Enhancing the Ductility of Sn-Ag-Cu Lead-Free Solder Joints by Addition of Compliant Intermetallics

H.X. XIE¹ and N. CHAWLA^{1,2}

1.—Materials Science and Engineering, School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ 85287-6106, USA. 2.—e-mail: nchawla@asu.edu

Tin (Sn)-rich lead (Pb)-free solders containing rare-earth (RE) elements have been shown to exhibit desirable attributes of microstructural refinement and enhanced ductility relative to conventional Sn-3.9Ag-0.7Cu lead-free solder, due to the unique mechanical properties of RE-Sn intermetallics. However, the roles of soft intermetallic phase in the enhanced ductility of Pb-free solder still need to be further investigated. In this paper, Ca and Mn were selected as doping elements for Sn-Ag-Cu solder. The mechanical properties of Ca-Sn and Mn-Sn intermetallics as a function of indentation depth were measured by nanoindentation using the continuous stiffness method (CSM). The microstructure and mechanical properties of as-reflowed Ca- and Mn-containing Sn-Ag-Cu solder joints were studied and compared with those of conventional Sn-Ag-Cu and RE-containing solder joints. It is shown that soft intermetallics result in higher ductility in Pb-free solders.

Key words: Lead-free solder, intermetallic, Young's modulus, hardness, nanoindentation, calcium, manganese

INTRODUCTION

Due to increasing demands to find replacements for Pb-Sn solder,¹ a series of rare earth (RE)-doped lead (Pb)-free solder alloys have gained significant attention due to their superior physical and mechanical properties.²⁻⁴ Previous investigations have shown that adding RE elements can refine the microstructure of Pb-free solders,^{5–7} refine the intermetallic particle size, $^{8-10}$ reduce the melting temperature, 11,12 decrease the thickness of the intermetallic layer that forms between solder and substrate,^{5,13} improve wettability,^{4,12} and promote a strong bond to semicon-ductors.^{14,15} Enhanced electromigration resistance,¹⁶ good thermal stability,^{17,18} and reasonable oxidation resistance¹⁹ have also been shown. In particular, RE-doped lead-free solders have been reported to have excellent mechanical properties, i.e., increased strength^{20,21} and strain to failure,^{9,22,23} and improved creep resistance.^{24,2}

We have shown that Pb-free solder alloys containing small amounts of $La^{17,22}$ and $\check{C}e^{5,18,23}$ exhibit a significant enhancement in ductility, in comparison with conventional Sn-3.9Ag-0.7Cu (SAC) solder. The proposed mechanism for this is based on the soft RE-Sn intermetallics⁵ formed inside RE-containing Pb-free solders.²³ However, while experiments do show that RE-Sn intermetallics enhance the ductility of RE-containing solders, the precise mechanisms for this enhancement have not been studied in detail. To understand the relationship between soft intermetallic particles and enhanced ductility, it is necessary to conduct mechanical tests on solder alloys with soft and hard particles, to simulate the effect of adding RE-Sn intermetallics to the microstructure. It has been reported that small addition of Mn can form MnSn₂ phase in Sn-rich Pb-free solder with modulus and hardness values (143.9 \pm 1 GPa and 8.9 \pm 0.1 GPa. respectively) significantly higher than RE-Sn and other traditional intermetallics formed in Pb-free solder.²⁶ CaSn₃ is formed in Ca-containing Sn-rich alloys. More importantly, it has the same crystal structure as CeSn₃ and LaSn₃ (cubic, L12),²⁷ but

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