



Characterization of the microstructure of tin-silver lead free solder



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ABSTRACT

Reliability and lifetime are the two most relevant design considerations in the production of safety critical assemblies. For example in a modern automobile dozens of electronic assemblies are integrated in which thousands of solder joints are mounting the electronic components to the printed circuit boards. There exists no standardised and universal observation method for characterising the fine microstructure of such solder joints. Previously we have developed a new method for the quantitative characterization of lead-free solder alloys and in present study the validity of the proposed method is demonstrated. Microstructure of Sn-3.5Ag lead free solder alloy was investigated by electrochemical impedance spectroscopy. Solder samples were solidified with different cooling rates in order to induce differences in the microstructure. Microstructure of the ingots was revealed by selective electrochemical etching. Electrochemical impedance spectra (EIS) were measured before and after the selective etching process. The complex impedance spectra contain information about microstructure of the solder alloys. Comparison and modelling of two EIS spectra allowed obtaining a characteristic parameter of surface structure of the etched specimens. The EIS measurements were complemented with small angle neutron scattering measurements and scanning electron microscopy, in order to correlate the EIS parameter with the magnitude of the interface of the β -Sn and Ag_3Sn phases.

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1. Introduction

Lead, being one of the most hazardous substances, has been banned from the electronic industry due to environmental considerations. This initiative has led to the development of new lead free solders for electronic applications [1–5]. All of these solders are Sn based materials with some minor composing elements [6,7]. Nowadays, excellent lead free solder alloys are available on the market, which satisfy the rigorous technical and operational requirements. SnAg (SA) and SnAgCu (SAC) alloys are considered to be the best substitutions for lead containing solders. In these solders Sn-rich dendritic/grainy matrix is formed, and an eutectic mixture of a Sn-rich phase and intermetallic Ag_3Sn particles are located in the interdendritic regions. The fine microstructure of Sn grains and intermetallic compounds (IMC) may be formed differently in function of soldering parameters. Since the macroscopic

properties of the solder joints are largely determined by the microstructure, its characterization is a current research topic.

During the lifetime of electrical assemblies the physical parameters of solder joint may change because of environmental effects. One of the most important processes that influences the solder joint, is the corrosion. This is the reason why the corrosion properties of any solder alloy are in the centre of interest [8–13]. For revealing corrosion properties of the lead free solder alloys, electrochemical methods are usually applied. Osório et al. applied different electrochemical measurements in order to find the correlation between microstructure and corrosion properties of solder alloys [8–10]. The electrochemical corrosion behaviour of Sn–Cu alloy samples was evaluated by electrochemical impedance spectroscopy (EIS) combined with potentiodynamic polarization. According to their results, the impedance response of different samples showed correlation with the microstructure. Independently from the measured electrochemical impedance spectra the examined Sn–Cu solder alloy samples had similar electrochemical corrosion properties, however this was not the case for the

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electrochemical corrosion behaviour of a Sn–Ag solder alloy. The directionally solidified solder samples inherited different microstructure morphologies, which were evaluated also by EIS. For higher cooling rates finer dendritic arrays and mixture of spheroids and fibre-like Ag_3Sn particles were found, which resulted in better corrosion resistance. The EIS measurement results of Osório et al. were in good correlation with their metallographic observations. Their method however is valid only for directionally solidified samples, and it cannot be used to study solder samples of industrial origin. Furthermore, they applied a selective chemical reagent to reveal the microstructure of their samples, but the level of selectivity could not be guaranteed due to the endothermic nature of the reaction. These limitations can be overcome by the improved characterization method proposed in the present work.

Conventional metallographic observation methods e.g. cross sectioning, provide only a restricted view on the structure of the solder joint. Our novel, recently published method of selective electrochemical etching [14,15], reveals the intermetallic structure of bulk solder and opens a new perspective in solder joint research. Due to the high selectivity of etching, the fine structure of intermetallic compounds is only slightly changed, therefore the original solder structure is revealed.

Previously we found that varying the technological processing conditions – for example the cooling rates – different solder microstructures developed [15]. The utility for qualitatively characterize the microstructure is already introduced and in the present study we propose an industrially applicable method, suited for quantitative characterization of different microstructures.

EIS is very sensitive to the geometry of the working electrodes [16], therefore it was successfully utilized to characterize the roughness of surfaces [17] and even to determine the pore size and shape in the case of porous electrodes [18–20]. Electrochemical etching forms complex surface determined by the microstructure of samples depending on the etching time. While there is no unequivocal relation between EIS characteristics and microstructure, it is safe to presume that the EIS response curves change in a continuous manner upon the variation of a certain parameter of the microstructure, or of the process in which the microstructure is formed. Determination of this relation would allow the usage of the EIS for quantitative characterization of the alloys microstructure.

For this purpose a series of casted solder alloys was prepared by varying the cooling rate and the EIS spectra measured before and after the etching process were compared. The electrochemical behaviour of the samples correlates with the processing parameters and this relation can be used to construct an indicator describing the microstructure.

2. Materials and methods

2.1. Sample preparation

A commercial, industrial grade solder alloy (ALPHA Vaculoy) of material composition Sn 96%, Ag 3.5% and Cu < 0.05% was used. The solder paste was heated up to 260 °C in a thermo resistant test tube in order to separate the metallic and non-metallic phases of the paste. After solidification of the solder ingot, the major part of the still liquid flux was removed and the ingots were grinded and weighed (32 g).

The solder ingots were molten again in a hot air reflow rework station and heated up to the temperature of 260 °C. Molten sample was immersed into a defined volume of tempered Galden liquid. After solidification of the solder, disc shaped samples were cut from the ingot for further analysis (see Fig. 1). Temperature of the solder was monitored with a thermocouple sensor connected to a data logger.

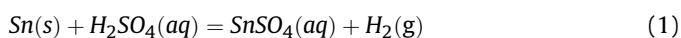
The sliced solder ingots were cold contacted with a measuring wire and they were embedded into a two component acrylic resin. The samples were rasped in a way that the size of their surfaces at the cross sectioning plane was approximately the same. The surface ratios of different samples can be seen in Table 1. The surface of the samples was finished with diamond suspension polishing.

Embedded and sectioned samples were placed in an electrochemical cell in which the selective etching and also the electrochemical measurements were performed.

2.2. Electrochemical methods

The electrochemical measurement of the samples consisted of three major steps. 1) Reference EIS measurement on the polished samples in 0.5 M NaCl solution; 2) β -Sn phase removal with selective electrochemical etching in 1 V/V% H_2SO_4 electrolyte; 3) EIS measurement on the etched samples, again in 0.5 M NaCl solution. These measurements were done in a standard three electrode measurement cell configuration, with the samples connected as working electrodes against a stainless steel basin counter electrode and saturated calomel (SCE) reference electrode with a Voltalab PGZ 301 potentiostat. During the measurements the samples were placed to a custom-made electrochemical cell-holder, fixed at 12 mm from the bottom of the stainless steel basin acting as the counter electrode. Only the electrolytes were changed between the three main measurement steps.

The selective removal of the β -Sn phase is possible due to the distinct redox potentials of the β -Sn and Ag_3Sn phases in the applied 1 V/V% H_2SO_4 electrolyte. The etching was done in chronoamperometry mode, where a fixed DV potential of –350 mV vs. SCE was applied for a given time and the resulting current was monitored. The etching time was chosen to be proportional to the surface area of samples and varied between 120 and 160 s (see the surface ratios in Table 1). The applied DC potential only etches the β -Sn phase (based on Eq. (1)), while it is not enough to remove the Ag_3Sn intermetallic compounds, which are hence left intact (Fig. 2).



During EIS a small amplitude alternating voltage (in our case a 10 mV peak-to-peak sine voltage) is applied on the working electrode at a fixed DC bias, and the resulting current is measured in function of the frequency (usually between 1 Hz and 50 kHz). The complex impedance of the system can be calculated from the measured current and the drive voltage and it characterizes the electrochemical behaviour of the cell. To qualitatively and quantitatively evaluate this behaviour various network models can be fitted on the measured impedance spectra, where the network elements represent the physical processes, which take place in the cell, more specifically on the surface of the working electrode. In the absence of Faradic processes (which cause electron flow from or to the working electrode, such as redox interactions) the simplest model which can be applied on the working electrode is a simple capacitor (representing the double layer capacitance, C_{dl}) which is charged and discharged with the applied alternating voltage. In practice the model is often extended with a serial resistance (representing the Ohmic resistance of the electrode (R_s) and the electrolyte) and a parallel resistance (representing the polarisation resistance of electrode (R_p) or the charge transfer resistance (R_{ct}) for the cases when Faradic processes also occur). To guarantee, that no Faradic charge transfer would take place during our EIS measurements – as a result of the 10 mV AC measurement signal – a negative DC bias of –700 mV vs. SCE was applied, which is around 150 mV lower than the measured open circuit potential (OCP, also named zero current potential, which was around –550 mV vs. SCE).

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