

Influence of Phosphorus Concentration in Electroless Plated Ni-P Alloy Film on Interfacial Structures and Strength between Sn-Ag-(Cu) Solder and Plated Ni-P Alloy Film

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One of the critical issues which needs to be solved in the packaging technology of high speed and high density semiconductor devices is the enhancement of micro-solder joint reliability and strength. The reliability and strength of the solder joints depend on the interfacial structures between metallization and lead free solder. Both the interfacial structures and the strengths of the solder joints between plated Ni-P alloy films with various P concentrations and various solder materials have been investigated. The places where intermetallic compounds crystallized were found to vary according to the P concentration in plated Ni-P alloy films and the composition of the solder. Pyramidal intermetallic compounds that formed on plated Ni-P alloy films had the following compositions: Sn-3.5 mass%Ag/Ni-2 mass%P, Sn-3.5Ag-0.7 mass%Cu/Ni-P(2, 8 mass%) and Sn-50 mass%Pb/Ni-P(2, 8 mass%). Whereas intermetallic compounds were crystallized in the solder of the Sn-3.5 mass%Ag/Ni-8 mass%P sample. A P-enriched layer was formed between the plated Ni-P alloy films and the intermetallic compounds. The thickness of the P-enriched layers of each sample increased with the reaction time. In experiments using the same solder material, the P-enriched layer of the solder/Ni-8 mass%P sample was much thicker than that of the solder/Ni-2 mass%P sample. In experiments with plated Ni-8 mass%P alloy films, the P-enriched layers became thicker in this order: Sn-50 mass%Pb/Ni-8 mass%P; Sn-3.5Ag-0.7Cu/Ni-8 mass%P; Sn-3.5 mass%Ag/Ni-8 mass%P. The strengths of the solder joints decreased with the P concentration in plated Ni-P alloy films for all solder materials. However, it was found that the strength degradation ratio varied with the solder materials and they increased in the following order: Sn-50 mass%Pb; Sn-3.5Ag-0.7 mass%Cu; Sn-3.5 mass%Ag. Therefore, it was found that the solder joint strength is very sensitive to the thickness of the P-enriched layer at the solder joint and the solder joint strength decreased with the thickness of the P-enriched layer independent of the solder materials.

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1. Introduction

In response to the miniaturization of products and the increasing speed of semiconductor devices there has been a recent reduction in the size of solder joints.¹⁾ Thus reliability enhancement at the micro solder joints is a critical issue to be solved for future high-performance semiconductor devices. The reliability of the joints may depend on the interfacial structure.^{2,3)}

Figure 1 show a schematic illustration of a Ball Grid Array (BGA) package structure. As shown in this diagram, electroless plated Ni film is commonly used as the metallization for solder joints and semiconductor devices because of its low cost and high corrosion resistance. Electroless plated Ni film contains phosphorous from several mass% through 10 mass% in order to employ hypophosphite as a reducing agent during plating.⁴⁾ So, Ni plated film will be referred to as Ni-P alloy film in this paper.

Recently, lead-free soldering processes have been investigated in order to eliminate the lead pollution caused by lead-bearing solder in semiconductor devices.^{5,6)} Sn-Ag based solder is one of the best candidates for a lead-free solder, because it has both good resistance to thermal fatigue and high ductility.⁷⁾

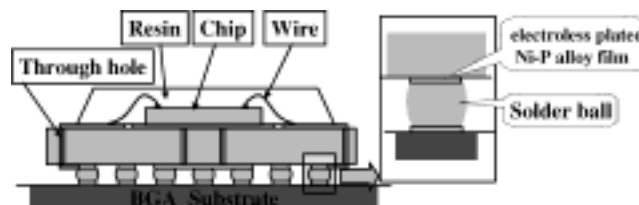


Fig. 1 A schematic representation of the BGA package.

Therefore, research into the interfacial structures between electroless plated Ni-P alloy film and solder is very important. It has been reported that reliability degradation occurs at the interface between plated electroless Ni-P alloy film and solder, when a P-enriched layer is formed at the interface during the soldering process.⁸⁾ However, no-one has yet confirmed the relationship between the interfacial structure, including intermetallic compound and the P-enriched layer, and the mechanical behavior of the solder joints.

The first purpose of the present paper is to investigate the interfacial structures formed during the soldering of plated Ni-P alloy films having various P concentrations with solder materials. Next, solder joint strength was investigated as a function of the solder materials and P concentrations in plated Ni-P alloy films. Finally, the relationship between the interfacial structure and the solder joint strength was investigated.

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Table 1 Metallization and soldering conditions.

Solder [mass%]	Mark	Plating [mass%]	Temp. [K]	Holding time [min]	Au plating [nm]
Sn–3.5Ag	Sn–Ag	Ni–[0, 2, 4, 8]P	513	1, 5, 10, 30	100
Sn–3.5Ag–0.7Cu	Sn–Ag–Cu	Ni–[0, 2, 4, 8]P	513	1, 5, 10, 30	100
Sn–50Pb	Sn–Pb	Ni–[0, 2, 4, 8]P	513	1, 5, 10, 30	100

2. Experimental Procedures

The specimens and experimental conditions are shown in Table 1. To observe the interfacial structure between plated Ni–P alloy films and solders, the Cu substrates were used made with the following procedure. 1 mm thick Cu plates were plated with 3 to 10 μm thick Ni–P alloy films containing 0, 2, 4 and 8 mass%P. Then, a 0.1 μm thick displacement Au layer was plated on top of the plated Ni–P alloy film in order to prevent oxidation and to enhance its wettability with solder as shown in Fig. 2(a). Figures 2(a) and (b) show the soldering process between a Cu substrate and solder. The Cu substrates were joined with 200 μm thick Sn–Pb, Sn–Ag and Sn–Ag–Cu solders. They were heated to 513 K for 1 to 30 min in a N_2 atmosphere. In order to evaluate the interfacial structure of the solder joints, these samples were polished on 1500 emery paper and then a buff was used for the final surface treatment of the samples. The cross-sectional structure of the interface was evaluated using a scanning electron microscope (SEM) and electron probe X-ray micro analyzer (EPMA).

The BGA substrate which consists of a 1.6 mm pitch and

a pad of 0.5 mm diameter is shown in Fig. 2(c). The pads on the BGA substrate were plated under the same conditions as that of the Cu substrate. 0.76 mm diameter solder balls were placed on the BGA substrates, and then they were heated to 513 K for 1 min in a N_2 atmosphere in order to inspect the strength of the solder joints shown in Figs. 2(c) and (d). Then, the strength of the solder joint was measured by using a cold bump pull (CBP) tester as shown in Fig. 2(e). The pull speed was fixed at 300 $\mu\text{m/s}$ for each test.

3. Results and Discussion

3.1 Evaluation of interfacial structures

First, we used EPMA to investigate where the intermetallic compounds and P-enriched layers formed in the solder joints. Figure 3 shows a cross-sectional SEM image (a), Ni– $\text{K}\alpha$ distribution image (b), Sn– $\text{K}\alpha$ distribution image (c), and a line analysis of P concentration (d) in the Ni–2 mass%P (abbreviated as Ni–2P hereafter)/Sn–Ag solder joint. By comparing the analytical results with the SEM image (a) and element distribution images (b), (c) and (d), we can identify the Ni–Sn intermetallic compound and the P-enriched layer as shown in (a). It can also be seen from (d) that the P-concentration of the P-enriched layer is about twice as high as that of the original value.

Figure 4 shows a cross-sectional SEM image of a Ni–8P/Sn–Ag solder joint (a), Ni– $\text{K}\alpha$ element distribution image (b), Sn– $\text{K}\alpha$ element distribution image (c), and a line analysis of P concentration (d) on the same place as (a). By comparing the analytical results with the SEM image (a) and element distribution images (b), (c) and (d), we can identify the Ni–Sn intermetallic compound and the P-enriched layer as shown in (a) as with Fig. 3.

Hence, the intermetallic compounds and the P-enriched layers were confirmed by the same process as shown in Figs. 3 and 4.

Figure 5 shows the cross-sectional SEM images of the joining interfaces between plated Ni–2P film and Sn–Pb, Sn–Ag, and Sn–Ag–Cu solders. Pyramidal intermetallic compounds were found to be formed along the interfaces between the plated Ni–P alloy film and the solders for all samples. For the Sn–Ag/Ni–2P and the Sn–Pb/Ni–2P joints, the Ni–Sn intermetallic compounds were formed as discussed in previous papers.^{9,10} Alternatively, Ni–Sn–Cu intermetallic compounds were formed at the Sn–Ag–Cu/Ni–P joints as reported.¹¹

Figure 6 shows the cross-sectional SEM images of the joining interfaces between plated Ni–8P film and Sn–Pb, Sn–Ag, and Sn–Ag–Cu solders. Intermetallic compounds were formed just above the P-enriched layer for Sn–Ag–Cu/Ni–8P and Sn–Pb/Ni–8P joints. However, in the case of Sn–Ag/Ni–8P joints, Sn–Ni intermetallic compounds were crystallized in the solder as reported in the previous paper.¹⁰

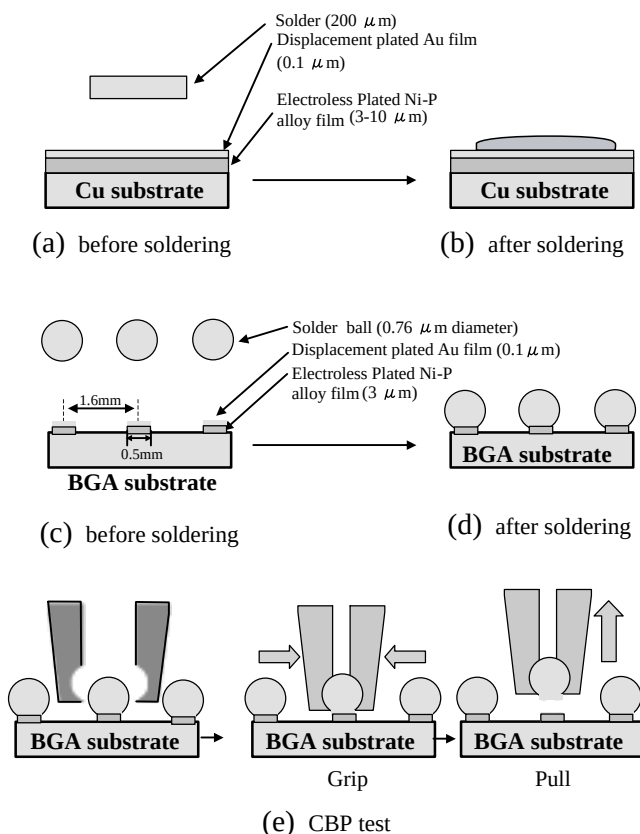


Fig. 2 A schematic representation of the procedures for soldering and the CBP test.

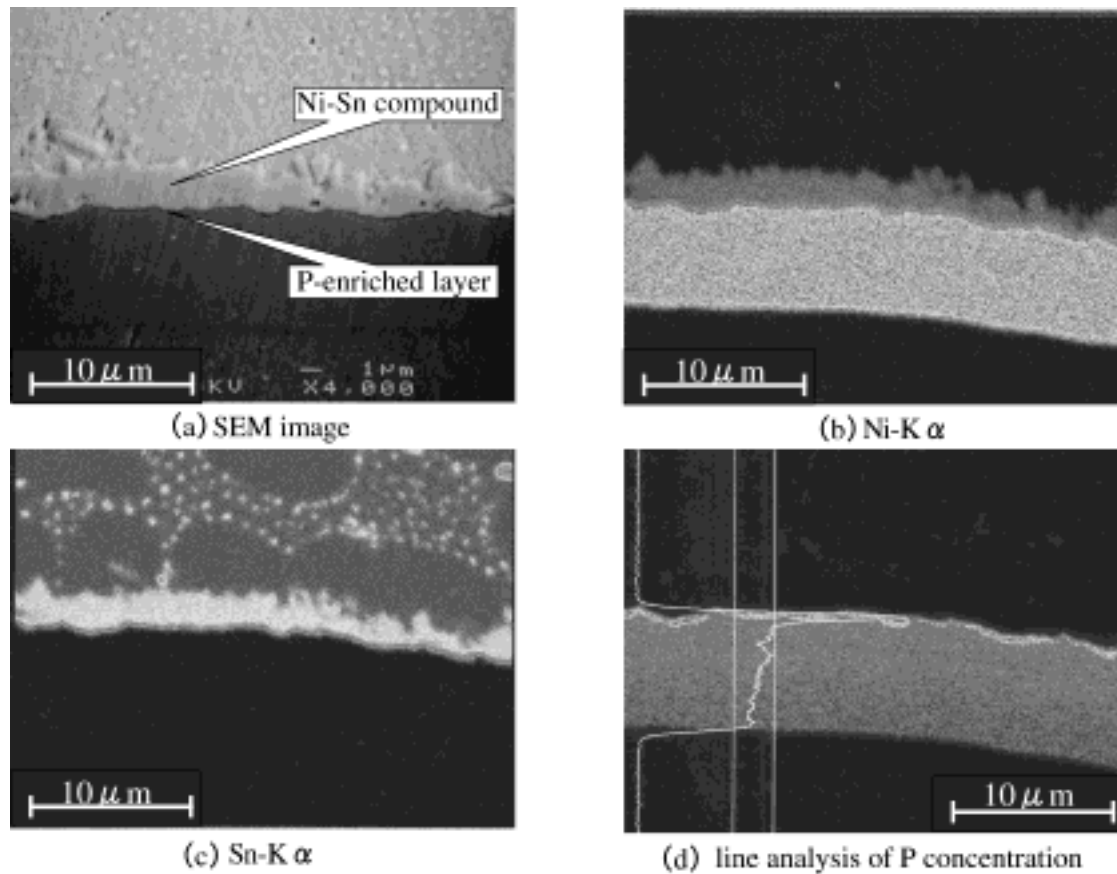


Fig. 3 The cross-sectional SEM image, element distribution images, and a line analysis of the joining interfaces between plated Ni-2 mass%P alloy films and Sn-3.5 mass%Ag solder.

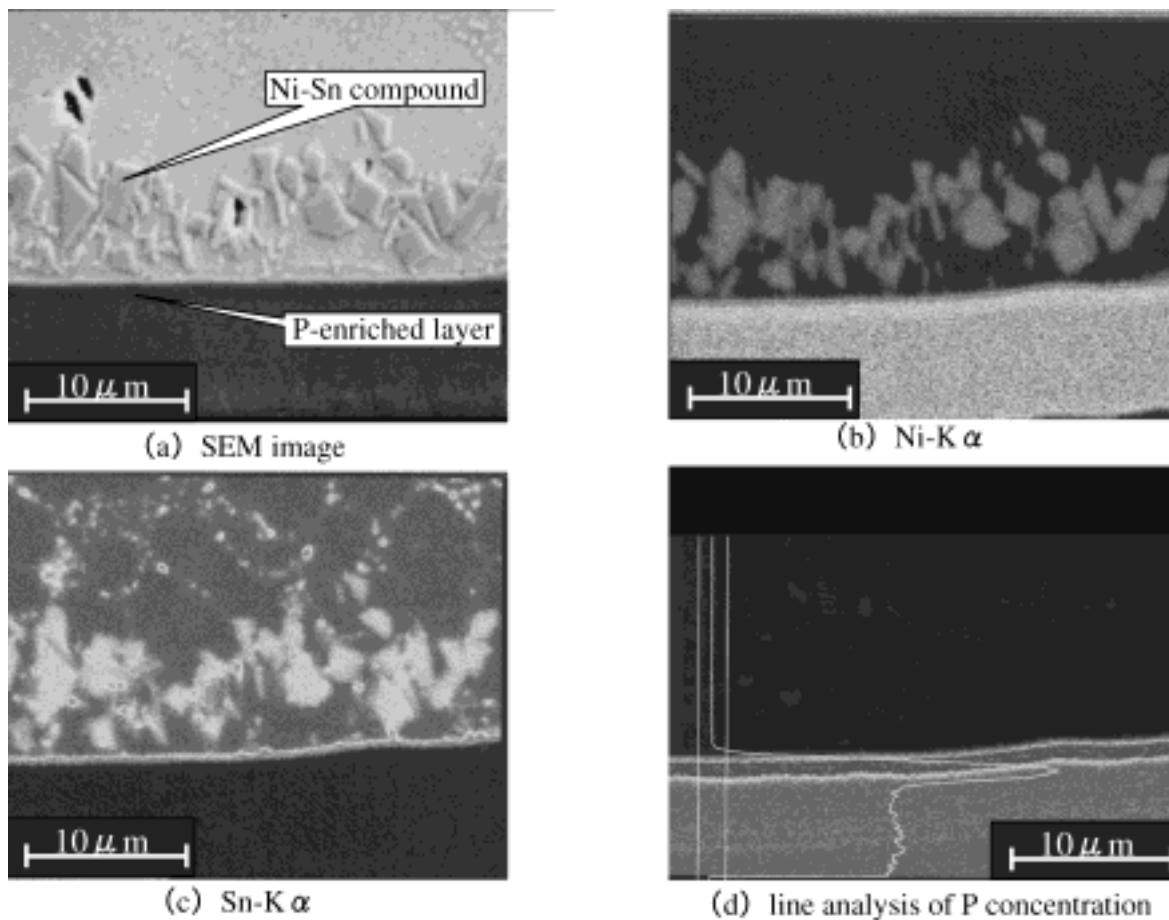


Fig. 4 The cross-sectional SEM image, element distribution images, and a line analysis of the joining interfaces between plated Ni-8 mass%P alloy films and Sn-3.5 mass%Ag solder.

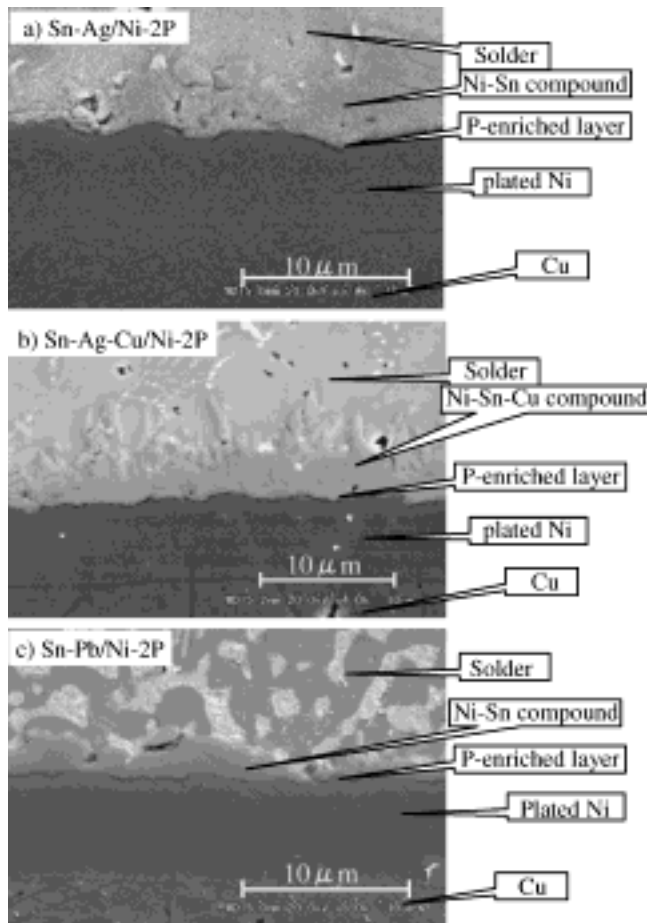


Fig. 5 Cross-sectional SEM images of joining interfaces between plated Ni-2 mass%P film and Sn-3.5 mass%Ag, Sn-3.5Ag-0.7 mass%Cu and Sn-50 mass%Pb solder.

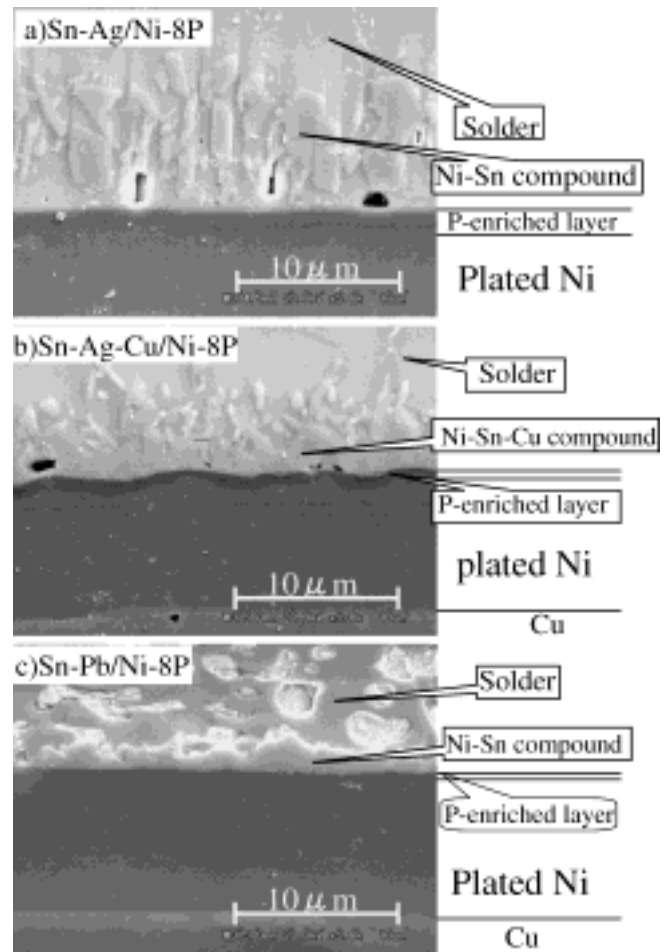


Fig. 6 Cross-sectional SEM images of the joining interfaces between plated Ni-8 mass%P film and Sn-3.5 mass%Ag, Sn-3.5Ag-0.7 mass%Cu and Sn-50 mass%Pb solder.

In Fig. 7, based on the above data, the thicknesses of the P-enriched layers were measured and plotted against the holding time at 513 K in N_2 atmosphere. The thickness of the P-enriched layers of each sample increases with the amount of reaction time at 513 K. In cases where the same solder material was used, the P-enriched layer of the solder/Ni-8P joints was much thicker than those of the solder/Ni-2P joints. It was also found that the thickness of the P-enriched layer varied with the solder material and they increased in the following order: Sn-Pb; Sn-Ag-Cu; Sn-Ag.

3.2 The strength of the solder joint

Figure 8 plots the pull strength of the solder joints between plated Ni-P (P: 0, 2, 4, 8 mass%) films and Sn-Ag(a), Sn-Ag-Cu(b) and Sn-Pb(c) solders as a function of the P concentrations in the plated Ni-P alloy films.

The strength of the solder joint decreased with P concentration in plated Ni-P alloy films for all samples. However, it was found that the strength degradation ratio depended on the solder materials and they increased in the following order: Sn-Pb, Sn-Ag-Cu, Sn-Ag. In order to identify the reason, the fractured surfaces were observed.

Figure 9 shows the SEM images of the fractured surfaces of the BGA substrate side of Sn-Ag/Ni-0P(a), Sn-Ag/Ni-2P(b), Sn-Ag/Ni-8P(c) joints after CBP test. Each fracture surface was evaluated with EDX to identify the point of frac-

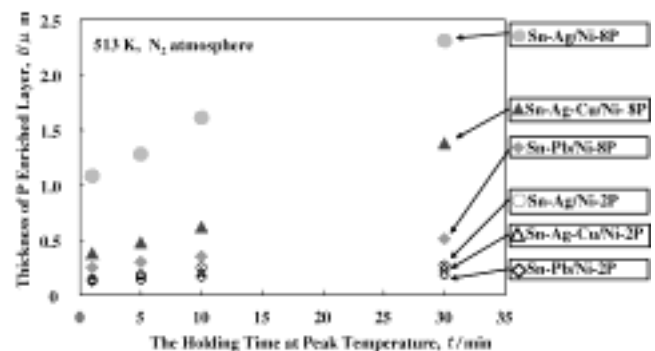


Fig. 7 The thickness of the P-enriched layer as a function of the holding time at 513 K.

ture. Figure 9(a) shows that Sn-Ag solder remained on the fractured surface of the BGA substrate side. This suggests that the strength of the joining interface between the solder and the plated Ni-P alloy film is strong. Figure 9(b) also shows that considerable Sn-Ag solder remained on the fractured surface of the BGA substrate side. However, the sample was partially fractured at the P-enriched layer, because Ni and P were observed on fractured surfaces of the BGA substrate side and that of solder ball side. Figure 9(c) indicates that the

sample was almost entirely fractured at the P-enriched layer, because Ni and P were observed on the entire fractured surface of the BGA substrate side and that of solder ball side. From the above results, it can be inferred that the fractured surface area at the P-enriched layer increases with P concentrations in the plated Ni–P alloy films.

Figure 10 shows the SEM images of the fractured surfaces between Ni–P(0, 2 and 8 mass%) alloy films and Sn–Pb solder after the CBP test. Each fracture surface was evaluated with EDX to identify the point of fracture. Figure 10(a) and

Fig. 10(b) show that Sn–Pb solder remained on the fractured surface of the BGA substrate side. Figure 10(c) shows that very small areas were fractured at the P-enriched layer in the sample, because Ni and P were observed on the fractured surfaces of BGA substrate side and that of the solder ball side.

We confirmed by using EDX the solder joints were fractured at the P-enriched layer, and they did not fracture at the intermetallic compound. Judging from these observations, the joint strength decreases as the area of P-enriched layer appearing on the fractured surface increases. The P-enriched layer is considered to be more brittle than the intermetallic compound.⁹⁾ So, the influence of the P-enriched layer on the solder joint strength degradation was greater than those of the intermetallic compound. Hence, a relationship might exist between strength degradation and an increase in the thickness of the P-enrich layer.

3.3 Relationship between the strength of the solder joints and the thickness of the P-enriched layer

Figure 11 shows the pull strength ratio of the various solder joints as a function of the thickness of the P-enriched layer. The strength ratio was defined as the ratio of the strength of the joints with P to these of the joints without P. The reason why we used the strength ratio instead of the pull strength is to remove the influence of the solder strength difference among

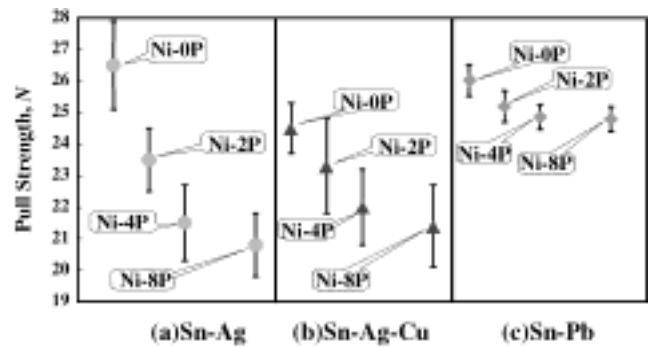
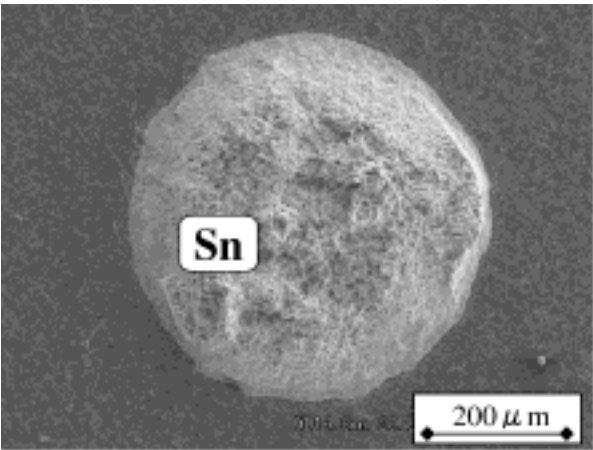
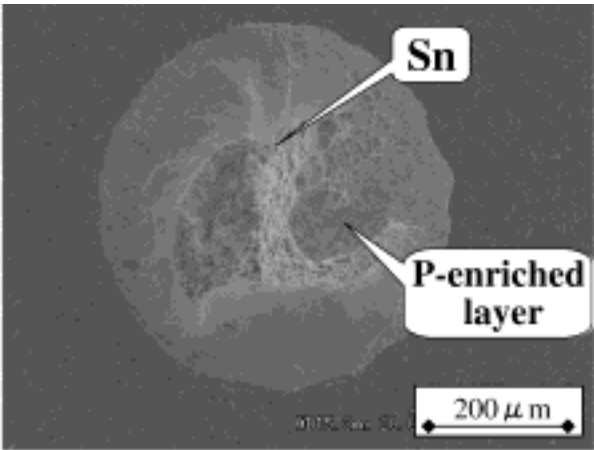


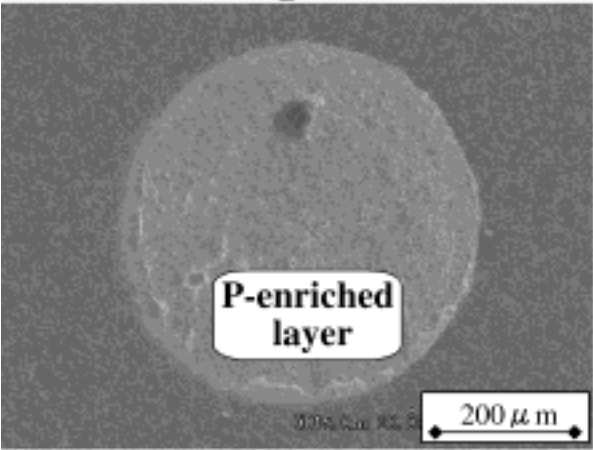
Fig. 8 The strength of solder joints between plated Ni–P films and solders as a function of the P concentration in the Plated Ni films.



a) Sn-Ag/Ni-0P



b) Sn-Ag/Ni-2P



c) Sn-Ag/Ni-8P

Fig. 9 The SEM images of the fracture surfaces of substrate side of Sn–Ag solder joints.

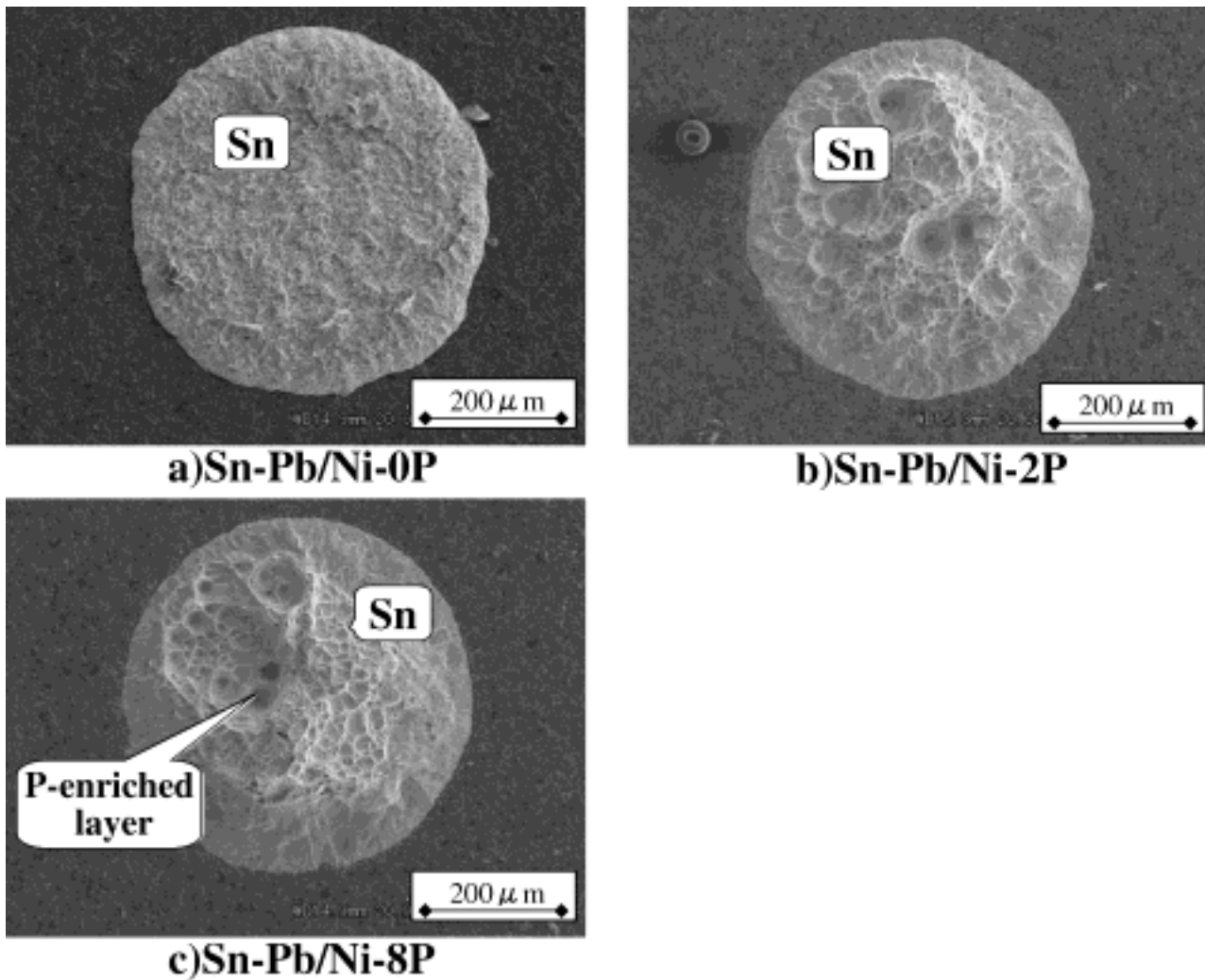


Fig. 10 The SEM images of the fracture surfaces of substrate side of Sn-Pb solder joints.

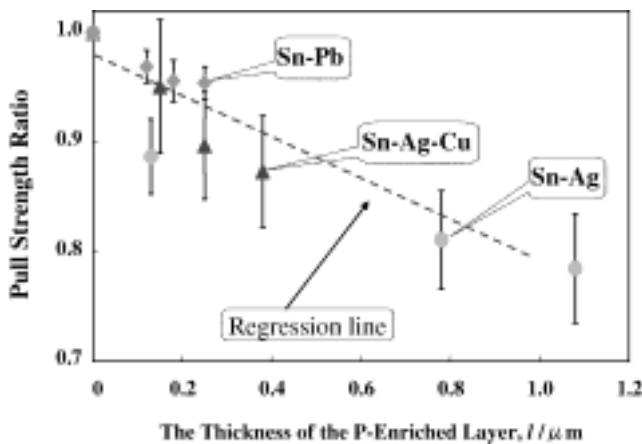


Fig. 11 The rate of the strength degradation as a function of the thickness of P-enriched layers.

the different solder materials.

The regression line was derived by least-square analysis. The correlation between the pull strength ratio of the various solder joints and the thickness of the P-enriched layer

was significant. The correlation coefficient was -0.80 for $[F(1, 173) = 307, p < 0.01]$ (p : level of significance). It can be seen that the degradation ratio of the pull strength is a linear function of the thickness of the P-enriched layer independent of the solder materials in the thickness range of the P-enriched layer from 0 to $1.08 \mu\text{m}$. Hence, it is reasonable to assume that an increase in the thickness of the P-enrich layer causes strength degradation in the solder joints. The main reason for this joint degradation may be due to the fact that the number of voids in the P-enriched layer increases with the thickness of P-enriched layer.⁹⁾

4. Conclusions

Our conclusions can be summarized as follows:

(1) In the case of the same solder, the P-enriched layer of the Ni-8 mass%P solder joints was much thicker than that of the Ni-2 mass%P solder joints.

(2) In the case of the plated Ni-8 mass%P films, the P-enriched layers became thicker in this order: Sn-Pb/Ni-P; Sn-Ag-Cu/Ni-P; Sn-Ag/Ni-P.

(3) The thickness of the P-enriched layers for each sample increased with the holding time at 513 K.

(4) Influence of P-enriched layer on the solder joint strength degradation was greater than those of intermetallic compound.

(5) The joint strength depends on the thickness of the P-enriched layer and decreases with the thickness of P-enriched layer independent of solder materials.

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