



Effect of Ti content and Y additions on oxidation behavior of SnAgTi solder and its application on dissimilar metals soldering



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ABSTRACT

Auger electron spectroscopy (AES) technology was utilized to investigate the oxidation behavior of SnAgTi solder by means of characterizing the chemical composition and the thickness of the oxide layer. The effect of Ti and Y elements on oxidation behavior was discussed. Cu and 1Cr18Ni9Ti was soldered with Sn4Ag2Ti0.5Y solder. The shear strength, the microstructure, and the composition of intermetallic compound phase of the soldered joint were measured. The result indicated that the oxide layer of SnAgTi solder mainly consisted of titanium oxide. A small amount of Y additions would further improve oxidation resistance because it could inhibit the oxidation of Ti in the molten solder and reduce the oxygen atoms entered into the solder. The composition of the oxide layer of Sn4Ag2Ti0.5Y solder was mainly Y_2O_3 and very little titanium oxide. The thickness of oxide layer and the depth of O containing layer became less with decreasing Ti content and adding Y element. The mechanical property and the microstructure of the Cu/1Cr18Ni9Ti soldered joint showed the good bonding between the parent metals and the solder. The study provides a fundamental understanding for the oxidation behavior of SnAgTi solder.

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1. Introduction

The solders provide the necessary electrical, mechanical, and thermal continuity in electronic assemblies. With the rapidly increasing needs of modern electronic components and devices with more features and higher power, the durability and reliability of solder joints are essential to the functionality and lifespan of an electronic product [1–3]. In the past decades, Tin–Lead (SnPb) alloys have been used extensively as joining materials for assembling and packaging because of their superior performance and low cost [4,5]. However, due to the environmental concern and impending legislation against Pb usage, the development and usage of Pb-free solder have been extensively increased, especially in the past 10 years [6,7]. Thousands of patents, papers concerning with Pb-free solders were authorized and published [8]. As the replacement of SnPb solder, the new Pb-free solders would be expected to perform equally well or better in most respects, such as melting point, wettability, thermomechanical properties, creep and fatigue performances etc. At present, various alloying elements have been studied, including Ag, Bi, Cd, Cu, In, Sb, Zn, Al [9–12]. Among them, SnAg alloy has emerged as one of the front runners to replace SnPb solders for its good wettability and mechanical properties [13–15]. In order to further improve its microstructure and properties, researches have been focused on the effects of adding minor alloying elements, such as Al, Bi, Co, Cu, In, Ni, Ti, Zn, and rare-earth (RE) elements into SnAg alloy [16–22].

Ti, as a special alloying element, has been added into SnAg alloy because Ti is a highly chemically active element and the atom has an incomplete d sub-shell, consequently it tends to react with other metals to form different intermetallic compounds in the alloying system. It was found that small amount of Ti additions in SnAg solder would not affect the melting point significantly, but could improve the bonding properties dramatically. Such SnAgTi solder is often considered as an active solder [23–25] for bonding of various metals including bonding of non-wettable materials, such as Ti, Al, Si, ceramics, glass, and graphite at low temperature (e.g. 250 °C) in air [26–29]. Based on thermodynamics, Tang et al. [25] investigated the effect of the activity of Ti on the interfacial reaction parameters of SnAgTi solder. The analysis indicated that the thermodynamic activity of Ti increased as Ti content increased from 0 to 2 wt.% at various Ag content in the alloys at 723 K. Chen et al. [26] recently reported that Ti additions to SnAg solders could effectively reduce the undercooling of solders, and therefore alter their microstructure by changing the solidification behavior. It is worth noting that SnAgTi solder has a very stable microstructure against extreme aging conditions. Wang et al. [27] Yu et al. [28] Tsao et al. [29, 30] and Kolenaka et al. [31] conducted the active soldering experiments of nonmetal (such as MAO 6061Al, Anodized 6061Al, MAO Ti, Al_2O_3 , and graphite etc.) using SnAgTi solder. Their studies focused on microstructure, activities, interfacial reactions, wettabilities, and mechanical properties of SnAgTi solder.

However, Ti is very easy to be oxidized, indicating SnAgTi solder is also easy to be oxidized. It has been reported that adding tiny amount of cerium could minimize the oxidation of SnAgTi solder [32]. Up to

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now, there are not enough reported experimental results to reveal the oxidation mechanism and how to control the oxidation of SnAgTi solder. In this work, we utilized Auger electron spectroscopy (AES) technology to investigate the oxidation mechanism of SnAgTi solder. The chemical compositions, the thickness of the oxide film, oxygen (O) concentration distribution were characterized and discussed. In addition, considering the much stronger affinity for oxygen than Ti, yttrium (Y) was proposed to be added in SnAgTi solder to prevent the oxidation of Ti. The solder was used to join the dissimilar metals to form Cu and 1Cr18Ni9Ti stainless steel joint, and the microstructure, elemental distribution and chemical composition of phases in the soldered zone were observed. This study provides a fundamental understanding of the oxidation mechanism of SnAgTi solder.

2. Experimental procedures

2.1. Oxidation behavior experiment

In this experiment, three solders of Sn–4.0 wt.%Ag–4.0 wt.%Ti (Sn4Ag4Ti), Sn–4.0 wt.%Ag–2.0 wt.%Ti (Sn4Ag2Ti), Sn–4.0 wt.%Ag–2.0 wt.%Ti–0.5 wt.%Y (Sn4Ag2Ti0.5Y) were prepared by vacuum arc melting. The base metal was annealed plates of commercial 6061Al alloy (Al specimen, wt.%: 0.28Cu, 0.61Si, 1.02 Mg, 0.20Cr, and the balance Al). The surface of 6061Al sheet was ground with silicon carbide grinding paper to 1200 grit, then cleaned with acetone. The solders were placed on the surface of polished 6061Al sheet followed by heating to 250 °C. After the solders melted, the pre-existed oxide film on the molten solders surface was crapped off following by the appearing of fresh molten solders. The samples were held at 250 °C for 80s. Then they were cooled down to room temperature and then ultrasonically cleaned.

In order to evaluate the oxidation behavior, chemical composition depth profiles of the heat-treated SnAgTi solders were analyzed by the Scanning Auger Nanoprobe (PHI-700, ULVAC-PHI Corporation) equipped with the coaxial field emission electron gun and Cylindrical Mirror Analyzer (CMA). The acceleration voltage of coaxial field emission electron gun used was 3 kV, and the ion gun was with 30° angle relative to the normal direction of samples. The chemical composition and the depth distribution of the treated SnAgTi solders were obtained through AES measurement with ion milling (sputtering).

2.2. Soldering of dissimilar metals

To show the application of the SnAgTi solder containing Y in the soldering of dissimilar metals, the fabricated Sn4Ag2Ti0.5Y alloy was selected as the solder to join Cu and 1Cr18Ni9Ti stainless steel. The size of the base metals sheets was 1 mm × 5 mm × 10 mm, and the size of Sn4Ag2Ti0.5Y solder foil was 0.5 mm × 5 mm × 10 mm. The soldering process was performed on the ultrasonic vibration soldering system as shown in Fig. 1. Before soldering, the surfaces of the two base metals and the solder foil were mechanically polished and then cleaned with acetone. The soldering process was as follows: 1) The Sn4Ag2Ti0.5Y solder was placed between Cu and 1Cr18Ni9Ti to form a lap specimen; 2) the lap specimen was heated to 250 °C in air; 3) the ultrasonic vibration soldering head with 5 W power at a frequency of 40 kHz was placed on the surface of the upper stainless steel surface to vibrate the molten solder for 20 s; 4) the molten solder wetted the base materials without flux, and filled into the gap between Cu and 1Cr18Ni9Ti sheets; 5) after the specimen was cooled down to the room temperature, the Cu/1Cr18Ni9Ti soldered joint was formed.

The Cu/1Cr18Ni9Ti soldered joint samples were cut, mounted, polished, and etched for cross-sectional microscopic evaluation. A scanning electron microscope (SEM, S-530, Hitachi Co.) equipped with energy dispersive X-ray spectroscopic analysis (EDS) and back scattering electron (BSE) detector was used to observe the microstructures and analyze the element distribution in the cross section of the soldered joint. EDS analysis and mapping were performed with an acceleration

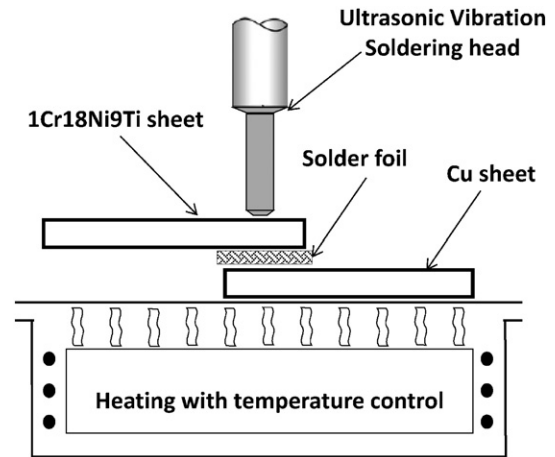


Fig. 1. Schematic diagram of ultrasonic vibration soldering system.

voltage of 20 kV. The microstructure and the chemical compositions of the soldered joint were determined by an electron probe micro-analyzer (EPMA, JXA8100, JEOL, Tokyo, Japan). The mechanical property of Cu/1Cr18Ni9Ti soldered joints was evaluated by shear testing at room temperature using a tensile testing machine (Instron) with a displacement rate of 2 mm/min.

3. Results and discussion

3.1. Composition analysis of Sn4Ag4Ti solder

Since the elemental identity and quantity of the detected elements in AES testing can be determined from the kinetic energy and intensity of an Auger peak, the concentrations of all elements in the surface of treated solders before and after ion milling (sputtering) can be measured.

Fig. 2 shows the chemical composition of the initial surface of the Sn4Ag4Ti solder. The elements of Sn, Ti, Ag, O and C were observed in the surfaces before sputtering. However, after sputtering, the O and C elements disappeared as shown in Fig. 3 suggesting that some oxides existed in the solder surface. It was further confirmed by the atomic concentration depth profiles as shown in Fig. 4.

In Fig. 4, the atomic concentrations of Sn, Ti, Ag and O were found to be 4%, 32%, 1%, and 63% on the initial surface, respectively. As the probing depth from Sn4Ag4Ti solder surface increased from 2 nm (1 min) to 22 nm (11 min), the atomic concentrations of Sn, Ag maintained the same levels without significant changes, while the Ti concentration increased from 32% to 42% and that of O decreased from 63% to 52%. It was clear that in the first sputtering period, O and Ti atoms held absolute majority in all the sputtered atoms, which suggested that titanium

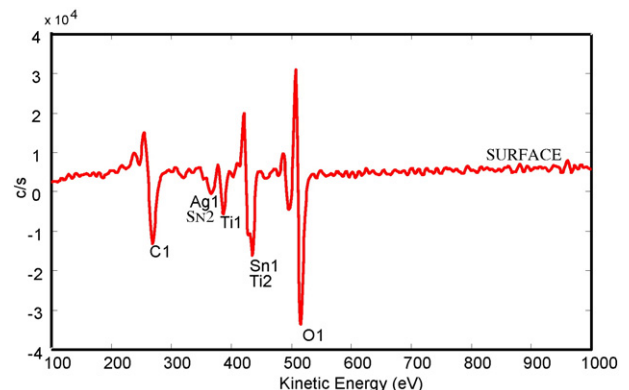


Fig. 2. The elemental mapping in the initial surface of the Sn4Ag4Ti solder.

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