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Sn concentration effect on the formation of intermetallic compounds in high-Pb/Ni reactions

M.H. Tsai*, W.M. Chen, M.Y. Tsai, C.R. Kao

Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan

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ABSTRACT

The reaction between high-Pb solders and Ni substrate was investigated to understand the Sn concentration effect on the formation of intermetallic compounds. Three PbxSn solders ($x = 1$, 3, and 5 wt.%) were reacted with Ni substrates at 400 °C for 2–240 min. The reaction products formed at the interface were related to the Sn concentration in the solders. When the Sn concentration was 5 wt.%, Ni_3Sn_4 formed first and followed by the formation of Ni_3Sn_2. When the Sn concentration decreased to 3 wt.%, Ni_3Sn_2 formed first and followed by the formation of Ni_3Sn. When the Sn concentration became 1 wt.%, only Ni_3Sn_2 was. This fascinating concentration dependency was rationalized by using the Pb–Sn–Ni isotherm. In addition, the deep penetration of Pb into the Ni substrate along the grain boundaries was observed. It was likely that the low interfacial energy between high-Pb and Ni caused such an unusual grain boundary penetration.

1. Introduction

Nickel-based under bump metallizations (UBM) are widely used in microelectronics packaging to prevent excessive intermetallic formation during processing and during operation of electronic devices [1–4]. High-Pb solders, such as 95Pb5Sn (wt.%, same below) are among the most widely used solders in flip–chip solder joints, and are currently exempt from the lead-free requirements for uses in flip–chip applications. The formation of a thin intermetallic layer between the solder and the UBM is desirable to achieve a good metallurgical bond; however, excessive growth of intermetallic layer may have deleterious effects. Often, the intermetallic layer is brittle and may degrade the mechanical properties of solder joints, leading to poor reliability of electronic devices [5,6]. In particular, Ni_3Sn_4 was found to be very brittle, and factures through this compound developed easily regardless its thickness [6]. Therefore, an understanding of interfacial reaction between solders and Ni-based UBM is necessary for improving the reliability of electronic products. The objective of this study is to investigate the reactions between Ni substrate and high-Pb solders with different Sn concentrations.

2. Experimental

Pure Ni substrates (99.99 wt.%) of 25 mm × 10 mm × 4 mm dimensions were mechanically mirror-polished on both faces to reduce the surface roughness, fully immersed into dilute hydrochloric acid (HCl) to remove Ni oxide on the Ni surface, then quickly spread with a commercial mildly activated rosin flux. Solder alloys of three different compositions, 99Pb1Sn, 97Pb3Sn, and 95Pb5Sn, were prepared by first melting high purity (99.99%) elements and then placing in a furnace at 300 °C for 1 week for alloy homogenization. Each fluxed Ni substrate was immersed in a fresh molten solder bath kept at 400 °C for 2–240 min. The amount of solder used in each soldering reaction was 12 g.

The soldered samples were further sliced for solder/substrate interfacial examination. After conventional metallographic grinding, the ion-milling polisher (E-3500; HITACHI, Tokyo, Japan) was used for final polishing. The ion-milling polishing has the benefit of less preparation damage and does not require surface etching by any chemical reagents. The compositions of the phases were determined by an electron probe micro-analyzer (FE-EPMA; JXA-8500F; JEOL, Tokyo, Japan) with average value of measurements from five different regions in the intermetallic layer.

3. Results

Fig. 1(a)–(c) shows a series of cross-sectional microstructure in backscattered electron mode for the 95Pb5Sn solder reacted with Ni at 400 °C for 2, 20 and 240 min, respectively. As can be seen in Fig. 1(a), a thin intermetallic layer formed at the interface, but its thickness was too thin to be accurately analyzed with FE-EPMA. From the results at longer reaction time, it was presumed to be Ni_3Sn_4. When the time reached 20 min, there was still only one intermetallic, and this compound was positively identified by FE-EPMA to be Ni_3Sn_4. Meanwhile, a few voids were observed between Ni_3Sn_4 and Ni, as shown in Fig. 1(b). When the soldering time reached to 240 min, both Ni_3Sn_4 and Ni_3Sn_2 were identified by FE-EPMA. The contrast between Ni_3Sn_4 and Ni_3Sn_2 was very weak, and thin dashed lines are added in Fig. 1(c) and (d) to help delineate these two compounds. As shown in Fig. 1(c) and (d), there were both voids and high-Pb phase (Pb) between Ni_3Sn_2 and Ni. Since

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* Corresponding author.
E-mail address: mh0617@gmail.com (M.H. Tsai).

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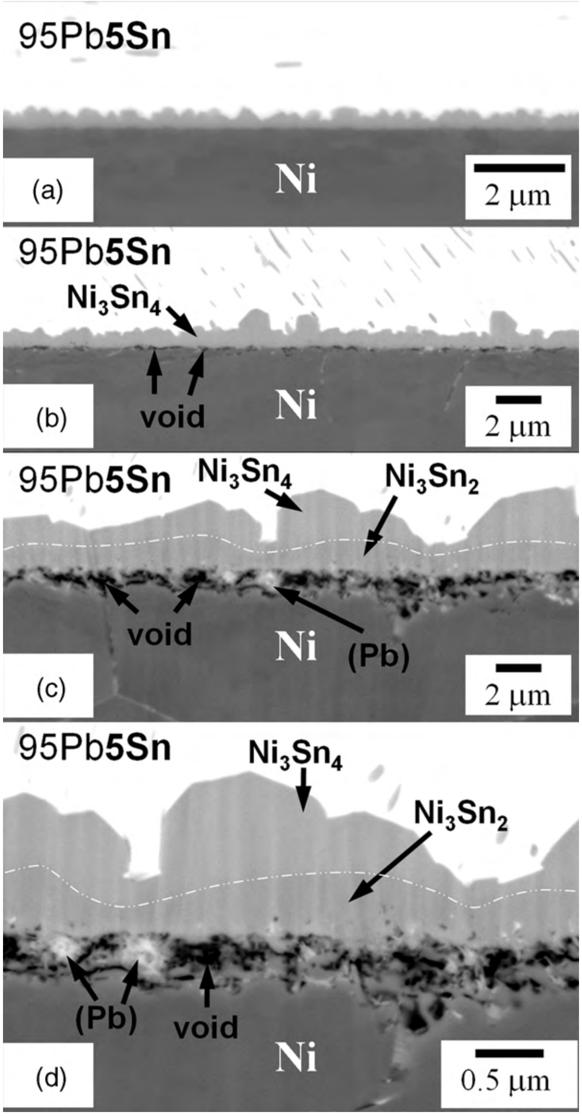

Fig. 1. (a)–(c) Microstructure evolution for the reaction between 95Pb5Sn and Ni at 400 °C for 2, 20, and 240 min, respectively. (d) Higher magnification micrograph for 240 min. The contrast between Ni_3Sn_4 and Ni_3Sn_2 was very weak, and thin dashed lines are added to help delineate these two compounds in (c) and (d).

the cross-sections in this study were all prepared by the relatively damage-free technique of ion-milling polishing, the voids and high-Pb phase (Pb) were not likely to be artifacts induced during sample preparation. The rationalizations for the formation of the voids and high-Pb phase (Pb) will be presented in the discussion section.

When the Sn concentration became 3 wt.%, a thin intermetallic layer formed at the interface after 2 min, as shown in Fig. 2(a), but its thickness was too thin to be accurately analyzed with FE-EPMA. From the results at longer reaction time, it was presumed to be Ni_3Sn_2. When the time reached 20 min, Ni_3Sn_2 formed at the interface, as shown in Fig. 2(b). A few voids were clearly visible between Ni_3Sn_2 and Ni. When the time reached 240 min, both Ni_3Sn_2 and Ni_3Sn formed at the interface as shown in Fig. 2(c). Again, the contrast between Ni_3Sn_2 and Ni_3Sn was very weak, and a thin dashed line is added in Fig. 2(c) to help delineate these two compounds. There were also voids and high-Pb phase (Pb) between Ni_3Sn and Ni.

When the Sn concentration was 1 wt.%, the results for 2 and 20 min the same as those of 97Pb3Sn in term of the types of compound formed, and the results are omitted here for the sake of brevity. When the reaction time reached 240 min (Fig. 3), only Ni_3Sn_2 formed, and Ni_3Sn was not observed. There were again voids and high-Pb phase (Pb) between Ni_3Sn and Ni, but the amount of voids and high-Pb phase (Pb) were less than those of 95Pb5Sn and 97Pb3Sn. In fact, a trend can be observed in Figs. 1(c), 2(c), and 3 that the amount of voids (Pb) decreased with decreasing Sn concentration in solders.

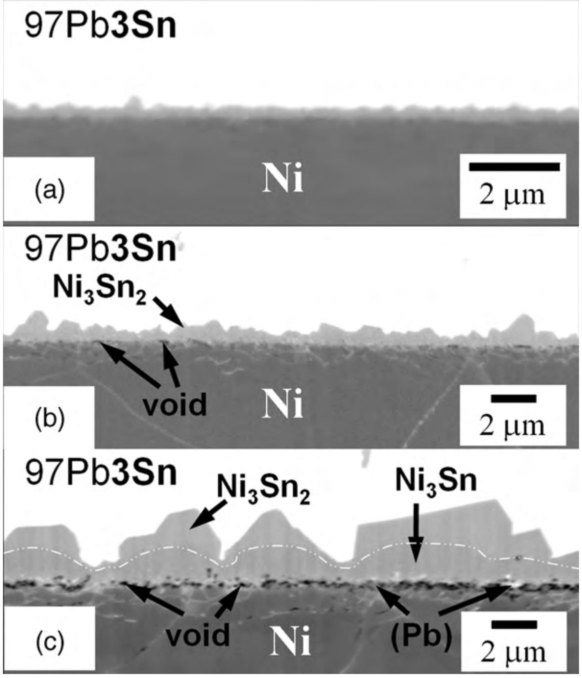

Fig. 2. (a)–(c) Microstructure evolution for the reaction between 97Pb3Sn and Ni at 400 °C for 2, 20, and 240 min, respectively. The contrast between Ni_3Sn_2 and Ni_3Sn was very weak, and a thin dashed line is added to help delineate these two compounds in (c).

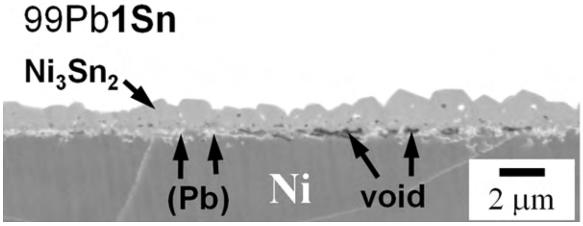

Fig. 3. Micrograph showing the interface between 99Pb1Sn and Ni reacted at 400 °C for 240 min. The only compound formed was Ni_3Sn_2.

4. Discussion

During the soldering reaction, the Sn atoms in solder reacted with Ni to form Ni–Sn intermetallics at the interface. If the amount of solder had been small, as in flip–chip solder joints, the Sn concentration in solder would have decreased as Ni–Sn intermetallics grew thicker. Nevertheless, in this study, the amount of solder was purposely set to be very large (12 g) compared to the amount of Ni–Sn intermetallics formed at the interface. Consequently, the Sn concentration in solder stayed nearly constant. This was done so that the Sn concentration effect can be clarified in this study first. Only after establishing the concentration effect, could one begin to investigate the volume effect. However, it should be emphasized that the results obtained in this study should only be used to interpret to results in real flip chip joints with an understanding of the volume effect.

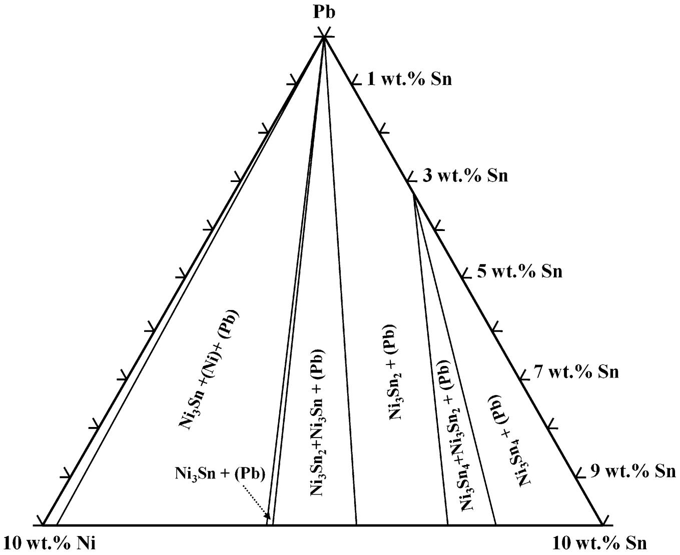

Fig. 4. Pb-rich corner of the Pb–Sn–Ni ternary isotherm at 400 °C. This isotherm was redrawn based on the information determined by Tu and Zeng [8].

According to the Ni–Sn binary phase diagram [7], there were three stable intermetallic compounds, Ni_3Sn, Ni_3Sn_2 and Ni_3Sn_4, that might form at the interface of binary Ni–Sn reaction at temperatures below 400 °C. For reactions in the PbSn/Ni ternary system, one needs to use the Pb–Sn–Ni isotherm at 400 °C, reproduced in Fig. 4 [8], as a reference map for discussion. In this study, when the Sn concentration was 5 wt.%, the Ni_3Sn_4 formed as the first intermetallic compound, and then Ni_3Sn_2 formed next to Ni_3Sn_4 at 240 min (see Fig. 1). When the Sn concentration was 3 wt.%, the first phase formed became Ni_3Sn_2, and then Ni_3Sn formed next to Ni_3Sn_4 at 240 min (see Fig. 2). When the Sn concentration was 1 wt.%, the first phase formed became Ni_3Sn_2, and Ni_3Sn_2 remained the only phase formed for reaction time as long as (see Fig. 3). For all the solder compositions used in this study, the first phase formed was consistent with the prediction of the Pb–Sn–Ni isotherm (see Fig. 4). In the 95Pb5Sn/Ni reaction, the Ni_3Sn_4 phase formed first, and now the interface represented a tie-line in the Ni_3Sn_4 + (Pb) two-phase field in the Pb–Sn–Ni isotherm shown in Fig. 4. When the Sn concentration in solder was 3 wt.% or 1 wt.%, the interface represented a tie-line in the Ni_3Sn_2 + (Pb) two-phase field, and therefore, Ni_3Sn_2 formed first next to the high-Pb solder. The first phase formed in the case of 95Pb5Sn is also consistent with the work of Lin and Jang [9].

As shown in Fig. 1(c), a voids + (Pb) region formed between Ni_3Sn_2 and Ni when the reaction time was long. Such a microstructure was quite similar to the massive spalling reported in the literature [10–17]. According to the theory of massive spalling [14–17], the massive spalling phenomenon is a process through which the interface responds to the shifting of the equilibrium phase. The massive spalling occurs because the original reaction product at the interface is no longer in local thermodynamic equilibrium with the solder, and this compound spalls away to make room for the nucleation and growth of the equilibrium phase. However, as pointed out earlier, the Sn concentration in this study would not change during the reaction because the supply of Sn was very large. Consequently, the formation of the voids + (Pb) region must be explained by another reason other than the massive spalling phenomenon.

The most likely explanation for the formation of the voids + (Pb) region is the interfacial energy effect. In fact, the penetration Ni grain boundaries by pure molten Pb had been reported at high temperatures (> 600 °C) [18,19]. They attributed this grain boundary penetration to the effect of low interfacial energy between molten Pb and Ni. The penetration started with the liquid grooving at the grain boundaries of exposed Ni surface [18,19]. In order to confirm whether the voids + (Pb) region was related to the grain boundary penetration reported at high temperatures (>600 °C) [18,19]. An experiment was carried out by reacting pure Pb with Ni at 400 °C for 240 min. The same experimental procedure as the other experiments of this study was used. Fig. 5 shows the interface of the reaction between pure Pb and Ni substrate at 400 °C for 240 min. It can clearly be seen that the Ni grain boundaries were decorated with a white phase. This white phase was in fact the molten pure Pb. In other words, Pb had penetrated into Ni along grain boundaries. Such observation was very difficult without resorting to ion-milling polishing technique. This is the first time that grain boundary penetration of Pb into Ni is observed at such a low temperature. Fig. 5 also shows that the Ni surface exposed to bulk of the molten Pb was very rough. In other words, molten Pb was able to break up the initially smooth Ni surface. This feature was similar to the microstructure of Ni substrate in 95Pb5Sn/Ni reaction at 400 °C for 240 min, shown in Fig. 1(d). Therefore, it is proposed that the voids between intermetallic layer and Ni were in fact originally occupied by the (Pb). These (Pb) penetrated into Ni along grain boundaries during soldering reaction, leaving behind those voids. These voids might also be the reason why NiSn compounds were reported to be quite weak in the literature [6]. The observation of this deep grain boundary penetration suggests that high-Pb solders are not compatible with Ni substrates. The combination of these two materials should be used in great caution.

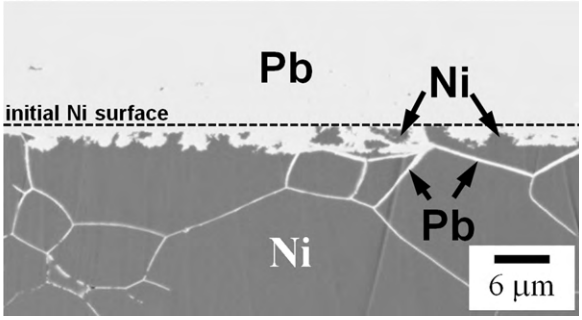

Fig. 5. Micrograph showing the interface between pure Pb and Ni reacted at 400 °C for 240 min. The molten Pb had penetrated into Ni along grain boundaries.

5. Conclusions

The types of Ni–Sn intermetallic compounds formed in high-Pb/Ni soldering reaction at 400 °C were related to the Sn concentration. When the Sn concentration was 5 wt.%, Ni_3Sn_4 formed first, and then Ni_3Sn_2 formed between Ni_3Sn_4 and Ni. When the Sn concentration decreased to 3 wt.%, the first compound formed was Ni_3Sn_2, and then Ni_3Sn formed between Ni_3Sn_2 and Ni when the time increased. When the Sn concentration was 1 wt.%, only Ni_3Sn_2 formed. This fascinating concentration dependency was rationalized by using the Pb–Sn–Ni isotherm.

Since the interfacial energy between molten Pb-rich phase and Ni was very low. The molten Pb-rich phase was able to penetrate into the interface between the intermetallic compound and the Ni substrate, creating the massive spalling phenomenon. When the reaction time was long enough, the Pb-rich phase was even able to wet the Ni grain boundaries, and penetrated deep into the grain boundaries. This suggests that high-Pb solders are not compatible with Ni substrates. The combination of these two materials should be used in great caution.

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