Effect of Zn Addition on Interfacial Reactions Between Sn-4Ag Solder and Ag Substrates

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In this study, the effect of Zn (Zn = 1 wt.%, 3 wt.%, and 7 wt.%) additions to Sn-4Ag solder reacting with Ag substrates was investigated under solid-state and liquid-state conditions. The composition and microstructure of the intermetallic compounds (IMCs) significantly changed due to the introduction of different Zn contents. In the case of Sn-4Ag solder with 1 wt.% Zn, a continuous Ag-Sn IMC layer formed on the Ag substrates; discontinuous Ag-Zn layers and Sn-rich regions formed on the Ag substrates under liquid-state conditions when the Sn-4Ag solders contained 3 wt.% and 7 wt.% Zn. If 3 wt.% Zn was added to Sn-4Ag solder, the Ag-Sn IMC would be transformed into a Ag-Zn IMC with increasing aging time. Rough interfaces between the IMCs and the Ag substrates were observed in Sn-4Ag-7Zn/Ag joints after reflowing at 260°C for 15 min; however, the interfaces between the IMCs and the Ag substrates became smooth for Sn-4Ag-1Zn/Ag and Sn-4Ag-3Zn/Ag joints. The nonparabolic growth mechanism of IMCs was probed in the Sn-4Ag-3Zn/Ag joints during liquid-state reaction, and can be attributed to the detachment of IMCs. On the other hand, the effect of gravity was also taken into account to explain the formation of IMCs at the three different interfaces (bottom, top, and vertical) during the reflow procedure.

Key words: Sn-Ag-Zn, lead-free solder, gravity, interfaces, intermetallic compounds

INTRODUCTION

Sn-Pb alloys have been used in electronic packaging for many years, however, lead and its alloys will be forbidden in many countries because of their toxicity, especially in electronic packaging. Therefore, it is an urgent task for electronic packaging and other fields to develop new lead-free solders to replace these conventional Sn-Pb solders.

At present, binary alloys, such as Sn-Ag, Sn-Cu and Sn-Bi, are important lead-free solders in electronic packaging. To further optimize the properties of these binary solders, Ag, Bi, Ni, and Cu are often added to these binary alloys. Recently, some researchers revealed that the addition of Zn can optimize the properties of solder joints. It was found that the presence of Zn in Sn-Ag solder often results in a significant improvement of the mechanical properties. For example, the tensile strength and elongation of Sn-3.3Ag-xZn (wt.%) solder were dramatically improved due to the introduction of Zn into Pb-10wt.%Sn alloy, which improves the high-temperature plasticity and refines the grain size. In addition, a small amount of Zn addition to a Sn-0.7Cu solder can refine the microstructure of the solders and retard the growth of an IMC layer. It was also found that the addition of Zn simultaneously improved the Vickers hardness, yield strength, and the ductility and restrained the formation of large Ag3Sn plates in a Pb-1.5Sb alloy.

On the other hand, Sn-Ag alloy is one of the good candidates to replace Sn-Pb solders because of its...
superior mechanical properties. As we know, the addition of Zn would improve the mechanical properties, so the ternary Sn-Ag-Zn phase diagram should be considered, as shown in Fig. 1. It is found that Ag-Zn IMCs will replace Ag-Sn IMCs during cooling and Ag-Zn particles tend to sediment in the lower region of the molten solder when using a low cooling rate. Song and Lin found that there were two peritectic transformations upon solidification for Sn-9Zn-Ag solders. And it is well known that Ag substrates have many superior properties, such as good conductivity, anti-oxidation, and wettability, which account for Ag substrates wide use in electronic packaging. A considerable number of researchers have focused on the interfacial reactions between Cu or Ni and lead-free solders. The effect of Cu addition on the interfacial reactions between Sn-9Zn and Ag substrates has also been investigated. However, there are limited data about the interfacial reactions between Sn-4Ag-xZn and Ag substrates. The main purpose of this study was to investigate the effect of Zn addition on the interfacial reactions between Sn-4Ag solder and Ag substrates.

**EXPERIMENTAL PROCEDURE**

In this study, Ag single crystals were used as substrates and three Sn-4Ag-xZn alloys (x = 1 wt.%, 3 wt.%, and 7 wt.%) were employed as solders. Firstly, a Ag single-crystal plate with dimensions of 40 mm x 80 mm x 10 mm was grown from Ag with a purity of 99.999% by the Bridgman method in a horizontal furnace. Secondly, the lead-free solders were prepared by melting high-purity (4N) tin, zinc, and silver in vacuum (<10⁻³ Pa) at 800°C for 30 min. The single-crystal Ag and the solders were cut and then ground with 800 grade, 1000 grade, and 2000 grade SiC papers and then carefully polished with 2.5 μm, 1.5 μm, and 0.5 μm polish pastes. They were then ultrasonically cleaned in ethanol for 10 min after polishing. In order to ensure that all the interfacial reactions were conducted under the same conditions, the three solders (about 0.5 g for each solder) were placed on different positions on a single-crystal Ag plate. Finally, the prepared samples were bonded in an oven with a constant temperature of 260°C for 15 min. One group of as-reflowed samples was isothermally aged at 160°C for 0 days, 2 days, 4 days, 7 days, and 11 days in order to study the IMC growth kinetics under the solid-state conditions. Another group of as-reflowed samples was isothermally aged at 260°C for various durations so as to reveal the IMC growth kinetics under liquid-state conditions. After solid- and liquid-state reactions, all the samples were observed with a LEO super35 scanning electron microscope (SEM) to detect the morphologies and thickness of the interfacial IMC layers. In order to decrease the error, both the integral area and the length of the IMC layers were measured using special software (SISC IAS V 8.0). The average thickness of the IMC layers can be calculated by using the following equation

\[ d = \int_{0}^{L_{0}} f(x) \, dx / L_{0}. \]  

where \( L_{0} \) is the length of the measured region, \( f(x) \) is the contour function of the IMC, and \( d \) is the average thickness of the IMC layer. To reveal the morphologies of the reactive phases between the Ag single crystal and the Sn-4Ag-xZn solders, some samples aged at 260°C for 22 h were deeply etched with 5% HCl + 3% HNO₃ + CH₃OH (v%) etchant solution to remove the excess Sn phase so that the reactive phases could be well exposed.

**EXPERIMENTAL RESULTS**

**Interfacial Reactions Between Sn-4Ag-1Zn and Ag**

Figure 2 shows interfacial morphologies of the couples under solid-state and liquid-state conditions after different periods. Under liquid-state conditions, there is only one IMC layer, which was detected as \( \text{Ag}_{72}\text{Sn}_{24}\text{Zn}_{4} \) (or \( \text{Ag}_{3}\text{Sn} \)) with energy-dispersive spectroscopy (EDS). Therefore, the reaction product of Sn-4Ag-1Zn and Ag is the same as that of Sn-4Ag and Ag. The reaction product of Sn-0.5Zn and Cu is the same as that of Sn and Cu too. Meanwhile, the interfaces become rougher with increasing aging time, as illustrated in Fig. 2 a–c, which is similar to previous results. However, the reaction products of the solid-state reaction are quite different from those of the liquid-state reaction; two IMC layers formed at the interface. One IMC layer is \( \text{Ag}_{58}\text{Sn}_{26}\text{Zn}_{16} \), and the second, gray layer (the inner Ag-Zn IMC layer) is \( \text{Ag}_{72}\text{Zn}_{24}\text{Sn}_{4} \) (Ag₃(Zn,Sn)). The thickness of the \( \text{Ag}_{72}\text{Zn}_{24}\text{Sn}_{4} \) layer remains unchanged with increasing aging time.