

Journal of Alloys and Compounds 455 (2008) 358-363

Journal of ALLOYS AND COMPOUNDS

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# Effect of Cr on the corrosion resistance of Cu-6Ni-4Sn alloys

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Received 25 June 2006; received in revised form 14 January 2007; accepted 21 January 2007 Available online 2 February 2007

#### Abstract

The corrosion characteristics of Cu–6% Ni–4% Sn–x% Cr alloys in an acid-chloride solution (0.1 M H<sub>2</sub>SO<sub>4</sub> + 0.0056 M NaCl) at pH 1.2, were studied as a function of the chromium content. Three kinds of Cu–6% Ni–4% Sn–x% Cr alloys were prepared by melting and casting, followed by thermomechanical treatments. The corrosion behavior of the Cu–6% Ni–4% Sn–x% Cr alloys was investigated using electrochemical corrosion test and surface analyses (optical microscopy, electron probe microanalysis and scanning electron microscopy). The addition of Cr was found to prevent the localized corrosion behavior, which is caused by the decreased Sn-rich precipitates in Cu–6% Ni–4% Sn–x% Cr alloys. These precipitates induced galvanic corrosion due to the difference of the chemical composition.

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Keywords: Cu-Ni-Sn alloy; Acid-chloride solution; Localized corrosion; Sn-rich precipitate; Galvanic effect

## 1. Introduction

Cu–Be alloys have been used for various applications in the electronics industry. In particular, these alloys exhibit high strength, elasticity and corrosion resistance, which makes them ideal for use as high performance connector materials in electronics applications [1]. However, they are harmful to the health, because beryllium oxide is generated during the melting process.

Cu–Ni–Sn alloys, which are made by adding Ni to Cu–Sn alloys, have good castability, strength, corrosion resistance and weldability. Recently, these alloy systems have been regarded as possible substitutes for Cu–Be alloys [2–6]. Traditionally, the addition of a small quantity of Zr to Cu alloys is considered to give rise to an improvement in their thermal resistance, conductivity and corrosion resistance. Also, it was reported that the addition of small amounts of Cr has similar effects [7].

The purpose of this study is to investigate the effect of chromium on the electrochemical characteristics of Cu–6Ni–4Sn alloys, in order to determine if it can improve the corrosion resistance in applications involving electronic materials.

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#### 2. Experimental

The alloys studied herein, viz. Cu–6Ni–4Sn–0% Cr, Cu–6Ni–4Sn–0.1% Cr and Cu–6Ni–4Sn–0.3% Cr, were prepared by melting and casting from commercial pure elements. The surface of each specimen was wet-polished to 600 grit with silicon carbide (SiC) paper and degreased with methanol prior to the experiment. For the electrical contact, copper was adhered to each specimen, after first being mounted in cured epoxy resin. To prevent crevice corrosion between the epoxy and specimen, the interface was sealed with silicon, leaving an exposed area of  $\emptyset$ 10.4 mm × 150 mm on the material surface for the electrochemical test. After etching with 60 ml H<sub>2</sub>O + 25 ml H<sub>2</sub>O<sub>2</sub> + 15 ml HNO<sub>3</sub>, the microstructures were observed. Also, SEM investigations were performed to the corroded surfaces of the tested specimens.

Potentiodynamic polarization tests were performed to evaluate the overall corrosion behavior. The electrochemical polarization of the sample was accomplished with an EG&G Model 273A potentiostat. All potentials were measured against a saturated calomel electrode (SCE). For each combination of material and electrolyte, the corrosion sample was allowed to stabilize in 0.1 M  $H_2SO_4 + 0.0056$  M NaCl solution (pH 1.2) which was aerated under ambient conditions, until the potential change was <1 mV/min. This potential was then taken as the open-circuit potential (OCP). To insure the reproducibility of the results, at least three replicate experiments were carried out.

## 3. Results and discussion

Fig. 1(a)–(c) shows the microstructures of the samples containing 0, 0.1, and 0.3% of Cr, respectively, which show that deformation bands are developed by cold working [8].

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Fig. 1. Optical micrographs of as-swaged and aged (a) Cu–6Ni–4Sn–0% Cr alloy with the addition of (b) 0.1% Cr; (c) 0.3% Cr.

In Fig. 1(a), precipitates can be seen in the grain boundary. In the case of Fig. 1(c), as the Cr concentration was increased, less precipitates were formed. These precipitates were principally composed of Sn (>80%) [9], which induced galvanic corrosion due to the difference of the chemical composition. Fig. 2 shows the results of the EDS analysis for the polished sample surface. The sample without Cr was observed to have Sn-rich precipitation. As the concentration of Cr was increased, the precipitates were distributed uniformly. Fig. 3 shows the potentiodynamic polarization curves of Cu–6Ni–4Sn alloys. All of the samples showed anodic dissolution behav-



Fig. 2. Observations of polished surfaces and composition using the SEM and EDS: (a) Cu-6Ni-4Sn-0Cr; (b) Cu-6Ni-4Sn-0.1Cr; (c) Cu-6Ni-4Sn-0.3Cr.

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