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Electrochemical studies of Pd-doped Cu and Pd-doped Cu-Al intermetallics for understanding corrosion behavior in wire-bonding packages

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ABSTRACT

This study investigated the electrochemical characterizations in the field of wire metallurgy (Pd concentration) and molding compound chemistry (chloride concentration) to find ways to reduce metallic entities' susceptibility to corrosion at ball-pad interfaces. The open circuit potentials and potentiodynamic polarization curves of various metallic entities found in a Cu(Pd)-Al bonding interface were obtained in near-neutral electrolytes of 100 ppm, 20 ppm, and 1 ppm of NaCl in high-purity water. From X-ray diffraction spectra, it was found that Pd could be homogeneously incorporated into Cu_9Al_4, the Cu-rich intermetallic compound (IMC) also referred to as γ but not into $CuAl_2$, the Al-rich IMC also referred to as θ for arc-melted specimens. For Cu-Pd alloys, at a given chloride concentration, increasing Pd concentration causes the value of open-circuit potential (E_{oc}) to increase and corrosion current density (i_{corr}) to decrease. Likewise, for a given amount of Pd in Cu-Pd alloy, decrease in the NaCl concentration causes the value of E_{oc} to increase and i_{corr} to decrease. Interestingly, for high concentration of Pd as in the case of Cu-9Pd, E_{oc} and i_{corr} became less sensitive to the NaCl concentrations investigated. This can be attributed to the Pd enrichment on the corroding surface that reduces the anodic dissolution rate of Cu. For Pd-doped γ intermetallics, increasing Pd concentration causes a systemic increase in the value of E_{oc}, but at a lower concentration of Pd, the value of i_{corr} was increased. The addition of Pd to γ causes an increase in the cathodic current density due to the high cathodic activity of Pd, while the passivation of Al in γ reduces the extent of the anodic current density reduction due to the addition of Pd, which leads to a higher value of i_{corr} at a low Pd concentration. This is true even when the NaCl concentration is as low as 1 ppm. On the other hand, the influence of NaCl concentration on the E_{oc} and i_{corr} of γ IMC was always observed, even with Pd addition.

1. Introduction

To manage the overall cost and performance of an electronic package, copper (Cu) wire has gained a significant share over gold (Au) wire for the wire-bonding process [1,2]. Oxidation concern of Cu during storage and the arc-melting process has prompted some manufacturers to use palladium (Pd)-coated Cu wire, due to the perceived high oxidation resistance of Pd [3]. The improved oxidation resistance enables Pd-coated wire to form a more spherical ball than bare Cu during the arc-melting process. In addition, the high solubility of Pd in Cu also improves the bonding strength [3–5]. As a platinum group metal, Pd is highly noble [6]. The bond interface formed with Pd-coated wire has shown an improved time-to-failure in the high accelerated stress testing (HAST) [5,7,8]. This improved time-to-failure has been attributed to a higher Pd concentration at the outer surface of the ball formed during the arc-melting process [5,7]. Therefore, the concentration effect of Pd on both the cathodic reaction kinetics and the anodic reaction kinetics of the relevant metallic entities needs to be fully characterized and compared such that the service reliability of Pd-coated Cu wire bonded electronic packages can be better evaluated.

Due to the size limitation, it is difficult to directly evaluate the electrochemical characteristics of various metallic entities using the ball-bonded joint. Bulk samples were recently used to examine the effect of Pd addition on the electrochemical characteristics of different metallic entities found in the Cu-Al interface [9]. However, only deionized water containing 25 ppm of NaCl with pH = 6 was used, so the findings of that study were limited. In addition to metallurgy, molding compound chemistry, especially the chloride concentration in the molding compound is another important factor that can affect the bonding

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Abbreviations: HAST, high accelerated stress testing; IMC, intermetallic compound; E_{oc}, open circuit potential; i_{corr}, corrosion current density; XRD, X-ray diffraction; FAB, free air ball; WE, working electrode; RE, reference electrode; CE, counter electrode; R_{soln}, solution resistance; $E_{applied}$, applied potential; E_{real}, corrected potential; ORR, oxygen reduction reaction; HER, hydrogen evolution reaction.

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failure rate significantly, as the anodic dissolution of Cu and Al is strongly influenced by the chloride concentration [8]. Therefore, it is necessary to vary the electrolyte's chloride concentration in order to gain a more complete understanding of the electrochemical behavior of Cu-Al metallic entities that vary by Pd addition.

In this study, the electrochemical characteristics of Pd addition on Cu and two other major IMCs, γ (Cu_9Al_4) and θ ($CuAl_2$) [10–12] were investigated using three electrolytes of 100 ppm, 20 ppm, and 1 ppm of NaCl in high-purity water. To simulate a thermosonic wire-bonding process [1], Pd was first arc-melted with Cu in an argon gas environment to form a Cu-Pd alloy. An appropriate amount of Al was then added to synthesize Cu-rich γ and Al-rich θ IMCs using an identical arc-melting process. X-ray diffraction (XRD) analysis was performed to investigate the Pd distribution in these two as-prepared IMCs. These samples were then encapsulated in epoxy and ground, or polished, to expose the known surface area necessary to carry out electrochemical characterization experiments. The cathodic and anodic polarization behavior of metallic samples containing different amounts of Pd was examined at near neutral electrolyte with 1 ppm, 20 ppm, and 100 ppm NaCl. Electrochemical properties such as open-circuit potentials (E_{oc}) and corrosion current density (i_{corr}) were compared as a function of Pd concentration as well as chloride concentration. These results provide the more complete electrochemical characterization needed to introduce particular strategies of reducing metallic entities' susceptibility to corrosion at the ball-pad interface of Cu-wire bonded electronic packages from the perspective of wire metallurgy and molding compound chemistry.

2. Material and methods

2.1. Preparation of Pd-doped intermetallic samples

In the ball-bonding process, the free end of Pd-coated Cu wire is first arc-melted to form a free air ball (FAB). This FAB is then welded on the Al pad with ultrasonic energy and compression force to form the ball bond [1]. To simulate this process, Cu-Pd alloys were prepared by the arc-melting process, and Pd-doped Cu-Al IMCs were prepared by adding appropriated amounts of Al to them. The electronic packaging industry commonly uses 20 μm-diameter Cu wire with 0.08 μm-thick Pd coating, providing an equivalent weight percentage of about 2% Pd in Cu [5,8]. Therefore, a Cu-Pd alloy containing 2 wt% Pd (Cu-2Pd) was used in this study. To further evaluate the effect of Pd concentration, Cu-Pd alloy with 9 wt% Pd (Cu-9Pd) was also prepared. Cu and these two Cu-Pd alloys were arc-melted again with appropriate amounts of Al to form the two major IMCs of interest, $(Cu\text{-}xPd)_9Al_4$, or γ, and $(Cu\text{-}xPd)Al_2$, or θ [10–12]. In this study, IMC samples made without Pd addition are labeled as #1, those made with Cu-2Pd are labeled as #2, and those made with Cu-9Pd are labeled as #3.

All samples used in this study were prepared through the arc-melting process under an argon atmosphere using as-received Cu, Pd, and Al of 99.99% purity from Kurt J. Lesker Company. A single arc furnace, model 5SA from Centorr Vacuum Industries, Inc., was used with a current of 80 A to generate the arc needed for melting these metallic samples. Repeated arc-melting steps were used to ensure the homogeneity of all samples. After these repeated arc-melting steps, the total weight loss for all samples used was about 0.2 wt% to 0.3 wt%. The weight fractions of Cu, Pd, and Al for all the samples studied are tabulated in Table 1.

Table 1
Nominal composition of the samples used.

Sample	Cu (wt%)	Pd (wt%)	Al (wt%)
Cu	100	0	0
Cu-2Pd	98.0	2.0	0
Cu-9Pd	91.0	9.0	0
γ#1: Cu_9Al_4	84.1	0	15.9
γ#2: $(Cu\text{-}2Pd)_9Al_4$	82.5	1.7	15.8
γ#3: $(Cu\text{-}9Pd)_9Al_4$	77.0	7.6	15.4
θ#1: $CuAl_2$	54.1	0	45.9
θ#2: $(Cu\text{-}2Pd)Al_2$	53.2	1.1	45.7
θ#3: $(Cu\text{-}9Pd)Al_2$	50.0	5.0	45.0

Crystal structures of the as-produced IMCs were examined by powder X-ray diffraction with the Rigaku Miniflex II™ benchtop X-ray diffractometer, and the diffraction patterns obtained were analyzed using a Jade® software package.

2.2. Electrochemical characterization

All samples were first soldered to a Cu wire for electrical connection and then encapsulated in an epoxy resin. A portion of specimen surface was exposed by the standard metallographic grinding technique using SiC paper up to 2400 grit. A schematic of the working electrode (WE) prepared by the above method is provided in Fig. 1. The exposed surface of the WE was degreased by ultrasonic cleaning using soapy water followed by a wash in deionized water. The area of the exposed surface was measured at the beginning of electrochemical measurements.

The electrochemical characterization, including open circuit potential and potentiodynamic polarization, were carried out at room temperature in a conventional three-electrode cell arrangement with Ag/AgCl (saturated with KCl) as the reference electrode (RE) and platinum foil as the counter electrode (CE), using a VSP modular 5 channels potentiostat from BioLogic Science Instruments. All electrochemical measurements were repeated 3 to 6 times by regrinding the previously used samples as well as at least two samples of the same composition to ensure data reproducibility. The electrolytes used for this study were 1 ppm, 20 ppm, and 100 ppm of NaCl in deionized water at pH = 6. The deionized water (≈18 MΩ·cm) was obtained from Barnstead™ Nanopure™.

Open circuit potential (E_{oc}) is the potential difference between WE and RE. To obtain a stable value of E_{oc}, the sample concerned needs to be immersed in the electrolyte for an extended period of time. In this study, the immersion time varied depending on the composition of WE, i.e., 2 h for Cu and Cu-Pd alloys and 24 h for γ and θ intermetallics. After immersion, E_{oc} was monitored for at least one additional hour, and the stable E_{oc} values were reported.

Potentiodynamic polarization measurements were carried out after the stable E_{oc} was obtained. Cathodic polarization curves were obtained

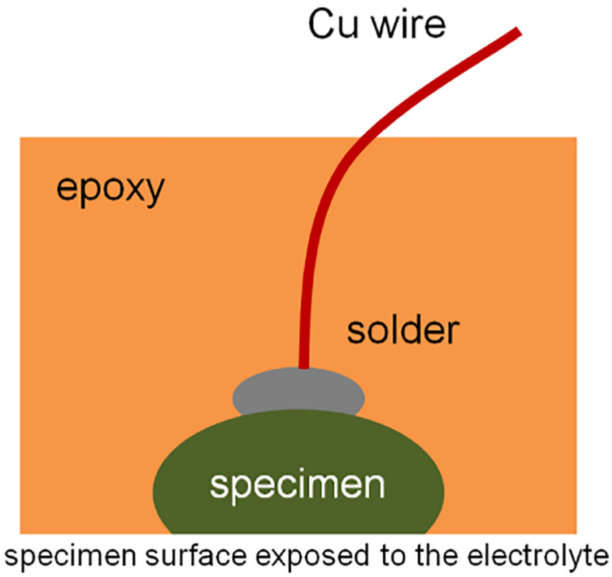

Fig. 1. Working electrode with known exposed surface area. Sample was first soldered to a Cu wire for electrical connection and then encapsulated in an epoxy resin. A portion of specimen surface was exposed by the standard metallographic preparation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)