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Stability of Ni₃P and its effect on the interfacial reaction between electroless Ni-P and molten tin

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Abstract

The stability of Ni₃P and its effect on the reaction with molten tin were evaluated in the present study by comparing the reaction behaviour of Ni-P coatings in the as-plated and heat-treated conditions. It was found that after the solder reaction a dark layer of Ni₃P was formed at the interface on Ni-P coatings in both conditions, but its thickness was thinner on heat-treated coatings than on as-plated coatings. From the compositional analysis on the cross-sections, it was found that not all the P ejected from the interfacial reaction between Sn and Ni-P was consumed by the formation of Ni₃P, as P was detected in a second layer of interfacial phase which also contained Ni and Sn. The formation of Ni₃P was found to be characteristic of a diffusion process, whilst the thickness of Ni-P coating consumed during the reaction was found to be linearly proportional to the reaction time. It is concluded that the Ni₃P phase formed during the solder reaction is not stable and therefore cannot act as an effective barrier to reactions with liquid solders.

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 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 Ni₃Sn₄ intermetallic compounds (IMC) at the interface, a layer of Ni₃P phase from the solder reaction-assisted crystallisation of amorphous Ni-P also precipitates adjacent to the IMC [8]. Whether the Ni₃P phase thus formed is stable, and what the effect of its precipitation is on the continuing growth of Ni₃Sn₄, are still in doubt. It has been proposed that Ni₃P may decompose to supply Ni atoms for the growth of Ni₃Sn₄ and that the ejected P atoms then diffuse back towards the Ni-P to

form Ni₃P [4, 6-8]. However, He et al. [5] ruled out the possibility of Ni₃P decomposition based on an analysis of the destination of decomposed P atoms. They also claimed that the formation of Ni₃P promoted the diffusion of Ni atoms and accounted for the faster growth of Ni₃Sn₄ 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] found that Ni₃P can act as a barrier layer for Ni diffusion and consequently suppresses the growth of Ni₃Sn₄, which in turn leads to the cessation of Ni₃P growth.

In this paper, electroless Ni-P coatings were deposited onto thin copper wires and heat-treated at 500°C for 2 hours before being dipped into a pure molten tin bath. 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 place in any intermetallic reactions. The purpose of the heat-treatment was to transform the amorphous Ni-P into the equilibrium state, which consists of crystallized Ni and Ni₃P, so that the reaction-assisted crystallisation of Ni₃P during the solder reaction may be avoided and the interference from its formation heat 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 Ni₃P and its effects on the solder reaction were investigated.

Experimental procedures

All 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 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 N₂ and 5% H₂ to avoid surface oxidation. The heat-treatment furnace was heated at a rate of 5 °C/min to 500 °C and was held at that temperature for 2 hours. The furnace was then cooled down at 5 °C/min to room temperature. The change in the deposit microstructure as a result of the heat-treatment was characterized by X-ray diffractometry using a Bruker D8 X-ray diffractometer, with Cu Kα radiation (λ=1.5406 Å), 2θ in the range of 25-90°, at a scan rate of 0.02 °/sec, a voltage of 40 kV, and a current of 40 mA.

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. The reaction temperature was 250 or 290 °C, 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 to avoid disturbing the reaction products at the interface.

Table 1 Electrolytes and deposition conditions for electroless Ni-P coatings

Composition and conditions	Formulation no.							
	1*	2	3	4	5	6**	7	8
NiSO ₄ ·6H ₂ O (g/l)	40	40	40	26	26	24	30	26
NaH ₂ PO ₄ ·H ₂ O (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 (°C)	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

All formulations except No 6 also contained 60g/l Na₃C₆H₅O₇·2H₂O, 66 g/l (NH₄)₂SO₄

Following dipping, the samples were mounted in electrically conductive resin and 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 for cross-sections like that shown in Fig. 1a. For cross-sections such as shown in Fig. 1b, the measurement was done along the short axis of the oval, where the distortion of thickness is the least due to an oblique section plane.

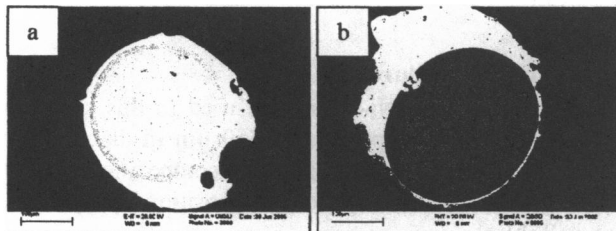


Fig. 1 SEM micrographs showing the cross-sections obtained under different conditions: (a) section plane normal to the copper wire; (b) section plane not normal to the wire

Results and discussion

The X-ray diffraction patterns for the as-plated and heat-treated Ni-P coatings are shown in Fig. 2. The breadth of the Ni XRD peak indicates that in the as-plated condition (Fig. 2a), the low P (2 wt%) coating is mainly nano-crystalline nickel. This is in agreement with results previously reported in the literature [10-12]. With increasing P content, the coating develops a fully amorphous microstructure owing to the increased disturbance from P atoms to the regular arrangement of Ni atoms. This amorphous microstructure can be inferred from the very weak and broadened diffraction peak for the coating with 14 wt% P. After the heat-treatment at 500 °C, it

can be seen from Fig. 2b that the diffraction peaks of Ni for the low P coating have become much stronger and sharper than before the heat-treatment, indicating that a grain coarsening process for the Ni has taken place. For coatings with medium (7.5 wt%) and high (14 wt%) P contents, the heat-treatment induced a phase transformation with the formation of well-crystallized Ni and Ni₃P phases. Therefore, it is confirmed that after the heat-treatment the Ni₃P phase has definitely precipitated from the amorphous matrix. Its stability during the reaction with molten tin can subsequently be assessed. It is necessary to note that the existence of Ni₃P in the coating with 2 wt% P, and Ni in the coating with 14 wt% P in the heat-treated state was not revealed by the XRD due to their small volume fractions.

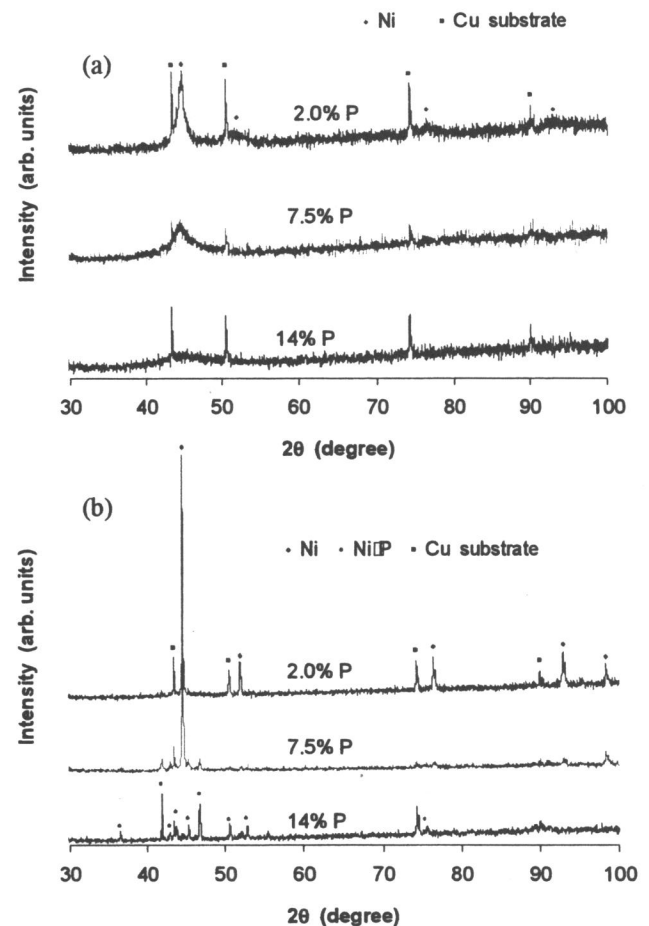


Fig. 2 X-ray diffraction patterns of Ni-P coatings in (a) the as-plated and (b) the heat-treated states

However, there is a possibility that during the heat-treatment, the P atoms in the Ni-P coatings may diffuse into the substrate [12], leading to a reduction of P content in the coating. The composition of the Ni-P coatings before and after heat-treatment was measured by EDS on the cross-sections and the results are shown in Fig. 3. It can be seen that for some coatings there seems to be a slight decrease in the P content after heat-treatment. Considering the overlapping of the error bars, this apparent slight decrease may however not be significant.

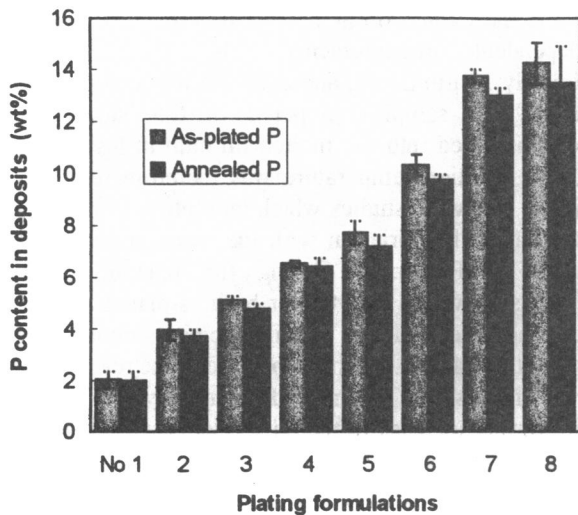


Fig. 3 Change in the deposit P content after heat-treatment for coatings from different plating formulations as given in Table 1

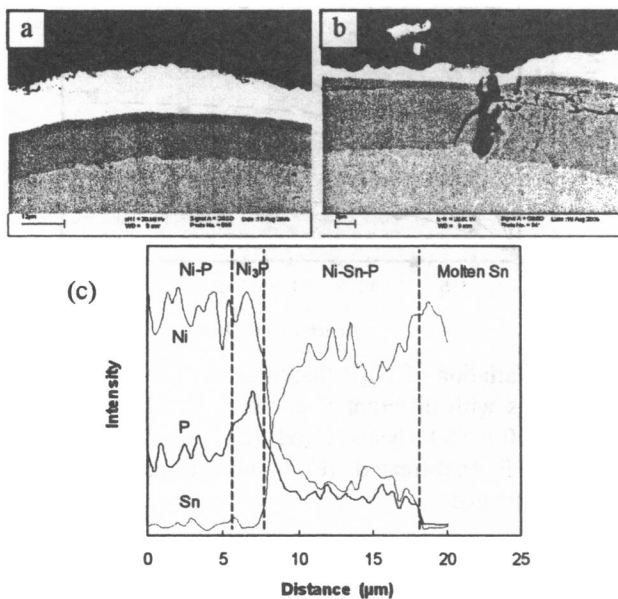
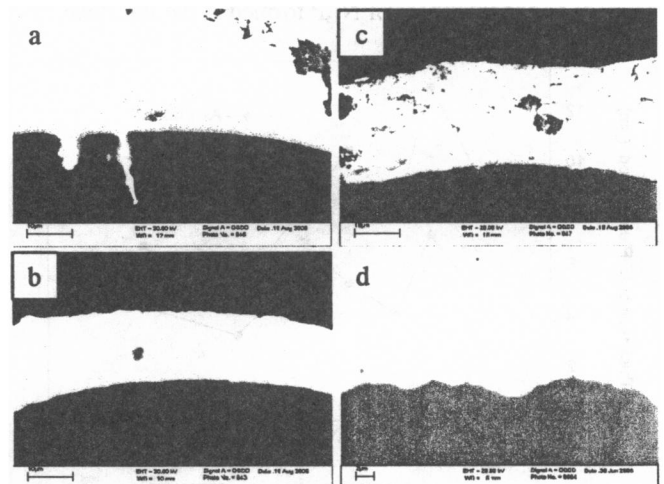


Fig. 4 The interfacial microstructure of Ni-P coatings with 14 wt% P in the as-plated (a) and the heat-treated (b) conditions after a reaction with molten tin at 250 °C for 12 minutes. (c) shows the line profiles of Ni, Sn and P at the interface shown in (a)

Figure 4 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. 4a 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 Ni₃P phase. Therefore this dark layer is assumed to be the Ni₃P phase as identified in previous

investigations [4,8]. The light grey layer next to the Ni₃P was expected to be the Ni₃Sn₄ IMC. However, the compositional analysis as shown in Fig. 4c indicated that it consisted of Ni, Sn and P. The presence of P in this layer suggests that P was lost into the molten solder side and that not all the P atoms ejected from the reaction between Ni and Sn were consumed by the formation of Ni₃P. To our knowledge, this is the first evidence of the loss of P into the solder, which may be enabled by the enhanced diffusion of atoms from the interface region into the bulk of molten tin due to the specific geometry of our thin copper wire samples. From the growth characteristics of the Ni₃P phase, Hung et al. [9] has also come to the same conclusion that there was a large loss of P during the reaction of their Ni₇₇P₂₃ coatings (approximately 14 wt% P) with molten eutectic Pb-Sn solder, but they didn't present any direct evidence for this.

For the heat-treated samples (as shown in Fig. 4b), a dark layer of Ni₃P also formed at the interface after the dipping experiment, although its thickness is thinner than that shown in Fig. 4a. The formation of such a single phase layer of Ni₃P on a two-phased Ni-P coating (i.e. Ni and Ni₃P) indicated that, during the reaction with molten tin, the Ni₃P phase formed during the heat-treatment prior to the dipping experiment had decomposed. The Ni atoms from the decomposition of Ni₃P reacted with molten tin, whilst the P atoms from the decomposition became enriched at the interface forming a new, continuous layer of Ni₃P. Therefore this could indicate that the



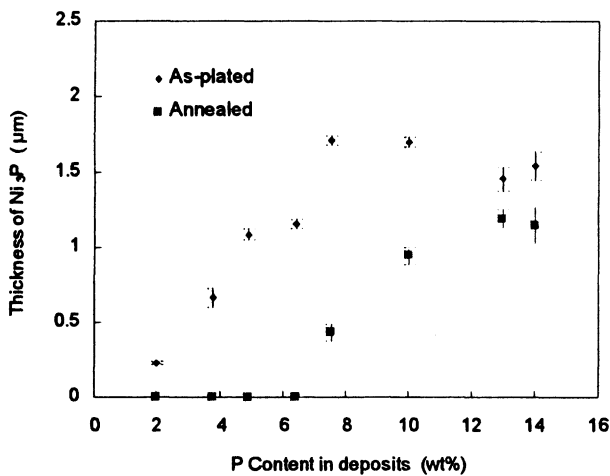
decomposition of Ni₃P is possible.

Fig. 5 Micrographs showing the interfacial microstructure of Ni-P coatings with low/medium P contents in different 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

The interfacial microstructure for Ni-P coatings with low/medium P contents is shown in Fig. 5. These interfaces showed a similar multilayered structure to those with 14 wt% P. The decrease in the thickness of Ni₃P as a result of heat-treatment is also apparent. For the coating with 2 wt% P in the heat-treated state, no Ni₃P was observed to form at the interface during its reaction with molten tin.

Fig. 6 shows the thickness of Ni_3P formed during the solder reaction with different Ni-P coatings at 290 °C 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 didn't 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 trend was observed, although the thickness of Ni_3P was apparently thinner than that formed on as-plated samples.

Fig. 6 Effect of the P content in the deposit and the heat-



treatment on the thickness of Ni_3P formed at the interface

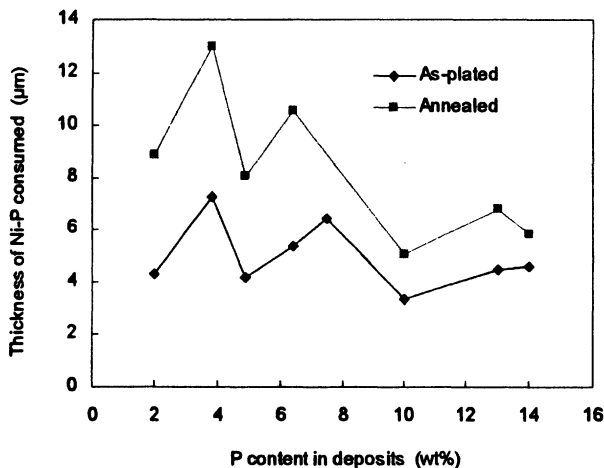


Fig. 7 Effect of the P content in the deposit and the heat-treatment on the thickness of Ni-P coatings consumed during the reaction with molten tin at 290 °C for 7 minutes

The effect of the P content in the deposit and the heat-treatment on the thickness of Ni-P coatings consumed during 7 minutes of solder reaction at 290 °C is shown in Fig. 7. The thickness of Ni-P coatings consumed during the reaction is defined as the thickness difference between the original Ni-P coating and the un-reacted Ni-P coating left underneath the Ni_3P layer after the dipping experiment. As can be seen from Fig. 7, Ni-P coatings after heat-treatment seemed to become more reactive with molten tin, whilst coatings with lower P contents seemed to be less resistant to the solder reaction.

It was found that the reaction rate between the electroless coatings and the molten tin at 290 °C 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 °C 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. 8. For both as-plated and heat-treated coatings, the thickness of Ni_3P increases rapidly at the beginning of the reaction. With an increase in the reaction time, the growth rate slows down and eventually there is no significant further increase in the Ni_3P thickness. This implies that the formation of Ni_3P is characteristic of a diffusion process.

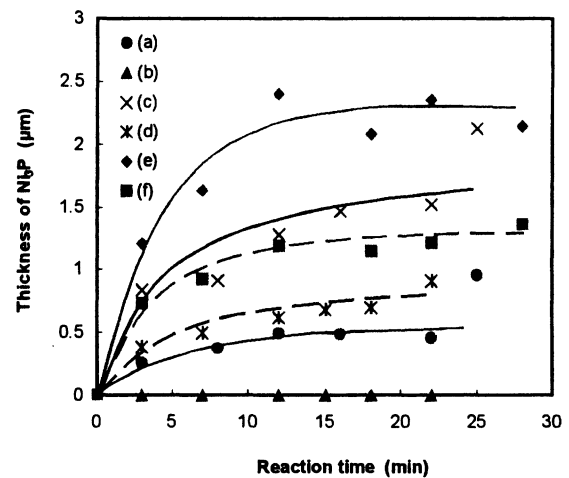
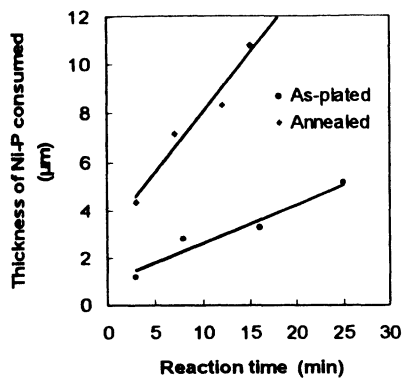
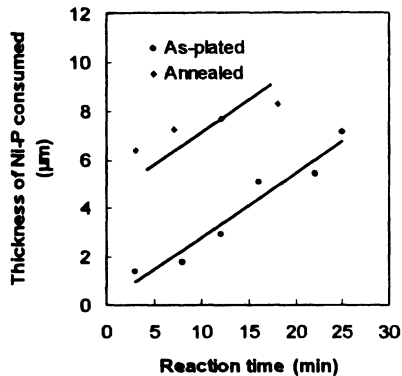


Fig. 8 Variation of Ni_3P thickness with reaction time for Ni-P coatings with different P contents. (a) 2.0 wt% P, as-plated; (b) 2.0 wt% P, heat-treated; (c) 7.5 wt% P, as-plated; (d) 7.5 wt% P, heat-treated; (e) 14 wt% P, as-plated; (f) 14 wt% P, heat-treated

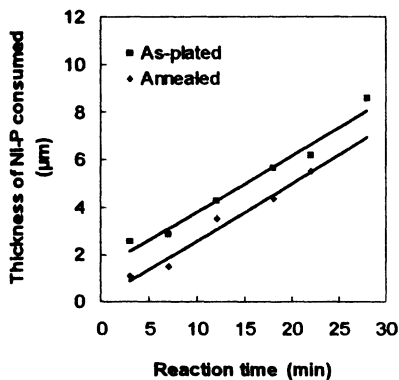
The thickness of the Ni-P coatings consumed during the solder reaction at 250 °C is shown in Fig. 9. No matter whether the coating is in the as-plated or the heat-treated state, the thickness of the coating consumed is linearly proportional to the reaction time. For the coatings with 2.0 wt% and 7.5 wt% P contents, their consumed thickness was much thicker in the heat-treated state than in the as-plated state. However, for the coating with 14 wt% P, the consumed thickness after the same reaction time was slightly thinner for the heat treated samples. However, considering the experimental error during the thickness measurement, this small difference may not be significant. Therefore the heat-treatment for the coating with high P content may not have a significant effect on its reaction rate with molten tin, although it has been found to promote the reaction between Ni-P coatings with low and medium P contents and molten tin, as shown in Fig. 9a and 9b.



(a) 2.0 wt% P



(b) 7.5 wt% P



(c) 14 wt% P

Fig. 9 The variation with reaction time in the thickness of Ni-P coatings consumed during the reaction at 250 °C.

The linear relationship between the thickness of the Ni-P coating consumed during the solder reaction and the reaction time implies that the reaction was under kinetic rather than diffusion control. The existence of a layer of Ni₃P at the interface didn't slow down the reaction rate at all. With reference to the decomposition of Ni₃P at the interface as stated earlier, it can be seen that Ni₃P couldn't act as an effective barrier for the reaction with molten tin.

Conclusions

It has been found that during the reaction of Ni-P coatings on thin copper wires with molten tin, P was lost to the solder side and not all the P was consumed by the formation of Ni₃P. The loss of P was more significant for Ni-P coatings in the as-plated state than for those after a heat-treatment prior to the solder reaction. The Ni₃P phase, either formed during the interfacial reaction or pre-existing as a result of the heat-treatment, was not stable. It decomposed to supply nickel

atoms for the interfacial reaction with molten tin. Therefore Ni₃P couldn't act as an effective barrier for the liquid solder reaction. As a result, the consumption rate of the Ni-P coatings was not slowed down, although the thickness of Ni₃P increased with increasing reaction time.

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