

Metallurgy and performance of electrodeposited copper for flexible circuits

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Keywords

Flexible circuits, Electrodeposition, Copper, Electronic packaging

Abstract

In this paper, we consider intrinsic properties of copper electrodeposited as plateaup on polyimide substrate, thermal response of electrodeposited copper and fatigue performance of copper and copper/polyimide construction. The critical material characteristics examined are grain morphology and structure, crystallographic texture, microhardness, uniaxial strength and ductility and isothermal cyclic fatigue life. Given optimum processing conditions, copper plateaup in flexible circuits displays fine grain structure, high ductility, adequate thermal stability, freedom from thermal embrittlement and excellent fatigue endurance over a wide range of strain amplitudes.

Presented at EURO TOM'99, 27 September-1 October 1999, Munich, Germany.

Microhardness hardness measurements, cross-section optical microscopy, grain size quantification and tensile/fatigue testing were conducted by M.G. Rozboril and M.G. Minor, X-ray diffraction by N.E. Bergkessel and optimization of electro-chemical parameters by J.T. Wang. Cross-section FIBCC-SEM analysis was performed at Accurrel, Sunnyvale, CA, and cross-section TEM by microtomy, ion milling and electropolishing by STEM, Woodbridge, CT. Planar TEM grain structure analysis was performed at University of Kentucky, Lexington, KY and cross-section FIBCC-TEM grain structure characterization at University of Central Florida, Orlando, FL.

1. Introduction

The flexible printed circuits in electronic packaging are the multi-layer polymer/metal constructions, with applications in computer disc drive, printer and medical devices. For the flexible polymer substrate, adhesion, thermo-mechanical dimensional stability, resistance to solvent absorption and etchability are four critical performance attributes which are influenced by polymer chemistry and/or microstructure (Weale *et al.*, 1993). The polymer of choice is polyimide since it can be processed at elevated temperatures to form planarized structures of high mechanical stability and low dielectric constant (Cummings *et al.*, 1982; Estes and Kulesza, 1983). Kapton E[1] is a high modulus polyimide film with low coefficient of thermal expansion (CTE) which provides excellent dimensional stability, superior resistance to solvent absorption and good etchability (Weale *et al.*, 1992; 1993). The Upilex-S[2] film offers lower moisture absorption and CTE more closely matched to copper (Egitto *et al.*, 1994). The thermo-mechanical stability is needed for flexible circuits to minimize movement of web features early in the process, which could prevent alignment/registration during subsequent photo processing (Weale *et al.*, 1992). Adequate adhesion ensures that the copper circuit lines remain in intimate contact with the substrate during processing and in the field, and no shorting out of circuit lines ensues.

Copper does not react with polyimide, bonds weakly with it and hence tends to diffuse into it (Tromp *et al.*, 1985; LeGoues *et al.*, 1988). Plasma treatment of polyimide leads to the bond scission of imide groups to form carbonyl and secondary amide groups; as a result, surface of the polyimide film changes from hydrophobic to hydrophilic (Inagaki *et al.*, 1994). The treatment removes a surface layer of polyimide, forming needle shaped surface protuberances and promoting improved adherence (Fronz, 1991). Furthermore, ion bombardment occurring in the DC-plasma configuration results in relatively high cross linking of the polymer surface; promoting improved cohesion strength in polymer and increased resistance to solvents and moisture diffusion (Egitto *et al.*, 1994). Even with the plasma treatment, the adhesion of copper to polyimide remains relatively weak (Chung *et al.*, 1994). A thin metal tie layer, such as chromium, separating copper and polyimide is effective in enhancing adhesion. Chromium reacts with polyimide at the interface and is thus bonded at the surface, forming a continuous layer on top of polyimide (LeGoues *et al.*, 1988). The prior plasma treatment of polyimide increases the reactivity of chromium with polyimide, and hence further increases the bond strength (Chung *et al.*, 1994).

Copper is electrodeposited typically on the plasma treated polyimide coated with thin sputtered tie coat layer (Cr, Cr/Cu or Cu/Ni) and with thin sputtered copper seed layer (Egitto *et al.*, 1994). This adhesiveless attachment of copper to the pretreated and precoated polyimide substrate has several advantages: thin

electrodeposited copper layer, thin overall metal/polyimide construction and ease of etching for the copper layer circuitization (Fronz, 1991). Distinctive characteristics of the polyimide are fully exploited. High-density fine-line applications requiring smooth surface and thin construction essential for fine line etching become feasible (Jiang *et al.*, 1998).

However, the deposited metal layers often result in web curvature (curl) due to residual stresses, especially when the metal is deposited only on one side of the web (Chen *et al.*, 1993). Since the laminate is subjected to through-hole forming operation for metal layer interconnect, tooling holes and photolithographic registration aids, the web should remain flat to permit good registration. The curling can be minimized by varying the thicknesses of chromium and copper sputtered layers (Chen *et al.*, 1993) and/or by manipulation of the copper electrodeposition parameters.

During the adhesion peel test, fracture may occur adhesively (Ahn *et al.*, 1996) at the metal/polyimide interface or cohesively (Iwamori, 1997) in polyimide a little below the interface (Jiang *et al.*, 1998; Pappas and Cuomo, 1991). High fracture energy and ease of plastic deformation of the metal layer contribute to the enhancement of peel strength (Pappas and Cuomo, 1991; Joh *et al.*, 1996). More ductile metal film has higher peel strength. Wide and long open grain or morphological boundaries assist the metal layer to be bent more easily during peeling. Easy bending of the metal film induces more extensive plastic deformation with relatively large contribution to the peel strength. Low yield strength of the metal layer reasonably accounts for high peel strength. The peel strength is thus more a measure of the plastic deformation accompanying the peel test rather than a measure of the fracture energy (Park and Yu, 1998).

It is clear that five critical parameters for plateaup are internal stresses, surface roughness, grain structure/morphology, strength and ductility. The first two are controlled by the choice of deposition parameters. In order to minimize curling, the internal stresses in the electrodeposit must balance the stresses in the sputtered layers; the balancing is specific to the design (dimensions, placement) of polyimide/metal layers construction. The choice of deposition parameters which may balance the internal stresses may not yield minimum surface roughness. Since the smooth surface is essential for fine line etching and, as we will establish in this study, also for fatigue performance, an optimum window of electrodeposition parameters is developed for acceptable levels of curl and roughness.

The intent of this study is to examine, within the framework of optimum electrochemical processing window, grain structure, fatigue performance and thermal response of strength and ductility of thin copper layer electrodeposited on polyimide substrate.

Circuit World
26/4 (2000) 7-14

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0305-9120]

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2. Experimental procedure

Commercially available 25 μm thick Kapton E (duPont) and 12.5 μm thick Upilex-S (UBE) polyimide films were utilized as substrate. Using roll-to-roll production system, plasma treatment, chromium tie layer deposition and copper seed layer deposition were conducted in sequence. The film surfaces were plasma treated in oxygen containing environment at low pressure. About 30nm chromium film was sputter deposited using 99.9 percent chromium target. About 200nm copper film was sputter deposited on the chromium layer using a planar magnetron and argon, utilizing 99.99+ percent copper target. An optimum electrodeposition processing window was established in the laboratory so that web curl and copper roughness were minimized. Electrodeposition was conducted on a roll-to-roll production unit using acidified sulfate solution to deposit 1 to 15 μm thick copper layer over the sputtered copper seed layer.

For copper electrodeposit less than 10 μm thick, Upilex-S film was used; for 10 μm and thicker copper, Kapton-E film was used. A set of samples was obtained, on the production unit, outside the optimum processing window; this yielded rough surface. For samples within the processing window, overpotential was varied. Another set of samples was obtained at relatively high overpotential to yield low amplitude, large wavelength deposit surface

profile. A third set of samples obtained at relatively low overpotential yielded virtually flat deposit surface. The deposit surface morphology for the three sets is illustrated in Figure 1.

The cross-section grain morphology was examined by optical microscopy and by focused ion (Gallium) beam channeling contrast (FIBCC) and SEM. The grain structure of electrodeposit was examined by TEM. For planar view TEM at mid-thickness, jet polishing was used. For cross-section TEM, either microtomy followed by jet polishing or FIBCC (Giannuzzi, 1996) was utilized.

Tensile tests were performed by monitoring crosshead movement, the details are presented in our earlier paper (Merchant, 1993). Room temperature tests were conducted at 1.7×10^{-2} /sec strain rate and above room temperature up to 473K at 4.2×10^{-4} /sec. Polyimide and polyimide/copper laminate were separately tested. Tensile behavior of the copper layer was determined by subtraction process described elsewhere (Marionczyk, 1996). Tukon hardness test procedure with 10g load, is described in our earlier paper (Merchant, 1995). The microhardness value is approximately proportional to the yield stress. The crosshead displacement tensile test procedure provides imprecise measure of the yield level (Merchant, 1997). However, the yield strength appears to be about 0.7 times the peak (ultimate) stress value at temperatures up to 473K.

Figure 1

Surface morphology of 15 μm plateaup. Optical cross-sections (a) rough surface, non-optimum processing, (b) profile surface, optimum window, high overpotential, (c) smooth surface, optimum window, low overpotential. Note vertical twin traces, (d) FIBCC - SEM cross-section

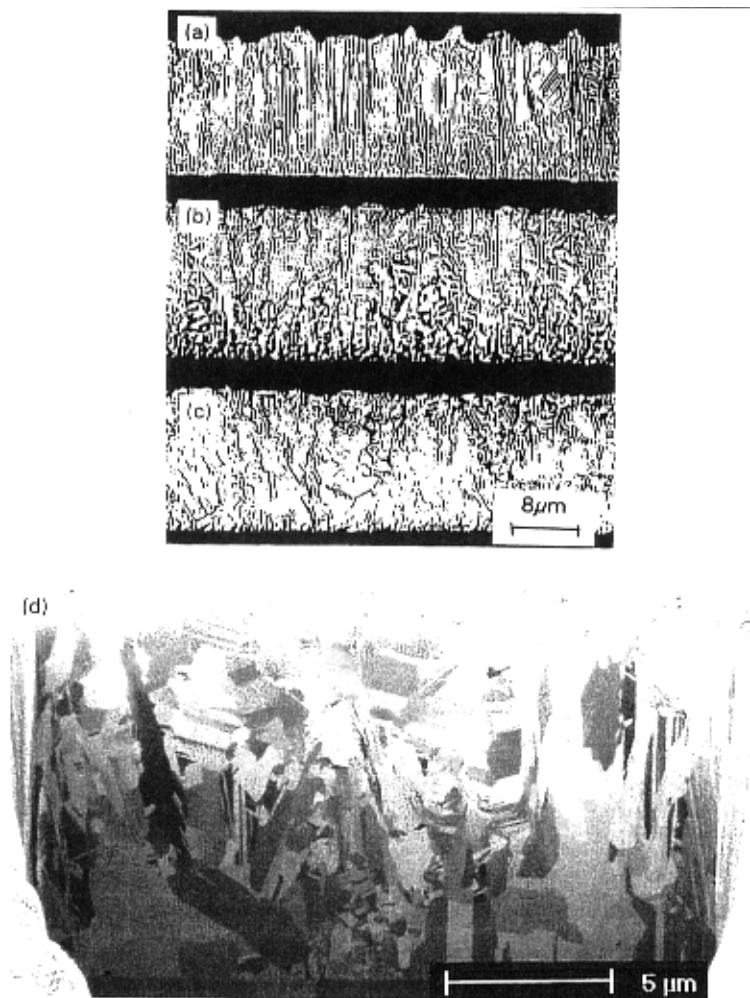


Figure 4
Grain size distribution in vertical and horizontal orientations for 3 μ m and 5 μ m plateups

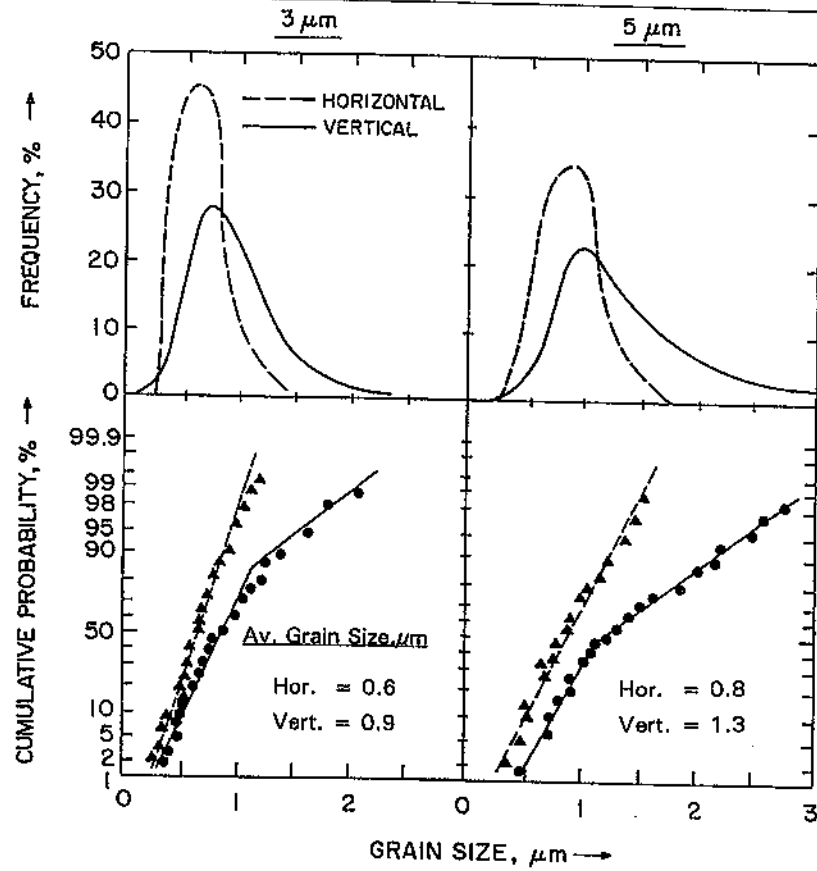
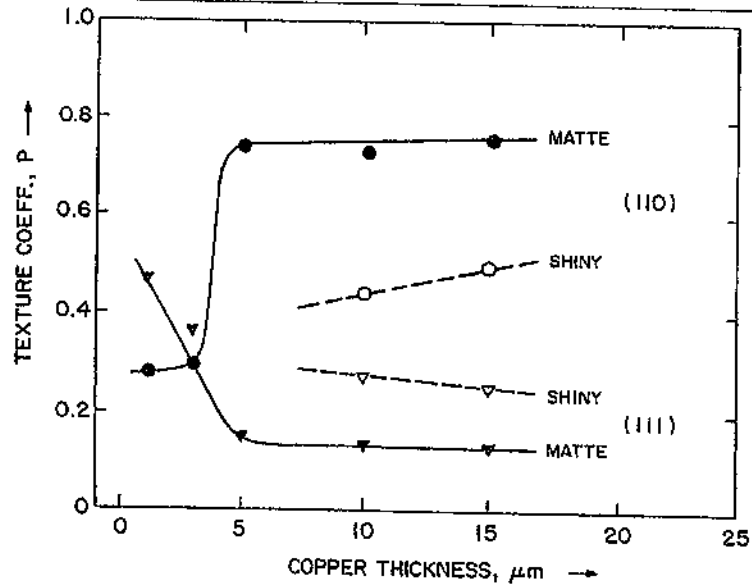


Figure 5
Effect of copper layer thickness on calculated texture coefficients (110) and (111)



grain structure of 3 μ m and 5 μ m layers is shown in Figure 3. The corresponding grain size distributions, based on about 50 independent observations, using vertical and horizontal intercepts are shown in Figure 4. For the vertical

orientation, long tail of frequency distribution and break in slope of cumulative distribution correspond to the elongated grains. The incidence of grain extension apparently increases with the layer thickness. The mean

Figure 6
Effect of 30 min. anneal on tensile properties and microhardness for "rough" 15 μ m plateup deposited outside the optimum deposition window

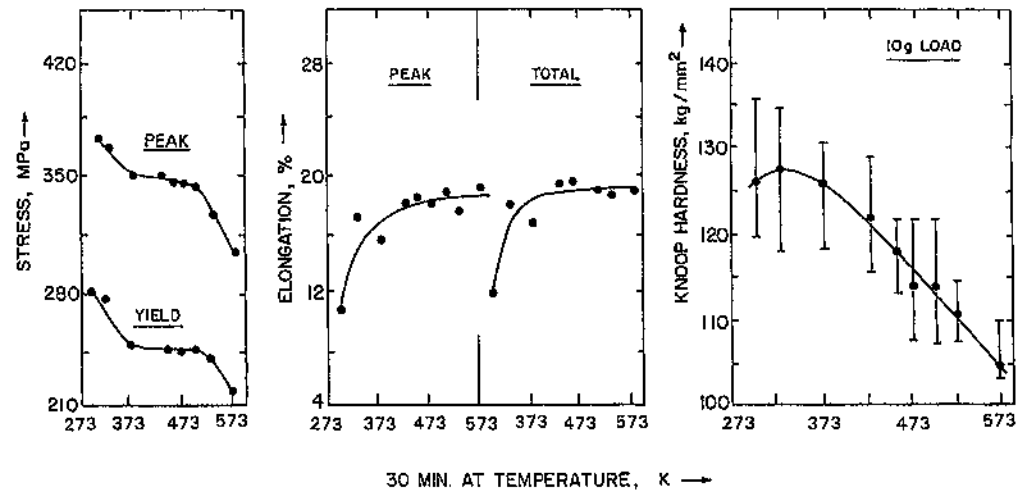
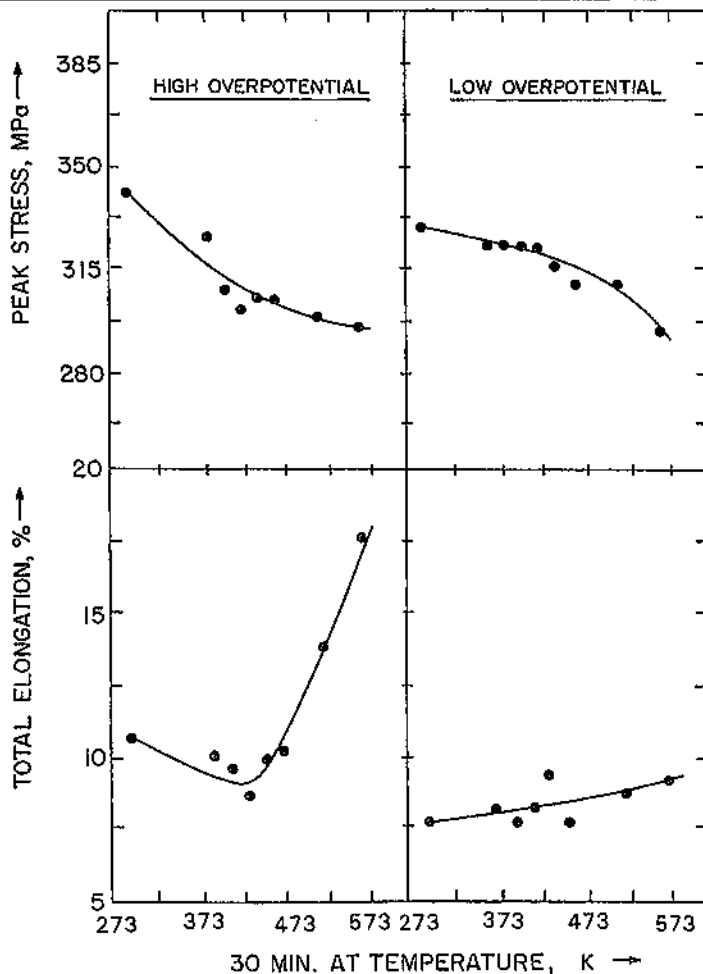


Figure 7
Effect of electrodeposition overpotential on annealing response for 15 μ m plateup deposited within optimum processing window



grain size in the vertical orientation is about 1.4 times that in the horizontal orientation, as predicted for the twin assisted growth (DeAngelis *et al.*, 1995).

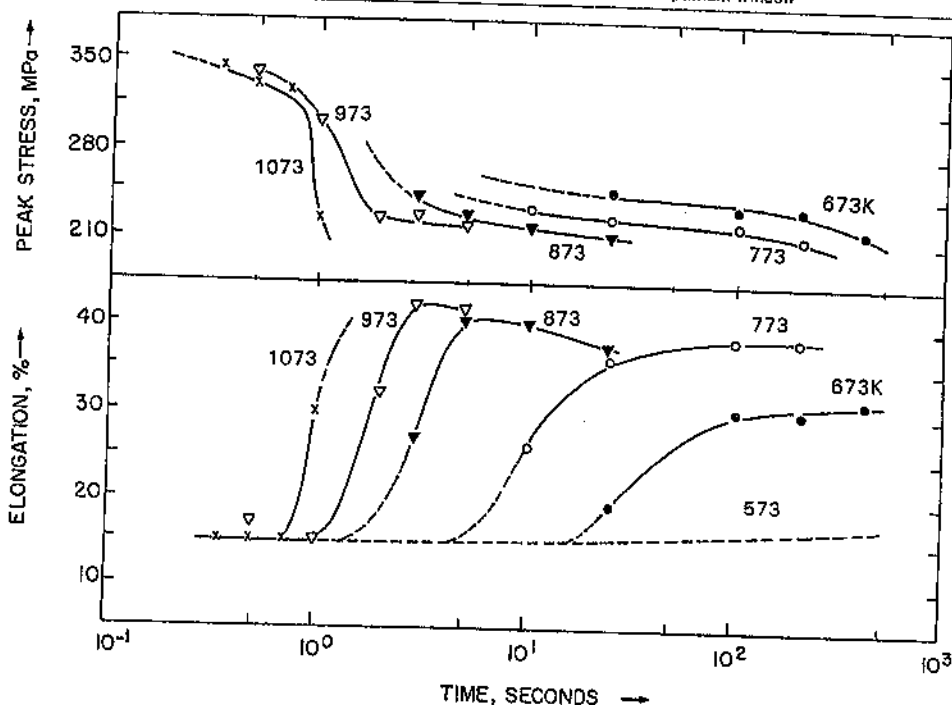
The calculated texture coefficient P using X-ray diffraction intensity data from the shiny (substrate side) and matte (air side) surfaces of the copper layer, as a function of copper layer thickness is shown in Figure 5. Note sudden jump in $P_{(220)}$ from near random ($P = 0.33$) for 3 μ m thickness to a strong texture ($P = 0.75$) for 5 μ m; also, evolution of $P_{(220)}$ from near random on the shiny surface to highly oriented on the matte surface. Owing to about 3 μ m subsurface penetration of the Cu-K radiation, it is not meaningful to differentiate between the shiny and matte surfaces for copper layer thicknesses 5 μ m and lower. In the cross-section TEM grain structure, the growth twins begin to appear for thicknesses 5 μ m and higher. Hence, grain extension in thickness direction is apparently due to the promotion of z-direction growth when $\langle 220 \rangle$ texture axis is parallel to $\{111\}$ twin plane (Bergstresser and Merchant, 1995).

3.2 Thermal response

The effect of 30 min. isothermal anneal between 296K and 573K on yield (0.2 percent strain cutoff) and peak (ultimate) stresses, peak (uniform) and total (fracture) elongations and microhardness for the "rough" 15 μ m plateup deposited outside the optimum window is shown in Figure 6. The yield stress curve runs parallel to and about 70 percent below the peak stress curve; the total elongation curve is only slightly above the peak elongation curve, indicating uniform elongation (no necking instability) almost to fracture. Already high ductility, apparently due to fine grain structure and freedom from porosity, is further improved by the anneal exposure. The microhardness anneal curve corresponds to the annealing events taking place at the plateup mid-thickness where the Takon indentations were made. Non-uniformity of softening is indicated by considerable scatter between 11 indentations for a given reading. The shape of anneal curve for microhardness is different from that for yield stress which averages annealing events across the whole specimen thickness.

Figure 7 shows the effect of overpotential on anneal response for plateup deposited within the optimum window. The anneal response in terms of elongation is significantly diminished by reducing the overpotential. Note a small dip

Figure 8
Short time - high temperature anneal response for 15µm plateau processed within optimum window



in elongation between 296K and 435K, apparently anneal induced embrittlement (loss of elongation), for the high overpotential sample. Figure 8 shows the high temperature/short time anneal response for the high overpotential sample. The peak stress appears to plateau around 200MPa and total elongation as high as 40 percent is achievable by judicious thermal exposure. For a required ductility level, an array of time/temperature combinations is possible as shown in Figure 9. The effect of test temperature on tensile properties, for the high and low overpotential plateaus, is shown in Figure 10. There is no evidence of extensive thermal embrittlement common with electrodeposits (Merchant, 1993). The normal metal behavior, increasing test temperature reduces strength and increases elongation, is observed: except that decreasing overpotential has a tendency to eliminate the test temperature effect on elongation.

3.3 Fatigue

The effects of anneal exposure at 453K, 60min. (coverlayer thermal lamination simulation, see Figure 12) and of copper attached to polyimide (Cu/PI) on strain control flex fatigue over a wide range of strain amplitudes ($\Delta\epsilon/2$) is shown in Figure 11 in the Coffin-Manson (C/M) format. The break in curve corresponds to transition from plastic (low cycle fatigue) to elastic (high cycle fatigue) response, the transition occurring for fatigue life (N_f) between 10^3 and 10^4 cycles. The effect of annealing (Figure 11a) is to enhance N_f , especially in the low cycle regime: the effect of attaching copper to polyimide substrate (Figure 11b) is to lower N_f in the low cycle regime but to enhance it dramatically in the high cycle regime. For the latter case, the effective strain accommodation due to good adhesion (no delamination) between polyimide and copper substantially reduces the C/M slope.

Figure 9
Anneal temperature and time for 20, 30 and 40 percent post-anneal elongation for 15µm plateau processed within optimum window

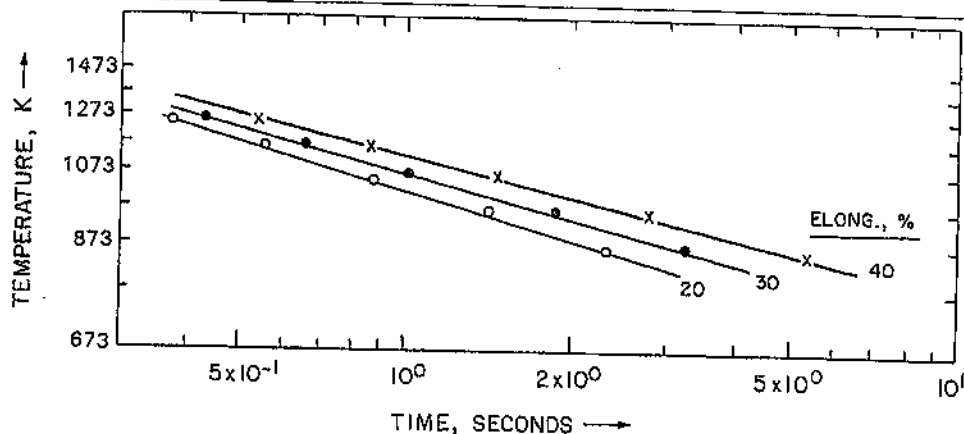


Figure 10
Effect of test temperature on tensile properties for 15 μ m plateup deposited within optimum processing windows

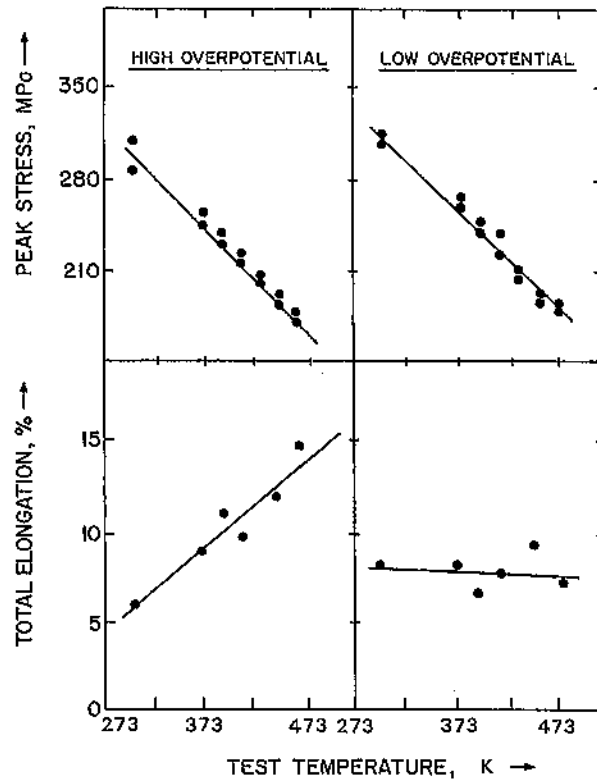


Figure 11
Strain-control flex fatigue Coffin-Manson plots for optimum processed 15 μ m plateup – effects of (a) annealing and (b) lamination

