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Tensile properties and morphology of pyrophosphate copper deposits

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New data which precisely define the effects of various operating parameters on the tensile properties of electrodeposits from the dimercaptothiadiazole/copper pyrophosphate system are presented. Two additive concentration ranges yielding high ductility and high tensile strength are delineated. Characteristic deposit microstructures are identified and correlated with the tensile properties. The results are interpreted in terms of the mechanism by which the additive functions, and implications for circuit board plating are discussed.

1. Introduction

For many applications, the tensile properties of copper deposits are extremely important. For example, through-hole deposits in high-reliability circuit boards must be relatively ductile to prevent cracking problems resulting from stress produced by excess thermal expansion of the board laminant material (compared to copper) during soldering operations (thermal shock), and must be sufficiently strong to resist flexing that can cause fatigue cracking during thermal cycling [1]. Copper pyrophosphate baths employing dimercaptothiadiazole (DMTD) additives are widely used for such applications but do not always yield acceptable results since the factors affecting the deposit tensile properties are not well understood. The tensile properties of electrodeposits are also of considerable interest from a fundamental standpoint since, in conjuction with the deposit morphology, they provide additional insight into the mechanism and kinetics of electrodeposition.

In previous studies performed in this laboratory [2], the elongation of pyrophosphate copper deposits was shown to depend strongly on the concentration of DMTD bath additive. This work involves a novel rotating cylinder tensile test method which has subsequently been refined and shown to yield even more precise data [3]. Recent mechanistic studies [4] suggest that the relatively complicated behaviour of copper pyrophosphate baths is a consequence of the complex DMTD additive system, which involves a balance between species that accelerate the copper electrodeposition rate (monomeric DMTD and copper ammine complexes) and the decelerating species (dimeric DMTD).

In the present paper, rotating cylinder data are presented which accurately define the effects of bath additive concentration, ammonia level, pH and current density on the tensile properties of pyrophosphate copper deposits. The effects of bath agitation and specimen heat treatment are also discussed. Based on deposit morphological data, the tensile test results are explained in terms of the relative effects of the accelerating/decelerating additive species. The implications for circuit board through-hole plating are also considered.

2. Experimental procedure

The apparatus and procedure used in this work were the same as previously described [3]. Unless otherwise noted, all plating was performed on a 304 stainless steel cylindrical mandrel (2.54 cm diameter × 1.3 cm width) at 38 mA cm^{-2} from air-saturated copper pyrophosphate baths (55° C) containing 22.5 g dm^{-3} Cu^{2+}, 175 g dm^{-3} $P_2O_7^{4-}$, 2.25 g dm^{-3} NH_3 (~ 8 ml dm^{-3} NH_4OH) and up to

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4 $cm^3 dm^{-3}$ of organic additive* whose active ingredient is a dimercaptothiadiazole. During deposition, the cathode was rotated at 750 rpm, which has been shown to correspond to the average agitation level typically attained within circuit board through-holes [5]. Baths were normally operated at pH 8.3 and were prepared from concentrates.† Anodes were machined from OFHC copper. The temperature was maintained constant within ± 1° C via water circulated through a jacket on a 1500 cm^3 cell. Baths were first pre-electrolysed [3], then heated for 16 h at the operating temperature to activate the additive [6].

Unless otherwise noted, plated specimens were heat treated in air at 120° C for 2 h. Tensile testing‡ was performed at a cross-head speed of 0.50 mm min^{-1} on specimens in the strip configuration [3]. The gage length and width were 3.00 and 1.3 cm, respectively. The elongation values reported are actual plastic elongation; values determined using the standard 0.2% offset technique [7] were as much as 1% higher. The deposit morphology was investigated by scanning electron microscopy performed on annealed deposit cross-sections which were mounted in acrylic resin, polished, and etched in fresh $NH_4OH/(NH_4)_2S_2O_8$ solution.

3. Results and discussion

3.1. *Additive effects*

Figure 1 shows the effect of additive concentration on the deposit elongation for as-plated pyrophosphate copper deposits and those annealed for 2 h at 120° C prior to testing. It is evident that annealing greatly enhances the elongation at both low and high additive concentrations. The corresponding plot for the deposit tensile strength is given in Fig. 2. Annealing is seen to significantly lower the tensile strength at lower additive concentrations. Since electrodeposits are usually annealed (either by design or inadvertently) in production processes, only annealed specimens are considered in the following discussion. The heat treatment used here is particularly appropriate since it simulates that to which circuit boards are normally subjected in fabrication steps subsequent to plating.

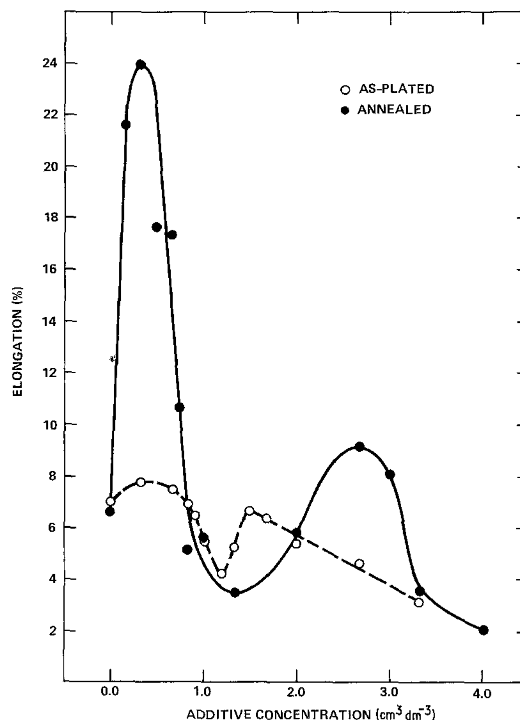

Fig. 1. Effect of additive concentration (batch A) on the elongation of as-plated and annealed pyrophosphate copper deposits.

Our previous mechanistic studies [4] provide the basis for understanding the variation in the deposit tensile properties with DMTD additive concentration. It was shown that this additive system involves an equilibrium between monomeric DMTD species that accelerate the copper deposition rate and dimeric DMTD species that produce a decelerating effect. The DMTD monomer, which can complex two Cu^{2+} ions at adjacent mercapto sites, apparently produces acceleration by facilitating Cu^{2+} discharge and, thus, nucleation of new growth centres. Deceleration is presumably associated with blockage of growth sites by the dimeric DMTD species.

Figure 3 shows the elongation, tensile strength and morphology of pyrophosphate copper deposits as a function of the additive concentration. In the absence of organic additive, deposition occurs preferentially in the direction perpendicular to the substrate, resulting in a columnar or needle-like microstructure (Fig. 3a). The moderate values for

* PY61-H, M&T Chemicals, Rahway, NJ.
† C10B and C11B, M&T Chemicals, Rahway, NJ.
‡ Model 1122, Universal Testing Instrument, Instron Corp., Canton, MA.

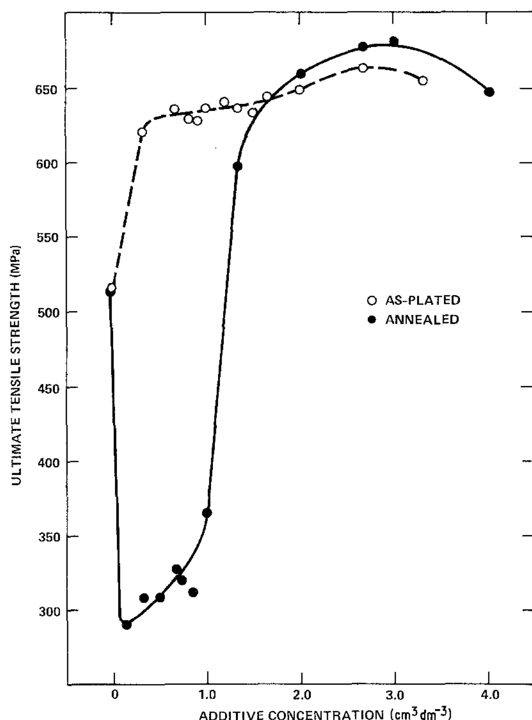

Fig. 2. Effect of additive concentration (batch A) on the tensile strength of as-plated and annealed pyrophosphate copper deposits.

the tensile strength and elongation in this case are not surprising when the pull direction (perpendicular to the columns/needles) is considered.

As additive is introduced into the bath, the columnar structure is lost and a chevron microstructure emerges (Fig. 3b and c). Other investigators [8, 9] have observed such chevron patterns (for acid copper deposits) and attributed them to preferred growth of extended pyramidal structures caused by dislocations [8] and the presence of depolarizing divalent sulphur species [9]. The latter is presumably analogous to the accelerating DMTD additive species in the copper pyrophosphate system. The extended pyramids are reported [8, 9] to grow in layers, with their bases oriented along ⟨1 0 0⟩ crystal planes. The change in growth habit, from oriented columns to more randomly-oriented extended pyramids, produced by accelerating additive species is associated with a sharp increase in the deposit elongation and a decrease in the tensile strength (Fig. 3).

At higher overall additive concentrations (0.3 to 1.0 $cm^3 dm^{-3}$), the elongation decreases sharply (producing a peak), the tensile strength begins to increase and nodules appear in the deposits (Figs. 3d–f). The nodules are more evident for deposits plated at additive concentrations just below those corresponding to the elongation minimum (Fig. 3f) and are apparently associated with very rapid deposition, produced by the increased concentration of accelerating additive species, at the available growth sites. Poor internodular cohesion would account for the low tensile strength/ elongation.

Above additive concentrations of 1.0 $cm^3 dm^{-3}$, deposits become finer-grained with fewer nodules (Fig. 3g–j), and the elongation and tensile strength increase, presumably because nodule growth is suppressed by the dimer additive species which is formed in higher concentrations. The decrease in both tensile properties at high additive levels presumably results from inclusion of excess organic material in the deposit.

Significant variations in the effective concentration of the proprietary additive from batch to batch, which were previously detected by cyclic voltammetric stripping analysis [6], are also reflected in the tensile test data. This is illustrated by the plots given in Fig. 4 of deposit elongation and tensile strength versus concentration of additive from a different batch. Although the qualitative features of the curves in Figs. 3 and 4 are the same, there are some quantitative differences. In particular, the elongation peak at higher concentrations occurs at 2.7 $cm^3 dm^{-3}$ additive in one case (Fig. 3) and 1.3 $cm^3 dm^{-3}$ in the other (Fig. 4). Since the dimer additive species predominates in this concentration range [4], the peak shift is apparently due to a difference in the concentration of active dimer produced during activation of the additive. This was demonstrated to be the case by cyclic voltammetric stripping analysis [6] of the two additive batches, which showed that the concentration corresponding to the elongation peak for each batch produces an approximately equivalent decelerating effect on the copper deposition rate. Also, the same deposit morphology was observed for corresponding features in the curves in Figs. 3 and 4. To some extent, such differences in the effective additive concentration appear to be associated with aging of the additive concentrate during storage. The elongation peak at low additive levels occurs at about the same concentration (0.3 $cm^3 dm^{-3}$) in

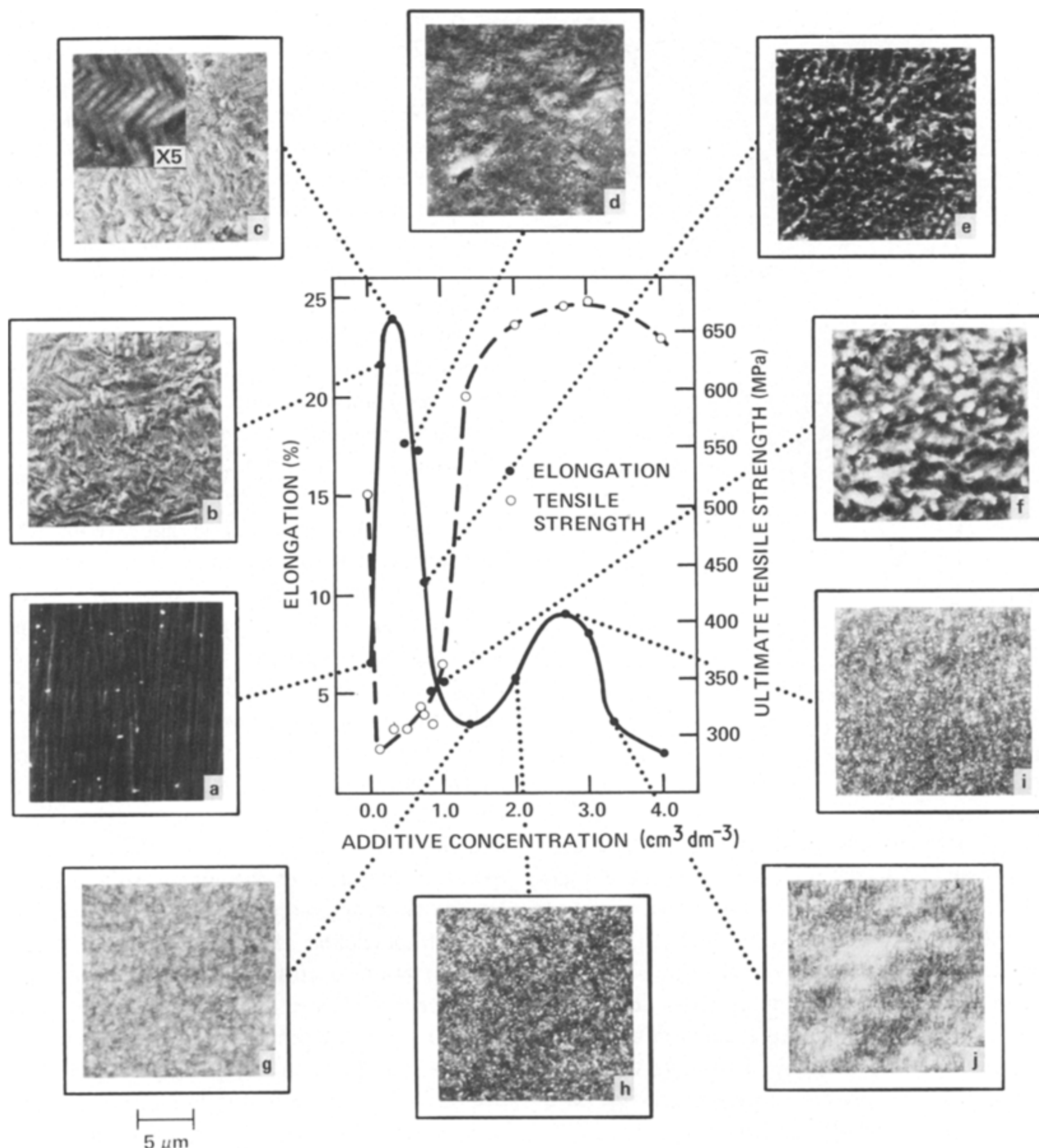

Fig. 3. Tensile properties and morphology of annealed pyrophosphate copper deposits versus bath additive concentration (batch A).

Figs. 3 and 4, as might be expected since the predominant species in this case is the monomer, which is in relatively high concentration [4] so that the effects of small concentration changes are not significant.

Three different batches of proprietary additive, designated A, B and C, were used in the present study. Based on cyclic voltammetric stripping analysis [6], the effective concentrations of batches B and C were, respectively, almost twice and three times that of batch A. Data reported in Figs. 1 to 3 were obtained with batch A; those in Figs. 4 to 7 with batch B; and those in Fig. 8 with batch C. Direct comparisons are only valid for data obtained using the same additive batch. As discussed above, cyclic voltammetric stripping analysis provides the basis for comparing data for different batches.

It should be mentioned that, when the differences in plating conditions and procedures are taken into account, the results presented here are in agreement with those reported previously [2]. In this earlier work, baths were not pre-electrolyzed and a large copper foil anode was employed,

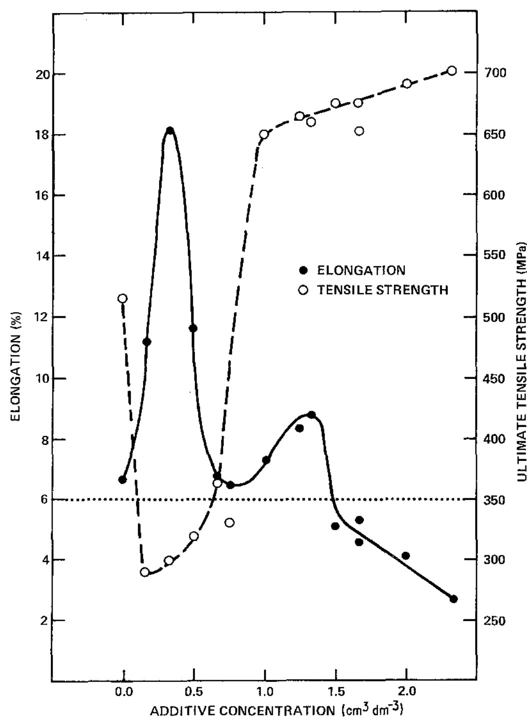

Fig. 4. Elongation and tensile strength for annealed pyrophosphate copper deposits versus concentration of additive from a different batch (batch B).

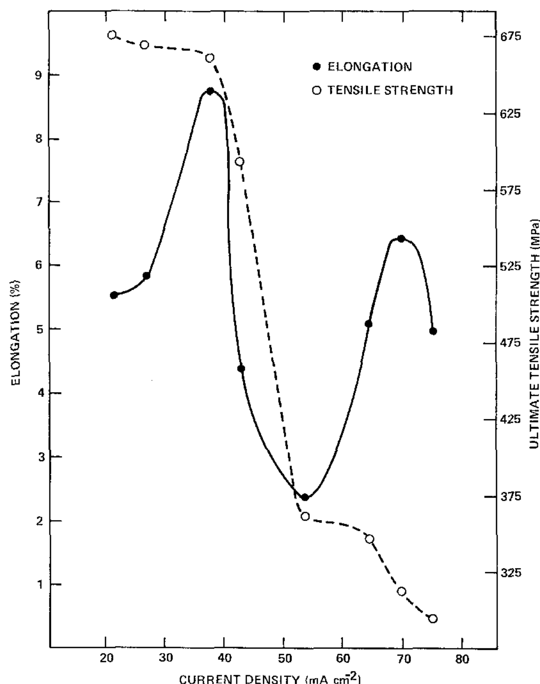

Fig. 5. Effect of current density on the elongation and tensile strength of annealed deposits from copper pyrophosphate baths containing 1.3 $cm^3 dm^{-3}$ additive (batch B).

instead of the special anode assembly used in the present studies, so that the results were considerably less reproducible. The cathode was also rotated at a significantly faster rate (2500 rpm) so that the additive concentration scale was compressed, i.e., the effects of changes in the additive concentration were less easily discerned. Consequently, the sharp peak in the deposit elongation in the lower concentration range (Figs. 3 and 4) was not resolved. The elongation value for the peak observed in the higher concentration range agrees (within experimental error) with the value given here (~ 9%), if the correction factor of 1.4 [3] appropriate for the band-shaped specimens used is applied.

3.2. *Practical implications*

These results have profound implications for electroplating operations employing copper pyrophosphate baths, particularly the circuit board through-hole plating process. Recent calculations indicate that the minimum tensile property values required to avoid cracking problems in circuit boards are 6% elongation and 350 MPa tensile strength [1]. Although these limits cannot be considered absolute, they provide reasonable guidelines against which the performance of plating baths can be evaluated for circuit board applications. It is evident from Figs. 3 and 4 that the minimal tensile properties required for high-reliability circuit board applications (represented by the dotted line in Fig. 4) are attained in only two relatively narrow additive concentration ranges. In the low range (< 0.1 $cm^3 dm^{-3}$), deposit elongation is more than adequate, but the additive concentration must be controlled very precisely (within $\pm$ 0.1 $cm^3 dm^{-3}$) to attain acceptable tensile strength. At such low concentrations, the additive also provides no levelling, since the accelerating additive species predominates [4] and a decrease in concentration lowers the deposition rate, the opposite of the desired effect [2]. In fact, the additive in this concentration range induces negative levelling, which leads to the irregular deposition within circuit board through-holes known as 'foldback' or 'foldover' if the additive level is slightly higher or other conditions change

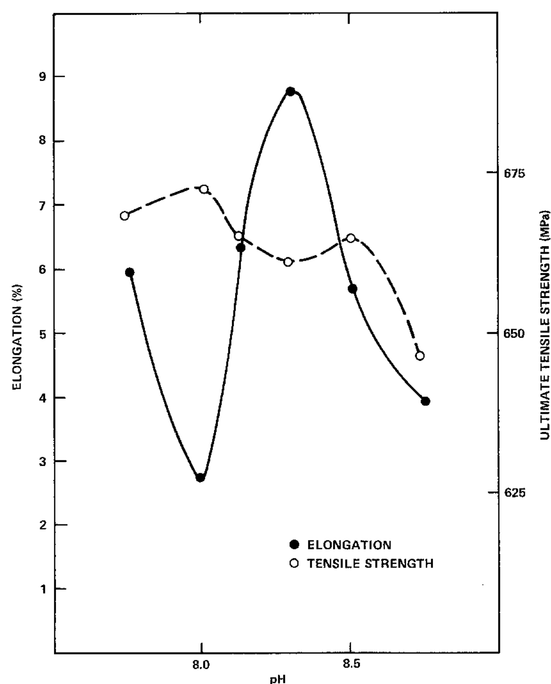

Fig. 6. Effect of pH on the tensile properties of annealed deposits obtained from copper pyrophosphate baths containing 1.3 $cm^3 dm^{-3}$ additive (batch B).

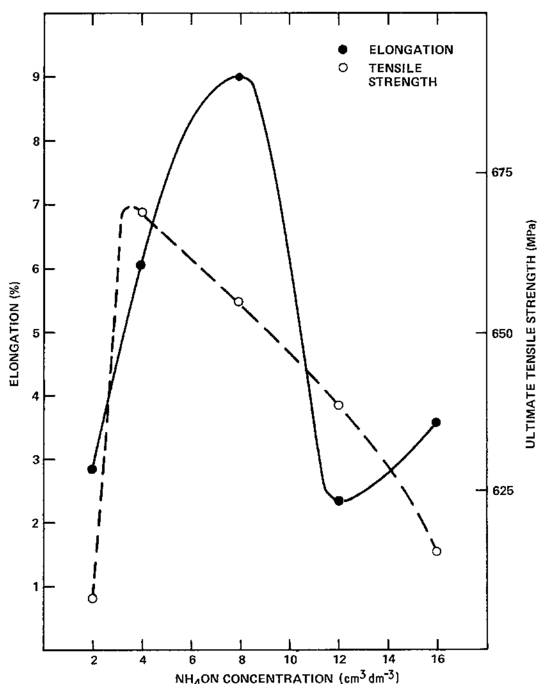

Fig. 7. Effect of ammonia concentration on the tensile properties of annealed deposits obtained from copper pyrophosphate baths containing 1.3 $cm^3 dm^{-3}$ additive (batch B).

so that an appreciable concentration gradient can be produced at the cathode surface [10]. Although the elongation is lower at the higher additive concentrations, acceptable values are attained over a much wider concentration range and the tensile strength is consistently high. Good bath levelling characteristics are also expected in the higher additive concentration range since the decelerating additive species predominates and an increase in its concentration decreases the copper deposition rate. Application of the cyclic voltammetric stripping method [6] to the analysis of production copper pyrophyosphate baths in various facilities has revealed that circuit boards can be plated successfully in either the low or high additive concentration ranges, although at the higher additive concentration a higher ammonia level is also apparently necessary [11]. In the low concentration range, the additive apparently functions primarily as a grain refiner.

3.3. *Current density/mass transport effects*

The effect of current density and electrolyte mass transport (bath agitation) on the deposit's mechanical properties can readily be understood in terms of the changes produced in the additive concentration at the cathode surface. Figure 5 shows plots of deposit elongation and tensile strength versus current density for baths having an additive concentration (batch B) of 1.3 $cm^3 dm^{-3}$. Since this additive level corresponds to a peak in the elongation (Fig. 4), decreasing the current density (below 38 mA cm^{-2}), which lowers the additive consumption rate and, thereby, effectively increasing the concentration of additive at the electrode surface, lowers the elongation (Fig. 5). Likewise, increasing the current density (above 38 mA cm^{-2}) lowers the surface additive concentration, and the elongation decreases. At sufficiently high current densities, the elongation goes through a second peak (at 70 mA cm^{-2}) which corresponds to the low concentration peak in Fig. 4. Strong support for this interpretation is provided by morphological data. For example, a chevron structure is clearly evident for deposits plated at 70 mA cm^{-2}, as expected by reference to Fig. 3. Note that an exact correspondence in peak positions (calculated from hydrodynamics by considering only additive effects) and peak

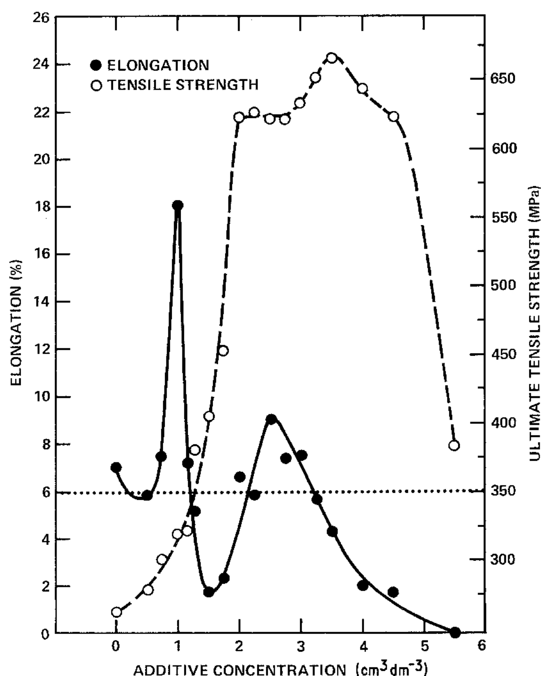

Fig. 8. Tensile properties of annealed pyrophosphate copper deposits versus additive concentration (batch C) in baths with twice the normal ammonia level.

heights between Figs. 4 and 5 is not expected since other solution species, whose surface concentrations also vary with current density, also affect the deposit elongation. Similar arguments apply to the tensile strength plot (Fig. 5), which is practically the mirror image of the corresponding plot in Fig. 4.

Bath agitation also affects the tensile properties primarily via changes in the surface concentration of the additive. This is demonstrated by the fact that the major features of the tensile test data in Figs. 3 and 4 are reproduced when the additive level is held constant and the rotation rate is varied. The surface additive concentration increases with $\omega^{0.7}$ (where ω is the cylinder rotation rate) [12].

3.4. *Other effects*

Other operating parameters which affect the tensile properties of copper pyrophosphate deposits do so primarily by influencing the additive equilibria or the balance between the effects of the various additive species. For example, as shown in Fig. 6 for baths containing 1.3 $cm^3 dm^{-3}$ additive, the deposit elongation is significantly reduced when the pH is either above or below normal (pH 8.3), apparently because of shifts in the equilibria for the various monomer and dimer additive species due to protonation/deprotonation reactions [13, 14]. The bath ammonia level also strongly affects the deposit tensile properties, as seen in Fig. 7, but in this case copper ammine complexes are formed which accelerate the deposition rate via nucleation of new growth sites, disturbing the balance between accelerating and decelerating additive species [4]. The magnitude of this effect therefore depends on the overall additive concentration. Copper ions are directly involved in the additive equilibria, but changes in the bath copper concentration have a relatively small effect on the deposit tensile properties since the copper ions are highly complexed so that the concentration of free Cu^{2+} remains very small. For example, variations in the copper concentration from 20 to 25 $g dm^{-3}$ in baths containing 1.3 $cm^3 dm^{-3}$ additive cause the elongation to vary by only ± 11% and the tensile strength by about 1%. Of course, the time and temperature for activation of the additive will also strongly affect its effective concentration and consequently the deposit tensile properties.

3.5. *High-ammonia operation*

The results presented above show that the widest possible control window for attaining moderately high elongation and high tensile strength for pyrophosphate copper deposits occurs at higher DMTD additive concentrations. However, a high bath ammonia level, twice the normal concentration, is apparently required for operation of production baths in this additive concentration range [11]. Note that additive precipitation problems have been encountered [15] under some conditions when pilot line baths were operated at high additive concentrations with the normal bath ammonia level (8 $cm^3 dm^{-3}$ NH_4OH).

A plot of deposit elongation and ultimate tensile strength versus the additive concentration for a bath containing twice the normal level of ammonia (16 $cm^3 dm^{-3}$ NH_4OH) is shown in Fig. 8. As in the case of the regular-ammonia bath, a broad elongation peak occurs at higher additive concentrations (2.0–3.2 $cm^3 dm^{-3}$) for

which elongations are greater than 6%, and the ultimate tensile strength is greater than 350 MPa (indicated by the dotted line in Fig. 8). Since the effective concentration of additive batch C is much greater than that of either batch A or B, the increased ammonia concentration obviously shifts both elongation peaks to considerably higher additive concentrations, the first peak from 0.3 to 1.0 $cm^3 dm^{-3}$. These shifts are most probably due to the associated increase in the concentration of copper ammine complexes, from which copper is readily electrodeposited [16] to nucleate new growth centres [4]. Thus, at higher ammonia levels, higher concentrations of decelerating additive species are required to limit the growth of the increased average number of growth centres and avoid nodule formation. A concomitant shift of the tensile strength curve (Fig. 8) to higher additive concentrations is also observed for the higher bath ammonia concentration. Note, however, that the deposit tensile strength is low (310 MPa) in the high-ammonia bath without additive present.

4. Summary and conclusions

The results presented here define the effects of dimercaptothiadiazole additive concentration, current density, bath ammonia level and pH on the tensile properties and morphology of pyrophosphate copper deposits. For the standard bath without additive present, deposits are moderately strong and ductile, and have a columnar microstructure. Small concentrations of additive enhance nucleation, resulting in a chevron microstructure, high deposit ductility, and low tensile strength. At intermediate additive levels, unchecked growth of centres nucleated by the additive, reflected in a nodular deposit microstructure, result in decreased deposit ductility. At higher additive concentrations, nodule growth is suppressed (deposits are fine-grained) by a decelerating additive species, formed by dimerization, and both the ductility and tensile strength increase. At very high additive levels, the ductility again decreases, presumably because of inclusion of excessive additive in the deposit. Current density and electrolyte mass transport effects can be understood in terms of the changes produced in the additive concentration at the cathode surface. The bath ammonia level and pH apparently affect the tensile properties primarily by influencing the additive equilibria or the balance between the effects of the various additive species.

Pyrophosphate copper deposits with good tensile properties can be attained in two additive concentration ranges. Operation in the higher range, which apparently requires a high ammonia level, is more desirable since the additive control window is wider and problems associated with deposit uniformity are minimized in this case. In view of the various factors which affect the activity of dimercaptothiadiazole additives in the copper pyrophosphate system, absolute additive concentration loses much of its meaning and bath control requires the use of methods, such as cyclic voltammetric stripping, that provide a measure of the effective additive concentration.

Acknowledgement

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