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Influence of solid-state interfacial reactions on the tensile strength of Cu/electroless Ni–P/Sn–3.5Ag solder joint

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Abstract

Tensile strength and fracture behavior of Cu/electroless Ni–P/Sn–3.5Ag (wt.% Ag) solder joint were investigated under high-temperature solid-state aging. The aging results showed that the Ni₃Sn₄ intermetallic phase grows at the electroless Ni–P/Sn–3.5Ag interface, along with the transformation of the underlying electroless Ni–P layer into Ni₃P compound. However, after complete consumption of the electroless Ni–P layer, a ternary Ni–Sn–P compound also starts to grow between Ni₃Sn₄ and Ni₃P layers in conjunction with the depletion of Cu from the Cu surface. It was found that while both the growth of Ni₃Sn₄ and depletion of Cu deteriorate the solder joint strength, the strength is deteriorated more with the latter. The growth of Ni₃Sn₄ and depletion of Cu were found to influence the failure mode and fracture surfaces of the solder joint, also. The failure mode changed from ductile to brittle and the fracture surfaces shifted from inside the bulk solder to the Ni₃Sn₄/Sn–3.5Ag interface due to the growth of Ni₃Sn₄. The failure mode became very brittle and the fracture surfaces shifted to the interface between Cu surface and Ni₃P or Ni–Sn–P layer due to the depletion of Cu.

Keyword: Electroless nickel; Solder; Mechanical reliability; Interfacial reactions

1. Introduction

Mechanical reliability of interconnects formed in low-cost solder flip-chip package is a critical issue. These interconnects are made of solder joining the chip-side under bump metallization (UBM) to the substrate metallization. Two types of solders, namely lead-containing and lead-free, are being used in the packaging industry. However, due to the legislation and environmental concerns, industry is promoting the use of lead-free solders. The lead-free solders are basically Sn-rich alloy constituting one or two more elements such as Ag, Cu, Au, and Bi. These high Sn-content solders react more rapidly with Cu UBM as compared to the lead-containing solders. The fast interfacial reactions result in large growth of brittle intermetallics and thereby in low mechanical reliability [1–3]. The intermetallic growth has been found to be minimized in the case of Ni UBM as the reaction between Ni and Sn is much slower than between Cu and Sn [4]. The Ni UBM can be deposited by various chemical and physical deposition techniques. Among them, electroless chemical deposition of Ni is becoming very popular due to its many advantages such as excellent selective deposition, good corrosion resistivity, strong adhesion, easy processing, and low-cost.

Electroless nickel is an amorphous Ni–P alloy (especially for $P > 12.5$ at.%) [5], which gets P from the hypophosphite reducing agent during the reduction of Ni from an ionic Ni solution. The presence of P in the electroless Ni–P causes its complicated interfacial reactions with solder [2–4,6–15]. During electroless Ni–P/solder interfacial reactions, mainly Ni_3Sn_4 intermetallic forms at the electroless Ni–P/solder interface along with the transformation of underlying electroless Ni–P layer into Ni_3P [7–9]. Recently, a thin Ni–Sn–P layer was also reported to form at the electroless Ni–P/solder interface [10], that grew during liquid-state aging [11,12]. More recently, it was found that this Ni–Sn–P layer can grow even during solid-state aging and can lead to the formation of Cu–Sn and Ni–Cu–Sn intermetallics in the Cu/electroless Ni–P/Sn–3.5Ag solder joint [14,15]. Although electroless Ni–P/solder interfacial reactions have been investigated thoroughly, the combined influence of all these interfacial reactions on the mechanical strength of solder joint has not been understood well, thus necessitating a thorough focused study.

Accordingly, in the present work, an attempt has been made to correlate the tensile strength of Cu/electroless Ni–P/Sn–3.5Ag solder joint with the interfacial reactions.

2. Experimental procedure

Cu (99.99%) plate of size of 70mm × 25mm × 6mm was used to fabricate multi-layered test sample Cu/Ni–P/Sn– 3.5Ag/Ni–P/Cu. The copper plate was surface cleaned, first by polishing down to 1 μm finish, then by ultrasonically cleaning with acetone for 10 min, then by etching with 20 vol.% HNO₃ solution for a few seconds, and finally by cleaning with de-ionized water. Electroless Ni–P was plated on the surface cleaned Cu plate in two steps. In the first step, Cu surface was activated using ruthenium-based commercial pre-initiator. Then, electroless Ni–P was plated on the activated Cu surface using commercial electroless nickel solution. Thin layer (~50 nm) of non-cyanide immersion gold was deposited on the electroless Ni–P surface to protect the surface from oxidation.

The electroless Ni–P coated Cu plate was cut into two plates of sizes of 40mm × 25mm × 6mm and 30mm × 25 mm × 6 mm, and then the two plates were joined with each other using Sn–3.5Ag solder. Fig. 1 illustrates the set-up used to join the plates. The joint was formed during the reflow process by placing a number of small pieces of solder wires on the small electroless Ni–P coated Cu plate and pressing them by the big plate. No-clean paste flux was applied on both the plates before placing the Sn–3.5Ag wires. The reflow process was carried out in IR reflow oven (ESSEMTEC RO-06E) which involved preheating at 150 °C for 100 s, then reflowing at 250 °C for 60 s, and finally cooling down to 160 °C in the oven. Alumina spacers of thickness of around 650 μm were used to maintain the uniform thickness of solder in between the plates. The joined plates were cut into a number of small samples of cross-sectional area of around 600 μm × 650 μm with the help of diamond saw. Fig. 2 shows the schematic diagram of test sample.

Solid-state thermal aging at 150 °C for 1000 h is a required reliability test for solder/UBM joint [4]. In this work, solid-state aging was carried out at higher temperatures (160–200 °C) to shorten down the aging duration. For thermal aging, as-prepared test samples were kept in the oven (Lenton WHT4/30) at 160, 180, and 200 °C

for 48, 100, 225, and 400 h. After aging, the samples were removed from the oven and cooled in air to room temperature. Five samples from each condition were tensile tested to obtain the average and the standard deviation. Tensile testing of solder joints was performed using INSTRON 5567 tensile tester at room temperature. A constant crosshead speed of 0.05 mm/min was used up to a complete fracture. JEOL JSM-6360A scanning electron microscope (SEM) was used for microstructure analysis. For cross-sectional SEM, samples were cold mounted in epoxy and polished down to 1 μm finish. After polishing, solder etching was carried out to reveal the microstructure in cross-section. Etching was done with 4 vol.% hydrochloric acid for a few seconds. Energy dispersive X-ray (EDX) spectroscopy was performed in the SEM to analyze the chemical composition of interfacial layers.

3. Results

3.1. Interfacial reactions

The thickness and P-content of as-plated electroless Ni-P layer were measured to be around 9.9 μm and 16 at.%, respectively. Fig. 3 is the line-scanned SEM images of Cu/electroless Ni-P/Sn-3.5Ag interfaces in the as-prepared and aged samples showing formation of various interfacial compounds (IFCs). In the as-prepared sample, two distinct colored IFCs, Ni_3Sn_4 and Ni_3P , formed at the electroless Ni-P/Sn-3.5Ag interface (Fig. 3a). The dark Ni_3P layer having a number of columnar voids formed within the electroless Ni-P layer as shown in Fig. 3a and b. In the samples aged at 160 and 180 $^\circ\text{C}$, a thin layer of ternary Ni-Sn-P compound was also found to grow between Ni_3Sn_4 and Ni_3P layers as shown in Fig. 3b. It is known that the Ni-Sn-P layer grows very slowly as long as electroless Ni-P layer remains underneath [15]. However in the samples aged at 200 $^\circ\text{C}$, after complete transformation of electroless Ni-P layer into Ni_3P , the Ni-Sn-P layer started growing very fast at the expense of Ni_3P layer (Fig. 3c and d). The elemental composition of this Ni-Sn-P layer was found similar to that of Ni_2SnP compound.

In the samples aged at 200 $^\circ\text{C}$, after complete transformation of electroless Ni-P layer into Ni_3P , a layer of voids also started growing at the Cu/ Ni_3P and Cu/Ni-Sn-P interfaces

as shown in Fig. 3c and d, respectively. In addition, a small amount of Cu (up to 5 at.%) was found in the Ni_3Sn_4 grown in these samples. The presence of Cu in Ni_3Sn_4 and growth of layer of voids at the Cu/ Ni_3P or Cu/ Ni-Sn-P interface imply that after complete transformation of electroless Ni-P layer into Ni_3P , Cu started depleting from the Cu surface to the Ni_3Sn_4 intermetallic through the Ni_3P and/or Ni-Sn-P layers. The extreme case of this Cu diffusion has been reported in our previous studies [14,15], where multi-layered Cu-Sn and Ni-Cu-Sn IFCs were found to form in the Cu/electroless Ni-P/Sn-3.5Ag solder joint.

3.2. Tensile strength and fracture analysis

Tensile strength of Cu/electroless Ni-P/Sn-3.5Ag solder joint as a function of aging duration at various aging temperatures is shown in Fig. 4. It can be seen that for a fixed duration, the strength decreased drastically with increase in aging temperature. The effect of increase in aging duration on the strength, however, varied with aging temperature. In the case of samples aged at 160 °C, the tensile strength increased slightly with increase in aging duration, whereas, it decreased considerably in the case of samples aged at 180 and 200 °C. The decrease in tensile strength was very severe in the initial 48 h of aging and after that the strength remained nearly constant.

In the as-prepared sample, as shown in Fig. 5, the failure mode was ductile and the fracture surfaces were inside the bulk solder. A large difference was observed in the failure mode and fracture surfaces of the samples aged at different temperatures. All the samples aged at 160 °C showed the same failure mode and location of fracture surfaces as the as-prepared samples showed. However in the samples aged at 180 °C, failure mode changed to brittle and fracture surfaces were at the $\text{Ni}_3\text{Sn}_4/\text{Sn-3.5Ag}$ interface (Fig. 6). The failure mode became very brittle and fracture surfaces were mainly at the Cu/ Ni_3P or Cu/ Ni-Sn-P interface in the samples aged at 200 °C (Fig. 7).

4. Discussion

The mechanical strength and fracture behavior of electroless Ni-P/solder joint were investigated in many studies [2,3,16–18]. It was reported [2,16–18] that the formation of

Ni₃P layer in the electroless Ni–P layer deteriorates the mechanical strength of electroless Ni–P/solder joint either due to the segregation of P [16–18] or due to the formation of voids [2]. However, in a recent study [3], the formation of voids in the Ni₃P layer was found not to affect the solder joint strength. Nevertheless, the change in Ni–P volume during its transformation and growth of Ni₃Sn₄ were reported [3] to be the reasons for deterioration in the joint strength. Further, the formation of Ni₃Sn₂ [17] and Ni₂SnP [10] at the Ni₃P/ Ni₃Sn₄ interface were also reported to be the main cause for brittle fracture in the solder joint. By considering the fact that all these investigations were done at different experimental conditions, it can be concluded that the electroless Ni–P/solder interfacial reactions deteriorate the mechanical properties of the solder joint. However, the main cause for this deterioration is still not clear because of different factors reported in the previous studies.

In the present work, tensile strength and fracture behavior of Cu/electroless Ni–P/Sn–3.5Ag solder joint were investigated under wide range of aging conditions to examine the mechanical reliability of the solder joint. It was found that as long as electroless Ni–P layer remains on the Cu surface, neither formation of Ni₃P layer nor formation of voids in the Ni₃P layer affect the solder joint strength. All the samples aged at 160 and 180 °C had the Ni₃P layer; nevertheless, the fracture occurred inside the bulk solder (Fig. 5) and at the Ni₃Sn₄/Sn–3.5Ag interface (Fig. 6), respectively. The formation of Ni–Sn–P layer was also found not to cause the brittle fracture in the solder joint, as in all the samples aged at 160 °C, ductile fracture occurred inside the bulk solder despite the presence of Ni–Sn–P layer.

It was found that the interfacial reactions deteriorate the tensile strength of Cu/electroless Ni–P/Sn–3.5Ag solder joint mainly due to the two factors. One is the growth of Ni₃Sn₄ intermetallic at the electroless Ni–P/Sn–3.5Ag interface and the other is the depletion of Cu from the Cu surface. The joint strength was found to deteriorate more severely due to the Cu depletion. In the case of samples aged at 180 °C, the strength decreased to ~28 MPa (Fig. 4) and the fracture surfaces were at the Ni₃Sn₄/Sn–3.5Ag interface (Fig. 6), whereas in the case of samples aged at 200 °C, the strength decreased to ~12 MPa (Fig. 4) and one of the fracture surfaces was always the Cu surface (Fig. 7).

Appearance of Cu surface as one of the fracture surfaces indicates that in the samples aged at 200 °C, the Cu surface lost its adhesion with the adjoining layer (Ni₃P or Ni–Sn–P). In these samples, electroless Ni–P layer completely transformed into Ni₃P and/or Ni–Sn–P layers (Fig. 3c and d). And then the Cu started depleting from the Cu surface to the Ni₃Sn₄ intermetallic through the Ni₃P and/or Ni–Sn–P layers. The depletion of Cu from the Cu surface resulted in the formation of layer of voids at the Cu/Ni₃P and Cu/Ni–Sn–P interfaces as shown in Fig. 3c and d, respectively. This layer of voids broke the mechanical and atomic interlocking between Cu surface and Ni₃P or Ni–Sn–P layer; thus caused a severe decrease in solder joint strength (Fig. 4) and a brittle fracture at the Cu/Ni₃P or Cu/Ni–Sn–P interface (Fig. 7).

5. Summary and conclusions

Influence of interfacial reactions was investigated on the tensile strength of Cu/electroless Ni–P/Sn–3.5Ag solder joint. It was found that the growth of Ni₃P or Ni–Sn–P layer does not affect the tensile strength as long as electroless Ni–P layer remains on the Cu surface. During interfacial reactions, the joint strength mainly decreases due to the growth of Ni₃Sn₄ and due to the depletion of Cu from the Cu surface. The growth of Ni₃Sn₄ results in a brittle fracture at the Ni₃Sn₄/Sn–3.5Ag interface. As Ni₃Sn₄ growth proceeds, Ni₃P layer grows within the electroless Ni–P layer. When the Ni₃P layer reaches the Cu surface, the Cu starts depleting from the Cu surface. The depletion of Cu results in the formation of a layer of voids at the Cu/Ni₃P interface, which further deteriorates the joint strength and causes a very brittle fracture at the Cu/Ni₃P interface.

Acknowledgements

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References

- [1] C.Y. Liu, C. Chen, A.K. Mal, K.N. Tu, *J. Appl. Phys.* 85 (1999) 3882–3886.
- [2] M.O. Alam, Y.C. Chan, K.N. Tu, *J. Appl. Phys.* 94 (2003) 4108–4115.
- [3] M. He, Z. Chen, G.J. Qi, *Metall. Mater. Trans. A* 36 (2005) 65–75.
- [4] K.N. Tu, K. Zeng, *Mater. Sci. Eng. R* 34 (2001) 1–58.
- [5] G.O. Mallory, J.B. Hajdu, *Electroless Plating: Fundamental and Applications*, American Electroplaters and Surface Finishes Society, Orlando, 1990.
- [6] C.Y. Lee, K.L. Lin, *Thin Solid Films* 249 (1994) 201–206.
- [7] J.W. Jang, P.G. Kim, K.N. Tu, D.R. Frear, P. Thompson, *J. Appl. Phys.* 85 (1999) 8456–8463.
- [8] Z. Chen, M. He, G. Qi, *J. Electron. Mater.* 33 (2004) 1465–1472.
- [9] P.L. Liu, Z. Xu, J.K. Shang, *Metall. Mater. Trans. A* 31 (2000) 2857–2866.
- [10] H. Matsuki, H. Ibuka, H. Saka, *Sci. Technol. Adv. Mater.* 3 (2002) 261–270.
- [11] Y.D. Jeon, A. Ostmann, H. Reichl, K.W. Paik, *Proceedings of ECTC (IEEE)*, 2003, pp. 1203–1208.
- [12] S.J. Wang, C.Y. Liu, *Scripta Mater.* 49 (2003) 813–818.
- [13] M. He, Z. Chen, G. Qi, *Acta Mater.* 52 (2004) 2047–2056.
- [14] A. Kumar, M. He, Z. Chen, *Surf. Coat. Technol.* 198 (2005) 283–286.
- [15] A. Kumar, Z. Chen, S. Mhaisalkar, C. C. Wong, P. S. Teo, V. Kripesh, *Thin Solid Films*, in press.
- [16] Z. Mei, M. Kaufmann, A. Eslambolchi, P. Johnson, *Proceedings of ECTC (IEEE)* (1998) 952–961.
- [17] P.L. Liu, J.K. Shang, *Metall. Mater. Trans. A* 31 (2000) 2867–2875.
- [18] S. Ahat, L. Du, M. Sheng, L. Luo, W. Kempe, J. Freytag, *J. Electron. Mater.* 29 (2000) 1105–1109.

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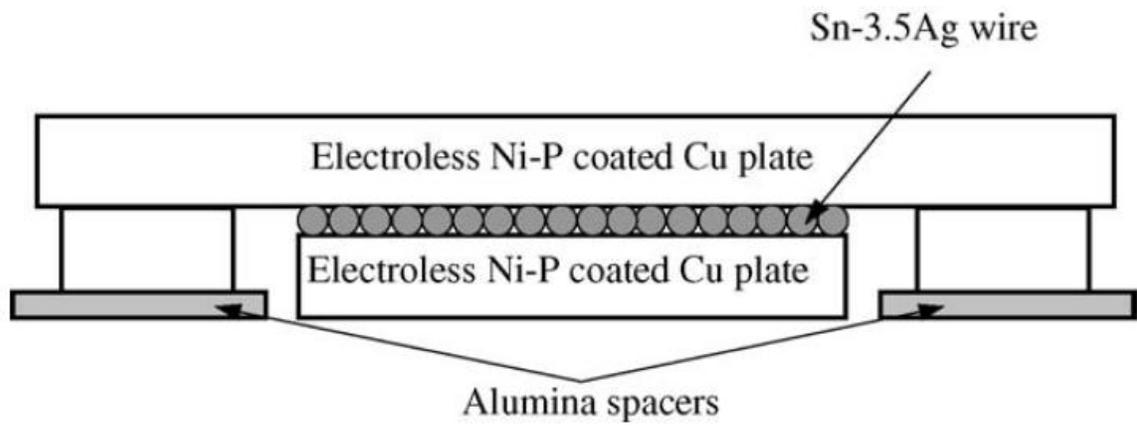


Fig. 1

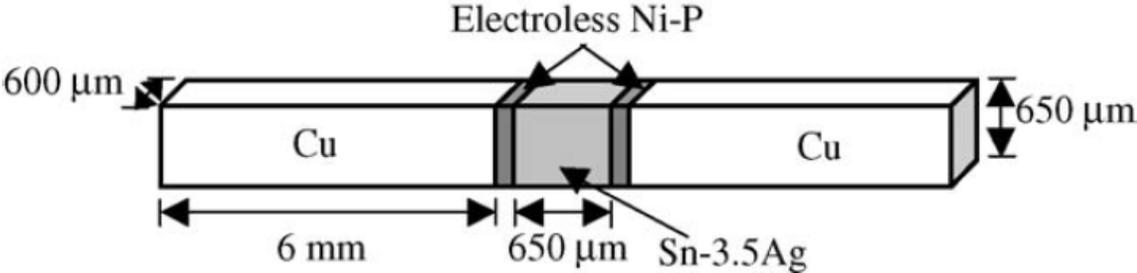


Fig. 2

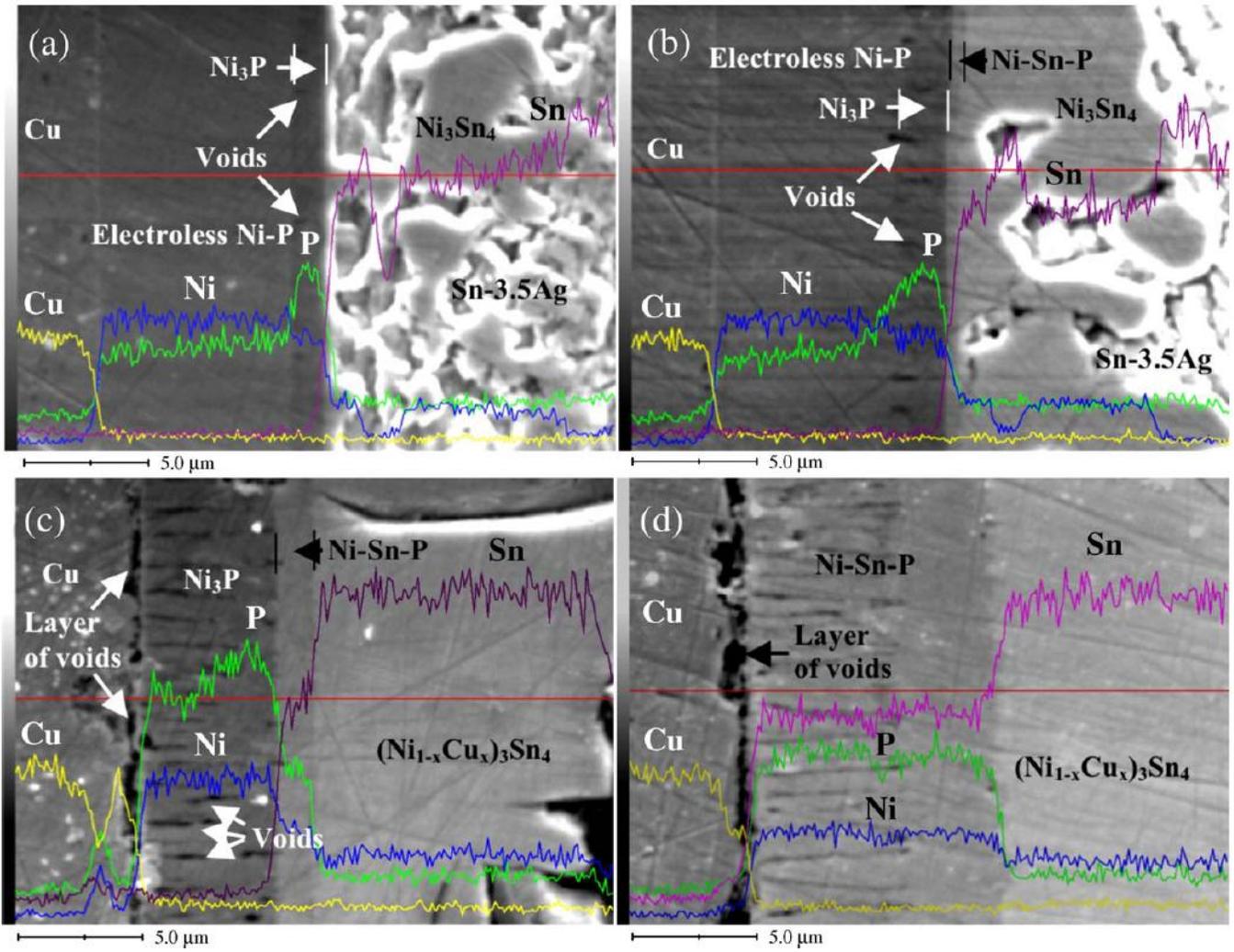


Fig. 3

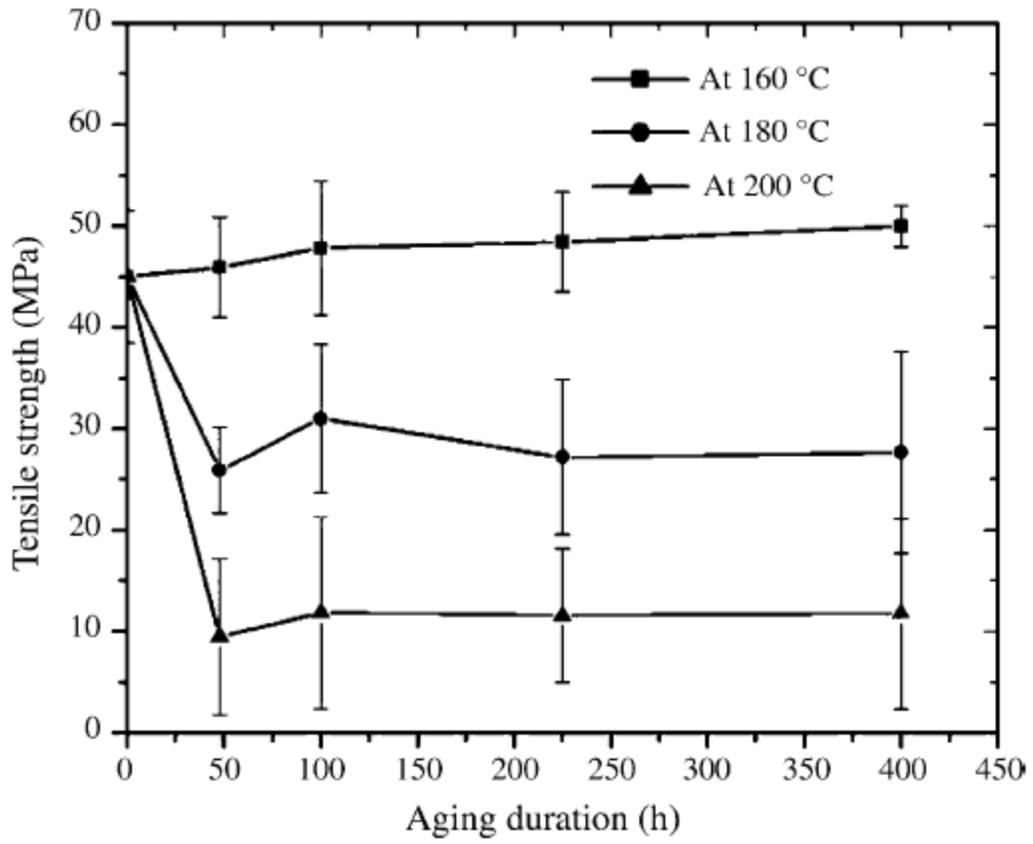


Fig. 4

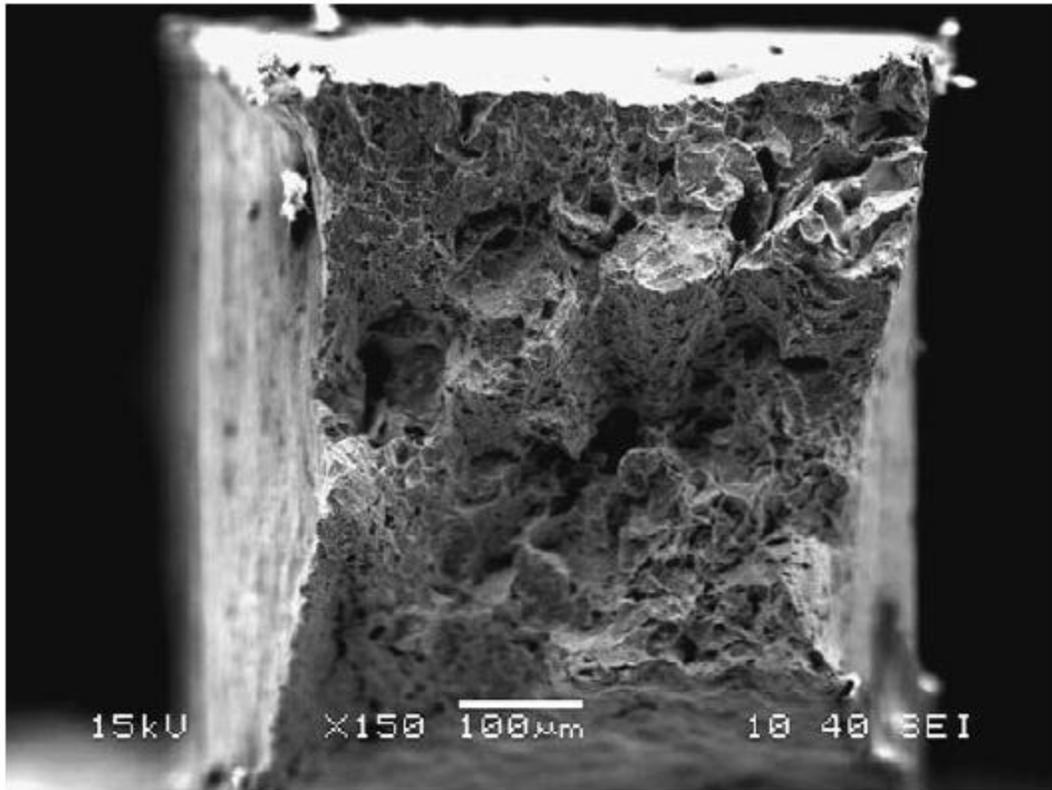


Fig. 5

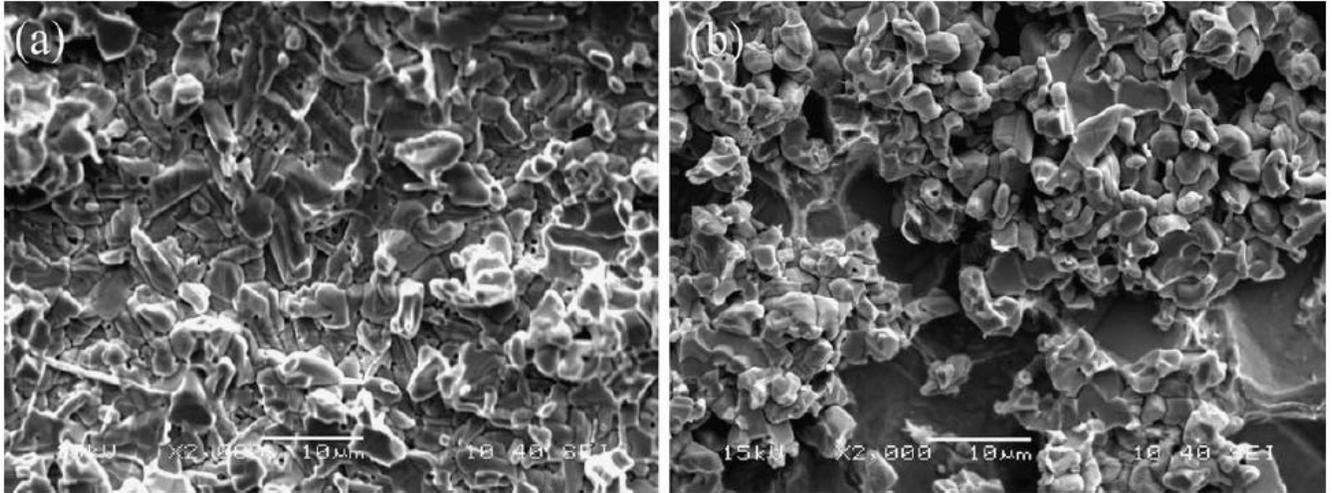


Fig. 6

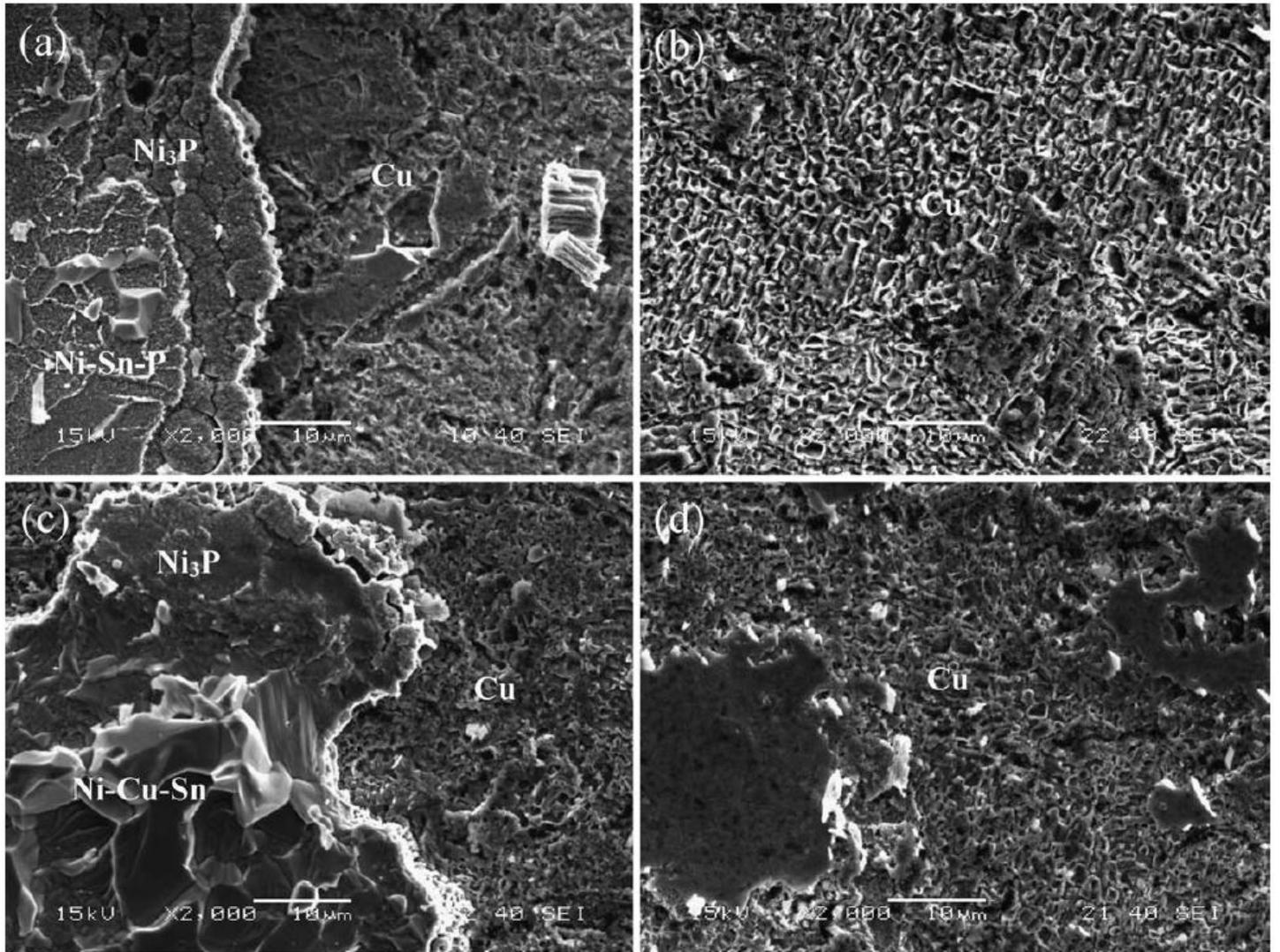


Fig. 7