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Adhesion improvement of copper/epoxy joints

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Copper oxides have been formed to improve the adhesive strength of copper/epoxy joints. Initial adhesive strength and durability of copper/epoxy joints were compared depending upon the type of oxides, black or red oxide. Although the initial adhesive strength of black oxide treated joints was worse than that of red oxide treated joints, the durability in acidic environment was better. In order to improve the durability of red oxide treated joints, 5-amino-indazole was applied to inhibit the corrosion of oxide layer in acidic medium. With the treatment of 5-amino-indazole, initial adhesive strength was increased by 50%, and durability was improved. The loci of failure for oxide treated joints were investigated with scanning electron microscope and X-ray photoelectron spectroscopy.

1. Introduction

The application of polymeric materials in the microelectronic industry has been growing rapidly because of low dielectric constant, good processability and cheapness of polymers. In many applications, it is essential to provide strong adherence between a polymeric surface and a metallic surface. In particular, adhesion between epoxy resins and copper is critical in the manufacture of multilayer printed circuit boards and the encapsulation of semiconductor chips.

Copper in its pure form exhibits poor adhesion characteristics for bonding to polymeric substrate because the natural copper oxide is mechanically weak and difficult to be wetted by the adhesives [1]. To improve copper adhesion, copper oxide formation on a copper surface by an oxidizing agent has been used from the early days of printed circuit technology. Recently, plasma treatments of a copper surface with fluorohydrocarbons has been introduced to avoid drawbacks, such as non-uniform thickness of oxide, undermining the conductor paths, and disposal problems of hazardous chemicals to the chlorite adhesion-promoting treatment [2, 3].

Adhesive strength of copper/epoxy joints obtained by the formation of copper oxide is good enough for the printed circuit technology, but the bond durability in acidic environments is very poor [4, 5]. Cyclic amine compounds such as imidazole and benzotriazole derivatives are used as corrosion inhibitors to improve the bond durability [6–8]. These coupling agents have active protons to form a complex with the cuprous hydroxide on the copper surface and functional groups such as amine and carboxylic acid to interact with epoxy resins [9].

In this study, adhesion strength was investigated by varying oxide formation conditions. Bond durability was examined with various pHs and temperatures, and improved using the cyclic amines as coupling agents. The adhesion mechanism was also studied by analysing the locus of failure.

2. Experimental procedure

2.1. Formation of copper oxides

The copper used was Poong San Corp. alloy no. C19400. Before forming copper oxides, the copper surface was degreased with chloroform, then natural oxide was removed by immersion in concentrated hydrochloric acid solution for 3 min, followed by rinsing with distilled water [10, 11]. Two different copper oxides, black oxide and red oxide, were formed depending upon the formation and treatment conditions of sodium chlorite and sodium hydroxide solution, as shown in Table I [12]. The formed oxide was rinsed with distilled water and dried in a convection oven at 110 °C for 30 min. Black oxide and red oxide were named after the colour produced due to the oxide thickness.

2.2. Formation of copper/epoxy joints

Diglycidyl ether of bisphenol-A (DGEBA, epoxide equivalent weight = 190, Kukdo Chemical Co.) 100 parts as an epoxy resin, nadic methyl anhydride (NMA) 80 parts as a curing agent, and benzyldimethylamine (BDMA) 2 parts as a catalyst were mixed and bubbles in the mixture were removed in a vacuum oven at room temperature. Epoxy resin was poured on to the copper oxide surface in a silicone rubber mould, and cured for 2 h at 140 °C under a pressure of 2 atm in a hot press to make the copper/epoxy joints.

2.3. Adhesion tests

A 90° peel test and a blister test [13–15] were used to measure adhesion strength. For the 90° peel test, copper foil was used with dimensions 0.055 mm thick

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and 1 cm wide. To avoid plastic deformation of copper foil in the 90° peel test, a blister test was employed, where a copper plate with dimensions 5 mm × 4.5 cm × 4.5 cm was drilled to make a hole of 11.5 mm diameter in the centre.

Fig. 1 shows the circular test cell and specimen. An artificial circular flaw was made with Scotch tape around the hole, and water was used as a pressurizing medium. The crack initiation pressure was measured to calculate the fracture energy from the equation derived by Andrews and Stevenson [16]:

cohesive fracture energy

$$2\tau = \frac{P_c^2 a}{E[f_1(h/a)]} \tag{1}$$

adhesive fracture energy

$$\theta = \frac{P_c^2 a}{E[f_2(h/a)]} \tag{2}$$

where

$$f_1\left(\frac{h}{a}\right) = \frac{1}{1-\nu^2}\left\{\frac{3}{32}\left[\left(\frac{a}{h}\right)^3 + \left(\frac{a}{h}\right)\frac{4}{1-\nu}\right] + \frac{1}{\pi}\right\}^{-1} \tag{3}$$

$$f_2\left(\frac{h}{a}\right) = \frac{1}{1-\nu^2}\left\{\frac{3}{32}\left[\left(\frac{a}{h}\right)^3 + \left(\frac{a}{h}\right)\frac{4}{1-\nu}\right] + \frac{2}{\pi}\right\}^{-1} \tag{4}$$

where h is the thickness of epoxy, a the radius of the crack, E Young's modulus of the epoxy, ν Poisson's ratio of the epoxy and P_c the crack initiation pressure.

TABLE I The formation and treatment conditions of oxidizing agents

Types of oxide	Black oxide	Red oxide
$NaClO_2$ (g)	37.5	37.5
NaOH (g)	50	6
$Na_3PO_4 \cdot 12H_2O$ (g)	100	25
H_2O (g)	1000	1000
Temperature (°C)	95	85
Reaction time (min)	15	2

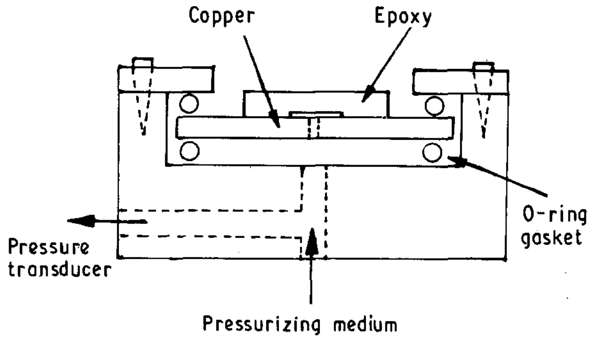

Figure 1 Schematics of the blister test cell.

2.4. Durability of copper/epoxy joints

The durability of copper/epoxy joints was examined in various solutions of pH 2, 7, and 12. The degradation of epoxy resins during the durability test was monitored by attenuated total reflection–Fourier transform infrared spectroscopy (ATR–FTIR).

In order to improve the durability, 5-amino-indazole (5-AIA) and benzotriazole-5-carboxylic acid (BTA-5-CA) were coated on copper oxide surfaces as coupling agents before applying epoxy resins. Defects in the coupling agent layer were tested by immersing the coupling agent-coated copper in 0.001 M sodium nitrate solution for 10 min [17]. Silver spots could be observed where silver cations had reacted with copper in areas where the coupling agents were uncoated.

2.5. Locus of failure

The locus of failure was investigated by SEM (Hitachi S-570) and XPS (Perkin–Elmer Phi-5400). The thickness of the copper oxides was measured by Alpha-step surface profiler (Tencor 200).

3. Results and discussion

3.1. Adhesive strength and locus of failure

Fig. 2 shows 90° peel energies of copper/epoxy joints depending upon treatment time in the sodium chlorite solutions. The red oxide is better than black oxide in promoting the adhesive strength of copper/epoxy joints, which is in agreement with the work of Slominski and Landau [4], and each oxide has a optimum thickness for the maximum adhesive strength. The red oxide treated joint shows the maximum peel energy of 1.1 kJ m^{-2} with the thickness of 200 nm, while the black oxide treated joint shows a maximum peel energy of 0.4 kJ m^{-2} with a thickness of 100 μm. It seems that each oxide has its minimum thickness to cover the copper surface without defects,

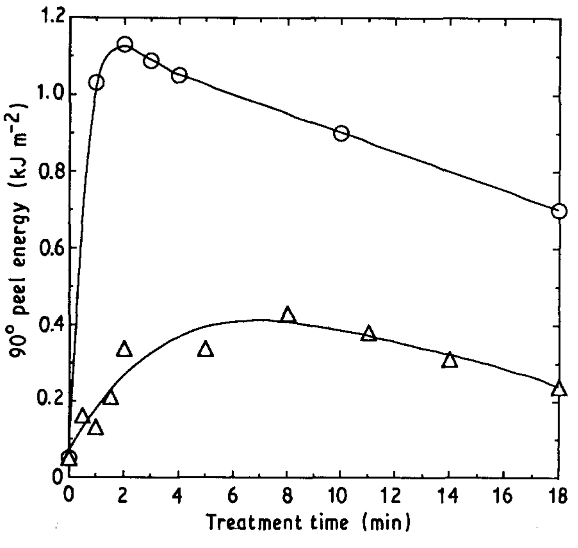

Figure 2 90° peel energy of copper/epoxy adhesive joints versus treatment time in chlorite solutions: (○) red oxide, (△) black oxide.

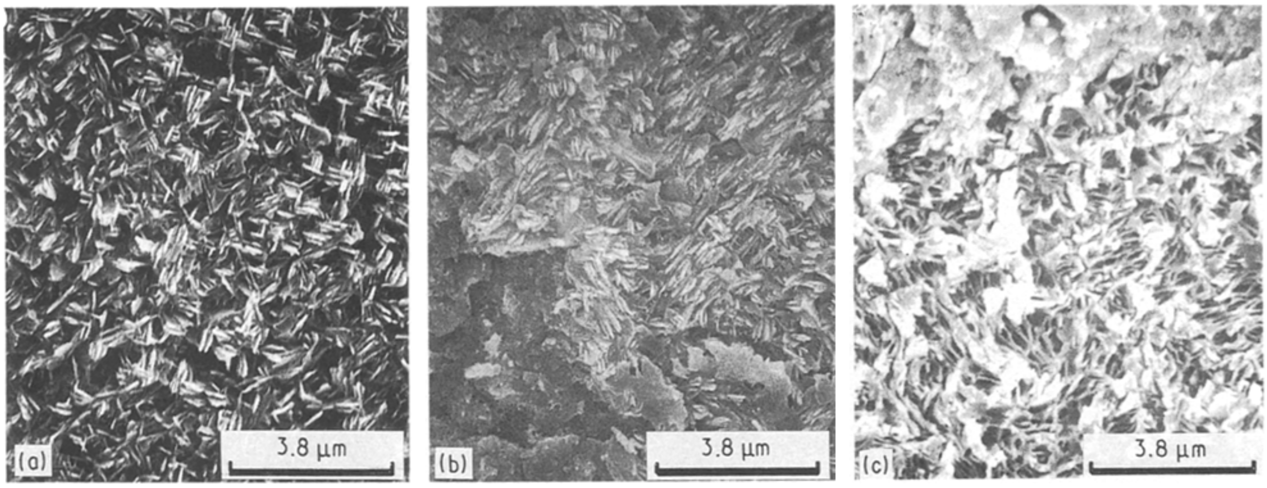

Figure 3 Scanning electron micrographs of peeled epoxy/black oxide joints: (a) black oxide surface, (b) peeled copper side, (c) peeled epoxy side.

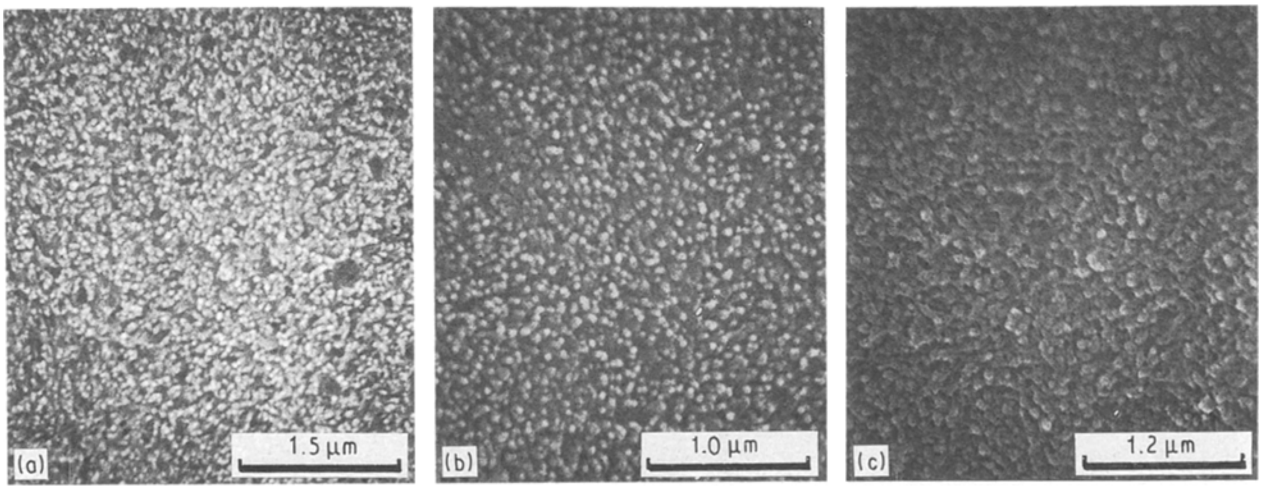

Figure 4 Scanning electron micrographs of peeled epoxy/red oxide joints: (a) red oxide surface, (b) peeled copper side, (c) peeled epoxy side.

and the probability of failure in the oxide layer increases with increasing thickness of coating beyond the minimum thickness.

The loci of failure of red oxide treated and black oxide treated joints were investigated by SEM and XPS. Fig. 3 shows the scanning electron micrographs of the black oxide surface, and the peeled copper side and epoxy side after the peel test. Both the peeled copper side and the epoxy side show needle-like structure which is the same morphology as the black oxide surface. Leaf-like structures shown in the bottom of the peeled copper side (Fig. 3b) and the top of the peeled epoxy side (Fig. 3c) are the bulk oxide, which implies cleavage through the bulk oxide. Scanning electron micrographs indicate that the locus of failure in the black oxide treated joint is mainly oxide itself and partially the interface of epoxy and oxide. Fig. 4 shows scanning electron micrographs of the red oxide surface, and the peeled copper side and epoxy side after the peel test. It can be seen in the micrographs of the oxide surfaces that the structure of red oxide is denser than that of black oxide, which could explain the better adhesive strength of the red oxide treated joint.

As shown in Fig. 4, the morphology of the oxide side is similar to that of the red oxide surface. The peeled epoxy side shows sparse red oxide and an unknown structure. It was difficult to identify the locus of failure of the red oxide treated joint from the micrographs, and XPS was employed to analyse both peeled surfaces. Weak peaks of copper 2p from cupric oxide were detected on the peeled epoxy side, as shown in Fig. 5, which implies that failure occurs through the bulk oxide near the epoxy layer. Fig. 6 shows the carbonyl and carboxylate peaks from the carbon 1s region, suggesting the failure of the bulk epoxy resin. The peaks of carboxylate in the peeled copper side and excess oxygen in the peeled epoxy side were observed from the oxygen 1s region shown in Fig. 7. SEM and XPS results indicate that the locus of failure of the red oxide treated joint is mainly the epoxy/oxide interface and partially the bulk oxide and epoxy near the interface.

3.2. Durability of copper/epoxy joints

The initial adhesive strength of the copper/epoxy joint improved by the formation of copper oxides, is good

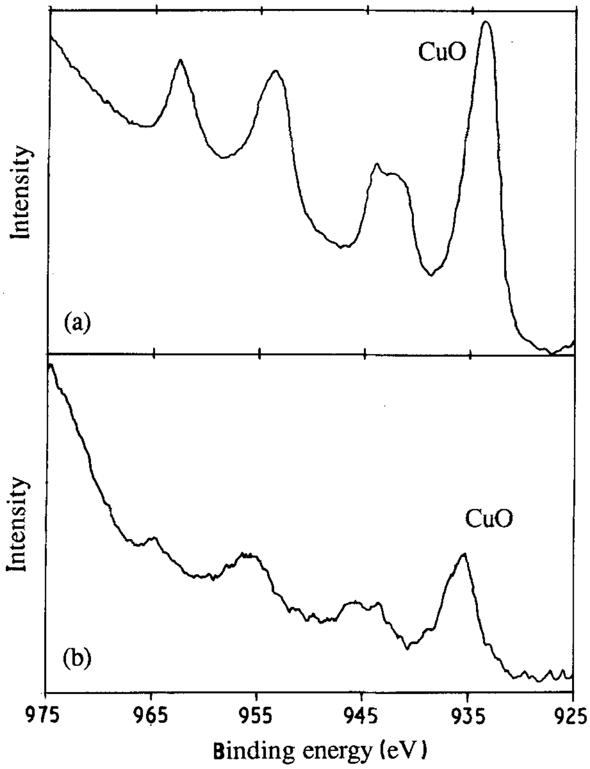

Figure 5 XPS spectrum of the copper 2p region: (a) peeled copper side, (b) peeled epoxy side.

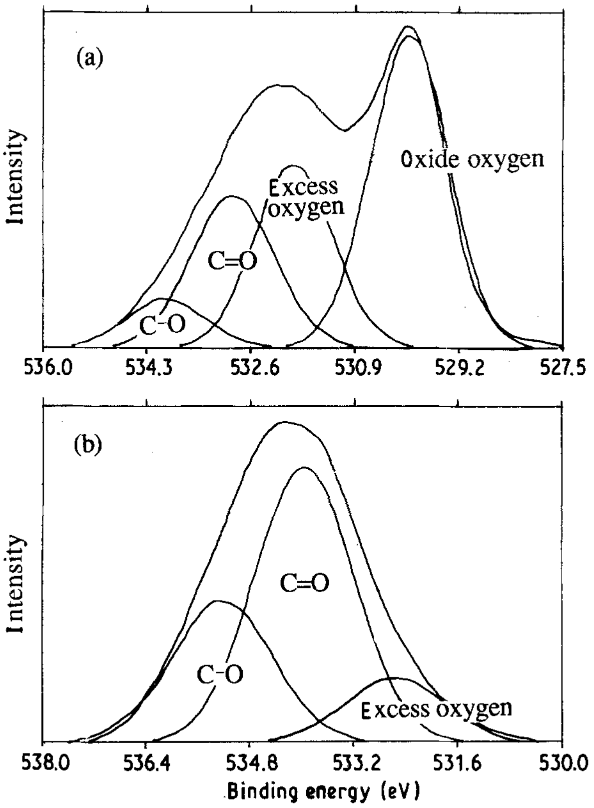

Figure 7 XPS spectrum of oxygen 1s region: (a) peeled copper side, (b) peeled epoxy side.

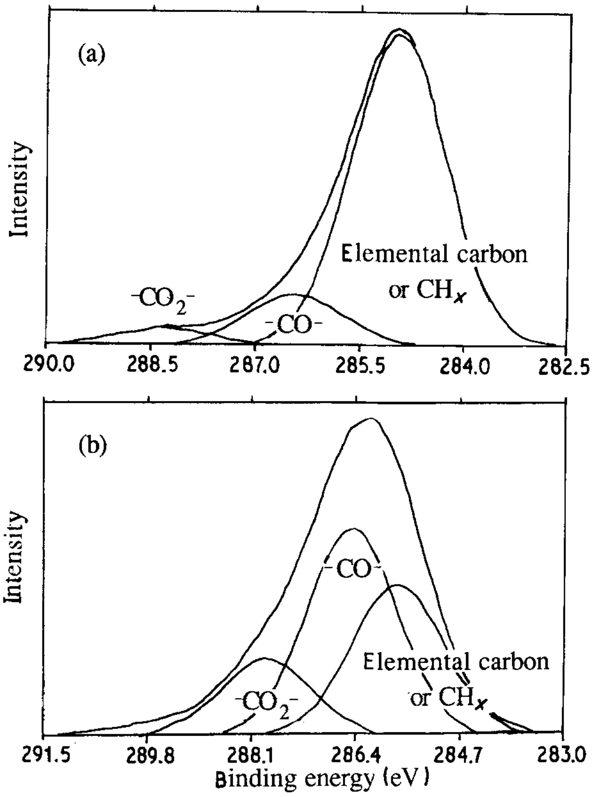

Figure 6 XPS spectrum of carbon 1s region: (a) peeled copper side, (b) peeled epoxy side.

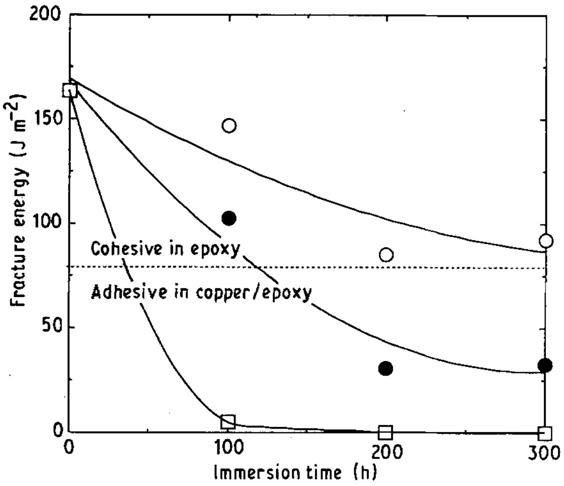

Figure 8 Durability tests of epoxy/red oxide joints in water of various pH at 80 °C: (○) pH 7, (●) pH 2, (□) pH 12.

enough for the printed circuit board (PCB) industry. However, because the copper/epoxy joint is exposed to various chemicals during the manufacturing process of PCB, the durability of joints is important, particularly in acidic environments. Fig. 8 shows the change of adhesive strength of epoxy/red oxide joints by blister testing after immersion in three different pH solutions of 2, 7, and 12 at 80 °C. In the blister test, cohesive failure of the epoxy resin occurs when the adhesive strength of the joints is higher than the fracture energy of the epoxy resin. Adhesive failure takes place below the dotted line in Fig. 8, where the fracture energy is less than 80 J m^{-2}. The adhesive strength decreases rapidly in the acidic and alkaline solutions as shown in Fig. 8. In the case of pH 2, by visual inspection the oxide layer was seen to be severely corroded. Fig. 9 shows ATR–FTIR analysis of cured epoxy immersed in the different pH solutions for 300 h at 80 °C. Compared with the control sample, the

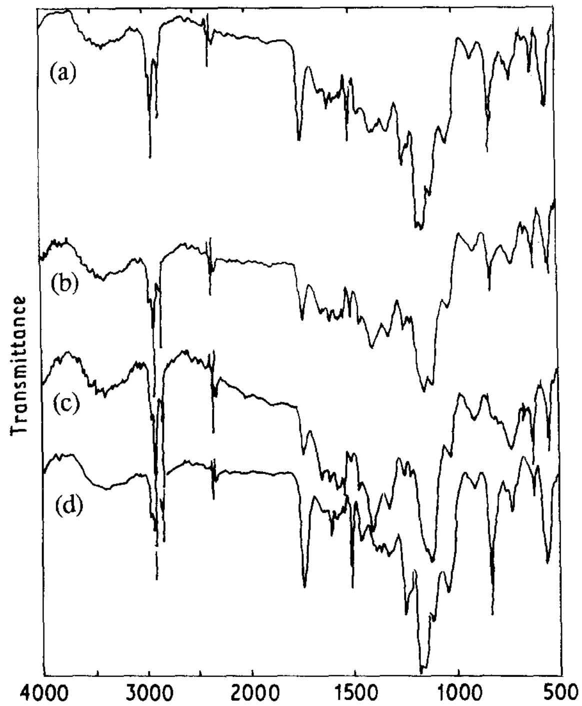

Figure 9 ATR–FTIR spectrum of epoxy immersed in water of various pH at 80 °C for 300 h: (a) control, (b) pH 7, (c) pH 12, (d) pH 2.

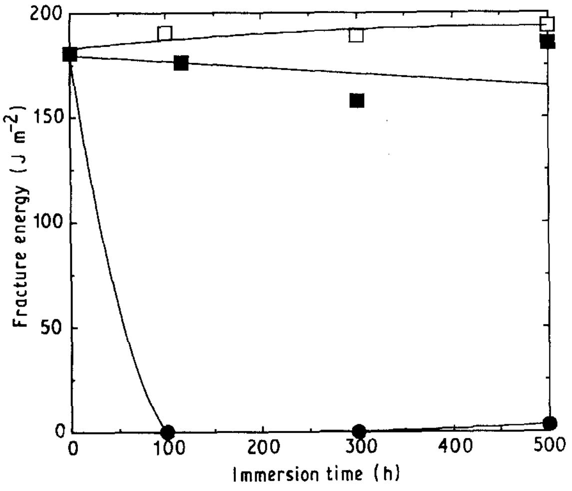

Figure 10 Durability tests of epoxy/red oxide joints in water of various pH at room temperature: (□) pH 7, (●) pH 2, (■) pH 12.

peak intensities from ester group (1739 and 1179 cm^{-1}) and ether groups (1248, 1155, 1035, and 829 cm^{-1}) of the epoxy resin decrease on increasing the pH from 7 to 12. But there is no change in the peak intensities of the samples immersed in pH 2 solution. It could be concluded that the joint strength decreases in acidic and alkaline solutions at 80 °C due to the corrosion of the oxide and to epoxy degradation, respectively. Fig. 10 shows the durability of copper/epoxy joints at room temperature, in which the adhesive strength does not decrease in solutions of pH 7 and 12, but the adhesive strength in the solution of pH 2 still decreases very steeply. Fig. 11 shows ATR–FTIR analysis of the cured epoxy immersed in the different pH solutions for 300 h at room temperature.

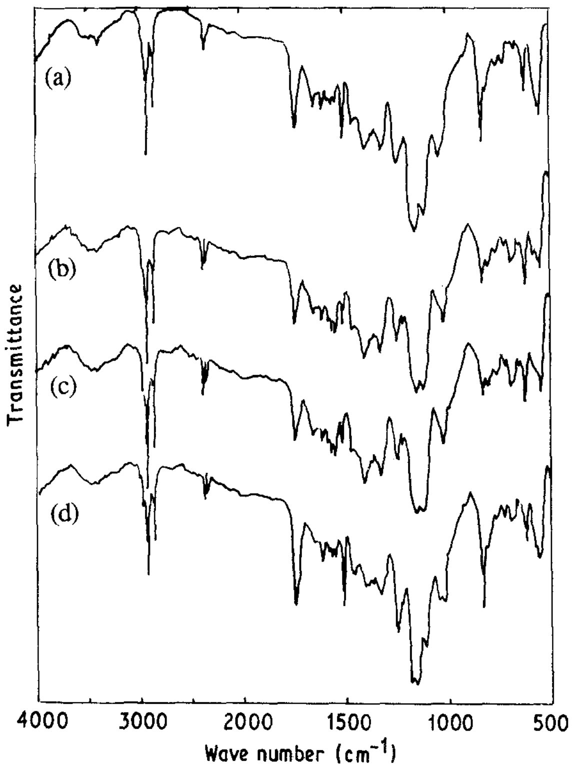

Figure 11 ATR–FTIR spectrum of epoxy immersed in water of various pH at room temperature for 300 h: (a) control, (b) pH 7, (c) pH 2, (d) pH 12.

Compared with the control sample, the relative peak intensities of ester and ether groups decrease in the pH 2 and pH 7 solutions, but there is no change in the pH 12 solution. It is observed from the FTIR study that epoxy resin has not deteriorated at room temperature even in alkaline solution.

The durability of black oxide treated joints was also studied in the pH 2 solution. As shown in Fig. 12, fracture energy is consistent until 400 h immersion in the solution of pH 2 at room temperature, and decreased slightly at 80 °C. Even though the initial adhesive strength of black oxide treated joints is weaker than that of red oxide treated joints, the durability of black oxide treated joints in an acidic environment is better than that of red oxide treated joints, because the black oxide layer is thick enough to stand for a long time.

3.3. Coupling agents for copper/epoxy joints

In order to improve the durability of red oxide treated joints, coupling agents such as BTA-5-CA and 5-AIA were applied after forming red oxide. Initial adhesive strength increased by 50% with both coupling agents, as shown in Table II. In the case of durability, BTA-5-CA applied joints were worse, but 5-AIA applied joints were better than the control sample.

As shown in Fig. 13, initial adhesive strength and bond durability were improved on increasing the number of coatings of 5-AIA solution at the concentration of 1 wt %. With an increasing number of coatings the number of defects in the 5-AIA layer examined in sodium nitrate solution was reduced, but the thickness of the 5-AIA layers was unchanged.

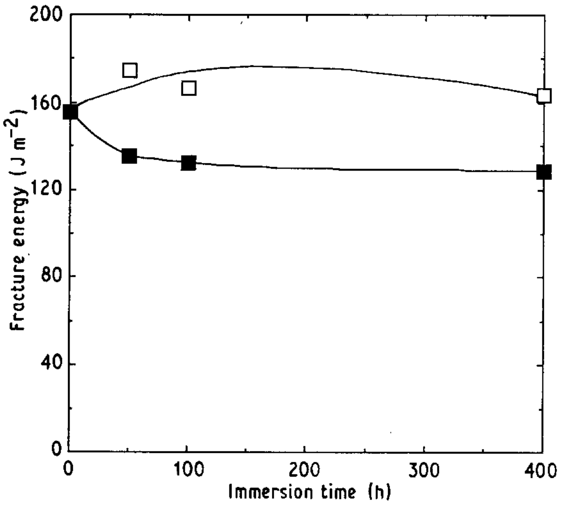

Figure 12 Durability tests of epoxy/black oxide joints in water of pH 2 at (□) room temperature (■) 80 °C.

TABLE II The effects of 5-AIA and BTA-5-CA on the 90° peel energy

Sample		90° peel energy (kJ m^{-2})
Natural oxide	Control	0.00
	5-AIA	0.18 ± 0.02
	BTA-5-CA	0.02 ± 0.01
Red oxide	control	0.78 ± 0.03
	5-AIA	1.22 ± 0.10
	BTA-5-CA	1.22 ± 0.02

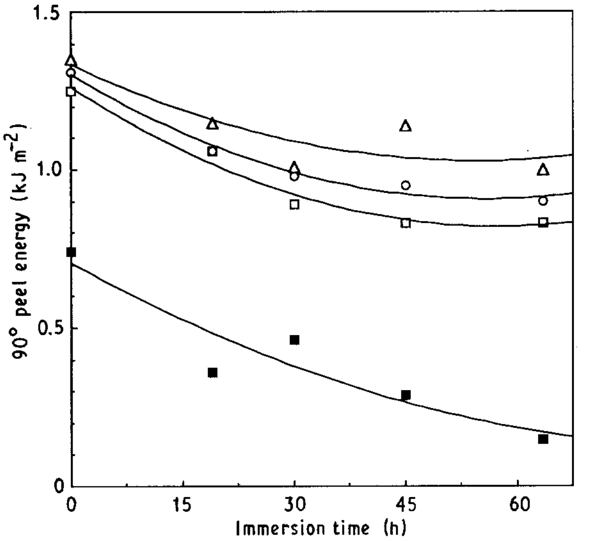

Figure 13 Effects of coating times of 1 wt % 5-amino-indazole solution on initial adhesion strength and durability of epoxy/red oxide joints in water of pH 2: (■) no coating, (□) two coatings, (○) six coatings, (△) twelve coatings.

Table III shows thickness of 5-AIA layers with the concentration of 5-AIA solutions where the thickness of the coatings was calculated from the weight difference between before and after coating. The effects of thickness of the 5-AIA layer on bond durability could not be seen as shown in Fig. 14.

TABLE III Thickness of 5-amino-indazole layer with varying concentration of 5-AIA/ethanol solutions

Concentration of 5-AIA (wt %)	Thickness (10^3 nm)
1.0	0.10
2.0	0.20
3.0	0.27
4.0	0.31

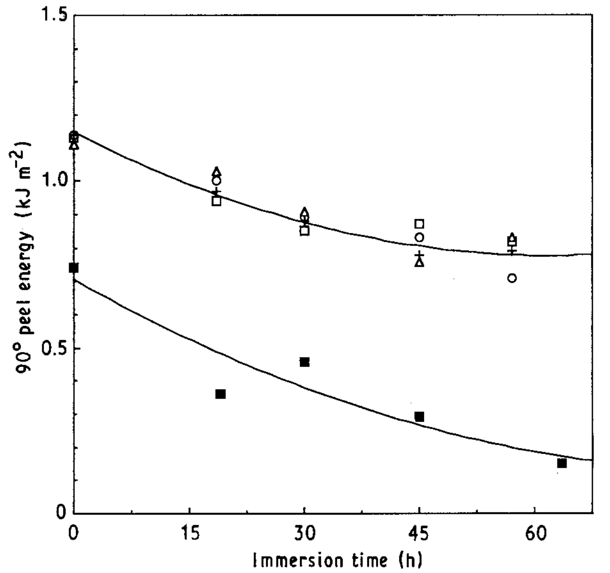

Figure 14 Effects of thickness of 5-amino-indazole layer on durability of epoxy/red oxide joints in water of pH 2: (■) no coating, (□) 1 wt %, (○) 2 wt %, (+) 3 wt %, (△) 4 wt % 5-amino-indazole solution.

4. Conclusion

Adhesive strength of copper/epoxy joints can be improved up to 0.4 and 1.1 kJ m^{-2} by the formation of black oxide and red oxide on the copper surface, respectively. Although black oxide treated joints show a lower initial adhesive strength than that of red oxide treated joints, they can endure 400 h in an acidic environment at 80 °C due to the thick oxide layer, which is better than for the red oxide.

In order to improve the durability of red oxide treated joints in acidic media, 5-amino-indazole was applied as a coupling agent. The initial adhesive strength was increased by 50% and durability was improved. The initial adhesive strength and bond durability were enhanced more with increasing number of coatings of 5-AIA.

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References

1. A. J. KINLOCH, in "Adhesion and Adhesives" (Chapman and Hall, London, 1987) p. 144.
2. S. V. BABU, V. Q. BUI, J. G. HOFFARTH and J. A. WELSH US Pat. 4810326 (1989).

3. K. K. CHAN and V. J. MALUEG, US Pat. 4 689 111 (1987).
4. L. J. SLOMINSKI and A. LANDAU, *Plat. Surf. Finish.* **69** (6) (1982) 96.
5. P. J. HINE, S. El. MUDDARRIS, and D. E. PACKHAM, *J. Adhes. Sci. Technol.* **1** (1) (1987) 69.
6. G. W. POLING, Final Report INCRA Project no. 185 (1979).
7. D. CHADWICK and T. HASHEMI, *Surf. Sci.* **89** (1979) 649.
8. J. M. PARK and J. P. BELL, in "Proceedings of the Symposium of Adhesive Aspects of Polymer Coating", edited by Mittal and Kashmiri Lal (Plenum, New York, 1983) p. 205.
9. J. C. BOLGER and H. E. MOLVAR Jr, *Soc. Plast. Eng. Tech. Pap.* **18** Pt. 1 (1972) 408.
10. T. LYMAN, H. E. BOYER, P. M. UNTERWEISER, J. P. HONTAS, L. R. MEHLMAN, W. J. CARNES and H. LAWTON, in "Metals Handbook", 8th Edn, Vol. 2 (ASM, Metals Park, OH, 1964) p. 635.
11. J. KRUGER and J. P. CALVERT, *J. Electrochem. Soc.* **11** (1964) 1038.
12. E. B. MURPHY, A. E. MASON and E. S. WAINWRIGHT, "Durable Copper-Polyimide Adhesive Bonds", MIT Lincoln Lab., Technical Report no. TR-652 (1983).
Bonds", MIT Lincoln Lab., Technical Report no. TR-652 (1983).
13. H. DANNENBERG, *J. Appl. Polym. Sci.* **5** (1961) 125.
14. M. G. ALLEN, M. MEHREGANY, R. T. HOWE, and S. D. SENTURIA, *Appl. Phys. Lett.* **51** (4) (1987) 241.
15. M. J. NAPOLITANO, A. CHUDNOVSKY, and A. MOET, *J. Adhes. Sci. Technol.* **2** (4) (1988) 311.
16. E. H. ANDREWS and A. STEVENSON, *J. Matter. Sci.* **13** (1978) 1680.
17. J. M. PARK and J. P. BELL, in "Proceedings of the Symposium of Adhesive Aspects of Polymer Coating", edited by Mittal and Kashmiri Lal (Plenum, New York, 1983) p. 205.

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