzed metallographically with a scanning electron microscope (SEM) (JEOL JSM5600, Tokyo, Japan). The compositions of the reaction phases were determined using electron probe microanalysis (EPMA) (JEOL JXA-8200SX, Tokyo, Japan). The thicknesses of the intermetallic compounds (IMCs) were measured with image-processing software (ImageJ, USA).

3. Results and discussion

3.1. Interfacial reactions in Sn–20In–xZn/Ag couples reacted at 150 °C

Fig. 1(a) shows the backscattered electron image (BEI) micrographs of the as-jointed Sn–20In–0.5Zn/Ag couple. A thin reaction layer can be observed in the as-jointed couple, which is presumed to be the ζ-(Ag,In) phase with 6 at %Zn formed during the reflow process at 230 °C according to compositional analysis and Chen et al. [20]. Fig. 1(b)–(d) shows the BEI micrographs of the Sn–20In–0.5Zn/Ag couples reacted at 150 °C for 50, 240, 480 h, respectively. Interestingly, irregular interfacial structures were developed after solid-state aging at 150 °C. As shown in Fig. 1(b), after a 50 h reaction, a porous reaction layer formed adjacent to the solder matrix (the γ-$InSn_4$ phase). Its composition was determined to be Ag-18.6 at %Zn-22.4 at %In using EPMA and it is presumed to be the ζ-(Ag,In) phase with 18.6 at %Zn. In addition, some dark phase regions can be found at the ζ-(Ag,In)/Ag interface, though they are too thin to be analyzed in the 50 h-reacted couple. With longer aging time of 240 h, as shown in Fig. 1(c), in addition to the porous ζ-(Ag,In) reaction layer and small dark phase regions at the ζ-(Ag,In)/Ag interface, large grains with non-uniform contrast under backscattered electron detector were formed at the γ-$InSn_4$/ζ-(Ag,In) interface. According to EPMA analyses, this non-uniform contrast originated from compositional difference. The compositions of the darker and brighter areas are Ag-37.0 at %Zn-13.0 at %In and Ag-33.5 at %Zn-15.0 at %In, respectively, and both are presumed to be the ζ-AgZn phase with some In content. After further prolonged reaction up to 480 h, as shown in Fig. 1(d), several microstructural changes can be found; i.e. the ζ-AgZn phase at the solder side became a continuous layer, the porous ζ-(Ag,In) grew thicker with loose structure at the solder side and dense structure at the Ag side, and the dark phase at the ζ-(Ag,In)/Ag interface grew thick enough so that its composition could be determined with confidence. The composition of the small dark phase regions is Ag-42.0 at %Zn-1.7 at %In and they are presumed to be the ζ-AgZn phase with 1.7 at %In. In summary, the reaction path across the Sn–20In–0.5Zn/Ag interface transferred from as-jointed γ-$InSn_4$/ζ-(Ag,In)/Ag to γ-$InSn_4$/ζ-AgZn/ζ-(Ag,In)/ζ-AgZn/Ag after solid-state aging at 150 °C where the ζ-AgZn phase at solder-side has higher In content and non-uniformed composition the ζ-(Ag,In) phase has a porous structure at the solder side and a dense structure at the Ag side, and the ζ-AgZn phase at the Ag side is smaller and has lower In content.

Fig. 2(a)–(d) shows the BEI micrographs of the as-jointed Sn–20In–1.0Zn/Ag couple, and the couples reacted 150 °C for 50, 120, 480 h, respectively. Similar microstructural developments can be found in Sn–20In–1.0Zn/Ag couples as in Sn–20In–0.5Zn/Ag couples. As shown in Fig. 2(a), a thin ζ-(Ag,In) phase with 15 at %Zn

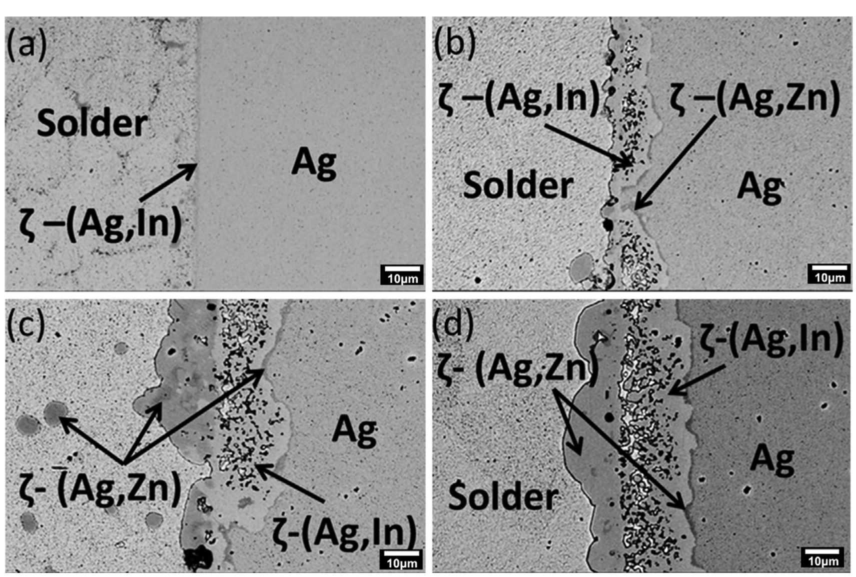

Fig. 1. BEI micrographs of the Sn-20In-0.5Zn/Ag couples reacted at 150 °C: (a) as-jointed (30 s at 230 °C), and for (b) 50 h, (c) 240 h, and (d) 480 h.