A comparative study of the interfacial reaction between electroless Ni-P coatings and molten tin

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Abstract

A comparative study of the reaction characteristics between molten tin and both as-plated and heat-treated Ni-P coatings was carried out, with a specific focus on the stability of the Ni_3P intermetallic layer and its effects on the subsequent reaction. It was found that a continuous layer of Ni_3P may be formed on both types of Ni-P during the interfacial reaction, despite the fact that heat-treated Ni-P is a two-phase mixture of Ni_3P and Ni. The Ni_3P formed on the heat-treated Ni-P was thinner than that on as-plated Ni-P. A mass conservation analysis of P revealed that no or limited P was lost into the molten tin when the Ni_3P layer was thin, whereas a significant loss of P took place as the Ni_3P thickness increased. It is proposed that the Ni_3P phase is stable and it may not undergo chemical decomposition during the interfacial reaction. The loss of P to the molten tin observed in the present study is most likely due to the crumbling of Ni_3P particles into the liquid phase, as a result of the enhanced mass transport due to use of thin copper wire substrates rather than a planar surface. Finally, the results show that the Ni_3P phase cannot act

as an effective barrier layer to the attack of molten tin toward the substrate. Defects in the Ni_3P were found to allow localised penetration of molten tin.

1. Introduction

Liquid solder interconnections for use in electronic assemblies exposed to high temperature environments have attracted much interest in recent years [1-3]. The major driving force behind this concept is that the use of a solder chosen such that it regularly becomes molten during normal operation of the equipment can prevent the build up of large thermal stresses in the solder joints and consequently the accumulation of damage due to the inelastic strains normally resulting from thermal cycling. A key issue in the practical implementation of this concept is to slow down the normally rapid interfacial reactions between the molten solder and the component and substrate metallization layers [3]. This may be partly achieved by applying a barrier layer of electroless Ni-P onto these metallizations, as it is well known that electroless Ni-P has a relatively slow reaction rate with solders compared with other common termination materials such as copper.

The interfacial reaction between electroless Ni-P alloys and liquid solders during reflow has been the focus of many studies [4-9]. However, the details of the reaction mechanism are still far from clear, as the presence of P complicates the situation. It is generally found that apart from the formation of Ni_3Sn_4 intermetallic compounds (IMC) at the interface, a layer of Ni_3P phase from the solder reaction-assisted crystallisation of amorphous Ni-P also precipitates adjacent to the IMC [8]. Whether the Ni_3P phase thus formed is stable, and what the effect of its precipitation is on the continuing growth of Ni_3Sn_4, are still in doubt. It has been proposed that Ni_3P may decompose to supply Ni atoms for the growth of Ni_3Sn_4 and that the ejected P atoms then diffuse back towards the Ni-P to form Ni_3P [4,6-8]. However, He et al. [5] ruled out the possibility of Ni_3P

decomposition based on an analysis of the destination of decomposed P atoms. They also claimed that the formation of Ni_3P promoted the diffusion of Ni atoms and accounted for the faster growth of Ni_3Sn_4 IMCs on electroless Ni-P than on pure Ni, by releasing the reaction heat as well as providing rapid paths for diffusion due to their fine columnar microstructure. However, Hung et al. [6,7] reported that Ni_3P can act as a barrier layer for Ni diffusion and consequently suppresses the growth of Ni_3Sn_4, which in turn leads to the cessation of Ni_3P growth.

The major conflict between the proposed explanations described above [4-9] for the liquid state interfacial reaction is centred around the stability of the Ni_3P phase, which is difficult to evaluate due to the fact that during the reaction the formation and the potential decomposition of Ni_3P phase are two simultaneous processes. The latter process, which takes place at the interface between the Ni_3P and IMC or molten solder, provides the P atoms needed for the formation of new Ni_3P phase at the interface next to the unreacted Ni-P [4,6-8]. Under such circumstances, samples with Ni_3P phase already precipitated prior to the interfacial reaction, could provide more insight into the stability of Ni_3P during the interfacial reaction, since interference from the simultaneous formation of Ni_3P does not exist.

In this paper, electroless Ni-P coatings were deposited onto thin copper wires and heat-treated at 500 ºC for 2 hours before being dipped into a pure molten tin bath. The purpose of the heat-treatment was to transform the amorphous Ni-P into the equilibrium state, which consists of crystallized Ni and Ni_3P, so that the reaction-assisted crystallisation of Ni_3P during the solder reaction may be avoided and therefore any interference from its heat of formation and fine-grained microstructure will not exist. By comparing the solder reaction behaviours of the Ni-P coatings in the as-plated and heat-treated conditions, the stability of Ni_3P and its effects on the solder reaction were investigated.

2. Experimental procedures

The pioneering study of liquid solder joints by Nowottnick et al. [2], used copper wires with a diameter of 2 mm to perform the dipping experiment. Following their work, all of the electroless Ni-P coatings used in this study were deposited onto thin copper wires (250 µm in diameter) to a thickness of approximately 15 µm. The choice of such thin copper wires as the substrate material was to avoid any significant change in the composition of the solder bath from the potential dissolution of the copper during the dipping experiment. The composition of the Ni-P coatings and the corresponding deposition conditions are given in Table 1.

The heat-treatment of the as-plated electroless Ni-P coatings was carried out under the protection of a flowing gas mixture of N_2 and 5% H_2 to avoid surface oxidation. The heat-treatment furnace was heated at a rate of 5 ⁰C/min to 500 ⁰C and was held at that temperature for 2 hours to enable the precipitation of Ni_3P and its growth into coarse grains. The furnace was then cooled down at 5 ⁰C/min to room temperature. The precipitation of Ni_3P and the resulting formation of a two-phased microstructure of well-crystallized Ni and Ni_3P in heat-treated Ni-P was confirmed by X-ray diffraction analysis. There was also a concern that the P atoms in the coating may diffuse into the substrate during the heat-treatment [10], leading to a reduction of P content in the coating. However, a compositional analysis indicated that the change in the P content in Ni-P coatings after heat-treatment was negligible.

The reaction of the Ni-P coatings with molten tin was studied by dipping the coated wires into molten tin (250 g, 99.96 wt% purity) held in a ceramic crucible. Pure tin was used as it is the major constituent of most solder alloys likely to be used in the applications envisioned for liquid solder joint technology and, due to its high reactivity, is generally the component which takes part

in the interfacial reactions. The reaction temperature was 250 or 290 ºC, whilst the reaction time was 3-28 min. The immersion depth of the samples was about 15 mm. Before dipping, all samples were coated in a strong flux (ACTIEC 5). Upon completion of the reaction step, the samples were withdrawn slowly from the solder bath.

Following dipping, the samples were mounted in electrically conductive resins and were metallographically polished for microstructural characterization and compositional analysis. These were carried out using a field emission gun scanning electron microscope (FEG-SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). The thickness measurements of the different phases at the reaction interface were performed at a randomly chosen location on the circumference of cross-sections, such as that shown in Fig. 1a. For cross-sections such as shown in Fig. 1b, the measurement was done along the short axis of the ellipse, where the distortion of thickness is the least due to an oblique section plane.

3. Results

3.1. Interface morphology

Figure 2 shows the interfacial microstructure of the coating with 14 wt% P in the as-plated and heat-treated states after the solder dipping experiment. For the as-plated samples, the interface shown in Fig. 2a exhibited a multilayered microstructure as typically observed for other solder/metallization combinations [4-9]. The dark layer adjacent to the remaining un-reacted Ni-P coatings was found by compositional analysis to consist of Ni and P. The P content of this dark layer is about 17 wt.%, which is very close to the stoichiometry of the Ni_3P phase (15 wt% P). Therefore, considering the solubility of P in Ni_3P, this dark layer is attributed to be the Ni_3P phase, as identified in previous investigations [4,8]. The light grey layer next to the Ni_3P was expected to be the Ni_3Sn_4 IMC. However, the compositional analysis as shown in Fig. 2c

indicated that it consisted of Ni, Sn and P. For the heat-treated samples (as shown in Fig. 2b), a dark layer of Ni_3P also formed at the interface after the dipping experiment, although its thickness was less than that shown in Fig. 2a.

The interfacial microstructure for Ni-P coatings with low/medium P contents after solder dipping for 12 minutes is shown in Fig 3. These interfaces showed a similar multilayered structure to those on samples with 14 wt% P. For these coatings, the P content in the dark layer next to the unreacted Ni-P was found to be approximately 15 wt%. This dark layer was therefore treated as Ni_3P. From the comparison of the interfacial microstructure of samples with and without a heat-treatment prior to the dipping experiment, the decrease in the thickness of Ni_3P formed on heat-treated samples is also apparent. Note that for the coating with 2 wt% P in the heat-treated state, no Ni_3P was observed to form at the interface during its reaction with molten tin (Fig. 3d).

Another characteristic of the interfacial microstructure of these Ni-P coatings after the dipping experiment is that for those which have a P content less than 11 wt%, no matter whether they were subjected to a prior heat-treatment or not, they suffered from localised penetration of molten tin along certain paths (as can be seen from Fig. 3a). Under higher magnifications, it was found that the preferential penetration occurred at the boundaries where two Ni-P nodules meet (Fig. 4a). Such boundaries may also be responsible for the formation of cracks or channels [6,9] in the Ni_3P layer formed during the liquid solder reaction. As shown in Fig. 4b, a boundary was found underneath the location where the continuity of the Ni_3P was interrupted.

3.2. Characterisation of Ni_3P growth

Figure 5 shows the thickness of Ni_3P formed during the solder reaction with different Ni-P coatings at 290 ℃ for 7 minutes. For the as-plated coatings, the Ni_3P thickness increased with increasing P content until about 8 wt%. A further increase in P content in the deposit did not lead to a further increase in the thickness of the Ni_3P phase. For the heat-treated samples, no Ni_3P phase was observed until the P content in the deposit was higher than about 6 wt%. After that a similar increasing trend of Ni_3P thickness with P content in the coating was observed, although the thickness of Ni_3P was apparently less than that formed on as-plated samples.

It was found that the reaction rate between the electroless coatings and the molten tin at 290 ℃ was too fast to enable time dependent measurements. The whole coating (approximately 15 μm thick), and even the whole copper wire for most of the samples prepared in this study, were completely dissolved into the molten tin bath in less than 15 minutes. The reaction temperature was therefore reduced to 250 ℃ in the following studies, which took place using a fresh molten tin bath. The variation with the reaction time of the thickness of Ni_3P formed during the reaction at this temperature is shown in Fig. 6. Except for the heat-treated low P coatings, where no Ni_3P was observed, the thickness of Ni_3P on all the other coatings increased rapidly at the beginning of the reaction. With increasing reaction time, the growth rate slowed down and eventually there was no significant further increase in the Ni_3P thickness.

3.3. Consumption rate of electroless Ni-P

The thickness of the Ni-P coatings consumed during the reaction, defined as the thickness difference between the original Ni-P coating and the un-reacted Ni-P coating left underneath the Ni_3P layer formed during the dipping experiment, is shown in Fig. 7. It can be seen that for the low P coatings, they appeared to be more reactive with molten tin in the heat-treated state than in the as-plated state. For the medium and high P coatings, their thickness consumed was found

to be linearly proportional to the reaction time, but independent of their heat-treatment history. Meanwhile, there was no significant difference between the coatings with medium and high P contents, in the thickness of Ni-P consumed.

3.4. Loss of P into molten tin

From the compositional analysis, it was found that some P was lost into the molten tin bath. However, in order to quantify the P loss, it is necessary to know the thickness of Ni_3P under the ideal condition of mass conservation, when all the P ejected from the interfacial reaction between Ni-P and molten tin is used for the formation of Ni_3P. As illustrated in Fig. 8, it is assumed that an electroless Ni-P coating with an original thickness of t_0, either on a planar substrate (Fig. 8a) or on a cylindrical substrate (Fig. 8b, and $2r \gg t_0$), has reacted with molten tin, forming a layer of IMC and Ni_3P at the interface. The thickness of Ni_3P is t_{Ni_3P}, while the thickness of the remaining unreacted Ni-P is t_{Ni-P}. The thickness of Ni-P consumed during the interfacial reaction is t_1, and $t_1 + t_{Ni-P} = t_0$. For a conservative reaction, the mass of P in the Ni-P coating consumed should be equal to that contained in the Ni_3P phase formed. Therefore for a sample with a unit surface area, the following equation results:

$$t_1 \rho_{Ni-P} c_{Ni-P} = t_{Ni_3P} \rho_{Ni_3P} c_{Ni_3P} \qquad (1)$$

where ρ_{Ni-P} and ρ_{Ni_3P} are the density and c_{Ni-P}, c_{Ni_3P} are the weight percentage of P in the Ni-P coating and the Ni_3P phase, respectively. Rearranging Equation (1), the following relationship between the thickness of Ni-P coating consumed (t_1) and the thickness of Ni_3P phase formed (t_{Ni_3P}) is obtained:

$$\frac{t_{Ni_3P}}{t_1} = \frac{t_{Ni_3P}}{t_0 - t_{Ni-P}} = \frac{\rho_{Ni-P} c_{Ni-P}}{\rho_{Ni_3P} c_{Ni_3P}} \qquad (2)$$

The density of Ni-P coating ρ_{Ni-P} in Equation (2) can be calculated from the empirical equation [10,11]:

$$\rho_{Ni-P} = \frac{113.6 - c_{Ni-P}}{12.7} \quad \text{(valid if } c_{Ni-P} < 13\%) \quad (3)$$

Since $\rho_{Ni_3P} = 7.823$ g/cm^3 and $c_{Ni_3P} = 15\%$, Equation (2) indicates that for a Ni-P coating with a known P content c_{Ni-P}, the thickness ratio $\dfrac{t_{Ni_3P}}{t_1}$ is a constant. So

$$t_{Ni_3P} = kt_1 = k(t_0 - t_{Ni-P}), \qquad k = \frac{\rho_{Ni-P}c_{Ni-P}}{\rho_{Ni_3P}c_{Ni_3P}} \qquad (4)$$

Normalising thicknesses t_1, t_{Ni_3P} and t_{Ni-P} to the original coating thickness t_0 so as to avoid interference from the variation of t_0 between different samples, one then obtains:

$$t_{Ni_3P}^* = k(1 - t_{Ni-P}^*) \qquad (5)$$

Where $t_{Ni_3P}^* = \dfrac{t_{Ni_3P}}{t_0}$, $t_{Ni-P}^* = \dfrac{t_{Ni-P}}{t_0}$.

Figure 9 shows the normalised thickness of Ni$_3$P phase ($t_{Ni_3P}^*$) plotted against the normalised thickness of Ni-P coatings consumed ($1 - t_{Ni-P}^*$) during the dipping experiment. The straight line is plotted from Equation 5, which gives the theoretical thickness of Ni$_3$P when no loss of P occurs. It can be seen from Fig. 9 that during the earlier stages of the interfacial reaction (except for the heat-treated low P coating), the actual thickness of Ni$_3$P measured is very close to the theoretical line, indicating that no or only a limited quantity of P is lost into the molten tin. However, as the reaction proceeds, the gap between the theoretical line and the experimental data point increases, which means that the loss of P during prolonged reaction increases.

4. Discussion

4.1 Interface microstructure

In this study, the interfaces formed as a result of the reaction between electroless Ni-P coatings and molten tin are characteristic of the following features:

(1) the presence of a continuous layer of Ni_3P on both as-plated and heat-treated Ni-P coatings (Fig 2 and Figs 3a, 3b);

(2) the loss of P to molten tin and the subsequent formation of a new layer consisting of Ni, Sn and P (Figure 2);

(3) the absence of a Ni_3Sn_4 layer, which can be observed on normal solder joints [4-9];

(4) the complete disappearance of Ni_3P on heat-treated Ni-P with less than approximately 7 wt% P (Figs 3c,3d, and Figs. 5,6);

(5) the localised penetration of Ni_3P and its underlying Ni-P by molten tin (Fig. 4)

The presence of Ni_3P on as-plated Ni-P after its reaction with molten tin is not surprising. Many previous investigations on the interfacial reaction between Ni-P and molten tin-based solders have observed a similar phenomenon. In view of the fact that, in as-plated Ni-P, P exists as an elemental solute in a Ni-based solid solution, Jang et al. [8] ascribed the formation of Ni_3P to the selective reaction of Ni in Ni-P with Sn in molten solders. As a consequence, P released from the selective reaction becomes enriched at the interface. The enrichment of P eventually induces a recrystallisation reaction which leads to the formation of Ni_3P.

For heat-treated Ni-P, no previous studies have been made on its reaction with molten solders. The formation of a similar layer of Ni_3P on heat-treated Ni-P in this study was somewhat unexpected, since unlike the elemental P in as-plated Ni-P, the P in heat-treated Ni-P has already precipitated out as Ni_3P prior to the reaction with molten tin. Heat-treated Ni-P was microstructurally a two-phased mixture of Ni and Ni_3P, probably in a laminated format [11] (also see Fig. 4). Therefore, the formation of a single-phased layer of Ni_3P on heat-treated Ni-P

seemed to indicate that the interfacial reaction was sustained by the outward diffusion of Ni atoms from the Ni phase, whilst the remaining Ni_3P phase coalesced into a continuous layer. This reaction mechanism is similar to that proposed by He et al. [5] for as-plated Ni-P, although the Ni_3P layer in the latter is formed by a recrystallisation reaction rather than a simple coalescing process.

Although It has been reported in the literature that some P had been lost into the molten solder [6,9], no direct evidence of the existence of P in phases other than Ni_3P was provided. All the claims were in fact based on the thickness ratio of Ni_3P and Ni_3Sn_4 phases [6]. Since Ni_3Sn_4 has a very irregular interface with solder [4-9], its thickness is difficult to measure accurately. In this study, the loss of P was proved by the direct detection of P in a Ni-Sn-P layer through the EDX analysis (Fig 2). As will be further explained later on, this loss was less likely due to the decomposition of Ni_3P. In contrast, it was believed that the enhanced mass transport of dissolving elements by our specific experimental setup was responsible for the loss of P and thus the formation of Ni-Sn-P. In this work, very thin copper wires (approximately 250 μm in diameter) were used as the substrate for the Ni-P plating samples, which were immersed in a large volume of molten tin for the interfacial reaction. It has been found that the mass transport rate of ions to and from a wire sample immersed vertically in a stationary electrolyte is inversely proportional to the third root of the wire radius [12]. The thinner the wire, the easier the mass transport. For the same reason of enhanced mass transport, Ni atoms dissolved from the reaction between Ni-P and molten tin may diffuse into the bulk of the molten tin so easily that the concentration of Ni atoms at the interface cannot accumulate to the level required for the formation of Ni_3Sn_4 IMCs. This explains the absence of large Ni_3Sn_4 particles from our samples, although they have been observed in other studies of solder joints with planar substrates [5,6,8]. Without the protection from such a solid layer of Ni_3Sn_4, the Ni_3P phase with a porous microstructure (with pores, or

possibly Kirkendall voids [5,8]) was subjected to the direct attack of molten tin. This led to the penetration of tin along the microstructural defects, which would eventually cause the crumbling of Ni_3P particles into the molten tin and the formation of a ternary layer of Ni-Sn-P.

In previous studies of the interfacial microstructure using TEM, a similar but much thinner (less than half a micron) ternary Ni-Sn-P alloy layer has also been identified in planar solder joints after solid state annealing [8,14]. The formation of such a Ni-Sn-P layer may also be due to the diffusion of Sn along the grain boundaries of Ni_3P, especially when all of the Ni-P has been reacted and there is therefore an insufficient supply of Ni atoms from underneath the Ni_3P to react with Sn from the solder [15].

In addition, the enhanced mass transport and the consequent absence of a layer of Ni_3Sn_4 IMC at the interface may also be responsible for the extreme reactivity of Ni-P observed in this study. For Ni-P on planar solder joints, an approximately 4 μm thick layer of Ni-P was found to be able to survive in molten eutectic Sn-Bi solder at 240 °C for about 48 hours before it failed by local penetration of liquid solder to the substrate [13]. However, it was found here that for Ni-P on thin wires, even a 15 μm thickness can be totally dissolved into the molten tin at 250 °C in less than 30 mins.

The complete disappearance of Ni_3P on heat-treated Ni-P with less than approximately 7 wt% P may be due to the small volume fraction of Ni_3P in such low P Ni-P coatings. As a result, there was a large volume contraction as Ni atoms diffused out to react with Sn and therefore a large tensile stress induced in the coalesced Ni_3P. This tensile stress could enhance the penetration of molten tin along Ni_3P boundaries, which may have caused the Ni_3P particles to crumble into the molten tin.

12

4.2 Ni₃P stability and its implications

As described in Section 3.2.4, the loss of P mainly occurred after longer periods of reaction when the Ni$_3$P became thicker. This result provides more support to the theory that during the interfacial reaction between electroless Ni-P and molten solder, the Ni$_3$P formed is stable and it does not decompose to release its Ni atoms [5]. The reason is that If Ni$_3$P were not stable and it did decompose during the interfacial reaction, there would be a greater chance for P atoms from the decomposed Ni$_3$P to diffuse into the molten tin (especially as, in this study, molten tin was in direct contact with Ni$_3$P), rather than to back diffuse through the solid Ni$_3$P or Ni-P phase. Although it has been proposed that the grain boundaries of fine Ni$_3$P may provide a fast diffusion path [4,8], the activation energy needed for the diffusion of P atoms in the solid phase is still much higher than that in the liquid tin. Therefore the decomposition of Ni$_3$P would mean a complete loss of P at any stage of reaction. Under the assumption of the decomposition of Ni$_3$P, it is difficult to explain the formation of Ni$_3$P on both types of Ni-P and no or limited loss of P at the early stage of reactions for as-plated Ni-P.

Although it is proposed that Ni$_3$P does not decompose, this does not imply that Ni$_3$P could form an effective barrier layer to protect the substrate from the attack of molten tin, which is of primary importance for the interfacial stability of liquid solder interconnections [3]. As can be seen from Fig. 7, the consumption rate of Ni-P was linear for both types of Ni-P coatings with higher P contents. This implies that Ni atoms from the remaining Ni-P underlying the Ni$_3$P layer can diffuse through the Ni$_3$P (up to a thickness of 2.0-2.5 µm) without any difficulty. The consumption rate of Ni-P was controlled by the chemical reaction of Ni and Sn. On the other hand, the Ni$_3$P formed, either by recrystallisation as for as-plated Ni-P or by the coalescence of existing Ni$_3$P particles, was not compact. The volume contraction and tensile stress developed during the

formation of Ni$_3$P, as discussed in Section 4.1, may tear it apart at the original boundaries of Ni-P nodules (Fig. 4), which is where these stresses concentrate. Such defects are believed to be the locations where the penetration of molten tin eventually started.

In order to improve the resistance of electroless Ni-P to the attack of molten tin and thus to maintain the interface stability of liquid solder interconnections, one possible approach is to introduce some high melting point elements into the coating, such as Cr, W and Mo [10,11]. As the coating reacts with molten solders, these elements get enriched at the surface. As a result, the diffusion of nickel atoms can be slowed down. Our recent work with electroless Ni-W-P alloys [16] has proved that the addition of W can greatly extend the service life of the barrier metallization.

5. Conclusions

In this study, we compared the reaction characteristics of different electroless Ni-P coatings with molten tin. Ni$_3$P was found to form on all as-plated Ni-P coatings. On heat-treated Ni-P, Ni$_3$P was observed only when the P content in the coating was higher than approximately 7 wt%. The thickness of Ni$_3$P was thicker on as-plated Ni-P than on heat-treated samples. No Ni$_3$Sn$_4$ was observed in any of the samples. Instead a new layer consisting of Ni, Sn and P was found, indicating the loss of P to the molten tin side. The absence of Ni$_3$Sn$_4$ is explained by the enhanced mass transport of dissolved Ni atoms, while the loss of P is ascribed to the crumbling of Ni$_3$P particles into the molten tin. A mass conservation analysis of P indicated that the loss of P mainly occurred when Ni$_3$P was thick. It is therefore proposed that, during the interfacial reaction, Ni$_3$P is stable and doesn't undergo chemical decomposition. The only source of Ni for the reaction is therefore the outward diffusion of Ni from the unreacted Ni-P. On as-plated Ni-P coatings, Ni$_3$P is formed by the enrichment of P and the consequently induced recrystallisation reaction; whist on heat-treated Ni-P coatings, Ni$_3$P is formed by the coalescence of already

precipitated Ni_3P particles due to the heat-treatment. However, Ni_3P cannot form an effective barrier against the attack of molten tin, since Ni atoms from the unreacted Ni-P underneath can diffuse through it without any difficulty, resulting in a linear consumption rate of Ni-P. Meanwhile, the defects in Ni_3P could also allow localised penetration of molten tin towards the substrate.

Acknowledgements

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TABLE 1 Electrolytes and deposition conditions for the electroless Ni-P coatings

Composition and conditions	Formulation No.							
	1*	2	3	4	5	6**	7	8
$NiSO_4 \cdot 6H_2O$ (g/l)	40	40	40	26	26	24	30	26
$NaH_2PO_2 \cdot H_2O$ (g/l)	11	11	11	16	16	24	14	16
pH	8.8	9.5	8.0	10.0	9.0	4.5	8.0	8.0
Temperature (ºC)	80	80	90	80	80	90	90	90
P content in deposits[†] (wt%)	2.0	3.8	5.0	6.5	7.5	10.0	13.0	14.0

* plus 0.6 mg/l thiourea
** plus 28 ml/l lactic acid and 2.2 ml/l propionic acid
[†] the P contents are for as-plated samples
All formulations except No 6 also contained 60 g/l $Na_3C_6H_5O_7 \cdot 2H_2O$, 66 g/l $(NH_4)_2SO_4$

FIG. 1. SEM micrographs showing the cross-sections obtained under different conditions: (a) section plane normal to the copper wire; (b) section plane not normal to the wire

FIG 2. The interfacial microstructure of Ni-P coatings with 14 wt% P in the as-plated (a) and the heat-treated (b) conditions after a reaction with molten tin at 250 ºC for 12 minutes. (c) shows the line profiles of Ni, Sn and P at the interface shown in (a)

FIG 3. Micrographs showing the interfacial microstructure of Ni-P coatings with low/medium P contents for different treatment conditions. (a) 7.5 wt% P, as-plated; (b) 7.5 wt% P, heat-treated; (c) 2.0 wt% P, as-plated; (d) 2.0 wt% P, heat-treated

FIG 4. Micrographs showing (a) the local penetration of a heat-treated Ni-P coating (7.5 wt% P) by molten tin at Ni-P nodule boundaries and (b) the formation of cracks in Ni_3P due to the boundary effect.

FIG 5. Effect of the P content in the deposit and the heat-treatment on the thickness of Ni_3P formed at the interface

FIG 6. Variation of Ni_3P thickness with reaction time for Ni-P coatings with different P contents. (a) 2.0 wt% P, as-plated; (b) 2.0 wt% P, heat-treated; (c) 7.5 wt% P, as-plated; (d) 7.5 wt% P, heat-treated; (e) 14 wt% P, as-plated; (f) 14 wt% P, heat-treated

FIG 7. The variation with reaction time in the thickness of Ni-P coatings consumed during the reaction at 250 ºC.

 FIG 8. Schematic illustration of the geometry of different phases at the interface of Ni-P on (a) planar substrates; (b) wire substrates with a diameter of 2r.

 FIG 9. The relationship between the thickness of Ni-P consumed and the thickness of Ni_3P formed during the interfacial reaction. The straight lines represent the mass conservative reaction of P. The data points were measured on the cross-section of samples.
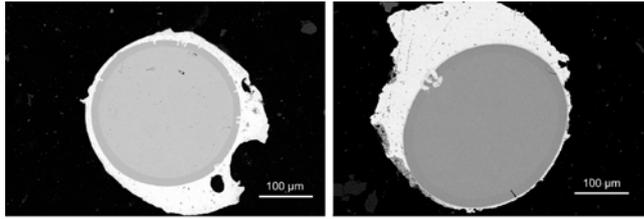
Figure 1

Fig 1
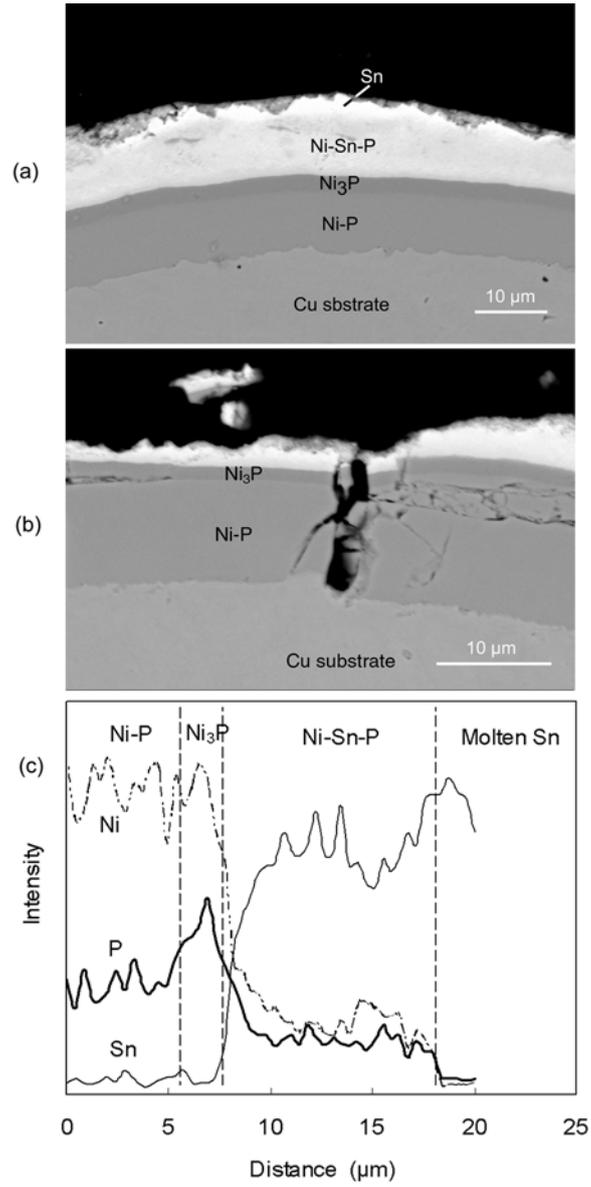
Fig 2
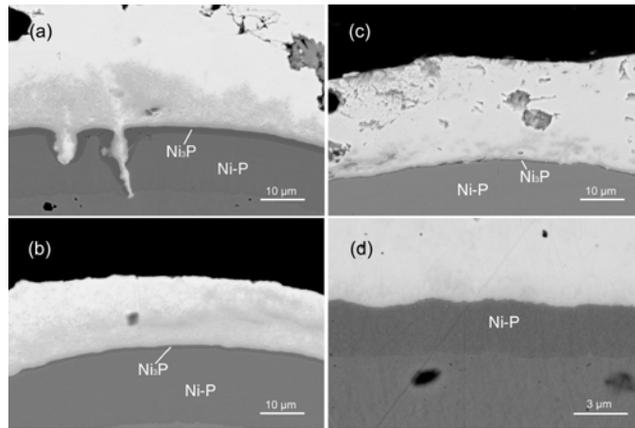
Fig 3
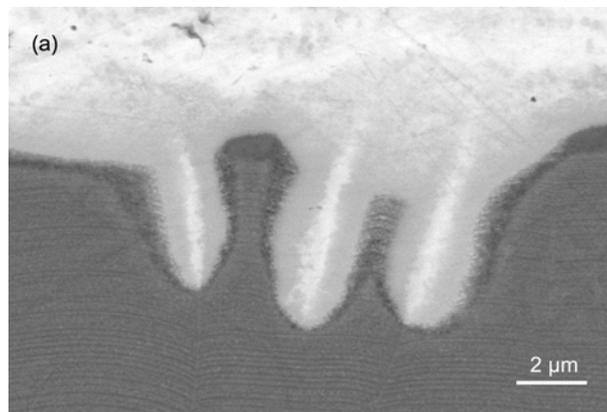
Fig 4a
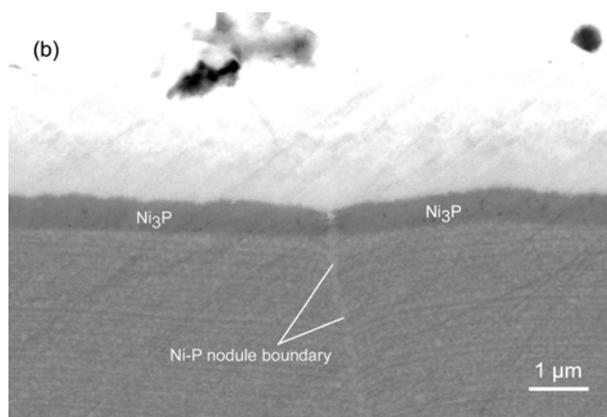
Fig 4b

Fig 5

Fig 6

Fig 7

Fig 8

23

Fig 9