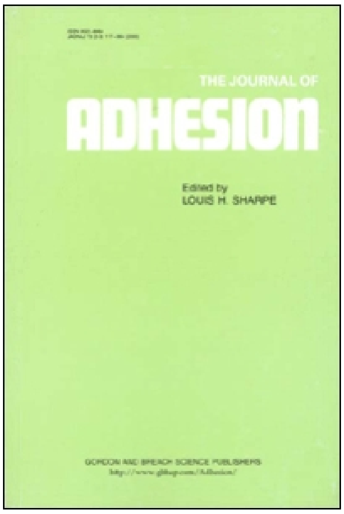

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Effects of Surface Modifications on the Peel Strength of Copper Based Polymer/Metal Interfaces with Characteristic Morphologies

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This paper summarizes a study on the effect of changes in surface chemistry on the peel strength of copper/polymer interfaces. Two different surface topographies were created and evaluated, one produced by cleaning and etching in sodium persulfate, the other by etching then mechanically roughening using 180 grit sandpaper. Both surfaces were then oxidized in an alkaline/oxidizing treatment to form cupric oxide. Ion implantation and benzotriazole priming modified the surface chemistry of the cupric oxide samples. After lamination to form an epoxy/copper interface, peel strength measurements were taken. The results showed that ion implantation degraded the peel strength while priming with benzotriazole improved the peel strength compared with the unmodified cupric oxide. In a separate comparison study, peel strength measurements were taken on interfaces formed from copper oxides with the same oxide structure but with widely different gross morphologies. "As laminated" adhesive strength was virtually the same. The bonded interfaces were aged at elevated temperature and the peel strength obeyed first order degradation kinetics. Two terms can be determined from the degradation studies, the first is the long term peel strength, $A(\infty)$, and the other is Ω, the degradation rate with units of time^{-1}. A value of $A(\infty)$ was 3.0 lbs/in for etched copper interfaces while $A(\infty)$ was 0.5 lbs/in for the sanded interfaces.

KEY WORDS surface chemistry of copper/polymer interfaces; effect of topography on peel strength; mechanical roughening; ion implantation; time dependent degradation of interface; chemical pretreatments; epoxy/glass prepreg.

INTRODUCTION

Because of the requirements for strong adhesion in printed circuits and other military electronics applications, there is a need for fundamental research on the adhe-

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sion of copper-based polymer/metal interfaces.[1-5] It has been difficult to achieve strong polymer adhesion with copper. The electronics industry is interested in two aspects of adhesion: the first is the initial adhesion immediately after lamination, the other is the long term adhesion of these interconnect structures. Researchers have specifically addressed whether structural or surface chemical interactions control adhesion. Many efforts have compared different adhesion promotion schemes for these interfacial systems.[6,7] Much of this research has centered on hot alkaline oxidizing treatments for copper before lamination. Other work has compared how priming copper with an organic pretreatment[8-10] or alloying schemes[11,12] have met with some degree of success.

Historically, the general investigative approach has been to determine how surface microstructure affects adhesion by altering the copper surfaces using different oxidizing treatments. These chemical treatments tend to affect both the surface oxide morphology as well as the level of copper oxidation. Since chemical and morphological structure are not necessarily independent, empiricism could lead to incorrect conclusions regarding how each treatment affects adhesion.

Tam and Robinson evaluated how the length of time in an $NaClO_2/NaOH$ oxidizing solution affected the peel strength of a series of oxidized copper/epoxy interfaces.[13] They found that peel strength increased with oxidation time. The improved peel strength was attributed to the preferential formation of CuO and to a stronger interaction between CuO and copper metal. There are also other published comparison studies with different oxidizing solutions.[6,14]

Other work has characterized the chemical interactions of the oxide during polymer/metal interface formation. Miller *et al.* observed the surface chemistry changes occurring to an oxidized copper surface after lamination to an epoxide laminate.[15] Using X-ray Photoelectron Spectroscopy, XPS, they found a reduction in the copper oxidation state from +2 to +1 after lamination. They attributed the reduction to a chemical reaction between CuO and the base copper underneath to form the thermodynamically more stable Cu_2O, following work by Evans *et al.*[16]

$$CuO + Cu \longrightarrow Cu_2O \tag{1}$$

They also cited potential chemical reactions between CuO and dicyandiamide, the curing agent for the epoxy.

Additional work in copper-based polymer/metal adhesion has established how surface chemistry variations affect adhesion of pure copper surfaces. Alloying of the copper surface by ion implantation[11] or immersion plating[12] could potentially improve adhesion. Also, priming the copper surface with an organic primer could improve adhesion.[8-10] The results are difficult to compare with the earlier oxidation research because the surface morphology was polished prior to treatment. The polished morphology is much smoother than the typical morphology generated from the oxidation research. In other, more recent, work the time-temperature effects on adhesion have been shown for the polybenzimidazole/copper interface.[10] Other pioneering work by Kinloch highlighted the need for understanding the mechanics of environmentally-induced adhesive failure in other bonded interfaces.[17]

Thus, there is a need to understand how surface chemistry variations affect the adhesion behavior of copper when the copper surface morphology is fixed and realistic. There is also an interest in understanding how adhesion changes with environmental aging. This study summarizes our efforts with two characteristic copper substrates.

EXPERIMENTAL

Oxygen Free High Conductivity (OFHC) copper foil was used. Each foil sample (3.4 mils (0.086 mm) thick, 8–10 inches (20.3–25.4 cm) in each lateral direction) was cleaned and initially prepared to produce two different morphologies. Surface morphology A was formed by etching the foil in a conveyerized machine with a sodium persulfate solution sprayed from jets at room temperature for two minutes. The foil was then oxidized in a (aqueous) bath of $NaClO_2$ (160 g/L) and NaOH (10 g/L) held at 68–71°C. The samples were held in the bath for two minutes, then rinsed with water and dried using compressed air. A micrograph of morphology A is shown in Figure 1. Surface modifications were performed on selected samples of morphology A after oxidation.

Morphology B surfaces were sanded using 180 grit sandpaper in two directions and rinsed in alcohol before immersing the samples in the oxidizing solution. Sanding residue was clearly observed being expelled into solution during oxidation. A micrograph is shown in Figure 2. Thus, samples A and B, with dramatically

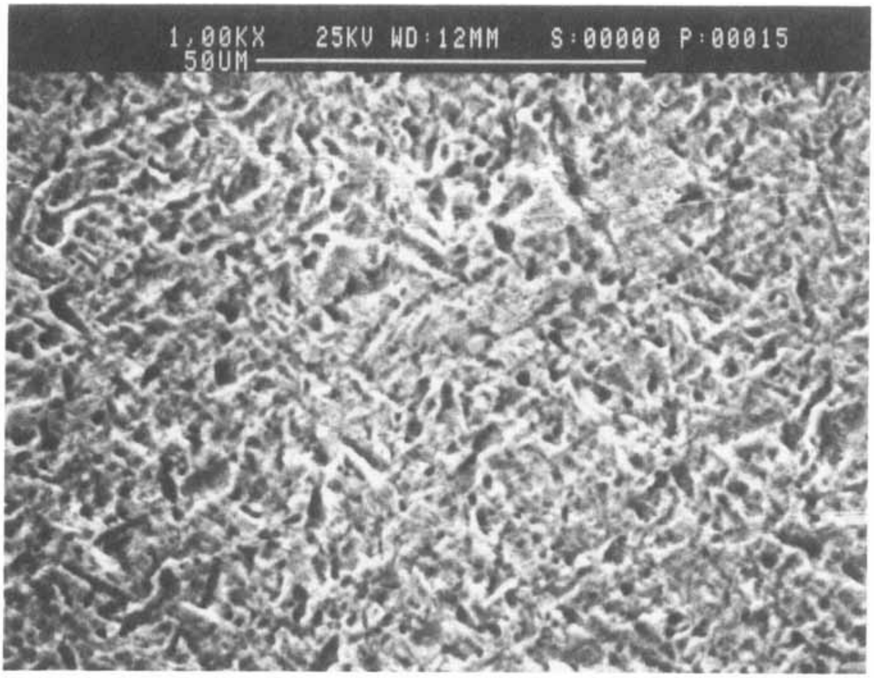

FIGURE 1 Scanning Electron Micrograph of the etched copper surface after the NaOH/$NaClO_2$ oxidation procedure between 68 and 71°C for 2 minutes (Sample A). No gross changes occurred in the morphology between the initial etch and the oxidation step.

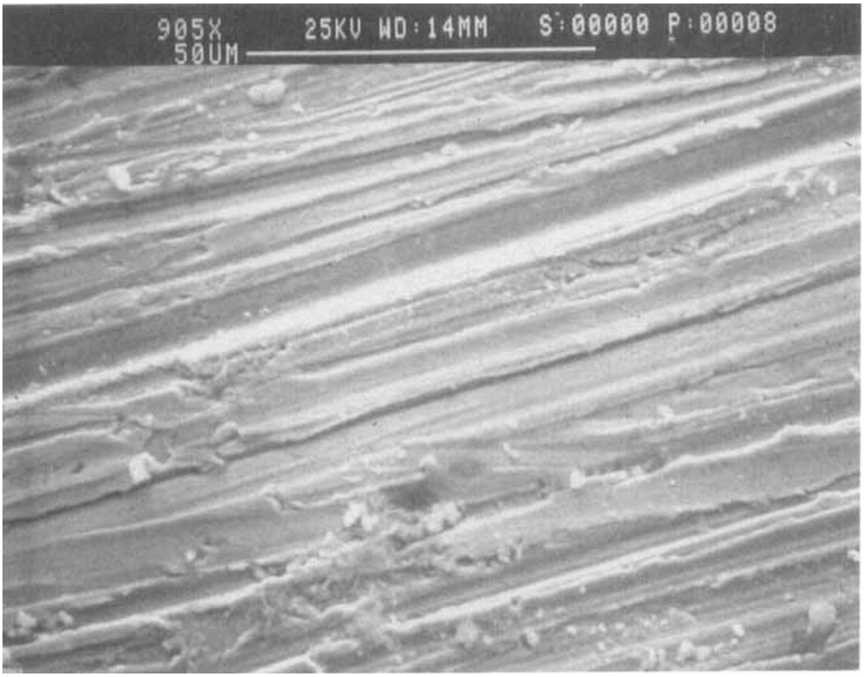

FIGURE 2 Scanning Electron Micrograph of the copper surface created by sanding the copper foil before the NaOH/NaClO$_2$ oxidation procedure between 68 and 71°C for 2 minutes (Sample B). No gross morphological changes occurred between the sanding and the oxidation.

different morphologies, were oxidized the same way. The particular oxidizing solution used in this study was rather benign and did not change the gross morphology of either A or B.

The surface chemical variations were achieved by priming the surface with a known copper complexing agent and by ion implantation. Priming of oxidized foil samples of morphology A was performed by immersing them into a solution of benzotriazole in ethylene glycol (45 g/L). The samples were immersed for 24 hours at room temperature, then removed and rinsed with copious amounts of deionized water until the ethylene glycol was removed.

Cr^+ ion implantation was also performed on oxidized foils with morphology A (Sample A1). The foils were subjected to a dose of 1×10^{16} ions/cm^2 with an incident energy of 40 KeV at Implant Sciences.[18]

Characterization of the oxide films was performed using XPS, Auger Electron Spectroscopy, AES, and depth profiling. These techniques determined how ion implantation and the different oxidation treatments affected the chemical structure of the copper. XPS was performed using a Surface Science ESCALAB Mark II with an Al Kα source emitting radiation of 1486.6 eV. AES was performed using a Perkin Elmer PHI 595 system with a LaB$_6$ filament and incident energies ranging from 3 and 10 KeV. The system was equipped with an Ar^+ sputtering gun. Published sensitivity factors for XPS and AES were used in determining atomic concentrations of the analyzed samples. Depth profiles and survey scans of these surfaces were taken after the oxidized samples were made and again after the surface modifications were performed. Profiling rates were determined to be 75 Å/minute relative to the sputtering rate of a 1000 Å thick Ta_2O_5 standard.

The foils were laminated to an epoxy glass laminate using a partially-cured epoxy coated glass prepreg. Miller and Laberge have explained how these partially-cured epoxy prepreg samples were laminated together.[15] The epoxy was a standard FR4 resin formed by chemical reaction of epichlorohydrin and tetrabromobisphenol A. The resin was cured partially with dicyandiamide prior to lamination with copper. The press cycle for final curing included a one-hour exposure at 177°C at 250 psi (15.5 MPa) in a flatbed press. Initial peel strength test samples were cut out of the laminated samples. The laminate samples were then aged for various times and samples were taken after these aging periods to gauge peel strength as a function of time at 150°C. A minimum of 4 samples per condition were tested.

Peel strength measurements were made with a floating roller peeler using guidelines outlined in ASTM Standard Test D3167-76. The load-elongation behavior was tracked using an Instron 1123 and the test measurements were taken using ¼ and ½ inch (6.4 and 12.7 mm) wide test strips. The test rate peeled 2 inches (50.8 mm) of the laminated foil per minute from the laminate.

RESULTS

The characterization results are shown for the different copper oxide samples in Table I. Two minute exposures in the $NaOH/NaClO_2$ oxidizing solution for both sample A and B produced CuO as measured by XPS. The XPS emission spectrum around the copper region for sample A is shown in Figure 3. It indicates that the prevalent oxide formation was CuO although the presence of some $Cu(OH)_2$ could not be ruled out. The main copper emission is found at 933.4 eV. The presence of shake up satellites for samples A and B further suggests CuO. The oxygen XPS spectrum for sample A found emissions at 529.6 eV, associated with CuO, and at

TABLE I
Surface characterization measurements

Sample type	Surface prep	Surface chemical modification	Primary oxide by XPS	Cu/O ratio by Auger
A	$Na_2S_2O_8$ etch/air dry	None	CuO	1.9
A1	same as A	Ion Implant Cr+ 1×10^{16} ions/cm^2	Cu_2O	2.5
A2	same as A	BTA primer in ethylene glycol	CuO	1.9
B	$Na_2S_2O_8$ etch/180 grit sand/IPA rinse/air dry	None	CuO	1.3

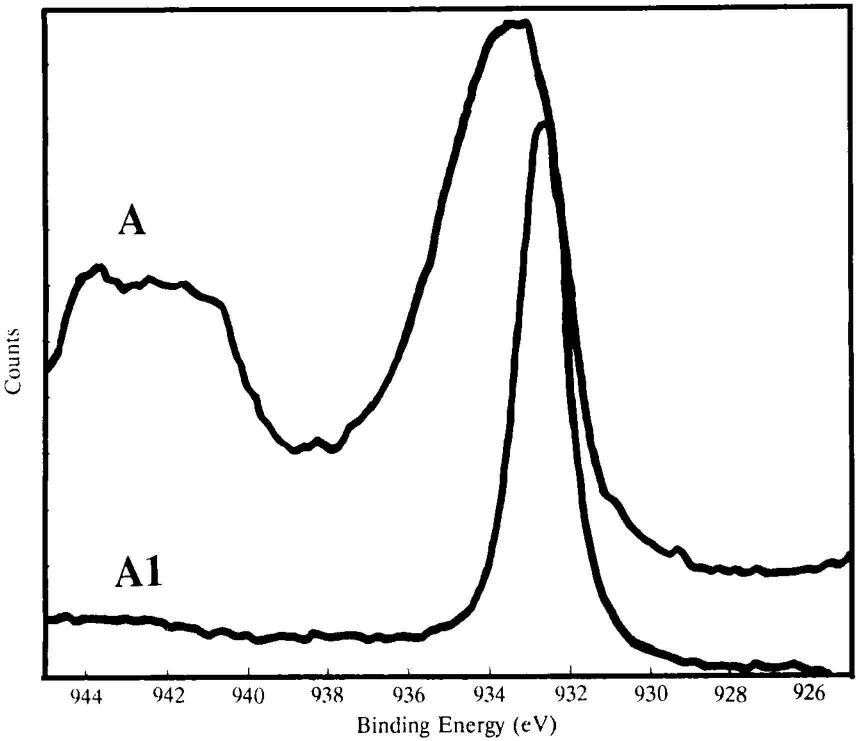

FIGURE 3 XPS high Resolution scan around the copper region comparing samples A and A1. The emission spectrum of sample A contains the primary peak at 933.4 eV and a secondary emission at 944 eV, indicative of both CuO and $Cu(OH)_2$. For the emission spectrum of A1, the 944 eV emission is eliminated and the primary emission has shifted to 932.3 eV, characteristic of Cu_2O.

531.5 eV related to either organic oxygen or $Cu(OH)_2$. The XPS spectrum of A1 is also shown in Figure 3 confirming the change in the copper oxidation state from +2 for sample A to +1 for sample A1 due to ion implantation. The shake up peaks for sample A1 are missing and the main copper emission has shifted down to 932.3 eV, characteristic of Cu_2O. XPS also detected trace amounts of chromium on the A1 surface. AES depth profiling measured a growth in the combined emissions of both chromium and oxygen, about 400 Å deep within the oxide layer. XPS was not performed on the primed cupric oxide samples, although some theoretical work by Zonnevylle and Hoffmann has suggested a chemical interaction between cupric oxide and azole-type primers.[19]

The etched specimens were found to have an average peak-to-valley height of 0.4 μm (±1 SD = 0.1 μm) as measured by the profilometer. The sanded specimens have an average height of 0.3 μm (±1 SD = 0.1 μm).

The peel strength results from laminated samples of these interfaces are shown in Figure 4. Surface chemical modifications of copper foil having the same surface morphology change the "as laminated" peel strength. Priming of the cupric oxide

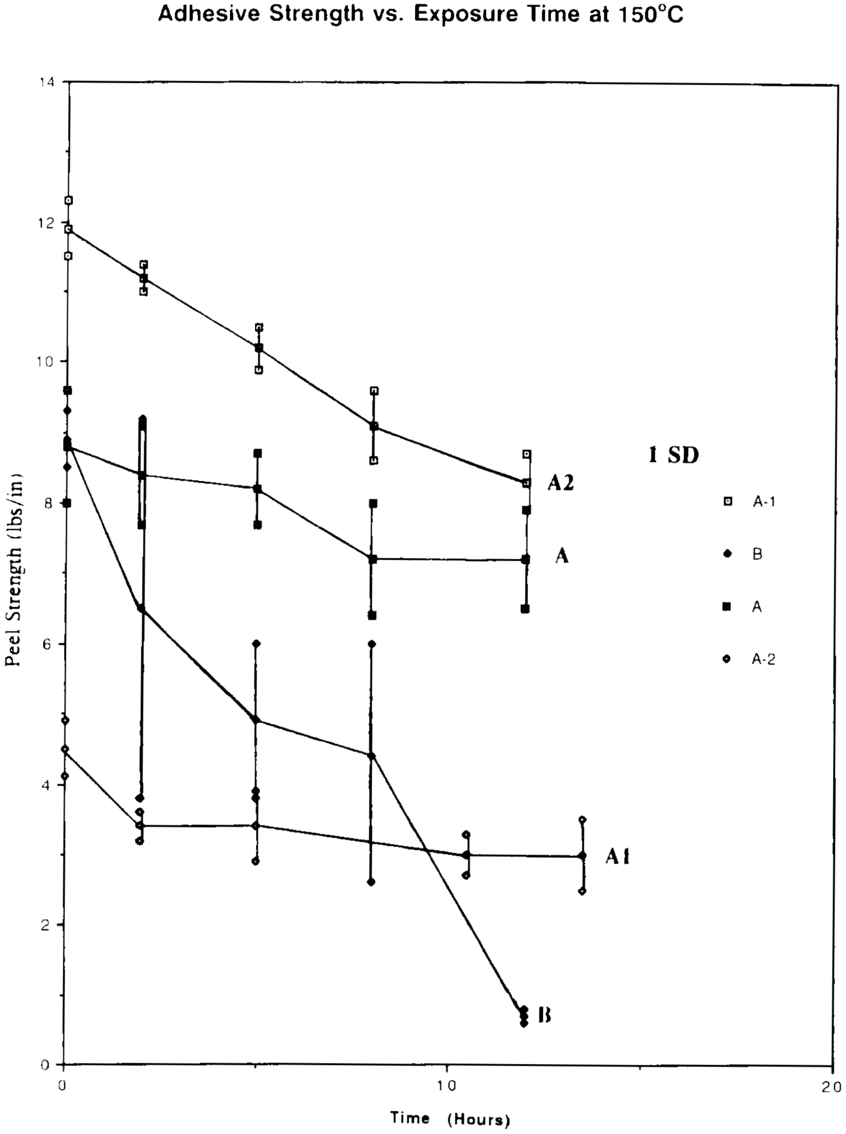

FIGURE 4 Adhesion as measured by peel strength as a function of elevated temperature aging at 150°C.

surface with morphology A (Sample A2) improved the peel strength over that of A. Ion implantation of sample A (Sample A1) decreased the "as laminated" peel strength compared with sample A.

It is interesting to note that, within statistical error, foils having morphologies A and B give nearly the same adhesive strength in the "as laminated" condition.

Figure 4 also shows how peel strength is affected by the elevated temperature exposure. While the peel strength of these interfaces decreased with time in all cases, the peel strength of some samples degraded more precipitously than others. While samples A and B have nearly the same "as laminated" peel strength, sample B, with the sanded morphology, degraded significantly faster than A. All of the etched interfaces appeared to have an asymptotic peel strength of about 3.0 lbs/in (0.53 N/mm), quite different from the B samples which degraded to near zero peel strength.

Microscopic observations of the interface after peeling gave some clues as to why the dramatic differences may occur. Electron micrographs of the etched (A) and sanded (B) surfaces after lamination and peel testing are shown in Figures 5 and 6. Samples with the etched surface show significant amounts of epoxy residue over the surface, while the samples which were sanded had epoxy residues only in the grooves. The A samples appeared to have a much larger tearing mechanism within the epoxy as opposed to failing at the interface between the copper and the epoxy. If the epoxy adhesion improved due to the keying effect indicated by Arrowsmith,[1] the etched samples would be more likely to retain peel strength than the sanded samples.

There was no observable difference between the morphology of the peeled

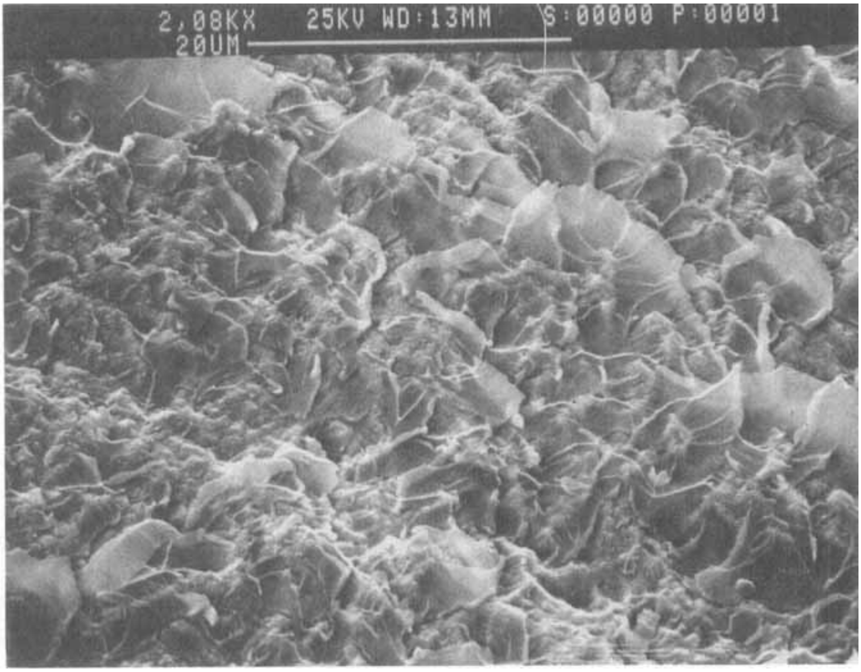

FIGURE 5 Scanning Electron Micrograph of a copper surface with morphology A after lamination and peel testing. Peel fractures in the epoxy are apparent as residues left on the copper suggesting fracture away from the interface.

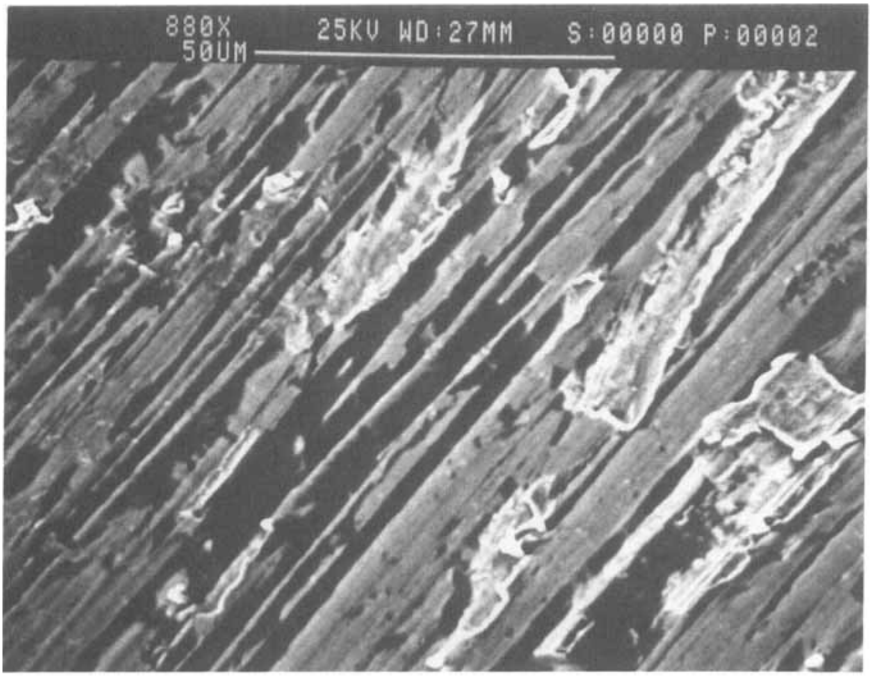

FIGURE 6 Scanning Electron Micrograph of a copper surface with morphology B after lamination and peel testing. Residual epoxy remains; however the regions of residue appear much more discrete.

surfaces which were modified (A1 and A2) and the unmodified peeled surface in sample A. The copper surfaces after peel testing all retained various amounts of residual epoxy on the surface.

The time dependent peel strength could be described using first order degradation kinetics. If A(t) is the peel strength at time t and A(0) is the "as laminated" peel strength, then the degradation can be written as:

$$\int \frac{dA}{dt} = \int [A(t) - A(\infty)]\,[-\Omega] \tag{2}$$

$$\frac{[A(t) - A(\infty)]}{[A(0) - A(\infty)]} = e^{-\Omega t} \tag{3}$$

where Ω is the degradation rate coefficient in hr^{-1}.

This is a two parameter fit for peel strength degradation with the independent parameter being the long time peel strength factor $A(\infty)$. If the peel strength results are analyzed using this equation, the values obtained for $A(\infty)$ and Ω are shown in Table II. It is clear from the results that $A(\infty)$ is much larger when the copper surface is etched than when it is sanded.

TABLE II
Peel test results for the discussed samples

Sample type	Initial adhesion A(0) lbs/in	S.D. (lbs/in)	$A(\infty)$ (lbs/in)	Ω (hr^{-1})	Corr. coeff.
A	8.8	0.8	3.0	0.04	.99
A1	4.5	0.4	3.0	0.30	.97
A2	11.9	0.4	3.0	0.03	.99
B	8.9	0.4	0.5	0.02	.95

DISCUSSION

The determination of peel strength as a function of time at elevated temperature is a better way of analyzing overall peel strength behavior than measuring the "as laminated" peel strength for interfaces in hostile environments. The kinetic expression for degradation generates two parameters and allows a more meaningful comparison than comparing the "as laminated" peel strength for a variety of similar interfaces. Clearly the comparison of A and B in terms of their initial peel strengths shows how problematic an approach using "as laminated" peel strength can be in understanding the time dependence of peel strength at a given temperature.

When comparing the peel strength of surface modified, etched samples with unmodified samples, several factors are noted. Priming improves peel strength over an unprimed copper oxide surface. These results are in line with those of Ishida[9,10] who found improved adhesion between copper and epoxy through the use of a benzimidazole complex agent. If the corrosion reaction (equation 1) cited by both Evans *et al.*[16] and Miller *et al.*[15] limits peel strength, then benzotriazole interaction with unoxidized copper (Sample A2) prevents reaction (1) and improves peel strength over the oxidized copper (Sample A). The peel strength improvement for the benzotriazole-treated copper interface, although slight, occurs over all exposure times. There is an activation energy for the corrosion reaction. Packham determined that the activation energy for this corrosion reaction was 18 KJ/mole at 500°K.[16] If one measures the degradation in peel strength with time at various temperatures, the activation energy for this process can be determined. It would be interesting to compare the activation energy for the cupric oxide/copper reaction with that for the diminishing peel strength.

Chromium ion implantation clearly degraded the peel strength. These results are contrary to those by Bridge *et al.*;[11] however, their results were for implanted copper samples, not copper oxides. The amount of implantation damage occurring within the oxide would be more than likely higher in the oxide than in the metal. Still, some important changes were measured in the oxide structure as a result of ion implantation using XPS. The surface oxidation state in the oxidized copper changed from +2 to +1 as a result of the implantation. Ion implantation could have provided the driving force for reaction (1) to occur. In addition, the oxide thickness decreased suggesting a sputtering effect. Clearly, ion implantation was less successful at implanting ions into the copper and cupric oxide than it was sputtering off the oxide, reducing the copper oxidation state in the oxide, and introducing implantation damage. All of these would serve, potentially, to decrease adhesion.

There are concerns about applying this technique across a wide spectrum of problems. Care should be taken to ensure that the elevated temperature exposure does not induce an unusual failure mode. Thus, for the instances of military hardware where thermal cycling in hostile environments is normal, this approach is acceptable.

CONCLUSIONS

The following conclusions can be drawn:

1. Given a characteristic morphology, chemical treatments performed to modify the surface chemistry of the eventual copper/polymer interface lead to differences in laminated peel strength.
2. The time dependent peel strength for these laminates can be described by a first-order kinetic expression with 2 parameters, the first is the long term peel strength factor, $A(\infty)$, and the other is the degradation rate, Ω. $A(\infty)$ is much larger for the etched surfaces than for the sanded surface indicating that the morphology may control this parameter.
3. "As laminated" peel strength is not a universal gauge of adhesion. Elevated temperature exposures of epoxy/copper laminates do not universally degrade their interfaces in the same way. The residual stress state established by the interfacial morphology is one determining factor in the peel strength degradation kinetics.
4. The work shows that morphological pretreatments, surface chemical treatments and the use environment (temperature, adhesion lifetime) must be specified in evaluating adhesion of a laminated interface.

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