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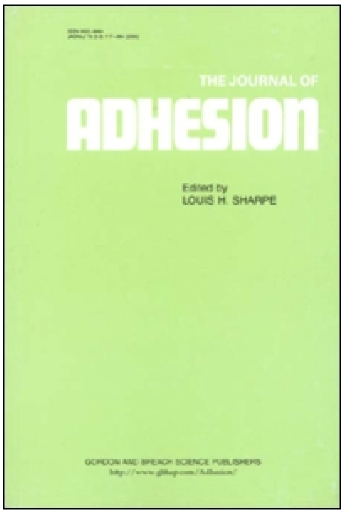

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Surface Chemical Characterization of Copper Oxide and its Relationship to Adhesion in Formed Epoxy/Copper Interfaces

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Surface Chemical Characterization of Copper Oxide and its Relationship to Adhesion in Formed Epoxy/Copper Interfaces*

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Experiments have been performed to comprehensively analyze copper oxides formed from a chlorite oxidation bath on copper bar stock and to measure the adhesion of an epoxy casting resin to the corresponding oxidized surfaces. Temperature conditions for the bath ranged from 25 to 90°C with oxidation times between 0.25 and 20 minutes. Adhesion testing of the epoxy/copper systems was performed using a 3-point bend testing rig and measuring the ultimate force and displacement at the moment of sample failure near the epoxy/substrate interface. The flexure testing configuration used the resin as a stiffening rib which created a deviation in the force-deflection curve from that of the originally-oxidized copper bar stock. As the oxidation temperature increased above 50°C, there was higher cohesion of the oxide layer formed on the copper and that led to a higher measured force at failure. On copper samples oxidized at lower temperatures, failure occurs within the oxide as a part of the latter remains on the resin side and lower adhesion was measured.

Keywords: Copper oxidation; chemical analysis; LEEIXS; XPS; SEM; epoxy/copper adhesion; mechanical testing; three-point flexure

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INTRODUCTION

There have been many adhesion investigations of copper-based materials in the literature [1 – 13]. Copper is a difficult substrate to bond due to (a) the catalytic activity of its surface oxide which alters adhesive curing conversion [14, 15], (b) the activity of copper in the presence of oxidizing and reducing agents from the environment [16], and (c) the poor intrinsic adhesion that is linked to the oxide layer at the oxide/metal interface [1, 4, 6, 8, 12, 17, 18]. Therefore, much work on improving adhesion between the copper surface and polymers has recently been reported which concerns particularly the chemically-formed copper oxides, namely the so-called black and red/bronze oxides [5, 6, 9 – 11, 16, 17].

Other efforts to increase polymer/copper adhesion have focused on the use of chemical coupling agents and other primers to enhance the chemical interactions between organic and copper [7, 8, 11, 12, 14, 18, 19]. These studies have often been performed on polished metal surfaces which have been treated with azole-type primers to maximize the chemical interaction between the curing polymer system and a modified metal surface and to minimize any sort of mechanical interlocking phenomena.

The goal of the present experiments was to analyze how chemical oxidation creates an adherent surface. This has been done by a thorough investigation of copper oxides formed by varying both processing times and temperatures using a standard wet oxidizing treatment and an evaluation of the bond strength of the interphase formed between an epoxy casting resin and copper oxide.

EXPERIMENTAL

Copper (OFHC – Oxygen Free High Conductivity) bar stock was punched into smaller samples (1 mm thick × 10 mm wide × 50 mm long) for this project. The copper specimens were prepared by mechanically polishing with 800 grit sandpaper, followed by a cleaning step in a 0.1 N HCl solution for 1 minute. After etching, each sample was rinsed in DI water and dried using a blowing nitrogen source. Each sample was then etched using a 20 g/l solution of $Na_2S_2O_8$ for

1 – 2 min and, after that, oxidized in a beaker bath solution of 45 g/l $NaClO_2$ and 10 g/l NaOH. The oxidizing bath temperature was controlled between 25 and 90°C using a hot plate and the immersion time ranged from 0.25 to 20 min, again followed by a rinsing and drying. The fluctuation in the temperature of the beaker bath was contained within 2°C. Of the group that was oxidized, a subset of samples was also subsequently immersed in a chelating primer solution during 16 h (benzotriazole (BTA) 40 g/l ethylene glycol). Following the priming procedure, these samples were rinsed in DI water 5 – 10 times to eliminate the ethylene glycol and dried.

The characterization effort used Low Energy Electron Induced X-ray Spectroscopy (LEEIXS), XPS and SEM. Our primary tool for characterization was LEEIXS, but other compositional analyses were collected using XPS. Morphological observations were collected using scanning electron microscopy.

LEEIXS measurements were carried out using a wavelength-dispersive X-ray spectrometer using an electronically-stabilized gas discharge tube which operates as an eletron source under the primary vacuum (1 – 15 Pa range) of the spectrometer. A schematic representation of the experimental set-up is given in Figure 1. The operating

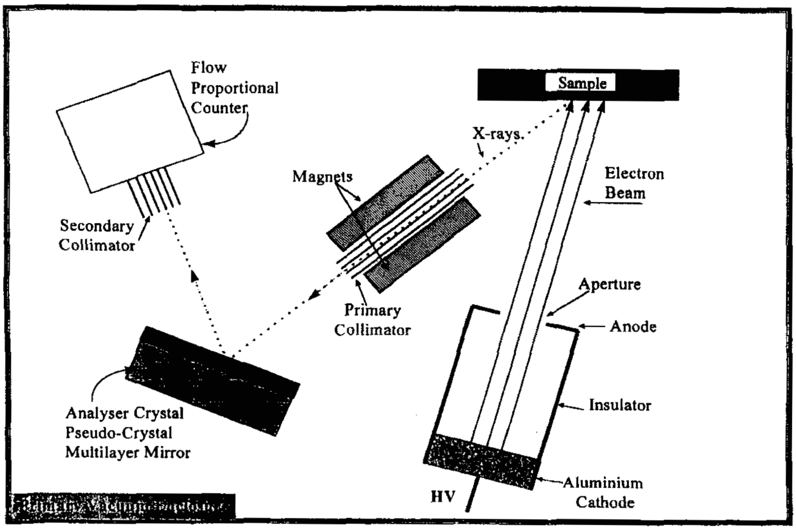

FIGURE 1 Schematic of the LEEIXS spectrometer.

voltage of the electron source was 4 kV with a current of 0.1 mA, creating an electron beam at the sample surface less than 1 cm in diameter. Emitted soft and ultra-soft X-rays (OK_α and $CuL_{\alpha,\beta}$) were dispersed by flat analyzing devices and detected by a flow proportional counter. Details about this technique are given in the literature [20]. LEEIXS is capable of probing the surfaces and near-surfaces of materials up to about 100 nm, the corresponding depth depending, among other parameters, on the incident electron beam energy and the nature of the sample.

The XPS unit was a Riber SIA 200 model using an Al Kα radiation source and a Mac 2 analyzer. The scanning electron microscope was a SEM 515 model from Philips. Given the conductivity of the specimens that were observed, there was no need for an additional conductive coating on the specimens. An image of an etched and oxidized surface of copper is shown in Figure 2.

After oxidation, a two-component epoxy adhesive (ARALDITE® AY 103 with hardener HY 991 from Ciba-Geigy™) was applied to the copper specimens. For the adhesion experiments that were performed in this study, oxidation times ranged between 4 and 5 minutes. A jig

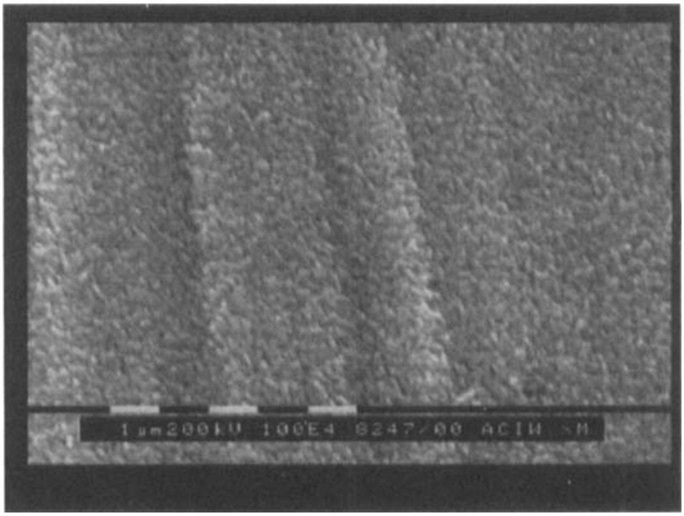

FIGURE 2 Scanning electron microscope micrographs of a copper oxide surface prepared through sanding and etching procedures, followed by oxidation for 5 min @ 80°C in the oxidation bath.

was used to perform the bonding procedure. The jig consisted of a metal plate to align each copper specimen and a silicone rubber gasket that created a moat for each copper specimen properly in the middle of the specimen. The casting resin was injected, using a syringe, into each moat following mixing of the two components. Curing was performed in an air oven in 80°C for 2 hours (according to specifications provided by the supplier) after which the samples were allowed to cool to room temperature for 24 hours prior to mechanical testing.

The bonded specimens were then tested with a three-point flexure device (Flex-3 Model from Techmetal fitted with a 1000 N load cell) using a published procedure [21, 22]. The force-deflection data that were collected were compared with the force deflection curve for the oxidized substrate. The positive deviation in the force-deflection curve of the bonded specimen arises due to the stiffening effect that the adhesive has on the compliance of the bar. In other words, the adhesive acts as a stiffening rib in altering the force-deflection curve. When failure arises, it is sensed in this force-deflection curve as the adhesive rib becomes decoupled from the metal substrate with a drop in the force-deflection curve toward that of the nonribbed substrate. The points associated with maximum force ($F_{\max}$) and maximum displacement ($D_{\max}$) can easily be identified for each series of samples associated with each process condition.

RESULTS AND DISCUSSION

Chemical Analysis Data

A representative graph showing the multiplexed Cu$L_{\alpha,\beta}$ LEEIXS output for bare and oxidized copper specimens is shown in Figure 3. Recognize that the corresponding spectrum contains two X-ray emission bands, CuL_α and CuL_β, each associated with different electronic transitions in copper atoms ($M_{4,5} \rightarrow L_3$ and $M_{4,5} \rightarrow L_2$, respectively). One also finds other elemental emissions such as OK_α (corresponding to $L_{2,3} \rightarrow K$ electronic transitions in oxygen atoms) by investigating other energy regions [23, 24].

The observed effect in comparing virgin and oxidized copper is the difference in the intensity of the two peaks in the spectrum, identified

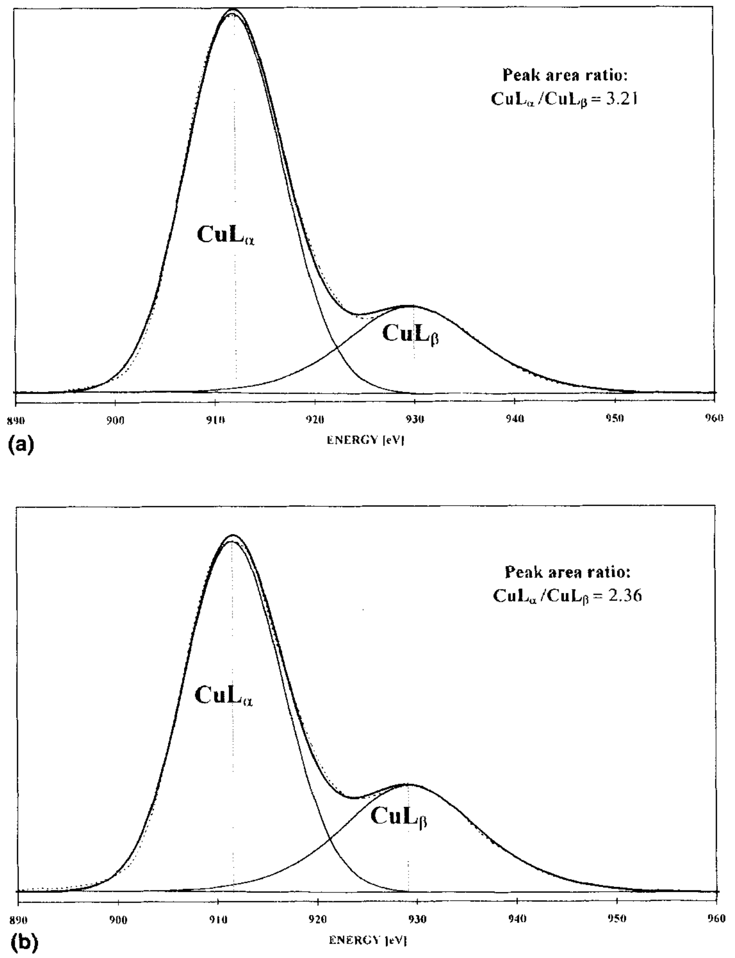

FIGURE 3 LEEIXS Cu$L_{\alpha,\beta}$ spectra for (a) metallic copper (b) CuO (incident electron energy 4 keV, TlAP crystal).

as L_α and L_β at maxima of 911.7 eV and 929.3 eV, respectively. By deconvoluting each spectrum, the ratio of intensity of the two partially overlapping emission bands can be determined. In the present case, and given the analyzer crystal (TlAP – Thallium Acid Phthalate, $2d = 2.571$ nm) used for dispersing the corresponding radiations, the spectral resolution is sufficient, so that the intensity maximum of each band L_α and L_β is unaffected by the contribution of its neighbor. As a result, each peak intensity can be directly measured after accounting for the baseline intensity. LEEIXS is sensitive to observing copper chemical states given the changes in the ratio of intensity of L_α to L_β resulting from oxidation [27, 28].

The influence of the oxidation time and temperature in terms of oxide growth characteristics can be observed by considering the variation of the CuL_α/CuL_β ratio. As shown in Figure 4, this ratio (about 3.2 for CuO and 2.4 for metallic copper) depends on the chemical state of copper. When the film oxide thickness increases, the contribution of the metal substrate decreases and, consequently, the CuL_α/CuL_β ratio decreases. The ratio drops fastest for samples processed at the highest oxidation temperatures because oxide growth rates are higher. The ratio reaches an asymptotic limit of approximately 2.5 for samples obtained at times beyond 15 minutes at the highest oxidation temperatures. This ratio characterizes cupric oxide as confirmed by the ratio obtained for stoichiometric cupric oxide specimens fabricated by physical vapor deposition (magnetron reactive sputtering) to a thickness greater than 1 μm thick [27].

Figure 5 shows OK_α (spectra in the 530 eV region) intensity growth for oxides obtained by varying both the bath temperature and immersion time. For a given temperature, increasing the immersion time linearly increases the intensity of OK_α (only emitted by the oxide

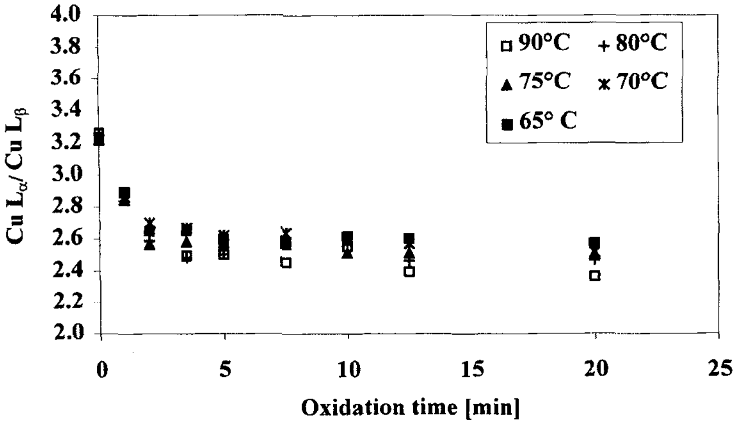

FIGURE 4 LEEIXS CuL_α/CuL_β intensity ratio as a function of treatment time for a series of oxidation temperatures.

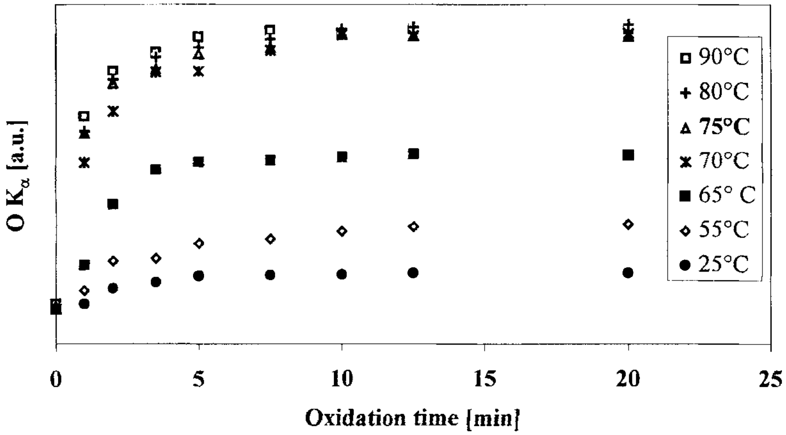

FIGURE 5 LEEIXS intensity variations of OK_α as a function of treatment time for a series of oxidation temperatures (incident electron energy 4 keV, TlAP crystal).

layer) up to oxidation times approaching 5 minutes; as the oxidation times increase beyond 5 minutes, the intensity reaches an asymptotic limit. The results show that, whatever the oxidation temperature may be, the oxide thickness reaches a plateau between 5 and 10 minutes. One can see the strong influence the oxidation temperature has on the OK_α intensity by taking isochronal lines across the LEEIXS intensity plots which are shown graphically in Figure 6. By measuring the intensity at the same oxidation time at different temperatures, the oxidation temperature demarcation between 55 and 70°C is clearly seen. Short times (2 min), even at the highest oxidation temperatures, lead to peak intensities of OK_α that could still rise with continued immersion. For a 2-min oxidation immersion the depth probed by LEEIXS is larger than the oxide layer thickness. As the oxide growth rate slows down when temperature increases, one observes a quasi-plateau at the end of the curve. Using the Feldman relation [20] for a given incident electron beam energy (4 keV) one can calculate for OK_α the maximum probed depth for oxygen in CuO. Knowing this value (102 nm) and recognizing that the OK_α intensity grows with continued oxidation time, the oxide thickness at 2 minutes is less than 102 nm and the corresponding growth rate is less than about 51 nm min^{-1}. The plateaus associated with OK_α intensity at longer times (at 5 and 12.5 minutes) are almost overlapping. The oxide thickness with samples

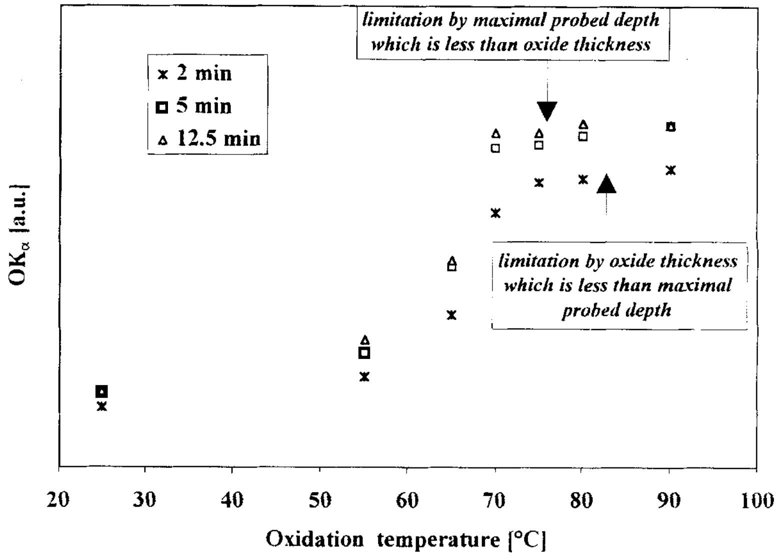

FIGURE 6 LEEIXS intensity variations of OK_α as a function of treatment temperature at specific times during the oxidation procedure (incident electron energy 4 keV, TlAP crystal).

processed at these longer times is likely to be larger than the probed depth for OK_α at 4 keV as shown by OK_α intensity obtained for CuO_x oxides (thicker than 1 μm) deposited by reactive magnetron sputtering.

The decreasing intensity of CuL_α with both increasing treatment time and bath temperature is shown in Figure 7. The signal variations of copper oxidized at 25°C show the most gradual change in CuL_α intensity. For all other process temperatures, the CuL_α LEEIXS intensities overlap. The same argument related to the probed depth can be used here to explain the results. Within three minutes of oxidation at any of the experimental temperatures the CuL_α intensity is invariant. The probed depth for CuL_α calculated from the Feldman relation at 4 keV is 97 nm, slightly smaller than that for OK_α. The copper signal invariance with oxide thickness before oxygen signal invariance is explained by the contribution of both the base metal and the formed oxide to CuL_α. This explains why the OK_α signal is easier to use.

The surface composition of copper oxides formed for various times (0 to 4 minutes) between 55 and 75°C was also determined by XPS.

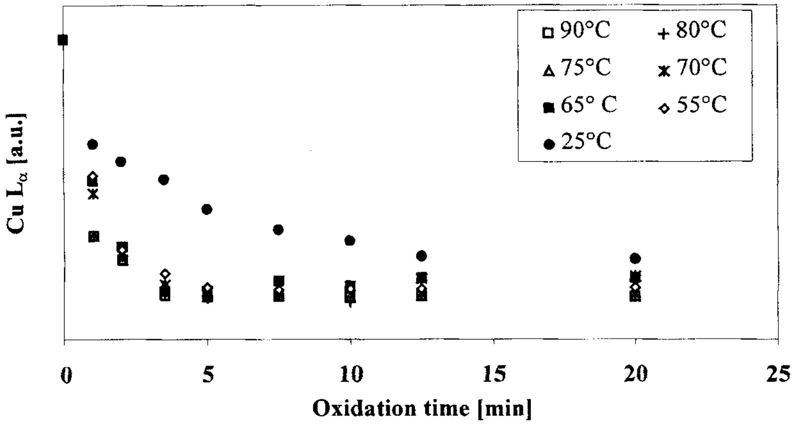

FIGURE 7 LEEIXS intensity variations of CuL_α as a function of treatment time for a series of oxidation temperatures (incident electron energy 4 keV, TlAP crystal).

The corresponding Cu2p spectra are shown in Figure 8. Spectrum (a) for the non-oxidized sample (sample only etched and persulfate-treated) is typical for copperr metal (Cu2p$_{3/2}$ peak at 932.6 eV). The other spectra (b), (c), (d), obtained from oxidized samples are characteristic of cupric oxide CuO (Cu2p$_{3/2}$ peak at 934.0 eV and presence of the Cu2p$_{3/2}$ multiplet structure at 942.6 eV [28]). The

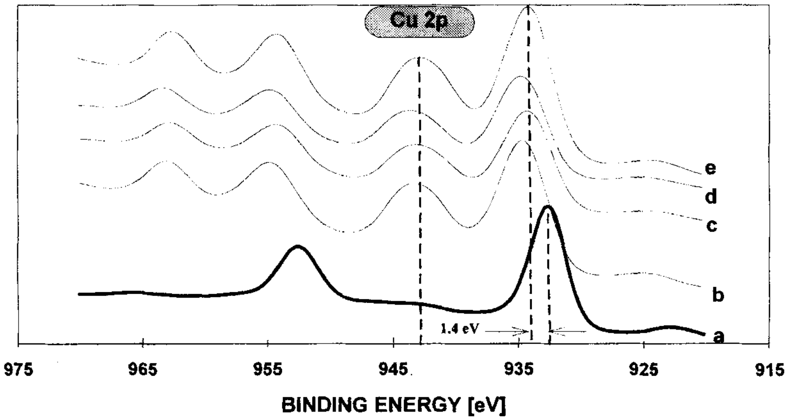

FIGURE 8 Cu2p XPS spectra: (a) non-oxidized sample; samples oxidized (b) at 55°C/1 min, (c) at 65°C/1 min, (d) at 75°C/1min, (e) at 75°C/4 min.

observed Auger lines in all of the oxidized cases are consistent with the interpretation of CuO [28]. This suggests that metallic copper is fully converted into cupric oxide on the outer surfaces even for the lowest temperature (55°C) and for the shortest time (1 min).

Mechanical Test Results

Data reported in Figure 9 show the influence of oxidation temperature on the 3-point flexure performance of the bonded joints. The results (F_{max} measurements and failure location) suggest that the low oxidation temperatures lead to an oxide coating that is weakly bound to the copper substrate, the failure appearing visually at the oxide/metal interface. When the bath temperature increases F_{max} increases, reaching an asymptotic limit of approximately 300 Newtons with failure occurring in the adhesive.

The use of maximum force in the determination of an adhesive failure is generally limited to the case of the failure within the initial linear region of the force-deflection curve for each specimen tested. As the adhesion at the polymer/metal interface rises, there is higher

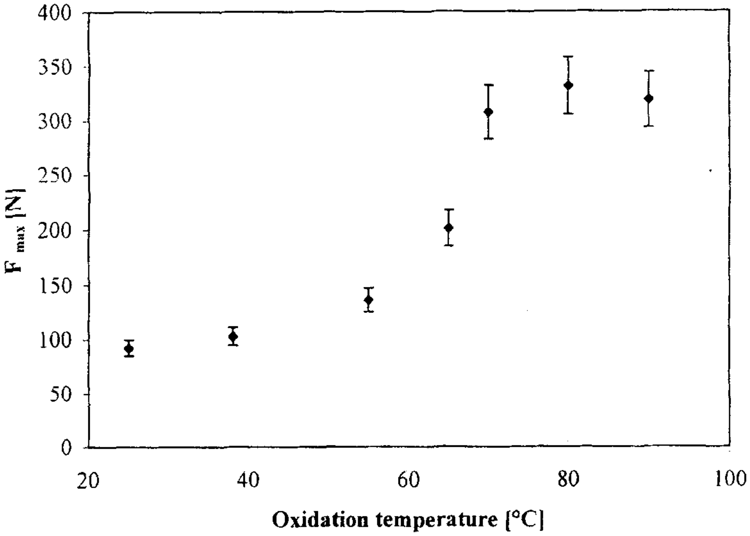

FIGURE 9 F_{max} for 3-point flexure tests on epoxy/copper systems as a function of oxidation temperature (oxidation time = 5 minutes).

potential for plastic deformation to occur in the substrate during the force-deflection experiment. For substrates oxidized above 70°C, failure of the bonded assembly occurs at loads that also plastically deform the substrate. Thus, another approach is needed.

The use of the maximum displacement in the flexure experiment is an alternative method to gauge the resistance to delamination. The interpretation of the results based on a maximum displacement is shown in Figure 10. A distinct rise in the maximum displacement is observed even above process temperatures of 80°C. When comparing these results with those from Figure 9, the sensitivity of F_{max} is lost at process temperatures above 70°C. The main reasons for the discrepancy between maximum force and maximum displacement interpretations are the low yield stress of the copper and the substantial plasticity of copper beyond the yield point. The displacement approach is clearly better.

A group of substrates, oxidized at 70, 80, and 90°C respectively, were aged in a humidity chamber at 90% humidity and 90°C. Following 250 hours of aging, substrates were removed from the chamber, bonded and flexure tested. The results of the aging experiments were mixed, but no specimen preparation condition led to a reduced maximum displacement.

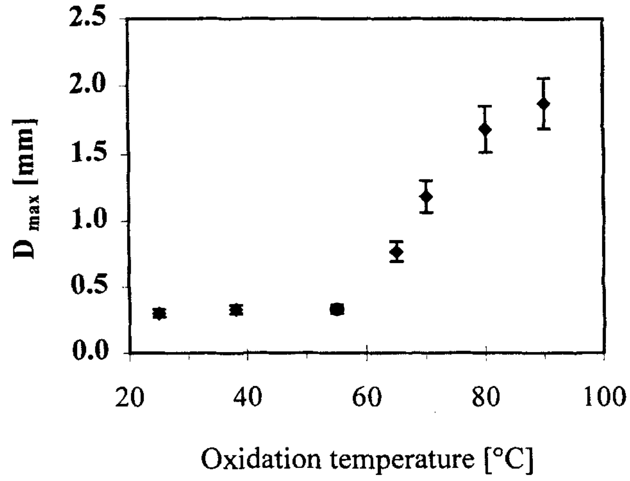

FIGURE 10 D_{max} for 3-point flexure tests on epoxy/copper systems as a function of oxidation temperature (oxidation time = 5 minutes).

Figure 11 shows the effect of the primer treatment on the maximum displacement results for the most favorable oxidation conditions (70 – 90°C). With oxidation temperatures of 70°C the influence of the primer is strongest in improving adhesion. The strength is so high for the treated specimens above 80°C that the failure occurs farther away from the true polymer/metal interfacial zone where the primer is located.

The results in this study are in conflict with the results obtained by Yun *et al.*, who found increased adhesion with primers used on specimens oxidized between 85 and 95°C [6], but not with another work performed at 70°C [8]. The main observation in these three studies is that the bath compositions are all different, therefore the oxidation kinetics are also not expected to be the same. It is not surprising to see changes in behavior for specimens processed through different oxidation baths.

To assess the need to actually oxidize the specimens at all, flexure testing was also performed on specimens at each of the other stages prior to the oxidation process. The flexure results of these specimens are included in Table I. While the performance for the non-oxidized specimens appears satisfactory, it is well-known that any level of thermal degradation leads to a rather dramatic drop-off in measured adhesive strength [19]. On the other hand, the presence of well-defined

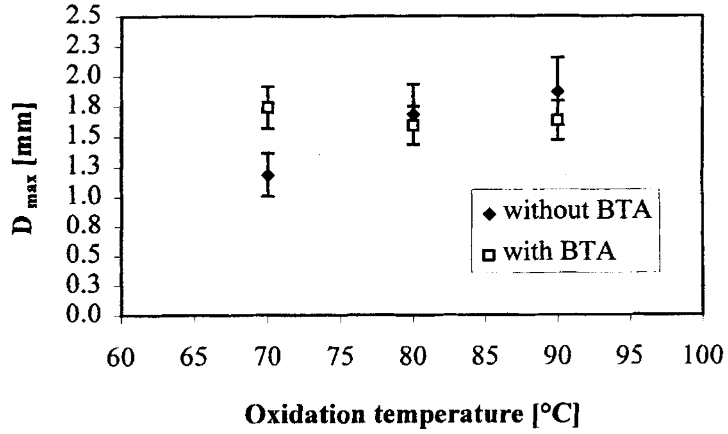

FIGURE 11 D_{max} for 3-point flexure tests on epoxy/copper systems as a function of the three highest oxidation temperatures with and without BTA.

TABLE I F_{max} and D_{max} measurements for epoxy/copper systems at intermediate process steps prior to oxidation and following oxidation of copper at various temperatures

Sample	*Fmax* [*N*]	*Error bar*	*Dmax* [*mm*]	*Error bar*
Degreased	140	14	0,37	0,12
Polished/degreased	277	12	0,92	0,15
Etched HCl + Persulfate	280	13	0,84	0,20
Oxidized 5 min @				
25°C	93	12	0,30	0,15
38°C	103	13	0,33	0,11
55°C	136	11	0,33	0,25
65°C	201	10	0,77	0,19
70°C	307	9	1,18	0,20
80°C	332	14	1,68	0,15
90°C	319	9	1,87	0,20

copper oxides allows one to improve the durability of epoxy/Cu assemblies in humid media [6]. In addition, it was shown that the kinetics of thermo-oxidative degradation of epoxy resins is lowered when the latter are in contact with CuO-type oxides [14] in comparison with the case where they are in contact with the natural, unorganized oxides present on etched copper substrates [29].

CONCLUSIONS

From the results presented, the following conclusions can be drawn:

- LEEIXS has proven useful as a complementary tool to XPS in characterizing thicker oxide coatings on copper,
- a strong correlation has been found between the formation of CuO and higher adhesion of an epoxy resin to the oxidized surface,
- oxidation temperatures above 70°C lead to copper oxides that show consistently higher adhesion with an epoxy casting,
- with flexure testing of compliant substrates, the use of maximum displacement is a stronger gauge of performance than the use of maximum applied force.

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