Interfacial Reactions between Ni Substrate and the Component Bi in Solders

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The reactions between Ni and liquid Bi at 300, 360, 420, and 480°C were studied. Bismuth is an important element in many electronic solders, while Ni is used in many printed circuit board surface finishes. It was found that the only intermetallic compound formed was NiBi3. The other intermetallic compound NiBi, which is thermodynamically stable at these temperatures, did not form. Reaction at 300°C produced a thick reaction zone, which is a two-phase mixture of NiBi3 needles dispersed in Bi matrix. The thickness of the reaction zone increased rapidly with reaction time, reaching 400 µm after 360 min. Reactions at 360 and 420°C produced very thin reaction zones, and the major interaction was the dissolution of Ni into liquid Bi. Reaction at 480°C produced extremely thin reaction zone, and the dissolution of Ni into liquid Bi was very fast and was the major interaction. It is proposed that the formation of the reaction zone is controlled by two factors: the solubility limit and the diffusivity of Ni in liquid Bi. Small diffusivity and small solubility limit, i.e., lower temperature, tend to favor the formation of a thick reaction zone. In addition to the NiBi3 formed within the reaction zone, NiBi also formed outside the reaction zone in the form of long needles with hexagonal cross section. The dissolution rate of Ni into Bi is comparable to that of Ni into Sn at the same temperature, and is much slower than the dissolution rates for Au, Ag, Cu, and Pd into Sn.

Key words: Bi-based solders, interfacial reactions, Ni substrate

INTRODUCTION

Lead-bearing solders are widely used by the electronics industry for packaging applications. These Pb-bearing solders include alloys such as 63Sn-37Pb (wt.%), frequently used for soldering printed circuit boards (PCBs), and 95Pb-5Sn, frequently used for chip-to-package connection. These solders have been used for years and meet the performance requirements quite well, but Pb in these solders posts potential threats to the environment. This environmental concern propels the search for the Pb-free replacements. Many Pb-free solders have been proposed as possible alternatives, and some of them have been used in industry for other reasons for quite some time. Bismuth is an important ingredient in many of these Pb-free solders, such as 90Sn-7.5Bi-2Ag-0.5Cu, 58Bi-42Sn, 68Bi-32In, 57Bi-26In-17Sn, and 66In-34Bi.1

In PCB manufacturing, the Cu surface mount pads are often coated with a solderable surface finish to maintain the solderability of a PCB over a period of shelf time. Currently, 63Sn-37Pb is one of the most common surface finishes. There is also a pressure from the environmental consideration to reduce the use of this Pb-bearing finish. Several Pb-free finishes utilize a Ni layer that is a few microns in thickness. These Ni-bearing surface finishes have the additional advantage of being very flat, making them ideal for fine lead-pitch surface mount components. To prevent oxidation of the Ni layer, the Ni surface is coated with another thin layer such as Au (0.15–0.25 µm) or Pd (0.02–0.05 µm).2 This thin Au or Pd layer dissolves into the solder during the soldering operation, and the Ni layer then comes into direct contact with the solder. Therefore, in Pb-free PCB soldering, the interactions between Ni and Bi have to be considered.

Lead forms a simple monotectic invariant with Ni, and is chemically inert to Ni.3 When Pb is in contact with Ni, the only interaction is the dissolution of Ni into Pb. In other words, Pb does not actively participate in the chemical reactions between Pb-bearing solders and Ni.

Bismuth is next to Pb on the periodic table and has many properties similar to those of Pb. In one respect, however, Bi is quite different from Pb. According to the Ni-Bi phase diagram shown in Fig. 1,3–5 there are
two intermetallic compounds in this system: NiBi and NiBi$_3$. Therefore, NiBi and NiBi$_3$ may form when Ni is exposed to Bi-bearing solders. In Bi-bearing solders, other common constituents such as Sn and In also can form intermetallics with Ni.3 The reactions of Bi-bearing solders with Ni can be very complicated and difficult to predict. For example, when 58Bi-42Sn solder is applied to Ni substrate, intermetallics of Ni and Bi (NiBi and NiBi$_3$) and intermetallics of Ni and Sn (Ni$_3$Sn, Ni$_3$Sn$_2$, and Ni$_3$Sn$_4$) will compete with each other to form. In such reactions, not all the possible intermetallic compounds predicted by the binary phase diagrams will form. Very often, only a few of the possible intermetallics become the reaction products. For some systems, the possibility of forming one or more ternary intermetallics also exists. In short, soldering reactions in such systems are complicated, and experimental studies are needed to reveal what exactly will occur in such reactions.

A literature search revealed that experimental study related to the reactions of Ni with Bi-bearing solders is very limited, and only one recent study was found.5,7 This is in sharp contrast to the rich literature for the reaction of Cu with Sn. Duchenko and Dybkov6,7 studied the reaction between solid Bi and Ni at 150–250°C, and found that only NiBi$_3$ form. The other intermetallic compound NiBi was not detected. The growth of NiBi$_3$ was parabolic, and the main diffusion species was determined to be Bi by marker experiment. No experimental study between liquid Bi and solid Ni could be found in the literature. The purpose of this paper is to study the reaction between liquid Bi and solid Ni in order to provide the basic data for the interactions of Ni with Bi-bearing solders.

**EXPERIMENTAL PROCEDURE**

The Ni was 99.995%-pure, with the shape of a disk measuring 5 mm in diameter and 0.5 mm in thickness. The mass of each disk was 0.088g. These Ni disks were cut from a 5 mm diameter rod and then metallurgically polished on both surfaces. One μm diamond abrasive was used as the last polishing step. The exact thickness of each disk was then recorded. These Ni disks were then cleaned with acetone, etched in a 50 vol.% HCl-H$_2$O solution for 10 s, and fluxed with a mildly activated rosin flux (RMA#5, Indium Corporation of America). The fluxed disks were vertically dipped into molten Bi baths at 300±0.5, 360±0.5, 420±0.5, or 480±0.5°C for time ranging from 10 to 360 min. The molten Bi, made of 4g, 99.9994%-pure Bi, was contained in a 10 mm inside-diameter vial. A fresh Bi bath was used for each Ni disk. When the predetermined reaction time was reached, the Bi bath together with the Ni disk was cooled down using an air-blower. The liquid Bi solidified with little disturbance and cooled to touch in about 90 s. The samples were then removed from the vials, mounted in epoxy, sectioned by using a low-speed diamond saw, and metallographically polished in preparation for characterization.

The reaction zone for each sample was examined by an optical microscope (OM) and a scanning electron microscope (SEM). The thickness of the reaction zone and the thickness of the unreacted Ni for each sample were measured at regular intervals on its optical or scanning electron micrograph. For each sample, about 30 data points were measured, and the average thickness was reported. The composition of the reaction product was determined using a JEOL JCX-733 electron microprobe, operated at 15 keV. During microprobe measurement, the measured x-ray was Kα and Mα for Ni and Bi, respectively, and the standards used were pure Ni and Bi for Ni and Bi signals, respectively. In microprobe analysis, the concentrations of Bi and Ni were measured independently, and the total weight percentage was within 100±1% in each case. For every data point, at least four measurements were made and the average value was reported. It was estimated that the accuracy of the alloy compositions determined in this study was within 1 wt.%. The crystal structures of the reaction products were determined by a diffractometer using Cu Kα$_1$ radiation.