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# *Tensile properties of acid copper electrodeposits*

DENNIS ANDERSON, RON HAAK, CAMERON OGDEN*, DENNIS TENCH, JOHN WHITE

*Rockwell International Science Center, 1049 Camino Dos Rios, Thousand Oaks, CA 91360, USA*

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For proprietary acid copper sulphate electroplating baths representing two major categories identified previously, deposit tensile properties are presented as functions of the bath additive and chloride concentrations. The effects of species that accumulate in the bath during circuit board plating and of variations in current density and the concentrations of copper sulphate and sulphuric acid are also discussed.

## 1. Introduction

Acid copper sulphate baths used in the manufacture of printed circuit boards generally employ proprietary additives to provide uniform deposits which have sufficient ductility and tensile strength to withstand thermally-generated stresses. Although several additive systems are commercially available, most of them are based on some combination of a polymer surfactant of a high molecular weight (e.g. polyethylene glycol) which apparently inhibits copper deposition by forming an adsorbed film on the cathode that mediates transport of species from the solution [1], and a sulphur-containing and/or nitrogen-containing organic species (e.g. disulphide or organic sulphonate), which induces levelling.

In an earlier paper [2], the tensile properties of deposits from eight commercial acid copper systems were measured as a function of bath agitation level. Control of the latter was attained by performing the deposition on a cylindrical cathode rotating at a constant velocity for which the rate of electrolyte mass transport is uniform and well defined [3]. Based on the results of these studies, baths could be placed in one of two categories depending on whether the tensile properties were found to be strongly (category A) or weakly (category B) dependent on the bath agitation level. In the case of category A baths, a maximum in elongation was observed. Interfacial depletion of the polymer surfactant additive component, which from patent literature is apparently employed at much smaller concentrations in category A baths, could partially account for the greater sensitivity of the tensile properties of the deposit to bath agitation in this case.

In the present work the plating parameters affecting the tensile properties of deposits from two commercial acid copper baths, one from each category, were evaluated in more detail. The rotating cylinder (RC) tensile test method was employed to ensure reproducible conditions at the cathode surface.

## 2. Experimental details

Baths chosen for study from categories A and B [2] were designated as bath A (Sel–Rex CUBATH® M) and bath B (Lea Ronal Copper Gleam® PCM) respectively and, unless otherwise noted, contained 68 (A) or 75 (B) $g\,l^{-1}$ $CuSO_4.5H_2O$, 9.2 (A) or 10.0 (B) vol % concentrated $H_2SO_4$, 50 (A) or 75 (B) $mg\,l^{-1}$ chloride, and $5.0\,ml\,l^{-1}$ additive, according to the manufacturer's recommendation. Solutions were prepared from reagent grade chemicals and ASTM class I deionized water (Barnsted Nanopure). Baths (1.5 litre) were operated at room temperature (22° C) and were used to plate only one specimen before being discarded. The copper foil anode was isolated in a separate compartment via ten porous Vycor frits (7 mm diameter),

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* *Present address*: Photocircuits, 31 Sea Cliff Avenue, Glen Cove, NY 11542, USA.

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symmetrically placed around the cathode compartment (2-litre Pyrex beaker) so as to provide a uniform current distribution.

Production bath specimens were obtained from circuit board manufacturers and were dummy plated before use to remove any residual additive present. Baths having various levels of accumulated species were prepared by diluting production baths with fresh baths having the same background composition. Note that 'accumulated species' is used as a general term to include both contaminants and possible excesses of additive component species resulting from a mismatch between consumption rates and the relative concentrations of the different components in the proprietary additive solution. Investigations into the effect of accumulated species involved four accumulation levels (0, 5, 20 and 50%) and five additive concentrations (0, 0.5, 1, 2 and 5 ml l$^{-1}$) for bath A, and three accumulation levels (0, 50 and 100%) and four additive concentrations (0, 2, 4 and 6 ml l$^{-1}$) for bath B. Undiluted bath B production specimens were not investigated since the accumulation level was atypically high because of a production power supply problem which was causing excessive additive consumption rates. It is not known to what extent this problem affected the nature of the accumulated species generated.

The rotating cylinder (RC) tensile test method has been described previously [3]. Specimens were plated at 30 mA cm$^{-2}$ to a final thickness of 50 $\mu$m on an Inconel 600 mandrel (2.54 cm in diameter, 1.27 cm wide) rotating at 750 r.p.m. This rotation rate was chosen to provide the rate of mass transport typically obtained within circuit board through-holes by vigorous air sparging [4]. After plating, samples were annealed in air at 120° C for 2 h, then pulled to failure under ambient conditions at 0.5 mm min$^{-1}$ in the as-plated configuration. The gauge length was 3.0 cm.

## 3. Experimental results

### 3.1. *Bath A data*

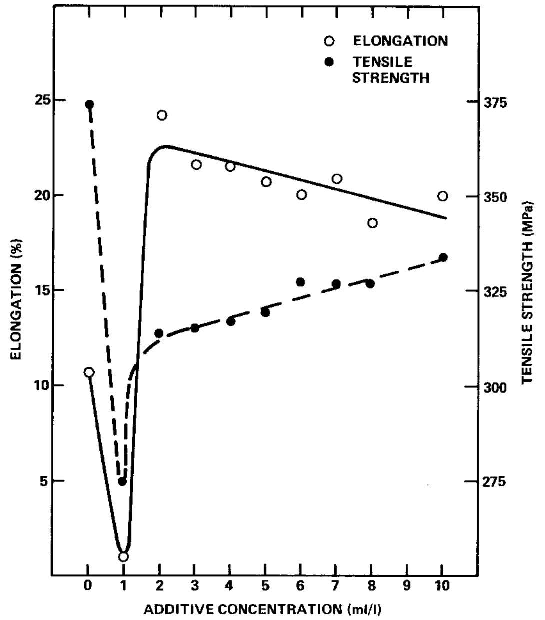

Fig. 1. Effect of the additive concentration on the tensile properties of deposits from bath A.

Fig. 1 shows plots of the tensile properties of deposits from bath A as a function of the bath additive concentration. Both the elongation and tensile strength are relatively insensitive to the additive concentration above 2 ml l$^{-1}$ but at 1 ml l$^{-1}$ minima of 1% and 250 MPa, corresponding to very poor deposit mechanical properties, are evident. At higher additive concentrations the elongation decreases and the tensile strength increases linearly.

The effects of variations in the plating current density and in the bath concentrations of copper, sulphuric acid and chloride on the tensile properties of bath A deposits may be summarized as follows. Variations in the copper and sulphuric acid concentrations of ±10% were found to exert negligible effects. As shown in Fig. 2, chloride initially enhances both the elongation and tensile strength, but concentration increases above 10 mg l$^{-1}$ have little effect on either property. Fig. 3 shows that the deposit elongation decreases sharply at current densities in the 50 mA cm$^{-2}$ range, whereas the tensile strength decreases monotonically over the current density range studied.

Investigations into the effect of species that accumulate in circuit board production baths involved variations in both the level of accumulated species and the additive concentration; data for bath A are summarized in topographs

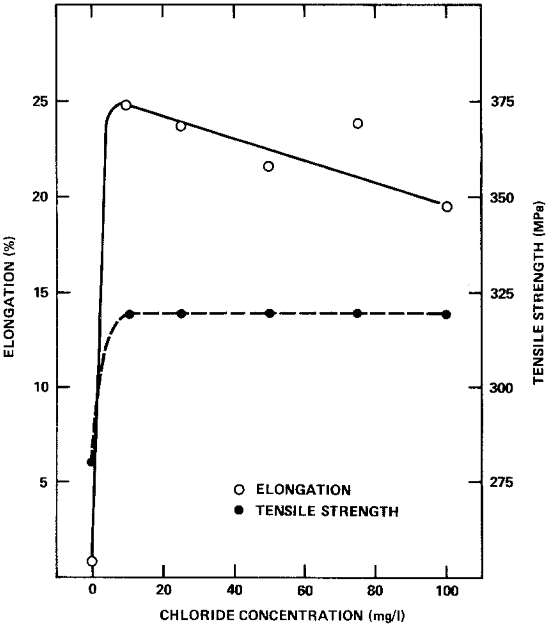

Fig. 2. Effect of bath chloride level on the tensile properties of deposits from bath A.

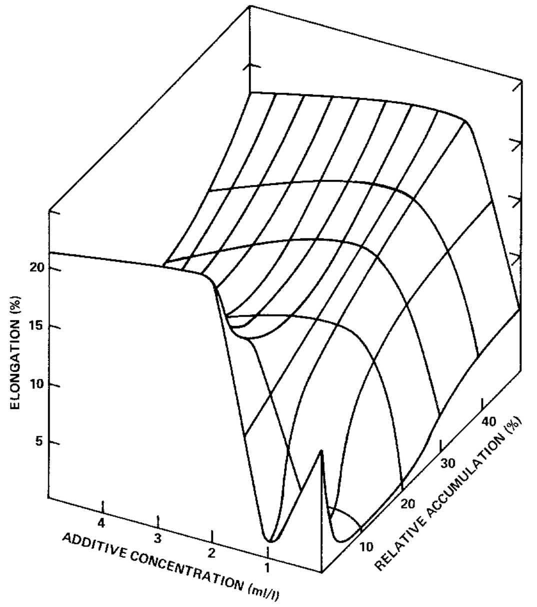

Fig. 4. Topograph of deposit elongation vs additive concentration and the relative level of accumulated species in production specimens of bath A.

(Figs 4 and 5). It is evident that, although low levels of accumulated species ($< 20\%$ accumulation) are somewhat detrimental, the tensile property values for higher accumulation levels approach or exceed those obtained for fresh baths. Essentially the major effect of accumulated species in well-aged production baths is to render the elongation less sensitive to the additive at low concentrations (in the $1\,\mathrm{ml\,l^{-1}}$ range).

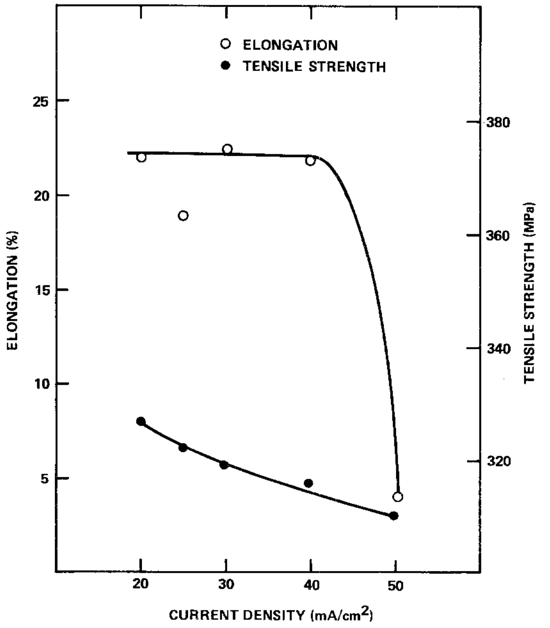

Fig. 3. Effect of plating current density on the tensile properties of deposits from bath A.

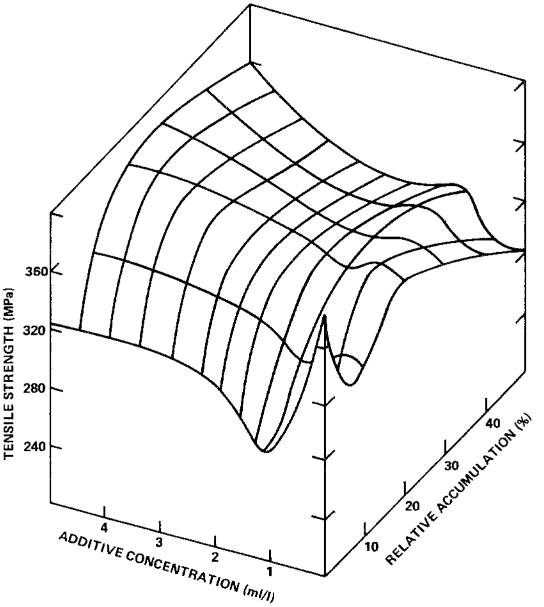

Fig. 5. Topograph of deposit tensile strength vs additive concentration and relative level of accumulated species in production specimens of bath A.

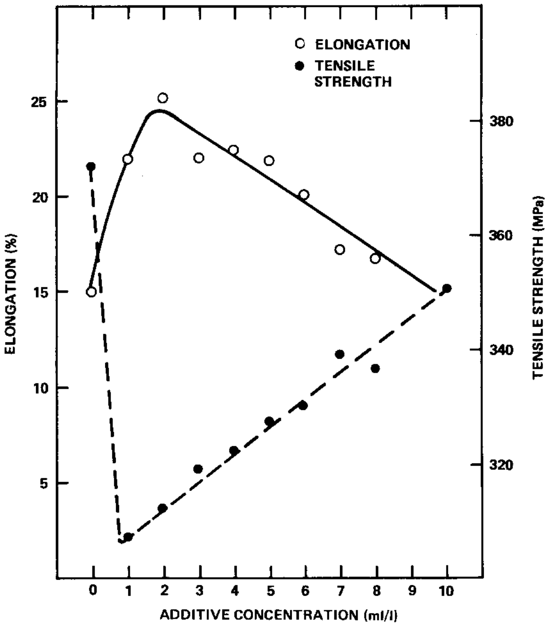

Fig. 6. Effect of additive concentration on the tensile properties of deposits from bath B.

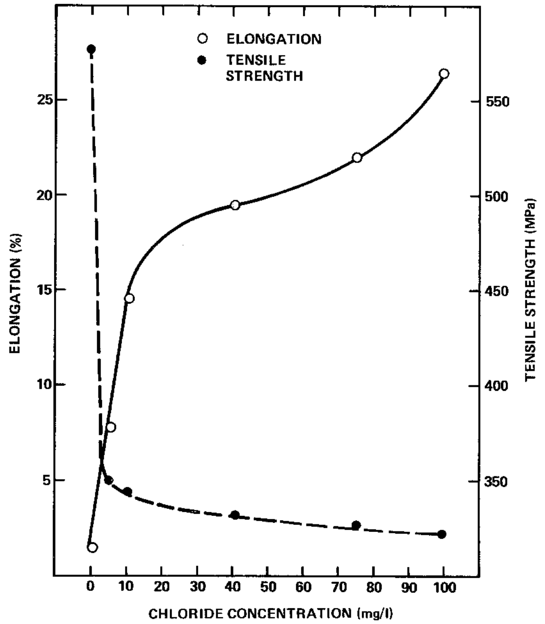

Fig. 7. Effect of bath chloride level on the tensile properties of deposits from bath B.

### 3.2. *Bath B data*

Fig. 6 shows plots of the tensile properties of deposits from bath B as a function of the bath additive concentration. The deposit elongation is seen to increase sharply with increasing additive concentration to a peak of ~25% at 2 ml l$^{-1}$ and then to decrease linearly, remaining reasonably high (> 15%), over the concentration range studied. On the other hand, the deposit tensile strength decreases sharply to a minimum of ~310 MPa at 1 ml l$^{-1}$ and then increases linearly to relatively high values. Fig. 7 shows that chloride dramatically enhances the deposit elongation and decreases the tensile strength up to about 20 mg l$^{-1}$, but produces much more gradual changes at higher concentrations. Fig. 8 shows that the tensile properties of bath B vary relatively gradually with current density. The sulphuric acid and copper concentrations were varied independently by ±10%; no effect was observed for the tensile strength, but such concentration increases decreased the elongation value by about 30% (from 22% to 15%) in each case.

Data for bath B production samples are summarized in Figs 9 and 10. Note that the relative accumulation scale in this case is reversed compared to that used for bath A. Accumulated bath species are seen to lower the absolute elongation values and introduce a shallow minimum in the 4–5 ml l$^{-1}$ additive concentration range. It is

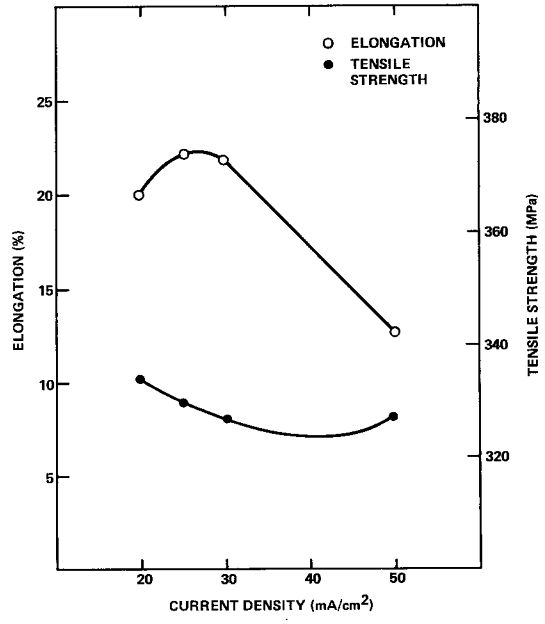

Fig. 8. Effect of plating current density on the tensile properties of deposits from bath B.

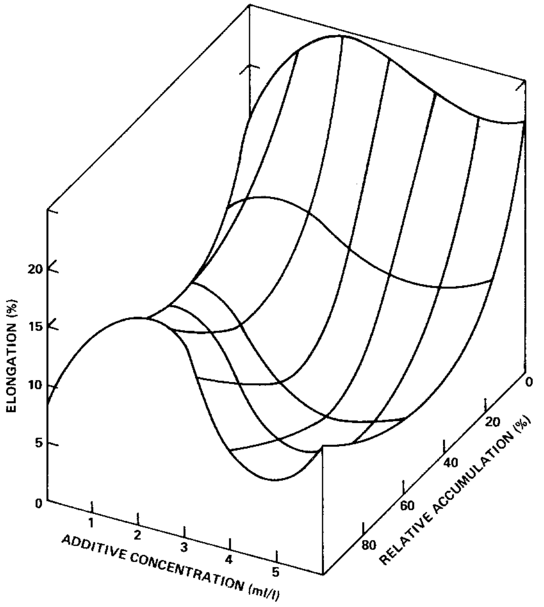

Fig. 9. Topograph of deposit elongation vs additive concentration and the relative level of accumulated species in production specimens of bath B.

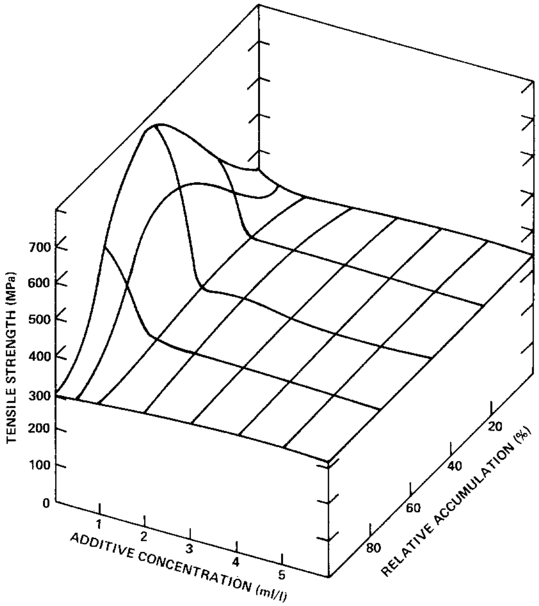

Fig. 10. Topograph of deposit tensile strength vs additive concentration and the relative level of accumulated species in production specimens of bath B.

evident that moderately high elongation values ($>10\%$) are obtained over a relatively wide additive concentration range (spanning $>4\,\mathrm{ml\,l^{-1}}$) in both fresh and well-aged baths (100% accumulation), but that the overall elongation values are significantly lower ($<10\%$) over most of the additive concentration range in baths with intermediate levels of accumulated species. This minimum in elongation with bath ageing could correspond to a mismatch in the relative concentrations of the additive components resulting from differences in their consumption rates. If this is the case, more consistent deposit tensile properties could be attained by properly matching the concentrations of the individual components in the proprietary additive solution with their respective consumption rates. From Fig. 10, it is evident that intermediate levels of the accumulated bath species greatly enhance the deposit tensile strength for low additive concentrations ($<1\,\mathrm{ml\,l^{-1}}$). The accumulated species generally have very little effect on the tensile strength at higher levels.

## 4. Discussion and summary

The tensile properties of deposits from bath A were found to go through pronounced minima at an additive concentration of $\sim 1\,\mathrm{ml\,l^{-1}}$ but this effect was not apparent for bath B. Since the patent literature, as well as voltametric studies [5] performed in our laboratory, indicates that additive A contains substantially less of the polymeric surfactant component than additive B, it is likely that these minima result from the surfactant concentration being inadequate to form the complete cathode film necessary to suppress copper deposition. In this case, excessively fast local deposition through holes in the cathode film would result in defects in the deposit and poor mechanical properties. Note that if this explanation is correct the deposit tensile properties for bath B would also exhibit such minima, but they would occur at a lower overall additive concentration (not investigated in this work) since additive B contains more of the polymeric surfactant component.

Species that accumulate with use in circuit board production baths generally lower the elongation of deposits from bath B, but at higher accumulation levels and lower additive concentrations tend to enhance the elongation of deposits from bath A. This is consistent with the model presented above since the surfactant species might be expected to be consumed relatively slowly (compared to the levelling/brightening components) and thus build up in the bath with use and be incompletely removed by dummying. Residual amounts of the surfactant would then enhance the effectiveness of that present in the proprietary additive solution, increasing the elongation at low additive concentrations. The detrimental effects of accumulated species in bath B may result from the larger concentration of polymeric surfactant additive species; decomposition products, presumably smaller polymeric chain fragments, might be expected to be included in the deposit, inducing brittleness.

A minimal amount of chloride is apparently essential to the ductility of deposits from both types of acid copper baths: the elongation in each case was found to rise dramatically for chloride additions in the 10 $\mathrm{mg\,l^{-1}}$ range. This effect can to some extent be attributed to improved nucleation associated with copper discharge from $CuCl^+$, which has recently been established as an intermediate in copper deposition from acid systems by the rotating ring–disc electrode technique [6]. However, our data also show that chloride enhances the deposit tensile strength for bath A while decreasing it for bath B, indicating that interactions between chloride and additive species are also involved. Note that chloride has been reported to interact with certain classes of polymers at electrode surfaces, affecting the formation of polymeric films [7].

Other parameters investigated were found to exert less dramatic effects on the deposit tensile properties. Reductions in the bath copper and sulphuric acid concentrations by 10% had no effect in either case, whereas equivalent increases significantly reduced the deposit elongation for bath B but not for bath A. On the other hand, current density effects were found to be stronger for bath A, with a sharper decrease in elongation occurring in the 50 $\mathrm{mA\,cm^{-2}}$ range. The latter may reflect breakdown of the inhibiting cathode film which may be prevented for bath B by the higher concentration of polymeric surfactant.

In general, although there are some specific differences, the deposit tensile properties provided by bath A and bath B are comparable. For freshly-prepared baths typical values obtained under a relatively wide range of conditions are 15–20% elongation and ~325 MPa tensile strength (maximum values, 25% and 375 MPa respectively). For aged production baths containing accumulated species this picture does not change dramatically although the overall deposit elongation values for bath B are lower. Note that bath B specimens containing an intermediate level of accumulation without added additive yielded a deposit tensile strength of ~750 MPa (Fig. 10), but this cannot be considered a usable value since the elongation in this case was < 5% (Fig. 9).

It is important to keep in mind that adequate control over electrolyte mass transport and bath composition is not always exercised during electrodeposition of test specimens and, in any case, tensile test results vary appreciably with sample configuration and pull test conditions so that absolute data comparisons for different systems or from laboratory to laboratory are often not possible. Fortunately data obtained for specimens plated (using the rotating cylinder method) and pull tested under conditions identical to those employed here are available for the copper pyrophosphate/dimercaptothiadiazole system.

For this pyrophosphate bath the deposit tensile strength is typically higher, ranging from 300 to almost 700 MPa depending on the additive concentration. Elongation values of 15–20% and tensile strengths in the 400 MPa range can be consistently attained by operating copper pyrophosphate baths at a low additive concentration. (Note that these results have been verified for operating circuit board production baths.) Even higher tensile strengths of about 650 MPa are obtained at a higher additive concentration range (for which additive control is less critical) but the elongation values in this case are only 6–8%.

These data indicate that the deposit ductilities obtained for pyrophosphate and acid copper baths are comparable but high ductility is provided by the latter over a much wider range of conditions. Thus when ductility is the only major tensile properties consideration, acid copper offers some advantage. However, the tensile strength provided by acid copper baths is always very low compared to that attainable with the pyrophosphate system, making the latter preferable for applications requiring high-reliability circuit boards for which copper deposits must not only be sufficiently ductile to avoid cracking under the thermal shock of soldering but must be sufficiently strong to resist flexing during thermal cycling that can lead to fatigue cracking [9].

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