



Electrochemical corrosion behavior of CeO₂ nanoparticle reinforced Sn–Ag based lead free nanocomposite solders in 3.5 wt.% NaCl bath



Ashutosh Sharma, Siddhartha Das, Karabi Das*

Department of Metallurgical and Materials Engineering, Indian Institute of Technology Kharagpur, Kharagpur 721302, India

ARTICLE INFO

Article history:

Received 3 May 2014

Accepted in revised form 9 November 2014

Available online 18 November 2014

Keywords:

Alloy
Metal matrix composites
Polarization
SEM
Electrodeposited films
Anodic dissolution

ABSTRACT

The corrosion behavior of lead free Sn–3.5Ag and Sn–3.5Ag alloy reinforced with different amounts of CeO₂ nanoparticles is investigated in 3.5 wt.% NaCl solution. Polarization and electrochemical impedance studies reveal that the corrosion current density (i_{corr}), the corrosion potential (E_{corr}), and double layer capacitance (C_{dl}) decrease, while the charge transfer (R_{ct})/polarization resistance (R_{p}) increase with the incorporation of CeO₂ nanoparticles (up to an optimum of ~12 wt.% of CeO₂ nanoparticles). The corrosion product, SnCl₂ is detected on the surface of Sn–Ag alloy which is coarse and loosely adherent to the surface, while Sn–Ag/CeO₂ possess finer corrosion products intact to the surface and thus increases passivity.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Lead-bearing solders are consistently in use for a relatively long time. However, the increased health concerns over the use of lead combined with strict legislations have enforced the fabrication of lead free solders. Therefore, a relatively large number of Pb-free solder alloys have been proposed, Sn being the primary or major constituent. The two other secondary elements that are used excessively with Sn are In and Bi. Other minor alloying elements are Zn, Ag, Sb, Cu, and Mg [1–3]. The most popular Pb free alloy system candidates are listed in a thorough review paper by Abtey and Selvaduray [3]. Although there are several advantages of Pb free solders over conventional Sn–Pb solders, yet they have some specific disadvantages [4,5]. The interfacial reaction of these solders with the substrates (Cu, Ni etc.) and thus the formation of several intermetallic compounds (IMCs) e.g., Cu₆Sn₅, Ag₃Sn and Cu₃Sn should be checked before they are actually used in practice. The situation becomes more severe when these solders are exposed to corrosive media/environment. This may change the micro-structure of corroded regions and degrade the reliability of solder joints by providing a crack initialization. In the case of marine applications, chloride compounds from sea water may react with the solder alloys and form soluble tin corroded products, which may corrode the solder joints and cause malfunction of electronic devices [6,7]. The residual salt deposits combined with humidity may also promote the accelerated deterioration of solders [8]. Failure may occur as a leakage through

corroded solder joints. Improper soldering (e.g., flux residue and gaps between soldered parts) can also severely enhance the corrosion process. Therefore, understanding of corrosion behavior of solders in marine environment is needed for the design and material selection for naval and defense electronics. There are a number of reports on the development of lead free nanocomposite solders where the interfacial reactions are minimized by reinforcing the solder with various nanoparticles [9–11]. However, limited information is available on the corrosion resistance of solder alloys and composites [12,13]. It has been found already that lead free solders exhibit better corrosion resistance as compared to Sn–Pb solders due to their lower passivation current density, lower corrosion current density and higher polarization resistance due to the formation of a highly passivated layer on the surface [14]. Recently, there are few notable reports on the corrosion behavior of metal matrix nanocomposites where nanoparticles are shown to increase the passivity of the matrix [15,16].

The present study is devoted to the corrosion behavior of eutectic Sn–Ag alloy and Sn–Ag composite reinforced with CeO₂ nanoparticles in 3.5 wt.% NaCl solution at room temperature. These observations may set a new direction in the development of the lead free solders when used in harsh marine applications.

2. Experimental details

2.1. Synthesis of composites

2.1.1. Materials

The details of the synthesis procedure of these composites can be found in our previous paper [10]. The materials selected for the

* Corresponding author. Tel.: +91 9868054950; fax: +91 3222 220 666, +91 3222 255 303.
E-mail address: stannum.ashu@gmail.com (A. Sharma).

electrodeposition are an electrolytic grade Sn plate with 99.95% purity as the anode and the cold rolled copper plate as the cathode. Nano-sized CeO₂ (20–30 nm) powder, prepared by means of High Energy Ball Milling (HEBM), is used as the reinforcement with varying concentrations.

2.1.2. Plating bath preparation

The electrolytic bath consists of tin(II) chloride (SnCl₂·2H₂O), tri-ammonium citrate (HOC (CO₂NH₄) (CH₂CO₂NH₄)₂), silver nitrate (AgNO₃), Thiourea and Triton X (C₁₄H₂₂O (C₂H₄O)_n) as a non-ionic surfactant. First of all, plating bath is prepared using a solution of 100 g of tri-ammonium citrate and 50 g of SnCl₂·2H₂O is dissolved in 1 l of deionized water. After that AgNO₃ is added in amount of 0.24 g/l of solution while thiourea is added as a complexing agent of silver to the solution. Ceria nanoparticles are added to the electrolyte for synthesis of nanocomposites. Triton X-100 is also added in the amount of 0.1 g/L in the plating bath which helps in dispersing the ceria nanoparticles in electrolyte. The solution is stirred and forms a clear solution after complete dissolution. The pH of the prepared bath is maintained at ~4. The monolithic as well as composites are synthesized from electrolyte containing varying concentrations of CeO₂ nanoparticles (0, 1, 2, 5, 10, 15, 20, 25 and 30 g/L). The corresponding deposited samples are designated as D0, D1, D2, D5, D10, D15, D20, D25 and D30.

2.1.3. Electroplating cell

The electrochemical cell consists of a tin plate as anode (99.8% pure, Merck) and a copper plate as cathode (polished and ultrasonically cleaned). They are kept parallel by a distance of separation of 3 cm. The whole assembly is immersed in a 500 mL beaker containing electrolytic solution at room temperature (≈ 28 °C).

2.1.4. Electroplating experiment

Pulse currents are supplied by Autolab PGSTAT with a peak current density of 0.2 A/cm². The deposition is carried out on a copper substrate with an exposed area of 6 cm². Tin plate is used as an anode. The deposited films are stripped off from the copper cathode under a running stream of water and washed with alcohol and dried in air before the evaluation of properties. In an effort to optimize the pulse parameters, a combination of different pulse on and off times is used and the quality of the obtained tin deposits (i.e., surface morphology, roughness) is carefully examined. The optimized pulse on-time (t_{on}) and pulse off-time (T_{off}) are kept constant at 0.001 and 0.01 s, respectively. The frequency is kept constant at 90 Hz. The electrolytic bath containing the CeO₂ particles is agitated continuously using a magnetic stirrer rotating at 300 rpm in order to keep the nanoparticles in suspension during the deposition process.

2.1.5. Structural characterization

The structure of the monolithic and composite samples is studied by a Bruker's D8 Advance X-ray diffraction (XRD) machine and the morphology of the samples are observed using a Carl Zeiss Supra 40 scanning electron microscope (SEM), and the compositional analysis is done by the energy dispersive spectroscope (EDS) attached with the SEM machine. The line profile analysis of the composites is also performed across the cross section of the sample using the EDS.

2.2. Corrosion Investigation experiments

2.2.1. Potentiodynamic polarization method – Tafel plot

Autolab PGSTAT 302N is used for corrosion measurements which can generate DC current waveform pulses up to 10 A. Experiments are conducted using the standard three electrode cell configuration with a platinum rod as a counter electrode, Ag/AgCl (1 M KCl) electrode as a reference electrode, and the sample as a working electrode. The surface area of the examined specimens exposed to corrosive medium is about 1 cm². A 3.5 wt.% NaCl aqueous solution with a measured pH of ~6.4 is

chosen as a corrosive medium. The sample is immersed in the corrosive medium for 30 min to attain steady state potential or open circuit potential (OCP). After attaining a stable OCP, the measurements are carried out by potentiodynamic polarization measurements from –1500 mV to +500 mV with respect to E_{corr}, at a scan rate and of 1 mV/s and step potential of 0.45 mV.

2.2.2. Electrochemical impedance spectroscopy (EIS)

The same three-electrode cell assembly and the instrument are used for the AC impedance measurements. The tin plated square samples are used as working electrode and the NaCl solution (3.5 wt.%) is used as the test solution. An excitation voltage of 10 mV (peak to peak) and an applied frequency ranging from 100 kHz to 10 mHz have been used. All the potential values in the text are relative to the 1 M KCl Ag/AgCl electrode. The values of solution resistance (R_s), double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) are obtained from Nyquist plots of the real (Z') versus imaginary (–Z'') components of the impedance. EIS measurements are conducted from –800 to +800 mV at room temperature. At least three samples were tested for each testing condition.

2.2.3. Corrosion rate

After the corrosion tests, the samples are cleaned with alcohol, dried in air and the surface morphology and composition of the corroded samples are examined. Corrosion rate is calculated by the Stern Geary relation embedded in the software program (General Purpose Electrochemical System, GPES, Eco Chemie module, version 4.9). In order to supply quantitative support for discussions of these experimental EIS results, Nova software module, 2.0 Version is used for equivalent circuit quantification.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the X-ray diffraction (XRD) patterns of as-deposited Sn–Ag alloy and Sn–Ag/CeO₂ nanocomposite coatings. The XRD pattern of nanocomposite coatings shows the presence of CeO₂ (111) peak which confirms the incorporation of CeO₂ in the coating. The peaks of Ag₃Sn intermetallic compound are also observed in all the samples. S. Ahat and his co-workers have also reported the presence of Ag₃Sn in a Sn–3.5Ag solder alloy, which improves the strength [17].

3.2. Microstructural investigations of as prepared samples

3.2.1. Scanning electron microscopy (SEM)

The surface morphology of monolithic Sn–Ag and Sn–Ag/CeO₂ composite is shown in Fig. 2(a–d). It is noticed that pure monolithic sample has a coarse grain structure (Fig. 2a–b), while on the addition of the CeO₂ nanoparticles inside the Sn–Ag alloy; the grain size is reduced and adopts a more regular shape as compared with the monolithic samples (Fig. 2c–d). This can be correlated to the two factors, (1) presence of more number of nucleation centers due to CeO₂ incorporation occurring during the co-electrodeposition and (2) the adsorption of CeO₂ on the cathode surface that increases the cathodic polarization and it results in finer grains. However, as noticed from the SEM micrographs the Ag₃Sn compounds are not clearly visible. This type of observation on the morphology of deposits can be found in recent studies on electrodeposited Sn–Ag solder [10,19].

3.2.2. Energy dispersive spectroscopy (EDS)

The amount of the reinforced ceria nanoparticles is evaluated by EDS analysis as shown in Fig. 3. It is observed that the amount of the incorporated nanoparticles increases rapidly to a peak value followed by a decrement of their concentration in the deposits.

Download English Version:

<https://daneshyari.com/en/article/1657309>

Download Persian Version:

<https://daneshyari.com/article/1657309>

[Daneshyari.com](https://daneshyari.com)