Journal of ELECTRONIC MATERIALS, Vol. 42, No. 2, 2013
DOI: 10.1007/s11664-012-2222-3
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Influence of Composition on the Morphology of Primary Cu_6Sn_5 in Sn-4Cu Alloys

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Alloys from the composition range Sn-(0.7 wt.% to 7.6 wt.%)Cu consist of primary Cu_6Sn_5 surrounded by a eutectic Sn-Cu_6Sn_5 mixture. The primary Cu_6Sn_5 intermetallics commonly adopt a coarse elongated morphology, which is not optimal for the mechanical properties of the soldered joint. This paper investigates the effect of trace elemental additions on the size and morphology of the primary Cu_6Sn_5 in Sn-4 wt.%Cu alloy with and without Ni additions. Elements investigated include ppm additions of Al, Ag, Ge, and Pb. It is shown that Al has a marked effect on the solder microstructure and refines the size of the primary Cu_6Sn_5, even at very low addition levels, in both binary Sn-Cu alloys and those containing additional Ni. The effect of Al is confirmed using real-time x-radiographic synchrotron observations of solidification.

Key words: Lead-free solder, Cu_6Sn_5, grain refinement, solidification, synchrotron

INTRODUCTION

Many Pb-free soldering alloys containing both Sn and Cu have a microstructure characterized by large volume fractions of Sn-Cu_6Sn_5 eutectic or eutectic variants containing these phases. In the composition range of 0.7 wt.% to 7.6 wt.% Cu the liquidus temperature increases from 227°C to 415°C, respectively, and solidification of the bulk alloy commences with the nucleation and growth of primary Cu_6Sn_5 intermetallic compounds (IMCs). However, it is generally accepted that large/coarse Cu_6Sn_5 IMCs have the potential to embrittle the microstructure and can be detrimental to the mechanical properties and reliability of the soldered joint.[1–3]

Cu_6Sn_5 is a relatively brittle phase in bulk solders, and interfacial solder–substrate IMCs often display visible cracking after thermal cycling.[4] This cracking can occur due to volumetric changes experienced during the polymorphic transformation between the hexagonal (high-temperature) and monoclinic (low temperature) Cu_6Sn_5 crystallographic variants,[5] which under equilibrium conditions, occurs at 186°C.[6] At practical cooling rates, hexagonal Cu_6Sn_5 is still present at room temperature but can undergo a transformation to monoclinic during typical service conditions.[7] At higher operating temperatures, this problem is compounded and polymorphic phase transformations become more likely unless prevented by the influence of additional elements known to stabilize the hexagonal phase, such as Ni[8] or Zn.[9]

Microstructural uniformity and stability have been identified as design goals for lead-free solder alloys to achieve a balance of mechanical properties under severe operating conditions.[1] As such, additions which promote refinement of Cu_6Sn_5, whether it is primary, eutectic, or interfacial, could help improve solder reliability. This is particularly true if these additions do not interfere with the stabilizing effect of elements that prevent the polymorphic Cu_6Sn_5 transformation. This paper investigates the effect of variations in composition on the solidification of primary Cu_6Sn_5 in Sn-4Cu alloy through the use of trace element additions of Al, Ag, Ge, and Pb. Following an assessment of the results, the effect of Al was investigated in more detail in both Sn-4Cu alloy and a similar commercial alloy (SN100C4;

(Received April 7, 2012; accepted August 2, 2012; published online September 5, 2012)