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Corrosion behaviour assessment of lead-free Sn–Ag–M (M = In, Bi, Cu) solder alloys

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Abstract

The corrosion behaviour of lead-free $Sn_{88.7}Ag_{2.3}In_{9.0}$, $Sn_{86.6}Ag_{3.0}Bi_{10.4}$, $Sn_{96.1}Ag_{3.1}Cu_{0.8}$ and $Sn_{90.4}Ag_{2.9}Cu_{6.7}$ solder alloys was investigated in 0.1 M NaCl solution and compared with that of the conventional eutectic $Sn_{73.9}Pb_{26.1}$ solder. Scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were used to characterize the samples prior and after the electrochemical tests. Potentiodynamic polarization curves show that $Sn_{88.7}Ag_{2.3}In_{9.0}$ and $Sn_{86.6}Ag_{3.0}Bi_{10.4}$ solders exhibit poor corrosion behaviour compared to that of $Sn_{73.9}Pb_{26.1}$. On the contrary, copper addition enhances the corrosion resistance of Sn–Ag solder alloys which exhibit improved passivity behaviour compared to $Sn_{73.9}Pb_{26.1}$ solder. Moreover, increasing the copper content from 0.8 to 6.7 at% results in a significant improvement of the corrosion behaviour of Sn–Ag solders. The presence of tin oxychlorides were detected at the surface of all the alloys investigated after the electrochemical tests. In addition, indium oxychlorides were also observed in the $Sn_{88.7}Ag_{2.3}In_{9.0}$ solder alloy.

Keywords: Lead-free solders; Tin-based alloys; Corrosion behaviour; Polarization curves

1. Introduction

The development of lead-free solders has become an important task for material scientists due to health and environmental concerns regarding the high toxicity of lead. The European Community, the US EPA (Environmental Protection Agency) and Japan, as well as the electronic industries have launched initiatives for reducing lead usage [1–3]. The European Project COST Action 531 [4], which started on March 2002 and will finish by March 2007, has the main objective of increasing knowledge on the alloy systems that can be used as lead-free solders. In the framework of this European Project, our group has contributed to the study of thermodynamic properties of Bi–In–Sn alloys [5] and the wetting behaviour of lead-free Au–In–Sn and Bi–In–Sn alloys on copper substrates [6].

One of the initiatives is the replacement of Pb-bearing solders with Pb-free solders which is perceived to be environmentally friendly. However, it is highly desirable for the lead-free candidate solder to have a melting temperature similar to Sn–Pb solders, good wettability, low cost, adequate strength and good corrosion resistance [7,8]. Among the various alloy systems, Sn–Ag solder is one of the earliest commercially available lead-free solders which provides better mechanical properties than those of the eutectic Sn–37Pb solder [9,10]. However, the high melting temperature of Sn–3.5Ag (221 °C) has limited its application to electronic packaging, since current manufacturing technologies are based upon the eutectic temperature of Sn–Pb (183 °C). From the viewpoint of lowering the melting temperature and improving mechanical and wetting properties, attempts were made to achieve this by systematic additions to form ternary and higher order solder alloys [11–18]. The additions of bismuth, indium, and copper were used with Sn–Ag solder. The addition of copper can slightly depress the melting point of Sn–Ag-based solders and increase wetting behaviour [11,12,18]. The Bi and In additions further depressed the melting temperature of Sn–Ag-based lead-free solder alloys [15,18,19]. One advantage of adding Bi into Sn–Ag system solder is also the improvement of solder wetting/spreading behaviour [13,14]. Indium as an additional component was also investigated and the mechanical properties of Sn–2.8Ag–*x*In ($x = 10$, 20 wt%)

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were reported [15,18]. However, no literature is available on the effect of bismuth, indium, and copper on the corrosion resistance of Sn–Ag-based solders. The present study thus investigates the corrosion behaviour of Sn–Ag–Bi, Sn–Ag–Cu and Sn–Ag–In solder alloys by polarization measurements performed in chloride-containing environments. Scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were used to obtain information about the surface composition of alloys after the polarization tests.

2. Experimental

Ternary alloys of about 2 g were prepared by melting the stoichiometric amounts of pure elements (Sn and Ag, 99.999 mass% purity, both supplied by Newmet Koch, Waltham Abbey, England; Bi, In and Cu, 99.999 mass% purity, all supplied by Ma Teck GmbH, Julich, Germany) in alumina crucibles, in an induction furnace under argon flow. The samples, enclosed under vacuum in flame sealed silica ampoules, were annealed for one week at 200 °C in a resistance furnace and then air-cooled. The microstructure of the alloys was investigated prior to and after the electrochemical measurements; light optical microscopy (LOM), scanning electron microscopy, and electron probe microanalysis based on energy dispersive X-ray spectroscopy, were used to check the overall composition of the different samples and analyse the coexisting phases. The microstructure of the alloys was investigated after preparing smooth surfaces of the specimen; the compositional contrast between the various phases was observed by means of a back-scattered electron detector (BSE). For quantitative EPMA, the samples were analysed at 20 kV acceleration voltage using cobalt as standard for calibration of the beam current, gain and resolution of the spectrometer. Finally, the X-ray intensities were corrected for ZAF effects using pure elements as standards.

Potentiodynamic polarization measurements were carried out in a single compartment cell using a standard three-electrode configuration: saturated calomel electrode (SCE) as a reference with a platinum electrode as counter and a sample as the working electrode. The surface area exposed to the test solution was 0.5 cm^2. The specimens were given a metallographic polishing prior to each experiment, followed by washing with distilled water and acetone. All the experiments were performed in aerated 0.1 M NaCl solution at room temperature (25 ± 0.1 °C). Potentiodynamic polarization curves were recorded in the potential range −1000 ÷ +250 mV versus SCE reference electrode at a scan rate of 0.5 mV s^{-1}, after allowing a steady-state potential to develop. IR drop compensation was achieved using current interruption method. All measurements were carried out employing an Amel System 5000 potentiostat controlled by a personal computer. For the sake of comparison, the polarization tests were also performed on the $Sn_{73.9}Pb_{26.1}$ eutectic alloy. Scanning electron microscopy and electron probe microanalysis were used to investigate the morphology and chemical composition of the alloy surface after the electrochemical tests.

3. Results and discussion

The nominal compositions of the lead-free solder alloys and the structural and compositional data obtained by EPMA of the phases observed are reported in Table 1.

Since the Sn-rich Sn–Ag–Cu alloys are considered to be among the best lead-free alloy systems, many studies have been made on their properties, microstructure, and on the effects of the formation of intermetallic compounds on their mechanical characteristics [18,20–22]. The evolution of lead-free solder microstructure with thermal treatment (annealing conditions and cooling rate) has been also studied [23,24].

Generally in these Sn–Ag–Cu alloys, having a near eutectic composition, we can observe the coexistence of three phases: βSn, ε phase Ag_3Sn and η phase Cu_6Sn_5.

Table 1
Microanalysis and crystallographic data of the alloys investigated

Alloy nominal composition (at%)	Phases analysis	Composition from EPMA (at%)	Structural type
$Sn_{96.1}Ag_{3.1}Cu_{0.8}$	(βSn)	$Sn_{99.7}Cu_{0.30}$	tI4–βSn
	η (Cu_6Sn_5)	$Cu_{54.2}Sn_{45.8}$	hP4–NiAs
	ε (Ag_3Sn)	$Ag_{73.8}Sn_{25.5}Cu_{0.7}$	oP8–β Cu_3Ti
$Sn_{90.4}Ag_{2.9}Cu_{6.7}$	(βSn)	$Sn_{99.8}Cu_{0.20}$	tI4–βSn
	η (Cu_6Sn_5)	$Cu_{54.5}Sn_{45.5}$	hP4–NiAs
	ε (Ag_3Sn)	$Ag_{74}Sn_{26}$	oP8–β Cu_3Ti
$Sn_{88.7}Ag_{2.3}In_{9.0}$	γ (Sn–In)	$Sn_{88.5}In_{11.5}$	hP5
	ζ (Ag–In)	$Ag_{70.4}In_{27.2}Sn_{2.4}$	hP*
$Sn_{86.6}Ag_{3.0}Bi_{10.4}$	(βSn)	$Sn_{98.5}Bi_{1.5}$	tI4–βSn
	(Bi)	$Bi_{93.6}Sn_{6.1}Ag_{0.3}$	hR2–α As
	ε (Ag_3Sn)	$Ag_{74.3}Sn_{25.7}$	oP8–β Cu_3Ti

The SEM micrograph of the $Sn_{96.1}Ag_{3.1}Cu_{0.8}$ alloy is reported in Fig. 1. The sample presents a typical three-phase appearance with a matrix of βSn where Cu_6Sn_5 (black crystals) andAg_3Sn (grey crystals with needle shape) are dispersed. The observed solubility of Ag in the η phase and of Cu in the ε phase are very small, likewise for the Cu and Ag solubility in Sn, in agreement with [25].

The microstructure of the $Sn_{90.4}Ag_{2.9}Cu_{6.7}$ alloy is shown in Fig. 2. We can see in this sample the matrix of βSn where many large crystals (black) of η phase Cu_6Sn_5 are precipitated and a few Ag_3Sn particles very finely dispersed in the matrix, similar to what was observed by [10].

The effects of indium on the microstructure and mechanical properties of Sn–Ag–In lead-free alloys have been reported by [15] and [18]. The SEM micrograph of the ternary $Sn_{88.7}Ag_{2.3}In_{9.0}$ alloy is reported in Fig. 3. The microstruc-

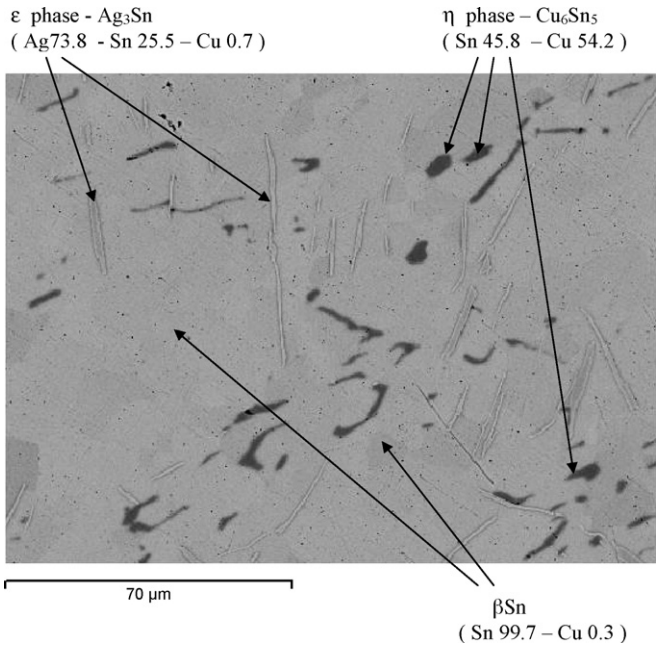

Fig. 1. SEM–BSE micrograph of the $Sn_{96.1}Ag_{3.1}Cu_{0.8}$ solder alloy. Grey phase (matrix): βSn; black crystals: η phase (Cu_6Sn_5); grey elongated crystals: ε phase (Ag_3Sn). The compositions of the phases (at%) are obtained by EPMA.