Journal of Alloys and Compounds 511 (2012) 176–188

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Intermetallic compound growth suppression at high temperature in SAC solders with Zn addition on Cu and Ni–P substrates

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ARTICLE INFO

Article history:
Received 14 July 2011
Received in revised form 7 September 2011
Accepted 8 September 2011
Available online 16 September 2011

Keywords:
Soldering
Lead-free solder
Intermetallic compounds
Sn–Ag–Cu alloys

ABSTRACT

The effect of adding 0.5–1.5 wt.% Zn to Sn–3.8Ag–0.7Cu (SAC) solder alloy during reflow and solid state ageing has been investigated. In particular, the role of the Zn addition in suppressing interfacial Intermetallic Compound (IMC) growth on Cu and Ni–P substrates has been determined. Solder–substrate couples were aged at 150 °C and 185 °C for 1000 h. In the case of 0.5–1.0 wt.% Zn on Cu substrate, Cu_3Sn IMC was significantly suppressed and the morphology of Cu_6Sn_5 grains was changed, leading to suppressed Cu_6Sn_5 growth. In the SAC–1.5Zn/Cu substrate system a Cu_5Zn_8 IMC layer nucleated at the interface followed by massive spalling of the layer into the solder, forming a barrier layer limiting Cu_6Sn_5 growth. On Ni–P substrates the $(Cu,Ni)_6Sn_5$ IMC growth rate was suppressed, the lowest growth rate being found in the SAC–1.5Zn/Ni–P system. In all cases the added Zn segregated to the interfacial IMCs so that Cu_6Sn_5 became $(Cu,Zn)_6Sn_5$ and $(Cu,Ni)_6Sn_5$ became $(Ni,Cu,Zn)_6Sn_5$. The effect of Zn concentration on undercooling, wetting angles and IMC composition changes during ageing are also tabulated, and a method of incorporating Zn into the solder during reflow without compromising solder paste reflow described.

1. Introduction

Interfacial reactions occur readily when a molten metal is in contact with a compatible solid metal (substrate). Such reactions involve interdiffusion between the liquid and solid metals and often result in the formation and growth of intermetallic compounds (IMCs) at the interface [1]. In this context, Pb–Sn alloys have been extensively studied and used for electronic interconnects. However, medical studies have shown that Pb is a heavy metal toxin that can damage the kidney, liver, blood, and the central nervous system [2]. Therefore, implementation of Sn-rich Pb-free solder manufacturing has become increasingly important in recent years due to the legislation to prohibit Pb in electronics products. Over the past two decades, considerable research has been carried out on Pb-free solders such as eutectic Sn–3.5Ag, Sn–0.7Cu, $Sn_xAg_yCu_z$ (SAC) and the IMCs formed with different substrates such as Cu, Ni, Ni–P during liquid and solid-state reaction [3–7]. From all these Sn-rich Pb-free solders, the SAC solder alloy has been identified as a promising candidate for electronics packages. However, many problems have been reported in SAC solder such as void formation in interfacial IMCs, higher IMC growth rates, spalling of interfacial IMCs during high temperature storage and large undercooling during solidification [8]. The problems become acute for high temperature applications when IMC growth rates accelerate.

During operation, electronic packages are usually subjected to a wide range of temperatures, especially in automotive, aerospace and traction industry applications. These components may experience temperature changes from −40 °C to 150 °C or even higher [9,10], driving IMC growth as a function of time and progressively converting ductile solder into brittle IMCs. This growth in solid-state is of particular technology concern, since it occurs continuously and may cause delayed and unpredictable problems.

The undercooling behaviour of Sn-rich Pb-free solders is also an issue, and the use of trace elements to reduce undercooling has been successful [11]. Previous research [11–14] suggests that the nucleation of β-Sn phases due to impurity elements, such as Zn, Co, and Fe reduces the undercooling of Sn-rich solder alloys. These various alloying elements also have major effects on solder/substrate reactions, as they are either soluble in the IMC layer (e.g., Ni, Au, Co, etc.), or form new interfacial IMC barrier layers (e.g., Fe, Al, P, etc.) [15]. Small additions of Zn into Pb-free solder have received much attention in comparison to the other alloying elements [8,14,16–19] because of: (i) significantly reduced undercooling, (ii) thinner and void-free IMCs at the interface. Despite the benefits of Zn, use of SAC + Zn solder alloy particles in the solder paste generally fails due to excessive oxidation of the particles resulting in incomplete particle coalescence during reflow. Other attempts to introduce Zn into the system during reflow of solder

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doi:10.1016/j.jallcom.2011.09.024

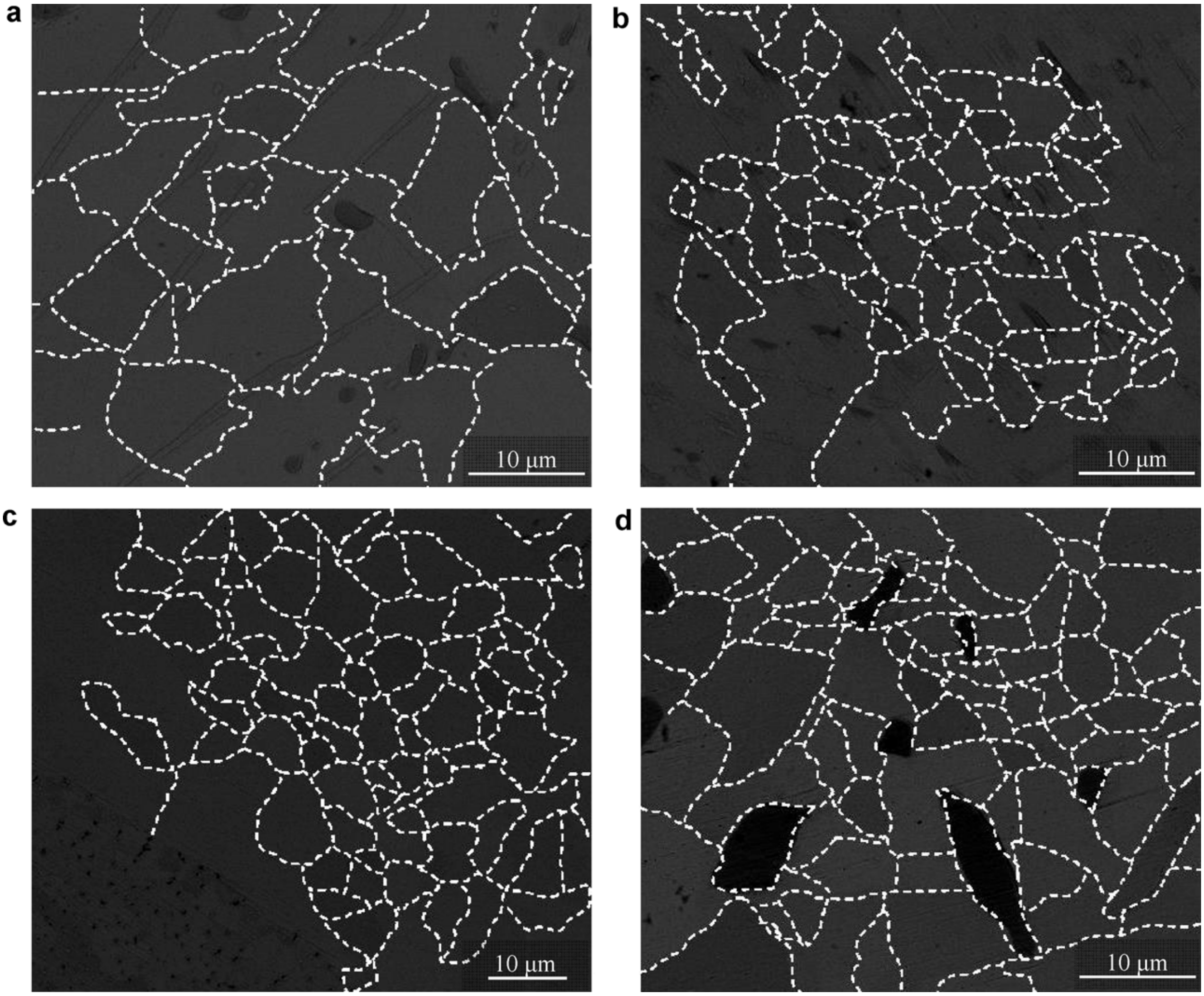

Fig. 1. SEM images showing the grain sizes in fabricated ingots of different solder alloys: (a) SAC, (b) SAC–0.5Zn, (c) SAC–1Zn, and (d) SAC–1.5Zn.

paste include the use of Cu–Zn substrates [20] and Zn compounds in the flux [21]. In this paper we extend the existing studies of IMC suppression to higher temperatures (150 °C and 185 °C) and increase understanding of the mechanism of IMC growth suppression. We also show that the mixing Zn particles in the 1–5 μm range into solder paste results in solder reflow and incorporation of Zn into the IMCs.

2. Experimental procedure

2.1. Alloy preparation

Sn–3.5Ag–0.7Cu (SAC) alloy was supplied by Henkel Ltd., UK. The SAC solder alloy with various amounts of Zn wt.% (0.5, 1, 1.5), subsequently referred to as SAC–0.5Zn, SAC–1Zn, and SAC–1.5Zn solder alloys, were fabricated in-house by dissolving the corresponding metallic foils at 420 °C for 20 min in a ceramic crucible using an electrical resistance furnace (all compositions in this article are given in weight percent unless otherwise stated). The fabricated ingot micrographs are shown in Fig. 1. There is no Zn segregation observed in any of the SAC–Zn solder ingots. Predetermined weights of solder were cut from the ingot and cleaned using acetone before soldering. The melting point and undercooling of solder alloys were measured by differential scanning calorimetry (DSC). The DSC experiment heating and cooling rate was fixed at 10 °C min^{-1} range from 25 °C to 250 °C. The undercooling (ΔT) is determined as the temperature difference between the melting point on the heating curve and the onset temperature of solidification on the cooling curve. DSC results are tabulated in Table 1.

2.2. Preparation of samples

Ni–P substrates were supplied by Schlumberger, Paris and consisted of Electroless Ni Immersion Gold (ENIG) bond pads on polyimide boards. The Cu substrates consisted of Cu coated FR4. The substrates were cut into 5 mm square plates with Cu thickness of 35 μm. Before reflowing, the substrate was cleaned using IPA (isopropyl alcohol), acetone and, finally, deionised water. For all of the alloys, 0.010 ± 0.003 g samples of solder alloy were cut from the solidified ingot, cleaned, coated by a thin layer of Henkel LF318 flux, and placed onto the substrate with a solder layer approximately 1.5 mm in maximum thickness and sent into a benchtop reflow oven (MRO

Table 1
Differential scanning calorimetry (DSC) test results for solder alloys.

Alloy composition (wt.%)	Onset melting temperature during heating (T_1) (°C)	Onset solidification temperature during cooling (T_2) (°C)	Undercooling $\Delta T = T_1 - T_2$ (°C)
Sn-3.8Ag–0.7Cu	217.73	199.89	17.84
(Sn-3.8Ag–0.7Cu)–0.5Zn	216.23	212.06	4.17
(Sn-3.8Ag–0.7Cu)–1Zn	216.65	212.61	4.04
(Sn-3.8Ag–0.7Cu)–1.5Zn	215.86	213.32	2.54