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Improved Electroformed Structural Copper and Copper Alloys

G.A. Malone, W. Hudson, B. Babcock, and R. Edwards
Electroformed Nickel, Inc., Huntsville, Alabama

November 1998

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SUMMARY

Electroforming offers a superior means for fabricating internally cooled heat exchange devices and engineering structures since the metal or alloy and near net shape of the part are created at the same time. Nickel or nickel alloys are often deposited because of the excellent mechanical properties obtained. Copper is deposited for many applications because of its good thermal conductivity, but it suffers from moderate yield strength as a structural material and loses mechanical strength at moderate or intermediate temperatures. Thermal performance improvements have been made in wrought coppers by alloying with small amounts of silver, zirconium, beryllium, nickel or cobalt. Most of these alloys are still inferior to electroformed nickel from a mechanical property standpoint. A severe need exists for an electroformable copper, or low alloyed copper, capable of competing with nickel at temperatures to 200°C or higher as it would find widespread use in aerospace and commercial products subject to more severe thermal environments.

The purpose of this program is the development and demonstration of electroformable copper and copper alloys having superior mechanical properties to those encompassed in the prior state-of-the-art while retaining good thermal properties. Specific technical objectives sought and the success in achieving each goal are described below:

1 Efforts to develop a copper or copper alloy electrodeposit having competitive mechanical properties with electrodeposited nickel were successful. Although 689 MPa (100 ksi) tensile strengths were exceeded in limited samples, it was not possible to maintain such strength over the long electroforming durations necessary in production facilities. Tensile strengths of 517 to 551 Mpa (75 to 80 ksi) were practical in production deposits while maintaining good yield strength and ductility. This was achieved with acid copper sulfate electrodeposits from a bath containing a single proprietary additive, PEG-B. These deposits respond well to heat treatment at 149°C to 371°C and were found to retain far higher yield strengths than wrought annealed OFHC grade copper. Unlike typical acid copper electrodeposits, these materials show good ductility at elevated temperature. Their cryogenic properties are outstanding. This material represents a major technical breakthrough in the use of electroformed copper for many structural components.

2. Low additive, non-alloyed electrolytic copper deposits were sought having yield strengths of at least 49.7 MPa (7.5 ksi) and 10 percent elongation in 5.08 cm at 371°C (700°F). This was not achieved at a test temperature of 371°C. However, these goals were met at a test temperature of 260°C (500°F) with deposits from acid copper sulfate baths containing only chloride ion as an additive, from similar baths containing xylose and triisopropanolamine, and from PEG-B baths.

3. Another goal was to demonstrate that low alloyed copper deposits could be produced having resistance to recrystallization at temperatures to 500°C (932°F) and superior strengths to conventional copper deposits. All deposits produced recrystallized to some degree at 371°C. However, after heat treating at 371°C, acid copper deposits from D+ xylose-TIPA additive baths, α/γ-alumina dispersion baths, and PEG-B baths exhibited better mechanical strength than conventional copper deposits. Dispersion strengthened material requires a much higher temperature

treatment to restore ductility.

It was also demonstrated that electrodeposited copper low alloyed with platinum could produce a heat treatable material having excellent microstructure after one hour at 371°C, outstanding ductility, and far superior yield strength to that of conventional electrodeposited copper (or wrought annealed copper).

4. It was shown that diamond-like materials (actually fullerenes) could be codeposited with copper to form a dispersion alloy of superior strength with no loss of thermal conductivity. It was also shown that dispersion stengthening could be utilized in all copper electrodeposits (including the copper-platinum alloys) by codeposition of submicron alumina particles.

5. Using the technology developed in this program, a deliverable compliant tube bundle thrust chamber was electroform fabricated in its entirety (except for the mechanically formed coolant tubes) with no welds or other thermal treatments employed. This is the first time such a device has been made entirely without thermal joining processes in order to preserve the mechanical properties of the copper.

INTRODUCTION

Copper has outstanding electrical and thermal conductivity that makes it a desireable material for fabricating many circuitry and heat exchange devices. It is easily deposited from many electrolytes with a wide variety of chemical compositions. Unfortunately, most baths yielding high strength deposits do not provide copper with good ductility. Best ductility is found in low to moderate strength deposits from acid sulfate, acid fluoborate, and the slightly alkaline pyrophosphate baths. Thermal conductivity is often of paramount importance -- especially in inner members (liners) for regeneratively cooled thrust chambers for space vehicle engines. To offset the low mechanical properties of pure wrought copper at moderate to intermediate temperatures, wrought copper is often alloyed with very small amounts of silver and/or zirconium. This provides better retention of yield strength at elevated temperatures than pure copper. As with many metals and alloys, copper may also be dispersion strengthened with refractory oxides and other compounds having high energies of formation. These particles block or delay dislocation movement under stress and deter the ability for grains to coalesce with neighboring grains at normal recrystallization temperatures.

With the availability of these wrought alloys, one might ask why we are interested in developing the electrodeposited counterparts. The first reason is that the elevated temperature wrought alloys such as NAR-alloy Z, NASA-Z, and Amzirc are very expensive to produce. Special metallurgical practices are necessary. Secondly, added to this cost is the labor intensive requirement for machining. On the other hand, electroforming produces the material and the near net shape of the product in a chemical solution which requires minimal maintenance and attention. Electroforming is essentially a longer than usual electroplating process whereby the deposit is made on a mandrel, or shape, which may be removed at a later time or left as part of the end product. Labor in electroforming is mainly in the mandrel preparation steps where masking and current directing shields are positioned to direct deposition to desired locations on the mandrel. It is also necessary to maintain the bath chemistry and operating parameters within designated limits to maintain deposit quality and mechanical properties.

There is an incentive for improving the mechanical properties of conventional unalloyed copper electrodeposits, since they are often deposited as a substrate for nickel electroforms where hydrogen embrittlement may be an issue. The bond strength of the nickel electroform to the primary substrate becomes highly dependent on the strength of this copper interface. Many commercial applications for high strength alloyed, or unalloyed, copper exist. Diamond turnable coppers are being actively sought. Improved high strength electronic circuitry is required, particularly where high density component integration results in higher thermal operating capability of the materials. This report will provide the reader with a better understanding of the mechanisms by which copper, copper alloys, and copper composites can be electrodeposited with greatly improved mechanical per-formance and physical characteristics. It is anticipated that this knowledge will generate a wider use of copper electroforms in many aerospace, defense, and commercial applications.

1. TASK I - DEVELOPMENT OF OPTIMUM PROPERTIES AND MICROSTRUCTURES IN CONVENTIONAL COPPER ELECTRODEPOSITS

1.0 Background

Safranek(1) summarized references prior to 1962 on the physical and mechanical properties of electrodeposited copper. Table I lists data from his references for copper deposits from acid copper sulfate electrolytes containing no additives. Acid copper sulfate electrolytes have been previously found in the literature and from prior studies to be the most useful in electroforming thick copper deposits with high strength and good ductility. This data indicates that not much was known of the mechanical properties of electrodeposited copper as of 1962. Safranek noted that for electrolytes without organic additives, the tensile strength is greatly influenced by cathode rotation as a means of solution agitation. However, the cathode rotational speeds of 1750 to 5500 rpm noted in Table I are not practical for most hardware that is electroformed.

TABLE I - HARDNESS, TENSILE STRENGTH, AND DUCTILITY OF COPPER ELECTROFORMED IN SULFATE SOLUTIONS WITH NO ADDITIVES(1).

Copper Concentration g/l	Sulfuric Acid Concentration g/l	Temperature °F	Current Density A/ft^2	Hardness, Knoop or Vickers	Tensile Strength Ksi	Elongation % in 2 in.
63	70	Not Reported	17	Not Rep'td	17. 1	11
63	70	Not Reported	46	Not Rep'td	22.2	16.
51	120	90	500	Not Rep'td	37.0[a]; 62.0[b]	Not Reported
51	120	90	2400	Not Rep'td	28.0[b]	Not Reported
51	120	122	500	Not Rep'td	49.0[b]	Not Reported
51	120	167	500	Not Rep'td	30.0[b]	Not Reported
Not Reported	Not Reported	Not Reported	40	81	36.1	22
63	50	65	9	Not Rep'td	28.3 to 31.6	Not Reported
63	5	65	9	Not Rep'td	33.4	Not Reported

[a] Properties for 12 inch diameter copper tubing rotated at 1750 rpm.

[b] Properties for 12 inch diameter copper tubing rotated at 5500 rpm

The American Electroplater's Society and the International Copper Research Association jointly sponsored AES Project No. 21 to study the physical properties of electrodeposited copper in order to stimulate its use in new applications. Lamb and Valentine(2) summarized about 160 papers dating back to 1899 that contained significant information on copper deposits, with most data being for the acid copper sulfate electrolyte. They and other investigators noted that there was significant lack of reproducibility of deposit grain sizes with coarsely crystalline deposits being the normal ones. These authors suggested that fine grained (additive-free) deposits are the result of trace impurities acting as grain-refining substances. This is in agreement with electrodeposited nickel theory whereby hydrated nickel oxides at the cathode surface aid or cause nucleation of fine grains. Copper does not form insoluble hydrous oxides under normal conditions in acid baths, so coarse grains are normally deposited.

For acid copper sulfate baths without addition agents, Lamb and Valentine could find only a very small effect of copper sulfate concentration on tensile strength. They also did not find any reliable evidence that increasing sulfuric acid concentration resulted in higher tensile strengths. Contradictory results were noted with regard to the effect of current density on tensile strength. This was likely due to current densities approaching or exceeding the limiting current density for the electrolyte agitation conditions. They concluded that tensile strength decreased markedly with increases in bath temperature. Increased bath agitation appeared to improve tensile strength, but as previously mentioned, the best tensile strengths were shown at impractical cathode rotation speeds such as 1500 to 5500 rpm.

As for ductility of deposits from acid sulfate baths without additives, Lamb and Valentine reported that ductility increased with an increase in tensile strength. This is contrary to the usual relation for wrought metals where ductility decreases with increased mechanical strength. These authors tried to evaluate hardness values for non-additive acid copper deposits by converting data from the many references to Diamond Pyramid Hardness values (DPH). They concluded that (1) hardness increased slightly with an increase in copper sulfate concentration, (2) the effect of increased sulfuric acid concentration was not determinable, (3) hardness increased slightly with increased deposition current density, and (4) a general decrease in hardness with increasing bath temperatures. They could not correlate hardness and tensile strength.

Lamb, Johnson, and Valentine[(3)] in 1970 reported the results of their own studies of copper deposits from acid sulfate and other electrolytes in what was probably the most comprehensive study ever conducted on electrodeposited copper. Acid copper sulfate bath compositions and operating conditions for their studies are shown in Table II.

TABLE II - BATH COMPOSITIONS AND OPERATING PARAMETERS FOR COPPER DEPOSITS FROM ACID SULFATE BATHS WITHOUT ADDITIVES[(3)]

Temp., °C		20			30				40				60		
		Current Density, A/dm^2													
Bath Symbol		0.5	2	4	0.5	2	4	8	0.5	2	4	8	4	8	20
Cu-1	H1	■				■			■		■				
	H2		■			■				■					
	H3				■	■	■								
Cu-2	H1					■						■			
	H2	■	■	■	■	■	■			■	■				
	H3		■		■	■	■	■				■		■	■
Cu-3	H1														
	H2														
	H3			■	■	■			■		■		■	■	

(shaded areas represent conditions that were used)

Definition of Bath Symbols

$CuSO_4 \cdot 5H_2O$				H_2SO_4			
Symbol	Moles/l	g/l	oz/gal	Symbol	Moles/l	g/l	oz/gal
Cu-1	0.35	87	12	H1	0.25	25	3.3
Cu-2	0.75	187	25	H2	0.40	39	5.2
Cu-3	1.1	275	36	H3	0.75	74	9.8

Test results for the deposition matrix shown in Table II based on bath composition and operating parameters are found in Tables III and IV.

TABLE III - EFFECT OF BATH TEMPERATURE ON PROPERTIES OF DEPOSITS FROM ACID SULFATE BATHS WITHOUT ADDITIVES(3)

Bath Symbol	Current Density A/dm^2	Bath Temperature °C	Tensile Strength		Yield Strength		Elongation in 2 Inches, %	Hardness, Knoop 200 g Load, Kg/mm^2
			Ksi	Mpa	Ksi	Mpa		
Cu1-H1	0.5	20	27	186	8	55	18	56
		40	30	207	10	69	24	57
Cu1-H2	2.0	20	31	214	9	62	28	59
		30	25	172	7	48	15	58
		40	24	165	8	55	13	47
Cu2-H2	0.5	20	26	179	7	48	25	105
		32	23	159	7	48	11	87
	2.0	20	32	221	11	76	33	61
		30	26	179	8	55	17	88
		40-45	22	152	8	55	10	67
	4.0	20	33	227	12	83	29	67
		30	30	207	9	62	24	53
		45	24	165	7	48	14	57
Cu2-H3	2.0	20	37	255	15	103	41	78
		30	29	200	9	62	19	54
	8.0	30	32	221	14	96	24	75
		40	37	255	15	103	44	80
		60	27	186	10	69	18	58
Cu3-H3	0.5	30	27	186	8	55	16	57
		45	32	221	10	69	34	57
	4.0	20	32	221	12	83	42	64
		45	26	179	8	55	15	51
		60	31	214	8	55	42	55

In most cases it was found that tensile strength and elongation decreased with increasing bath temperature, although a reverse effect was noted in some cases where other bath variables may have been influential. Yield strength trends paralled tensile strength trends. This trend also applied to hardness; that is, hardness decreased with increasing temperature, although the effect was generally small.

They examined the effect of thickness on properties of deposits and noted that thin deposits (1 to 6 mils thick) were significantly stronger but less ductile than deposits 18 mils thick. This was explained on the basis that the initial layers of the deposit tend to continue the structure of the substrate metal for a short distance up to 3 to 5 mils. Beyond this distance, the grains of non-additive bath deposits become much coarser and thus affect mechanical properties. These investigators noted that the acid sulfate deposits from non-additive baths are extremely columnar and this columnar condition is suppressed by certain amine additions. Use of a pyrophosphate bath can produce very uniform equi-axed grains. These structures would account for the great variation in copper electrodeposit mechanical properties.

TABLE IV - EFFECT OF CURRENT DENSITY ON PROPERTIES OF DEPOSITS FROM ACID SULFATE BATHS WITHOUT ADDITIVES(3)

Bath Symbol	Bath Temperature °C	Current Density A/dm^2	Tensile Strength Mpa	Tensile Strength Ksi	Yield Strength MPa	Yield Strength Ksi	Elongation in 2 Inches, %	Hardness, Knoop 200 g Load, Kg/mm^2
Cu1-H1	40	0.5	30	207	10	69	24	57
		4.0	29	200	8	55	32	46
Cu1-H3	30	0.5	20	138	8	55	8	56
		2.0	28	193	8	55	16	58
		4.0	34	234	13	90	15	79
Cu2-H2	20	0.5	26	179	7	48	25	105
		2.0	32	221	11	76	34	61
		4.0	33	227	12	83	29	67
	32	0.5	23	159	7	48	11	87
	30	2.0	26	179	8	55	17	88
		4.0	30	207	9	62	24	53
	40	2.0	22	152	7	48	10	85
	45	2.0	21	145	8	55	10	49
		4.0	24	165	7	48	14	57
Cu2-H3	30	0.5	33	227	10	69	41	62
		2.0	28	193	9	62	19	54
		4.0	34	234	11	76	46	66
		8.0	32	221	14	96	24	75
	60	8.0	27	186	10	69	18	58
		20.0	20	138	7	48	5	58
Cu3-H3	30	0.5	27	186	8	55	16	57
		2.0	30	207	9	62	29	55
	45	0.5	32	221	10	69	34	57
		4.0	26	179	8	55	15	51
	60	4.0	31	214	8	55	42	55
		8.0	31	214	10	69	33	59

These same investigators noted a dominant trend for an increase in tensile strength and elongation with increase in current density, but the effects were not large. Some exceptions were noted where limiting current density for the bath conditions was approached or exceeded and codeposition of impurities probably occurred. They considered that there was a loose correlation of increased hardness with increased current density, but the effects were small.

They examined the effects of copper sulfate concentration on properties and concluded that there was no significant effect on tensile strength or hardness. They did note that elongation appeared to improve with increased copper sulfate concentration. As for the effect of sulfuric acid on the deposit properties, their test results indicated a consistent increase in tensile strength and elongation with an increase in acid concentration from the medium range to the high range. They also noted that there was a trend for hardness to increase with increasing acid concentration. It should be noted that chlorides were not added to their baths. Bath volumes ranged from 27 to 30 liters. Solution agitation at the cathode was provided by air spargers. Continuous filtration was used with cotton filter media. An interesting observation by these investigators was that the average tensile strength of all of their non-addition agent acid sulfate deposits was 29 ksi while the tensile strength of annealed tough-pitch copper was 31 ksi. The average elongation of these same acid sulfate deposits was 24%, while that of the wrought copper counterpart was 45%.

Lamb, Johnson, and Valentine briefly examined the use of periodic current reversal to produce copper deposits from the acid sulfate bath. They noted that tensile strength and hardness increased significantly with the use of current reversal (PR). Malone[(4)] compared periodic current reversal with conventional direct current deposition of copper from the acid sulfate bath. He demonstrated that very thick, uniform grained deposits could be produced with PR that had significantly better mechanical properties than those for the dc plated specimens. Table V summarizes Malone's test results and plating parameters for copper deposits without periodic current reversal using a bath of nearly identical composition to Bath Cu2-H3 employed by Lamb, Johnson, and Valentine.

TABLE V - MECHANICAL PROPERTIES OF ACID COPPER SULFATE DEPOSITS ELECTROFORMED WITHOUT PERIODIC CURRENT REVERSAL

Electrolyte: Copper Sulfate 187.5 g/l, Sulfuric Acid 75 g/l.

Panel No.	Bath Temp. °C	Current Density		Specimen Thickness		Mechanical Properties				
						Ult. Strength		Yield Strength		Elongation % in 2 in.
		A/ft²	A/dm²	in.	mm	Kpsi	MN/m²	Kpsi	NM/m²	
1	32.2	30	3.23	0.023	0.584	18.2	125.5	9.9	68.3	12
				0.024	0.610	21.7	149.6	8.5	58.6	11
				0.030	0.762	21.7	149.6	8.9	61.4	13
2	32.2	45	4.84	0.032	0.813	41.3	284.8	19.7	135.8	29
				0.027	0.686	42.2	291.0	20.1	138.6	26
				0.025	0.635	41.4	285.5	20.4	140.7	29
3	32.2	45	4.84	0.099	2.515	18.9	130.3	10.0	69.0	11

The mechanical properties reported in Table V would be expected to approximate those of Lamb, Johnson, and Valentine from Table IV, Bath Cu2-H3, bath temperature 30°C, and current densities of 2 to 4 A/dm^2. This was not found to be true. Although lower ductility was found in Malone's copper deposits, the tensile and yield strengths were significantly higher than those of Lamb, et al. The samples from Malone's studies were much thicker than those of Lamb and his co-workers; however, the mechanical property differences were more likely due to the fact that Malone used pumped solution flow over the cathode surface as opposed to air agitation to move the electrolyte. Malone also used 100 liter baths; much larger than the 27 to 30 liter jars used by Lamb, et al. Malone also used polypropylene cartridges for continuous bath filtration in contrast to the cotton filters employed by the other investigators.

Table V provides mechanical property data that establishes trends with regards to current density and thickness variations for acid copper sulfate deposits where PR is not used. Increasing current density led to deposits with greatly improved mechanical properties (including ductility). However, on increasing deposit thickness to about 0.1 inch, the mechanical properties degraded immensely. It is likely that this was caused by formation of coarse grains and surface roughening which decreased actual surface current density. These properties resemble those for the thinner specimen deposited at only 3.23 A/dm^2. This explains the need for a deposition method which will maintain fine copper grain size while promoting a smooth surface of more constant area. Periodic current reversal appears to provide such controls at a sacrifice in deposition rate due to the reversal (deplating) cycles. Malone$^{(4)}$ found that best mechanical properties were obtained with a forward to reverse cycle ratio of 2:1 or less, Table VI. As a result, periodic reversal was investigated in the current studies.

TABLE VI - MECHANICAL PROPERTIES OF ACID COPPER SULFATE DEPOSITS ELECTROFORMED WITH PERIODIC CURRENT REVERSAL$^{(4)}$
Electrolyte: Copper Sulfate 187.5 g/l, Sulfuric Acid 75 g/l.

Panel No.	Periodic Current Cycle	Bath Temp. °C	Current Density		Specimen Thickness		Mechanical Properties				
							Ult. Str.		Yield Str.		Elongation % in 2 in.
			A/ft^2	A/dm	in.	mm	Kpsi	MN/m	Kpsi	MN/m	
PR-1	8 sec. forward	32.2	30	3.23	0.031	0.787	35.1	242.0	12.4	85.5	36
	4 sec. reverse				0.027	0.686	30.0	206.9	8.1	55.8	30
					0.025	0.635	26.1	180.0	14.0	96.5	17
PR-2	8 sec. forward	32.2	45	4.84	0.019	0.483	44.7	308.2	20.5	141.3	31
	4 sec. reverse				0.019	0.483	55.1	379.9	25.6	176.5	31
					0.017	0.432	44.2	304.8	19.2	132.4	30
PR-3	8 sec. forward	32.2	60	6.46	0.036	0.914	40.6	279.9	16.7	115.1	36
	4 sec. reverse				0.035	0.889	36.1	248.9	14.9	102.7	39
					0.030	0.762	35.6	245.5	12.6	86.9	38
PR-4	8 sec. forward 4 sec. reverse	32.2	60	6.46	0.086	2.184	37.5	258.6	17.3	119.3	35

Best mechanical properties were found under the conditions under which Panels PR-2 and PR-3 were produced. Panel PR-4 demonstrated that excellent mechanical properties could be maintained over very great plating thicknesses. Lamb, Johnson, and Valentine also examined mechanical properties of acid sulfate copper using periodically reversed current. For a cycle of 5 seconds forward current and 2 seconds reversed current, a bath temperature of 30°C and a current density of 4 A/dm^2, they obtained deposits having 43 ksi tensile strength, 20 ksi yield strength, and 26 percent elongation in 5 cm (2 in). These results are in good agreement with those of Panel No. PR-2 in Table VI.

Lamb, Johnson, and Valentine$^{(3)}$ and Malone$^{(4)}$ investigated mechanical properties and microstructures of copper deposits from pyrophosphate baths. Most of the copper pyrophosphate bath compositions fit into the ranges shown in Table VII. All of the investigators used low pressure filtered air supplied by oil-less carbon vaned blowers to spargers to provide the very high solution agitation required for the pyrophosphate bath. Lamb, Johnson, and Valentine tried various means of bath agitation and concluded that air agitation was superior to mechanical agitation, since the latter resulted in rough, nodular deposits. They noted only minor variations of mechanical properties as temperature was adjusted from 50 to 60°C and current density was varied from 2 to 4 A/dm^2. Tensile strengths ranged from 38 to 40 ksi, yield strengths from 20 to 22 ksi, and elongations were 33 to 39 percent in 5 cm.

They did not define pyrophosphate deposit thicknesses, so it is presumed that most were of a similar thickness to the acid sulfate deposits (0.018 to 0.020 in).

TABLE VII - NORMAL RANGE OF CHEMISTRY AND OPERATING CONDITIONS FOR COPPER PYROPHOSPHATE BATHS(5)

Copper Metal, g/l	18.8 to 30.0
Pyrophosphate-Copper-Ratio	7.4:1 to 8.0:1
Ammonia, g/l	0.375 to 2.25
Potassium Nitrate, g/l	5 to 10
pH	8.0 to 8.5
Temp, °C	46.1° to 57.2°C
Current Density, Cathode*	2.16 to 3.24 Amp/dm^2 (20 to 30 Amp/ft^2)

*High densities possible with good aitation of electrolyte.

Malone(4) demonstrated similar mechanical properties in pyrophosphate copper deposits to those found by Lamb, Johnson, and Valentine.

Malone also noted that the pyrophosphate bath is one of the more difficult electrolytes to operate and control for very thick deposits due to the need for uniform vigorous agitation of the electrolyte over all sufaces being electroformed and due to the more complex bath chemistry which must be frequently corrected to maintain proper pH and pyrophosphate-to-copper ratio. Although Malone's previous studies agreed with Lamb, Johnson, and Valentine that agitation did not significantly affect tensile and yield strengths, he found that cathode boundary solution agitation was critical to good ductility. Table VIII shows data leading to this conclusion.

TABLE VIII - EFFECTS OF AIR AGITATION AND CHEMISTRY IMBALANCES ON MECHANICAL PROPERTIES(4)

Rating	Panel Nos.	Mechanical Property Range					Related Electrolyte Chemistry or Operating Conditions
		Ult. Strength		Yield Strength		Elongation % in 2 in.	
		Kpsi	MN/m^2	Kpsi	MN/m^2		
Poor	1, 6, 7, 8, 10	56.7 to 83.8	390.9 to 577.8	35.0 to 68.5	241.3 to 472.3	4 to 12	Inadequate electrolyte filtration, or high copper metal and low pyro/cu ratio (below 7:1)
Poor	16	43.7 to 44.5	301.3 to 306.8	27.5 to 29.3	189.6 to 202.0	8 to 10	Badly misaligned air agitation system
Fair	9, 15, 20	38.7 to 53.3	266.8 to 367.5	22.7 to 36.4	156.5 to 251.0	14 to 21	Non-optimum placement of air agitation system, or marginal pyro/cu ratio (Panel 20 only)
Good	25	42.2	291.0	27.2	187.5	28	Bath chemistry optimum, air agitation alignment changed during electroforming.
Excellent	12	43.3 to 45.9	298.6 to 316.5	24.5 to 25.7	168.9 to 177.2	27 to 37	Bath chemistry optimum, air agitation near optimum

Malone found that those deposits having inadequate solution agitation during electroforming had fine columnar or duplexed (both equi-axed and fine columnar) grain structures as shown in Figure 1. The normal (desired) microstructure for pyrophosphate deposits is shown in Figure 2. Although the ductility of the duplexed deposit was acceptable, it was not as good as that of the totally equi-axed microstructure in Figure 2. Each moderately coarse grain in this structure is composed of fine subgrains. Mechanical properties for both specimens illustrated are found in Table VIII.

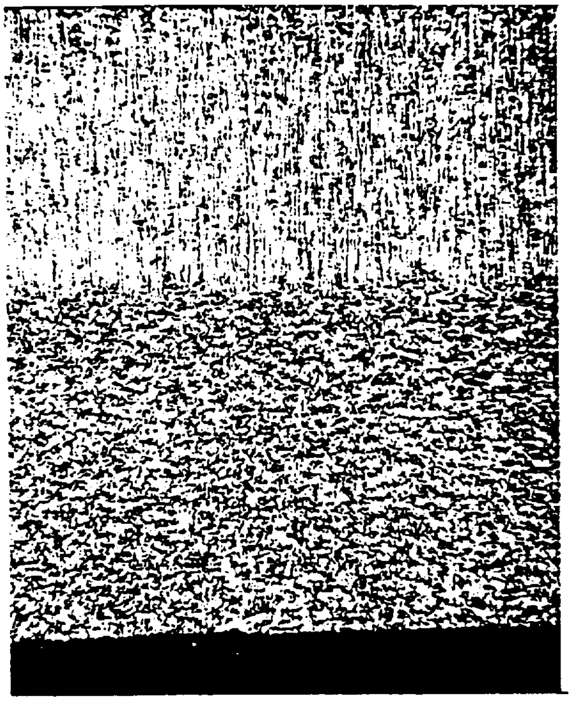


Figure 1. Duplex Grain Structure in Copper Pyrophosphate Deposits with Varied Solution Agitation.

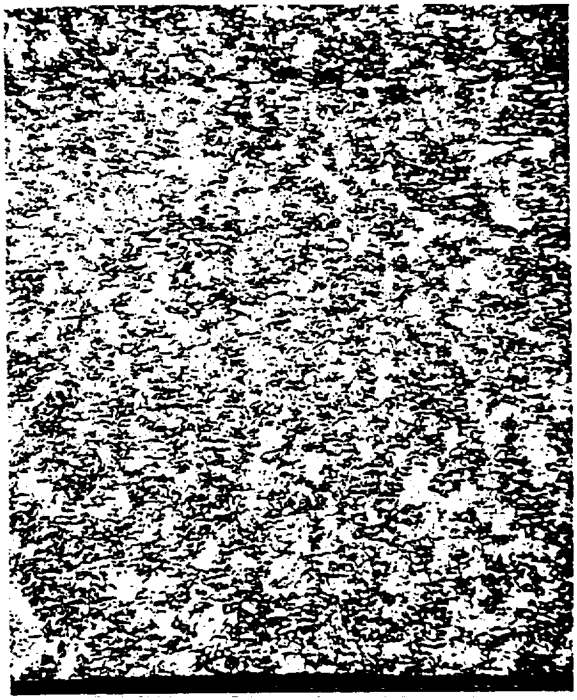


Figure 2. Normal Equi-axed Grain Structure in Copper Pyrophosphate Deposits with Uniformly Vigorous Bath Agitation.

The copper pyrophosphate bath has rarely been used for electroforming due to the continuous need for chemical monitoring and complexities involved in providing a vigorous and uniform means of solution agitation at the cathode surface, particularly where complex three dimensional topography is an issue. It should also be noted that the bath operates at a far higher temperature than the acid sulfate bath, and this prohibits use of many of the waxes used as channel fillers in many electroforming operations. However, the equi-axed grain structure is a desireable feature for producing multidimensionally uniform mechanical properties. Copper in this particular bath is highly complexed by the inorganic pyrophosphate anion, and this may account for the unusual microstructures observed in Figures 1 and 2..

The copper fluoborate bath can also be used for electroforming, but it is highly corrosive and requires special facility equipment to overcome this problem. Lamb, Johnson, and Valentine(3) investigated this bath and reported the mechanical properties shown in Table IX. These properties are inferior to those obtained with periodic current reversal in the acid sulfate bath, consequently the fluoborate bath was excluded from the current program.

TABLE IX - BATH CHEMISTRY, OPERATING PARAMETERS, AND DEPOSIT MECHANICAL PROPERTIES FOR COPPER FLUOBORATE BATHS

Bath Chemistry or Operating Conditions	Conc. g/l	Bath Temperature °C	Current Density A/dm^2	Tensile Strength		Yield Strength		Elongation in 2 Inches, %	Hardness, Knoop, 200 g Load, kg/mm^2
				Mpa	Ksi	Mpa	Ksi		
$Cu(BF_4)_2$	177	30	2.0	138	20	62	9	7	53
HBF_4	12	30	8.0	255	37	110	16	31	81
Boric Acid	12	60	8.0	221	32	76	11	16	56
pH	0.8-1.0								
$Cu(BF_4)_2$	366	30	8.0	248	36	103	15	31	71
HBF_4	22	50	20.0	227	33	83	12	29	60
Boric Acid	22								
pH	0.4-0.6								

1.1 Current Program Studies of Copper Deposits from Non-Additive Electrolytes

Since many readers will be unfamiliar with copper electrodeposition, the Principal Investigator has presented a lengthy and detailed background to provide reasons for the development and demonstration approach taken in the Task I studies. The results of this work form a basic foundation of conventional copper deposit properties and microstructures from which improvements can be measured in subsequent tasks.

1.1.1 Pulse and Periodic Current Reversal Screening Tests at Southern Illinois University at Carbondale (SIU)

Under subcontract, Southern Illinois University (SIU) performed one liter beaker studies on acid copper sulfate baths without additives. Chloride ion was not added to these baths. Deposition was carried out using pulsed deposition in the forward current mode and pulsed plating with current periodically reversed. A summary of deposition and hardness test data is found in Table X. Dr. Lalvani and Jaw-Ching Kang of SIU concluded that pulse plating corresponding to relatively high duty cycles (duty cycles well in excess of 50 percent) led to higher hardness values when pulse durations were in seconds rather than in milliseconds.. When pulse durations were in milliseconds, they found that (contrary to the literature claims) no improvement in hardness was realized. They also examined relatively large forward and small reverse peak currents and concluded that no significant improvement in hardness was obtained. However, when they applied high current density pulse in the forward deposition mode with no reverse current, significant hardness improvements were found. It should be recognized that these baths contained no chloride which might significantly affect hardness results. The effect of trace chloride ion in acid copper electrolytes will become significant when mechanical properties deposits from such baths are evaluated in this investigation.

TABLE X - SIU STUDIES OF PULSED DEPOSITION OF COPPER FROM ACID SULFATE ELECTROLYTES WITHOUT ADDITIVES

SIU	Pulse Duty Cycle		Fwd Pulse Time		Rev Pulse Time		Peak CD		Average CD		Thickness	Knoop
Sample	Fwd	Rev	On	Off	On	Off	(A/dm²)		(A/dm²)		Of Deposit	Hardness
Number	%	%	(Msec)	(Msec)	(Msec)	(Msec)	Fwd	Rev	Fwd	Rev	µm	25g Load
P27	40	0	4	6	0	0	18.8	0	7.52	0	440	99.8
P28	40	0	2.67	4	0	0	12.5	0	5.0	0	210	78.5
P29	40	0	2.67	4	0	0	18.8	0	7.52	0	410	82.3
P30	80	0	16	4	0	0	6.3	0	5.04	0	420	85.9
P31	80	0	16	4	0	0	9.4	0	7.52	0	320	91.6
P32	80	0	8	2	0	0	6.3	0	5.04	0	270	125.3
P34	67	100	8	4	4	0	7.5	1	5.0	1	230	61.6
P51	75	80	1500	500	800	200	7.5	1	5.63	0.8	220	94.9
P52	67	100	8000	4000	4000	0	7.5	1	5.0	1	150	92.6
P53	67	75	8000	4000	3000	1000	7.5	0.8	5.0	0.6	270	84.8
P54	67	75	8000	4000	3000	1000	7.5	1.3	5.0	0.9	170	84.8
P55	67	100	8000	4000	4000	0	7.5	1.2	5.0	1.2	190	106.3
P56	67	75	8000	4000	1500	500	7.5	0.8	5.0	0.6	150	100.6
P57	73	75	8000	3000	1500	500	7.5	0.8	5.45	0.6	180	105.7
P58	80	80	8000	2000	4000	1000	7.5	0.8	6.0	0.6	120	107.0
P59	75	75	3000	1000	1500	500	7.5	0.8	5.63	0.6	140	110.3
P60	67	75	8000	4000	3000	1000	8.5	1.0	5.7	0.75	130	112.3
P61	67	75	8000	4000	3000	1000	9.5	1.2	6.34	0.9	160	114.3
P62	67	100	8000	4000	4000	0	9.5	1.2	6.34	1.2	260	114.3
P63	73	75	8000	3000	1500	500	9.5	0.8	6.91	0.6	240	111.7

1.1.2 ENI Studies of Non-additive Acid Copper Sulfate Electrolytes Using 100 Liter Baths

Initial copper deposition studies were made in four liter beakers with the intent to screen various plating parameters and later repeat these conditions in much larger baths. Beaker sized baths were evaluated with and without selenium as an additive. Use of selenium as an additive was based on Safranek's(1) suggestions that tensile strength and ductility were improved while grain size was reduced. Difficulties were encountered with these baths due to the large cathode size to bath volume necessary to deposit samples large enouugh for mechanical property testing. Shielding was required to obtain uniform deposit thicknesses, and this blocked electrolyte agitation produced by a magnetic stirring rod in the beaker. Continuous filtration was not used; however the bath was filtered after plating each sample. These conditions resulted in blocked electrolyte agitation produced by a magnetic stirring rod in the beaker. This resulted in poor sample quality. Most specimens exhibited inadequate elongation when tested for mechanical properties. The best specimen electroformed in the preliminary 4 liter beaker trials was deposited at 4.3 A/dm² using periodic current reversal of 8 seconds forward and 4 seconds reverse and a stirring bar speed of 300 rpm. The mechanical properties of this deposit were 42.4 ksi tensile strength, 15.6 ksi yield strength, and 19 percent elongation in 5 cm. The bath contained 220.2 g/l copper sulfate pentahydrate, 75.6 g/l sulfuric acid, 42 ppm chlorides, and was operated at 29.4°C.

All subsequent studies were conducted in 100 liter tanks containing a weir compartment to isolate the continuous 20 micron rated filtration system. The filtration return was through a bulkhead fitting in the weir base and then through a perforated sparger pipe in the bottom of the tank. This size tank accommodated a 1000 watt heater equipped with a thermostatic control. An in-tank pump, in addition to the weir pump, was used to direct solution flow to the surface of the cathode. This permitted use of varied solution agitation at the surface being electroformed. An illustration of the typical tank and equipment used in the majority of studies in Tasks I and II is found in Figure 3. To simplify description of solution agitation conditions, the following code has been used throughout this report:

1. "A" designates conditions of no agitation other than solution return from the weir or (in the case of beaker experiments) natural convection.
2. "B" designates indirect flow of the electrolyte whereby the flow direction is not at the cathode.
3. "CO" designates solution flow directed at the cathode through open pipe fittings without nozzles. A number preceeded by a dash indicates how many open pipe fittings were employed (i.e., CO-2 means that two open flow pipes were used.
4. "CN" indicates that plastic spray nozzles were used to provide cathode agitation. A suffix preceeded by a dash describes the number of nozzles used in a pattern.
5. "MS" designates that a magnetic stirrer was used in a beaker experiment.
6. "AA" indicates that air agitation was supplied by a low pressure oil-less pump.

Figure 3. Illustration of Typical 100 Liter Copper Electroforming Facility

Using acid copper baths with no additives, the influence of modest chloride content on mechanical properties was evaluated. Figure 4 summarizes electrolyte compositions, deposition parameters, mechanical properties, and microstructures obtained when less than 50 ppm of chloride ion was present in the bath. Figure 5 provides similar data for when 50 to 100 ppm of chloride was present. The effect of chloride, even in small amounts was quite remarkable. Ultimate strengths and yield strengths increased significantly when the chloride ion content changed from below 50 ppm to above 50 ppm. Ductility was very satisfactory at both levels of chloride ion. The improved mechanical properties from the increased chloride concentration are a result of the much finer columnar grain structure in the deposits as seen when photomicrographs in Figures 4 and 5 are compared.

Rocketdyne Division of Boeing$^{(5)}$ specifies addition of D$^+$ xylose in acid copper electrolytes used in producing the cooling channel close-outs on NAR-loy Z combustion chamber liners for the Space Shuttle Main Engines. This pentose serves as a reducing agent to minimize codeposition of copper oxides which would degrade thermal performance and mechanical properties at elevated temperatures. The Principal Investigator in the current study also employs this additive and phosphorized oxygen-free copper anodes for copper electroforming in thrust chamber production.

Earlier work by Malone$^{(6)}$, Phase I preceeding this program, demonstrated that proper bath purification and anode operation would result in a low oxygen acid copper deposit, Figure 6. However, it was also demonstrated in this samer work that use of the D$^+$ xylose compound would promote low oxygen in the deposit, even when a significant amount of an organic additive was present, Figure 7. In order to utilize this organic chemical in combination with other organics in Task II, it was first necessary to determine if mechanical property changes were introduced by the xylose compound. If no changes were observed, it would be possible to expand the definition of "additive-free" acid copper sulfate baths to include those containing D$^+$ xylose. To perform this study, two 100 liter acid copper sulfate tanks were purified by treatment with 30% by volume hydrogen peroxide to break down any organic contamination. Both baths were heated to 60°C to remove excess peroxide and continuously carbon treated for at least two days with the heaters turned off. Both electrolytes contained chloride ion in the range of 50 to 100 ppm. Reagent grade D$^+$ xylose was added to each bath to provide a concentration of 0.70 g/l.

After allowing the D$^+$ xylose to dissolve and mix over a twenty-four hour period, 15.24 cm by 19.05 cm mechanical property test panels were electroformed in each tank. Electroforming conditions, bath chemistries, and test results (including microstructures) are presented in Figure 8. A comparison of this data with that shown in Figure 5 indicates that there are no changes in mechanical properties, hardness, or microstructure when the only variation in deposition conditions is the presence (or absense) of D$^+$ xylose. This means that D$^+$ xylose containing baths can be grouped with conventional non-additive acid copper baths with regards to effects on mechanical properties.

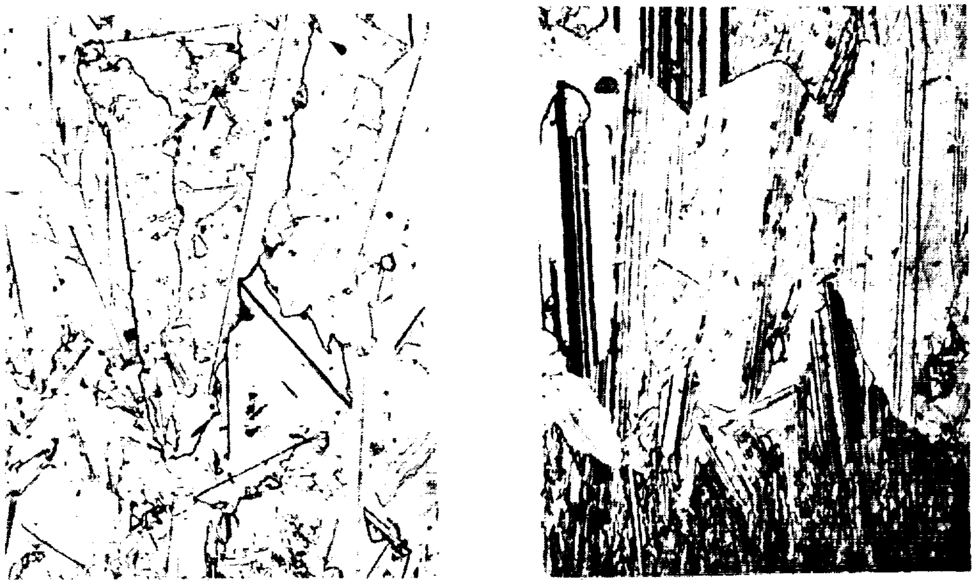
1.2 Task I Summary and Conclusions

The use of periodic current reversal appears to enhance ability to produce thick electroforms of copper with improved mechanical properties and uniform microstructures. Electroformed copper

EFFECT OF CHLORIDE ION CONCENTRATION ON MECHANICAL PROPERTIES AND MICROSTRUCTURE OF ADDITIVE-FREE ACID COPPER SULFATE DEPOSITS
(LESS THAN 50 PPM CHLORIDE ION)

Chemistry	**Sample 4-NA-01**	**Sample 5-NA-01**
$CuSO_4$ $5H_2O$	221.7 G/L	229.2 G/L
H_2SO_4	75.6 G/L	68.1 G/L
Chloride Ion, By Weight	30 PPM	35 PPM
Operating Parameters		
Bath Temperature	26.7°C	26.7°C
Periodic Current Reversal, Forward Time	8 Seconds	8 Seconds
Periodic Current Reversal, Forward CD	4.84 A/dm^2	4.84 A/dm^2
Periodic Current Reversal, Reverse Time	4 Seconds	4 Seconds
Periodic Current Reversal, Reverse CD	4.84 A/dm^2	4.84 A/dm^2
Electroyte Agitation Code	CN-4	CN-4
Continuous Filtration	20 Microns	20 Microns
Deposition Time, Hours	99.25	96.00
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	29.82	22.33
Yield Strength, ksi	9.59	8.02
Elongation, % in 5.08 cm	23.0	19.0
Hardness, Vickers 100 g Load	74	71
Thickness, cm	0.213	0.221

Microstructures (Magnification 100X)



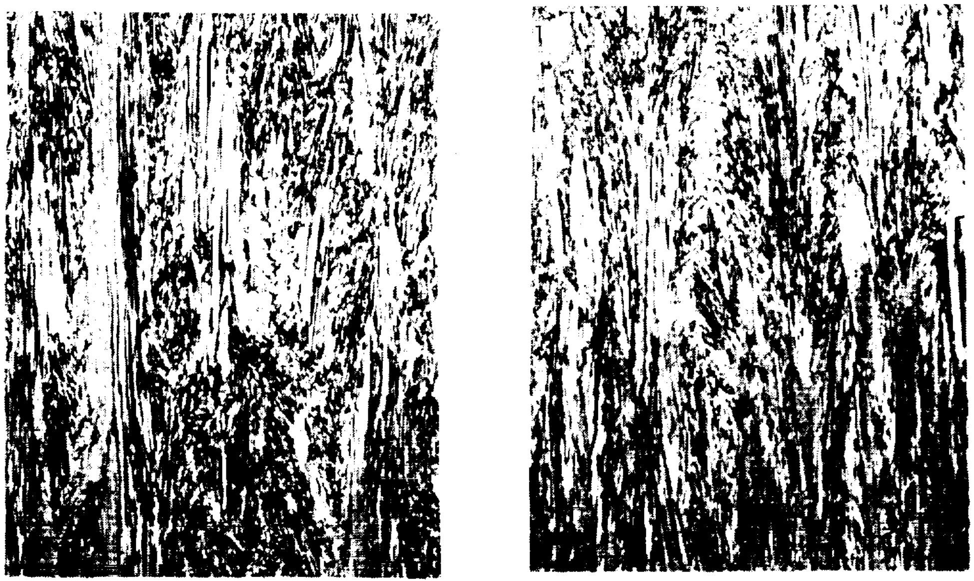
Sample 4-NA-01

Sample 5-NA-01

Figure 4. Data for Acid Copper Sulfate Deposits from Electrolytes with Less Than 50 PPM Chloride Ion and Containing No Additives.

EFFECT OF CHLORIDE ION CONCENTRATION ON MECHANICAL PROPERTIES AND MICROSTRUCTURE OF ADDITIVE-FREE ACID COPPER SULFATE DEPOSITS (BETWEEN 50 AND 100 PPM CHLORIDE ION)

Chemistry	**Sample 4-NA-02**	**Sample 5-NA-02**
$CuSO_4\,5H_2O$	239.6 G/L	226.2 G/L
H_2SO_4	74.1 G/L	68.9 G/L
Chloride Ion, By Weight	81 PPM	61 PPM
Operating Parameters		
Bath Temperature	26.7°C	26.7°C
Periodic Current Reversal, Forward Time	8 Seconds	8 Seconds
Periodic Current Reversal, Forward CD	4.84 A/dm^2	4.84 A/dm^2
Periodic Current Reversal, Reverse Time	4 Seconds	4 Seconds
Periodic Current Reversal, Reverse CD	4.84 A/dm^2	4.84 A/dm^2
Electroyte Agitation Code	CN-4	CN-4
Continuous Filtration	20 Microns	20 Microns
Deposition Time, Hours	96.75	99.25
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	46.30	43.16
Yield Strength, ksi	27.59	24.78
Elongation, % in 5.08 cm	22.0	15.0
Hardness, Vickers 100 g Load	108	103
Thickness, cm	0.147	0.201
Microstructures (Magnification 100X)		



Sample 4-NA-02 Sample 5-NA-02

Figure 5. Data for Acid Copper Sulfate Deposits from Electrolytes with 50 to 100 PPM Chloride Ion and Containing No Additives.

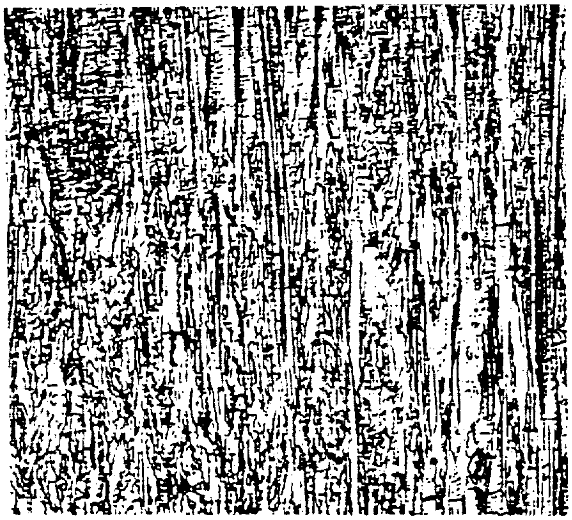
EFFECT OF BATH PURIFICATION AND PROPER ANODE MANAGEMENT ON MECHANICAL PROPERTIES, MICROSTRUCTURE, AND IMPURITY CONTENT OF ADDITIVE-FREE ACID COPPER SULFATE DEPOSITS (WITH 50 TO 100 PPM CHLORIDE ION)

Chemistry	**Sample A-2 (Tank 001)**
$CuSO_4 \cdot 5H_2O$	229.9 G/L
H_2SO_4	72.6 G/L
Chloride Ion, By Weight	75 PPM
D' Xylose	None

Operating Parameters	
Bath Temperature	30.6°C
Periodic Current Reversal, Forward Time	8 Seconds
Periodic Current Reversal, Forward CD	4.84 A/dm^2
Periodic Current Reversal, Reverse Time	4 Seconds
Periodic Current Reversal, Reverse CD	4.84 A/dm^2
Electroyte Agitation Code	CN-4
Continuous Filtration	15 Microns
Deposition Time, Hours	92.00

Mechanical Properties and Deposit Thickness	
Ultimate Strength, ksi	46.85
Yield Strength, ksi	25.56
Elongation, % in 5.08 cm	30.0
Hardness, Vickers 100 g Load	Not Determined
Thickness, cm	0.137

Microstructures (Magnification 100X)



Deposit Chemistry:

Oxygen	12 ppm
Carbon	10 ppm
Hydrogen	0.9 ppm
Sulfur	6 ppm

Sample A-2 (Tank 001)

Figure 6. Data for Acid Copper Sulfate Deposits with Low Oxygen and No Additives.

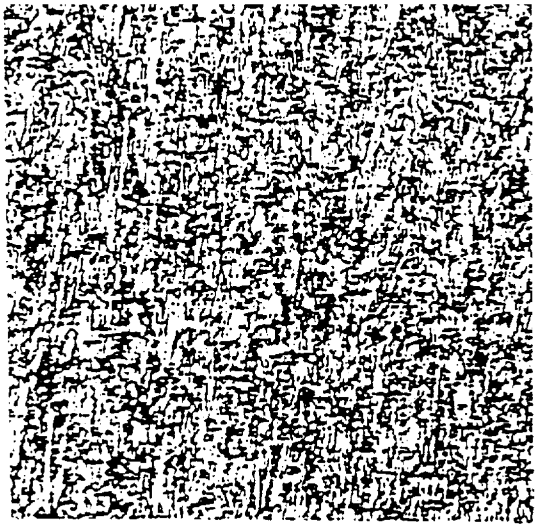
EFFECT OF D^+ XYLOSE ON MECHANICAL PROPERTIES, MICROSTRUCTURE, AND CHEMISTRY OF DEPOSITS FROM ACID COPPER SULFATE BATHS CONTAINING OTHER ORGANIC ADDITIVES AND CHLORIDE ION

Chemistry	**Sample CU-B**
$CuSO_4$ $5H_2O$	210.0 G/L
H_2SO_4	78..6 G/L
Chloride Ion, By Weight	75 PPM
D^- Xylose	0.2 G/L
Triisopropanolamine	0.1 G/L

Operating Parameters	
Bath Temperature	28.3°C
Periodic Current Reversal, Forward Time	12 Seconds
Periodic Current Reversal, Forward CD	4.31 A/dm^2
Periodic Current Reversal, Reverse Time	6 Seconds
Periodic Current Reversal, Reverse CD	4.31A/dm^2
Electroyte Agitation Code	CN-4
Continuous Filtration	20 Microns
Deposition Time, Hours	96.00

Mechanical Properties and Deposit Thickness	
Ultimate Strength, ksi	57.30
Yield Strength, ksi	37.25
Elongation, % in 5.08 cm	29.0
Hardness, Vickers 100 g Load	Not Determined
Thickness, cm	0.191

Microstructures (Magnification 100X)



Sample CU-B

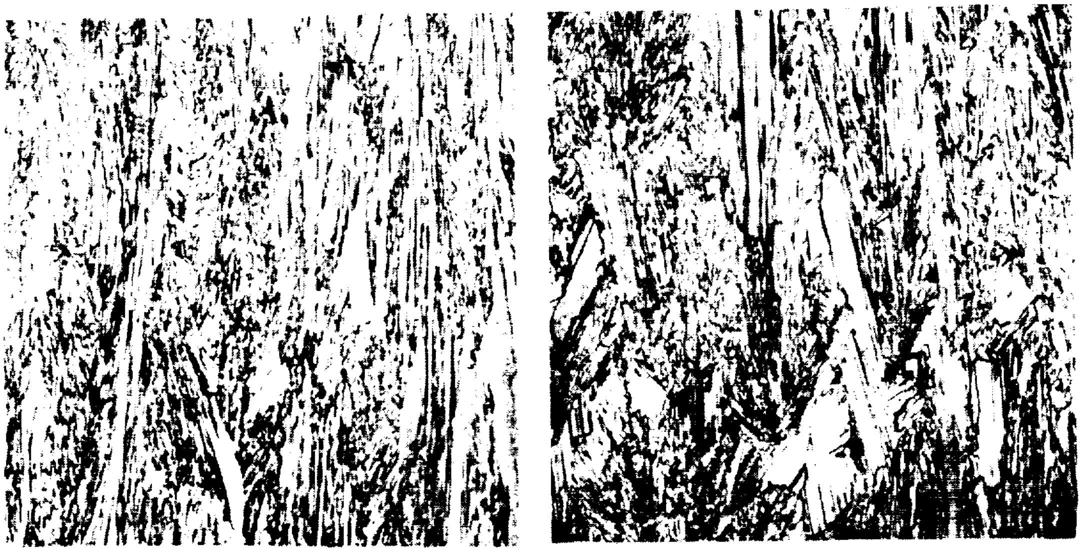
Deposit Chemistry:

Oxygen	9 ppm
Carbon	<5 ppm
Hydrogen	7.6 ppm
Sulfur	<5 ppm

Figure 7. Data for Acid Copper Sulfate Deposits from Electrolytes with D^+ Xylose.and Other Organic Additives Demonstrating Low Oxygen Content

EFFECT OF D^+ XYLOSE CONCENTRATION ON MECHANICAL PROPERTIES AND MICROSTRUCTURE OF ADDITIVE-FREE ACID COPPER SULFATE DEPOSITS (WITH 50 TO 100 PPM CHLORIDE ION)

Chemistry	**Sample 4-NA-03**	**Sample 5-NA-03**
$CuSO_4\,5H_2O$	229.9 G/L	225.4 G/L
H_2SO_4	72.6 G/L	68.1 G/L
Chloride Ion, By Weight	81 PPM	61 PPM
D^+ Xylose	0.7 G/L	0.7 G/L
Operating Parameters		
Bath Temperature	26.7°C	26.7°C
Periodic Current Reversal, Forward Time	8 Seconds	8 Seconds
Periodic Current Reversal, Forward CD	4.84 A/dm^2	4.84 A/dm^2
Periodic Current Reversal, Reverse Time	4 Seconds	4 Seconds
Periodic Current Reversal, Reverse CD	4.84 A/dm^2	4.84 A/dm^2
Electroyte Agitation Code	CN-4	CN-4
Continuous Filtration	20 Microns	20 Microns
Deposition Time, Hours	97.00	96.00
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	46.85	44.39
Yield Strength, ksi	25.56	23.76
Elongation, % in 5.08 cm	30.0	27.5
Hardness, Vickers 100 g Load	Not Determined	105
Thickness, cm	0.137	0.184
Microstructures (Magnification 100X)		



Sample 4-NA-03

Sample 5-NA-03

Figure 8. Data for Acid Copper Sulfate Deposits from Electrolytes with D^+ Xylose.

specimens from the mildly alkaline pyrophosphate bath and the acid copper sulfate type baths have been shown to produce very similar mechanical properties that would be considered acceptable for providing a baseline standard for measuring improvements sought in the subsequent tasks of this program. Use of the acid copper sulfate bath is preferred from a standpoint of operational ease. The acid sulfate bath requires the presence of chloride ion in the amount of 50 to 100 ppm by weight to obtain good mechanical properties and microstructures. The use of periodic current reversal appears to enhance ability to produce thick electroforms of copper with uniform mechanical properties and microstructures. Use of D^+ xylose to reduce oxygen content of the deposit does not affect mechanical properties or microstructure. The D^+ xylose appears to reduce oxygen content in the acid copper deposits, even when other organic additives are present in small concentrations. However, it has also been shown in prior Phase I work that low oxygen contents are obtained when proper bath purity and anode operation controls are maintained.

From this task it has been shown that good mechanical properties can be produced over a wide range of thicknesses from standard acid copper sulfate baths containing very small chloride ion additions. Use of periodic current reversal (PR) enhances the ability to produce very thick electroforms. From the test data presented in this task, it is possible to establish a baseline for room temperature mechanical properties of copper electrodeposited at 4.94 A/dm^2 from non-additive baths as follows:

Bath Type:	Conventional Acid Sulfate		Conventional Acid Sulfate With PR	
Chloride Ion, By Wt.:	Under 50 PPM	Over 50 PPM	Under 50 PPM	Over 50 PPM
Data Source:	Reference 3	Reference 4	This Report	This Report
Sample No:	Cu2-H3, 30°C, 4 A/dm^2	Panel 2, 32°C, 4.8 A/dm^2	4-NA-01	4-NA-02
Ultimate Strength, ksi	34	41	30	46
Yield Strength, ksi	11	20	10	28
Elong. In 5 cm, %	46	29	23	22

Elevated temperature performance of this baseline copper electrodeposit will be discussed in later tasks where mechanical property improvement comparisons are to be made.

2. TASK II - DEPOSITION OF COPPER WITH IMPROVED PROPERTIES FROM ADDITIVE CONTAINING ACID COPPER BATHS

2.0 Background

Safranek(7) reported that copper electrodeposits have been produced from copper cyanide baths and from acid and alkaline copper sulfate baths (with organic amine additives) having tensile strengths ranging from 60 to 93 ksi and yield strengths from 38 to 57 ksi. However, the high strength deposits exhibited low elongation, generally less than five percent in a 5.08 cm gauge length. His summary of high strength copper data is found in Table XI.

TABLE XI - PROPERTIES OF HIGH-STRENGTH ELECTRODEPOSITED COPPER(7)

Tensile Strength Ksi	Yield Strength Ksi	Elongation in 5.08 Cm %	Internal Stress Ksi	Deposit Density G/cc	Bath Temperature °C	Current Density A/dm^2	Plating Bath
71	43	7	7.1	8.913	30	5	Acid Cu Sulfate (1)
93	Not Reported	3					Acid Cu Sulfate(2)
81	Not Reported	4	7.8	8.913	60	2	Copper Cyanide(3)
66	Not Reported	18	7.4	8.908	60	1	Copper Cyanide(3)
86	57	10	5.1	8.917	80	6	Copper Cyanide(4)
60	44	4	-6.0	8.906	55	4	Acid Cu Sulfate(5)
69	41	4	-4.0	Not Reported	55	2	Alk. Cu Sulfate(5)

Notes: (1) 187 g/l Copper Sulfate, 74 g/l Sulfuric Acid, 3.5 g/l Triisopropanolamine
(2) Copper Sulfate, Molasses, Thiourea (exact composition not reported)
(3) 25 g/l CuCN, 6 g/l Free NaCN, 15 g/l Sodium Carbonate
(4) 40 g/l CuCN, 10 g/l Free NaCN, 30 g/l Sodium Carbonate, pH 11.8 to 12.8
(5) 100 g/l Copper Sulfate, 20 g/l Ammonium Sulfate, 80 ml/l Ethylenediamine, 4 ml/l Ammonia

Safranek noted that these strengths were higher than the 50 ksi normally found in hard, cold-rolled copper sheet and were partially due to its extremely fine grain size. From the data in Table XI, one would expect deposits from the copper cyanide baths to be of interest to electroformers. It should be noted that such baths operate at much higher temperatures than the acid sulfate baths, and this would have a serious impact on the use of waxes employed in recess passages such as coolant channels in thrust chambers. The toxicity of large cyanide baths needed in most electroforming shops would make such solutions undesireable environmentally and from a safety standpoint. This investigator knows of no cyanide bath being used for electroforming of engineering (structural) hardware in this country.

Lamb, Johnson, and Valentine(3) included organic and inorganic additives to various copper electrolytes studied prior to 1970. Their evaluation of the effects of these additives on mechanical properties and microstructures was too extensive to reproduce herein; however, reference to their results, where appropriate, will be made throughout this report. Since they provided mechanical property test data for room temperature testing before and after annealing at various temperatures, test data for "as deposited" samples pulled at elevated temperatures, fatigue test data, and microstructural information, their results shall be used as a standard for comparison and evaluation of the results achieved in the present studies. Table XII summarizes information for deposits from additive baths warranting continued study in the present work. Bath symbols used in this table refer to electrolyte formulations defined in Table II of Task I.

TABLE XII - RESULTS FROM LAMB, JOHNSON, AND VALENTINE STUDIES OF COPPER DEPOSITS FROM ACID SULFATE BATHS CONTAINING ADDITIVES(3)

Panel Number	Bath Symbol	Addition Agent Name	Addition Agent Concentration, g/l or Other Variable	Bath Temp. °C	Current Density A/dm²	Tensile Strength Ksi	Yield Strength Ksi	Elongation In 5.08 Cm %	Knoop Hard., 200g Load, Kg/mm²
166	Cu2-H2	SeO_2	0.0001g/l Se	30	2	47	17	21	123
172	Cu2-H2	SeO_2	0.0010 g/l Se	30	2	44	16	24	108
064	Cu2-H1	Gelatin	0.003	30	2	40	19	26	91
065	Cu2-H1	Gelatin	0.003	30	2	41	22	23	88
066	Cu2-H2	Gelatin	0.003	30	2	45	28	8	82
081	Cu2-H3	Gelatin	0.01	30	2	53	31	10	131
083	Cu2-H3	Gelatin	0.10	30	2	40	34	0.4	148
068	Cu2-H1	PSA	1.0	30	2	36	15	31	97
069	Cu2-H2	PSA	0.7	30	2	33	11	35	73
070	Cu2-H2	PSA	1.0	30	2	36	15	34	99
073	Cu2-H3	PSA	1.0	20	2	40	18	28	93
071	Cu2-H3	PSA	1.0	30	2	34	13	32	84
071B	Cu2-H3	PSA	1.0	30	2	36	14	34	90
072	Cu2-H3	PSA	1.0	40	2	30	9	23	88
076	Cu2-H3	PSA	1.0	40	4	33	12	31	87
077	Cu3-H3	PSA	1.0	30	2	34	13	32	82
086	Cu2-H3	Thiourea	0.005	30	2	20	6	10	70
088	Cu2-H3	Thiourea	0.015	30	2	28	12	9	76
216	Cu2-H3	Thiourea +NDS	0.015 Thiourea 0.5 NDS	30	2	39	13	20	99
093	Cu2-H3	TIPA	3.5	30	2	41	19	26	109
108	Cu2-H3	TIPA	3.5	30	2	39	19	7	129
337	Cu2-H3	TIPA	3.5	30	5	71	43	7	144
219	Cu2-H3	Eth. Alc.+ Molasses	0.3 2.0	30	2	27	13	9	61
160	Cu2-H3	Beta-NQ	0.1	30	2	36	14	8	119
091	Cu2-H3	NDS	1.8	30	2	31	9	29	67

Note: PSA = Phenolsulfonic Acid; NDS = 1,5-Naphthalenedisulfonic Acid; Beta-NQ = Beta-Naphthoquinoline; TIPA = Triisopropanolamine

Other additives were included in the studies of Lamb, Johnson, and Valentine; however, the results did not meet the objectives sought in the present work. It should be pointed out that these investigators did not use acid copper sulfate electrolytes with small chloride additions. This may have led to the generally disappointing yield strengths observed in their deposits. The hardnesses were expressed in Knoop values while hadnesses in the present studies were expressed in Vickers using a 100 gram load (unless described otherwise). On the basis of the above data, it was apparent that triisopropanolamine (TIPA) was a beneficial additive for increasing yield strength and tensile strength. Gelatin also had a beneficial effect on mechanical properties, but good ductility required a low concentration of this additive. The use of very small amounts of selenium dioxide improved mechanical properties, particularly tensile strengths. Safranek suggested that this was due to grain refinement.

Based on the general correlation of high hardness to high mechanical strength, the selection of acid copper sulfate electrolytes with selenium dioxide, gelatin, and TIPA for continued study was made. To this list was added a series of organic amines, polyethylene glycol ethers, polyoxyethylene glycol ethers, and a few substances recommended in a screening study performed under subcontract by Southern Illinois University.

2.1 Screening Tests at Southern Illinois University at Carbondale (SIU)

Dr. S. Lalvani, Jaw-Ching Kang, and several graduate students performed numerous acid copper sulfate deposition studies using several organic additives suggested by the Principal Investigator of this study. Since a large number of test deposits were to be made using different additives and operating conditions, one liter baths were employed. New baths were used for each additive, and the use of small baths led to a smaller volume of wastes to be dispositioned. Cylindrical 304L Stainless Steel cathodes were used without rotation. Solution agitation was maintained by a magnetic stir bar. Since the test samples were too small to accommodate mechanical property testing, measurement of expected mechanical property performance was based on Knoop hardness at various indentor loads. Although this is not always indicative of the mechanical strength of a material, it does provide a rapid method of screening for further evaluation.

As a baseline, the Principal Investigator provided test specimens of known mechanical properties from which Knoop hardness values (KHV) could be determined at the test loads being employed by SIU. These two specimens were electroformed in Phase I studies using large production tanks. Sample Ph-I-A was produced from an acid copper sulfate solution containing about 0.2 g/l of D^+ xylose and 1g/l of triisopropanolamine (TIPA). Sample Ph-I-B was produced from a similar bath without the TIPA. TIPA is a tertiary amine having known ability to refine grain size in electrodeposited copper. It was found that surface roughness affected hardness results which led to testing after polishing each sample. Results are shown in Table XIII. Both production baths contained chloride ion at a concentration between 50 and 100 ppm by weight.

TABLE XIII - KNOOP HARDNESSES AND MECHANICAL PROPERTIES OF ACID COPPER SULFATE DEPOSITS SUPPLIED BY THE PRINCIPAL INVESTIGATOR

Sample Number	Additives Name	G/l	Ultimate Strength Ksi	Yield Strength Ksi	Elongation In 5.08 cm %	Knoop Hardness Polished to 1 µm Finish 10 g	25 g	50 g	Knoop Hardness Polished to 0.05 µm Finish 10 g	25 g	50 g
Ph-I-A	D^+ Xylose	0.2	88.98	70.49	13	-	118	132	77	112	128
	TIPA	1.0									
Ph-I-B	D^+ Xylose	0.2	50.42	30.30	25	-	109	116	70	87	94

Sample Ph-I-A deposited at 2.15 A/dm^2, conventional dc, 26°C bath temperature.

Sample Ph-I-B deposited at 2.15 A/dm^2, periodic current reversal (20 sec forward, 4 sec reverse), and 31°C bath temperature.

Using a one liter acid copper sulfate bath with no chlorides and no organic additives, SIU deposited a pure copper of 590 μm thickness having Knoop hardnesses of 95 and 110 for 25g and 50g loads, respectively, and a surface polished to 1 μm finish. Correlation graphs were developed by SIU for conversions of Knoop hardness numbers between the 25 gram load tests and the 50 gram load tests. Metallographic examination disclosed a fine grain structure at the start of plating, but a coarser grain developed with increasing thickness. This would indicate that the presence of chloride ion and periodic current reversal contribute to more uniform grains and hardnesess in copper from acid sulfate baths without additives.

Early SIU studies compared the hardening effects of the $D^+$and D^- stereoisomers of xylose on acid copper sulfate deposits. Although D^+ xylose has been used for many years by a prominent aerospace manufacturer to reduce oxygen content in copper electrodeposits, no reported evaluation of the D^- xylose stereoisomer has been made. In this series of deposition studies, SIU also compared the relative effects adding TIPA to separate electrolytes containing either D^+ xylose or D^- xylose. These results are reported in Table XIV. With TIPA not present it appears that D^- xylose promotes higher hardnesses than does equivalent concentrations of the D^+ xylose stereoisomer. The addition of TIPA appears to override this difference. These baths contained 200 g/l of copper sulfate and 75 g/l of sulfuric acid.

TABLE XIV - HARDNESS STUDIES ON COPPER DEPOSITS FROM ACID SULFATE BATHS CONTAINING D^+ AND D^- XYLOSE STEREOISOMERS OR SIMILAR STEREOISOMERS WITH TRIISOPROPANOLAMINE (TIPA)

SIU Sample Number	D^+ Xylose Concentrat. g/l	D^- Xylose Concentrat. g/l	TIPA Concentrat. g/l	Current Density A/dm^2	Deposit Thickness μm	Surface Polish μm	Knoop Hardness Numbers Indentor Load of: 25 g	50 g
009	0.0	0.2	0.0	5.0	250	1.0	127	148
012	0.2	0.0	0.0	5.0	160	1.0	94	99
036	0.0	0.2	0.0	5.0	220	0.05	110	134
037	0.2	0.0	0.0	5.0	280	0.05	90	104
021	0.5	0.0	0.5	2.5	210	0.05	137	84
026	0.0	0.1	1.0	5.2	220	0.05	202	246
023	0.1	0.0	1.0	5.0	190	0.05	141	148
020	0.0	0.2	1.0	5.0	210	0.05	144	176
027	0.0	0.2	1.4	5.8	300	0.05	130	155
024	0.2	0.0	1.4	5.0	220	0.05	147	96
028	0.0	0.1	1.6	5.0	310	0.05	130	124
025	0.1	0.0	1.6	5.3	200	0.05	177	216

Acetaminophen was evaluated as an additive (with and without D^- xylose), and results are summarized in Table XV. The acetaminophen appeared to promote high hardness in the deposits, but the high hardnesses shown at the higher current densities may have been due to brittleness as a result of exceeding the limiting current density. This study was continued at ENI and is reported later. These baths, and all subsequent baths, contained 200 g/l copper sulfate and 75 g/l sulfuric acid unless otherwise indicated.

SIU also conducted experiments with benzocaine and hexadecyltrimethylammonium bromide and found no benefits to be derived from either. In fact, both chemicals had adverse effects on the solutions. Extensive work was performed using ethanolamine hydrochloride (EHCl), EHCl with D$^+$ xylose, and EHCl with D$^-$ xylose, Table XVI. EHCl as the only additive appears to increase copper deposit hardness when intermediate current densities are used. Increasing the current density further does not appear to improve hardness; it may actually increase brittleness. A near linear increase in hardness was noticed when current density was increased with D$^+$ xylose present at 1 g/l. Hardnesses were higher for any particular current density with the D$^+$ xylose present than without. Use of the D$^-$ xylose isomer did not result in hardness improvements; in fact, hardness decreased at current densities of 7.5 A/dm^2.

TABLE XV - EFFECTS OF ACETAMINOPHEN WITH AND WITHOUT D$^-$XYLOSE ON ACID COPPER SULFATE DEPOSIT HARDNESSES

SIU Sample Number	Acetaminophen Concentration G/l	D$^-$ Xylose Concentration G/l	Current Density A/dm^2	Deposit Thickness µm	Knoop Hardness (Normalized to 0.05 µm Surf.) 25g Load	50g Load
043	1.0	0.0	3.8	230	136	162
048	1.0	0.0	5.1	320	79	56
044	1.0	0.0	6.1	290	168	171
042	1.0	0.1	7.8	320	227	200

TABLE XVI - EFFECTS OF ETHANOLAMINE HYDROCHLORIDE (EHCl) AND D$^+$ AND D$^-$ XYLOSE STEREOISOMERS ON ACID COPPER SULFATE DEPOSIT HARDNESS

SIU Sample Number	Concentrations of: ECHl G/l	D$^+$ Xylose G/l	D$^-$ Xylose G/l	Current Density A/dm^2	Deposit Thickness µm	Knoop Hardness (Normalized to 0.05 µm Surface) 25g Load
052	1.0	0.0	0.0	2.5	119	113
060	1.0	0.0	0.0	2.5	140	95
051	1.0	0.0	0.0	5.0	250	155
058	1.0	0.0	0.0	5.0	200	147
053	1.0	0.0	0.0	7.5	430	144
059	1.0	0.0	0.0	7.5	260	150
061	1.0	0.1	0.0	2.5	220	132
054	1.0	0.1	0.0	5.0	350	163
055	1.0	0.1	0.0	7.5	450	187
056	1.0	0.0	0.1	5.0	600	165
057	1.0	0.0	0.1	7.5	300	145

Triethanolamine hydrochloride (TEAHCl) was also investigated by SIU. Using this amine with no other additive, significant hardness increases were noted, even at low current densities. Increasing current density from 2.5 to 5.0 A/dm^2 increased hardness, but further increase in current density resulted in no change. This indicates there is a limiting current density above which brittle deposits result from additive entrapment and burning. Table XVII shows the plating conditions and hardness results for samples involving TEAHCl, including those with D$^+$ and D$^-$ xylose isomers as additional additives. These xylose stereoisomers did not show significant hardness improvements when used with TEAHCl in an acid copper sulfate bath containing 200 g/l of copper sulfate and 75 g/l of sulfuric acid.

The next copper deposit hardness study involved diethylenetriamine (DETA) with and without the D^+ and D^- xylose isomer additives. The effect of this organic compound on hardness was much the same as noted for most of the other amines; the hardness increased with increasing current density, Table XVIII.

TABLE XVII - EFFECTS OF TRIETHANOLAMINE HYDROCHLORIDE (TEHCl) AND THE D^+ AND D^- XYLOSE STEREOISOMERS ON ACID COPPER SULFATE BATH DEPOSIT HARDNESS

SIU Sample Number	TEAHCl Concentrat. g/l	D^+ Xylose Concentrat. g/l	D^-Xylose Concentrat. g/l	Current Density A/dm^2	Deposit Thickness µm	Surface Polish µm	Knoop Hardness Numbers (Normalized for 0.05 µm Surface):	
							10 g Load	25 g Load
066	1.0	0.0	0.0	2.5	110	0.05	111	137
069	1.0	0.0	0.0	5.0	130	0.05	123	164
072	1.0	0.0	0.0	7.5	210	0.05	123	177
067	1.0	0.1	0.0	2.5	100	0.05	127	151
071	1.0	0.1	0.0	5.0	180	0.05	104	130
073	1.0	0.1	0.0	7.5	220	0.05	124	167
068	1.0	0.0	0.1	2.5	120	0.05	101	125
070	1.0	0.0	0.1	5.0	160	0.05	111	137

TABLE XVIII - EFFECTS OF DIETHYLENETRIAMINE (DETA) AND THE D^+ AND D^- XYLOSE STEREOISOMERS ON ACID COPPER SULFATE BATH DEPOSIT HARDNESS

SIU Sample Number	DETA Concentrat. g/l	D^+ Xylose Concentrat. g/l	D^-Xylose Concentrat. g/l	Current Density A/dm^2	Deposit Thickness µm	Surface Polish µm	Knoop Hardness Numbers (Normalized for 0.05 µm Surface):	
							10 g Load	25 g Load
075	1.0	0.0	0.0	2.5	140	0.05	85	145
076	1.0	0.0	0.0	5.0	300	0.05	89	152
077	1.0	0.0	0.0	7.5	260	0.05	83	140
078	1.0	0.1	0.0	2.5	180	0.05	60	104
079	1.0	0.1	0.0	5.0	220	0.05	68	112
080	1.0	0.1	0.0	7.5	270	0.05	84	154
081	1.0	0.0	0.1	2.5	150	0.05	83	144
082	1.0	0.0	0.1	5.0	260	0.05	78	120
083	1.0	0.0	0.1	7.5	270	0.05	88	167

Tetraethylene pentamine (TEPA) was the final amine investigated in one liter baths by SIU. This organic compound was of particular interest because it is highly polar and of known benefit in strengthening the surface charge of dispersion particles in copper electrolytes. Use of this substance was made in Task IV of this program. This provided an opportune time to measure the effects on acid copper deposit hardness before introducing dispersion strengthening particles. The acid copper bath was the standard 200 g/l copper sulfate, 75 g/l sulfuric acid bath (without chlorides). Operating conditions and hardness data for the TEPA and TEPA-xylose isomers are found in Table XIX. Under most operating conditions, the use of these additives in the combinations shown does not appear to significantly affect hardness. High hardnesses in the samples plated at 7.5 A/dm^2 were likely due to brittleness from the excessive current.

TABLE XIX - EFFECTS OF TETRAETHYLENE PENTAMINE (TEPA) AND D^+ OR D^- XYLOSE STEREOISOMERS ON ACID COPPER SULFATE DEPOSIT HARDNESS

SIU Sample Number	TEPA Concentrat. g/l	D^+ Xylose Concentrat. g/l	D^-Xylose Concentrat. g/l	Current Density A/dm^2	Deposit Thickness µm	Surface Polish µm	Knoop Hardness Numbers (Normalized for 0.05 µm Surface):	
							10 g Load	25 g Load
161	0.4	0.1	0.0	2.5	220	0.05	99	117
162	0.4	0.0	0.1	2.5	220	0.05	95	108
163	0.4	0.1	0.0	5.0	240	0.05	108	108
157	0.4	0.1	0.0	5.0	210	0.05	123	117
159	0.4	0.0	0.1	5.0	210	0.05	100	122
158	0.4	0.1	0.0	7.5	230	0.05	244	179
164	0.4	0.1	0.0	7.5	220	0.05	120	112
160	0.4	0.0	0.1	7.5	210	0.05	164	140

2.2 Additive Studies at Electroformed Nickel Using 100 Liter Baths

Three 100 liter acid copper sulfate baths were used concurrently at ENI to further evaluate the screening tests performed by SIU and to evaluate additional organic additives. These tanks and their support equipment were described in Task I and illustrated in Figure 3. Each electrolyte contained chloride ion in a concentration of between 50 and 100 ppm by weight. Each electrolyte was reused after each series of studies on individual additives.

At the end of each study, the electrolyte was treated with 30 percent by weight hydrogen peroxide to destroy the prior organic additive. Reaction time was usually overnight with continuous solution circulation. The bath was then heated to 60°C for one hour to drive off any excess peroxide. It was then carbon treated through a 6.8 kg carbon charge for two to three days. During this period the bath was cooling to ambient temperature. The carbon charge was replaced and treatment continued. The carbon filtration system was replaced by a filtration chamber containing 20 micron polypropylene filters. As a general rule, the successful removal of organics was accompanied by a color and clarity of the acid copper electrolyte that was easy to distinguish. The purified bath was of a lighter blue and very translucent. The organic containing baths were a deep aquamarine color with little translucence. Carbon treatment was probably in excess to insure bath purity between studies.

Use of additives to enhance mechanical properties in electrodeposited metals and alloys is of little value if some means of measuring the useful bath life of such agents can not be found. A means of such measurement was introduced in these studies by ENI. Where an additive, or combination of additives, appeared to promote improved mechanical properties, a series of consecutive specimens were electrodeposited to sufficient thicknesses to cause a very large number of ampere-hours of plating to be accumulated. Each specimen was tested for mechanical properties. Since the accumulated ampere-hours for each sequential specimen and the bath volume was known, it was possible to relate mechanical property performance with accrued ampere-hours per liter of electrolyte. This may prove more desireable for control in production facilities, since analytical measurements of the organics present would be expensive and difficult due to the possibility of breakdown products. If mechanical property measurements might cause production delays, at least the hardness values can be easily checked from independent samples run in the tank during production, and these can be tracked against accrued ampere-hours.

2.3 Studies Using Selenium Dioxide in Acid Copper Sulfate Electroyltes

Selenium dioxide was the only additive in Task II that was not an organic compound. Safranek(7) characterized the effects of selenium on acid sulfate copper deposits as increasing mechanical properties while decreasing grain size. This warranted examining this additive in the present studies. Once added to the bath, it is difficult (if at all possible) to remove. It is probable that it could eventually be removed by long term electrolyzing, but this would be an expensive and time consuming task. The effects of this compound on mechanical properties was studied in the same manner as with organics

2.3.1 Acid Copper Sulfate Baths With Selenium and 50 to 100 PPM Chloride Ion

One of the 100 liter acid copper sulfate facilities was adjusted to contain 71 ppm by weight of chloride ion. Selenium dioxide was added to a concentration of 0.00015 g/l. A series of mechanical property test panels was electroformed using various combinations of bath temperature, current density, and periodic current reversal timing. All test panels measured 15.24 cm by 19.05 cm to permit machining of at least four useful tensile bar specimens. This size was used throughout Task II in order to provide a uniform standard of comparison and to accumulate significant ampere-hours usage per unit of bath volume. Mechanical property test data for these specimens is found in Table XX. Metallographic examination of the various samples (Figures 9a, 9b, and 9c) revealed very fine

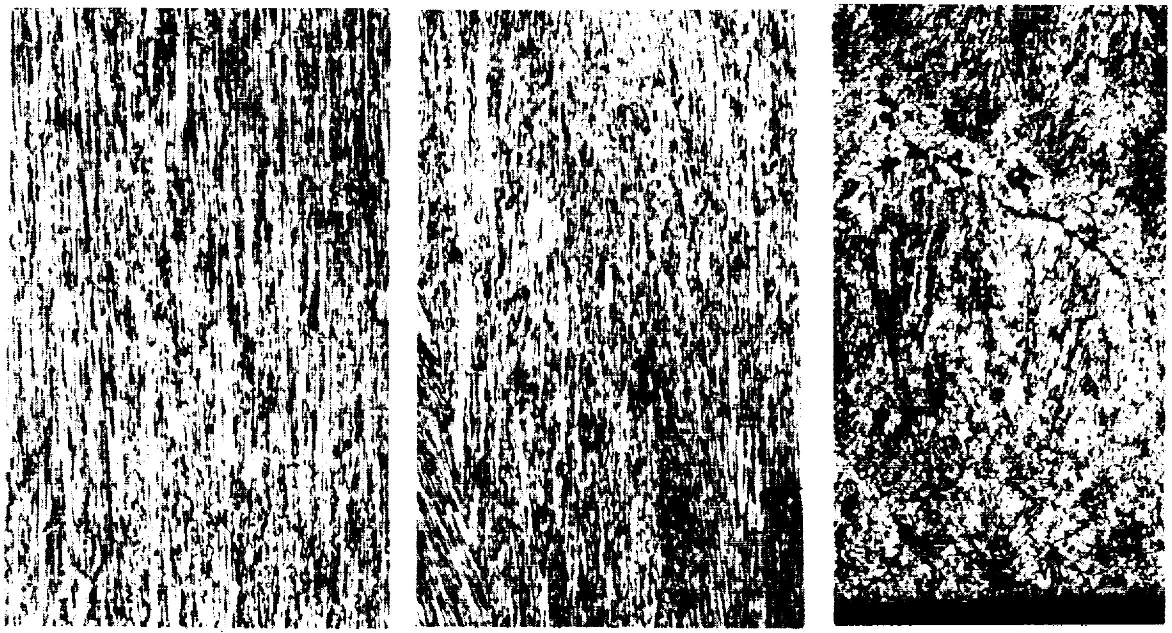
TABLE XX - MECHANICAL PROPERTIES OF DEPOSITS FROM ACID COPPER SULFATE BATHS WITH OPTIMUM CHLORIDE ION CONTENT AND 0.00015 G/L OF SELENIUM DIOXIDE

ENI Sample Number	Selenium Dioxide (g/l)	Bath Temp. (°C)	Current Density (A/dm^2)	PR Timing		Mechanical Properties			Vickers Hardness Number 100 g Load
				Forward (Sec)	Reverse (Sec)	Ult. Str. Ksi	Yield Str. Ksi	Elongation % in 5.08 Cm	
3-SE-01	0.00015	26.7	4.84	8	4	48.96	28.63	18.5	107
3-SE-02	0.00015	26.7	4.84	12	4	49.21	26.36	21.0	112
3-SE-03	0.00015	32.2	4.84	8	4	42.25	22.50	8.5	109
3-SE-04	0.00015	32.2	4.84	12	4	49.02	25.91	25.0	116
3-SE-05	0.00015	26.7	6.45	8	4	51.32	30.65	26.5	107
3-SE-06	0.00015	26.7	6.99	8	4	29.65	27.60	4.0	100
3-SE-07	0.00015	26.7	6.45	12	4	50.26	29.74	10.5	114
3-SE-08	0.00015	26.7	4.84	80	40	33.97	25.30	4.0	105
3-SE-09	0.00015	26.7	6.99	80	40	Too Brittle for Testing			

EFFECT OF SELENIUM DIOXIDE ADDITIONS ON MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS FROM ELECTROLYTES WITH 50 TO 100 PPM BY WEIGHT CHLORIDE ION

Chemistry	**Sample 3-SE-01**	**Sample 3-SE-05**	**Sample 3-SE-06**
$CuSO_4 \cdot 5H_2O$	217.9 g/l	216.4 g/l	211.2 g/l
H_2SO_4	56.2 g/l	66.7 g/l	68.1 g/l
Chloride Ion, By Weight	71 ppm	71 ppm	71 ppm
Selenium Dioxide	0.00015 g/l	0.00015 g/l	0.00015 g/l
Operating Parameters			
Bath Temperature	26.7°C	26.7°C	26.7°C
Periodic Current Reversal, Forward Time	8 Seconds	8 Seconds	8 Seconds
Periodic Current Reversal, Forward CD	4.84 A/dm^2	6.45 A/dm^2	6.99 A/dm^2
Periodic Current Reversal, Reverse Time	4 Seconds	4 Seconds	4 Seconds
Periodic Current Reversal, Reverse CD	4.84 A/dm^2	6.45 A/dm^2	6.99 A/dm^2
Electrolyte Agitation Code (Page 13)	CN-4	CN-4	CN-4
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	72.0	54.5	48.5
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	48.96	51.32	29.65
Yield Strength, ksi	28.63	30.65	27.60
Elongation, % in 5.08 cm	18.5	26.5	4.0
Hardness, Vickers 100 g Load	107	107	100
Thickness, cm	0.150	0.141	0.199

Microstructures (Magnification 100X)



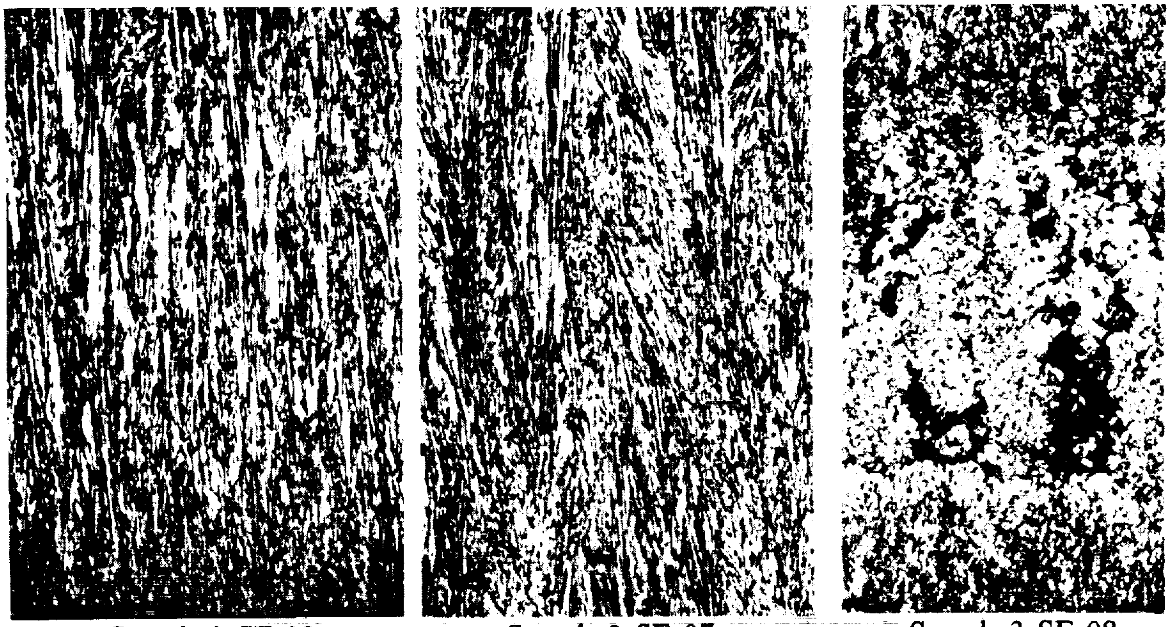
Sample 3-SE-01 Sample 3-SE-05 Sample 3-SE-06

Figure 9a. Data for Acid Copper Sulfate Deposits from Electrolytes with 50 to 100 PPM Chloride Ion and 0.00015 g/l of Selenium Dioxide Using Periodic Current Reversal.

EFFECT OF SELENIUM DIOXIDE ADDITIONS ON MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS FROM ELECTROLYTES WITH 50 TO 100 PPM BY WEIGHT CHLORIDE ION

Chemistry	**Sample 3-SE-02**	**Sample 3-SE-07**	**Sample 3-SE-08**
$CuSO_4 \cdot 5H_2O$	218.7 g/l	216.4 g/l	192.5 g/l
H_2SO_4	56.9 g/l	68.1 g/l	83.9 g/l
Chloride Ion, By Weight	71 ppm	71 ppm	71 ppm
Selenium Dioxide	0.00015 g/l	0.00015 g/l	0.00015 g/l
Operating Parameters			
Bath Temperature	26.7°C	26.7°C	26.7°C
Periodic Current Reversal, Forward Time	12 Seconds	12 Seconds	80 Seconds
Periodic Current Reversal, Forward CD	4.84 A/dm^2	6.45 A/dm^2	4.84 A/dm^2
Periodic Current Reversal, Reverse Time	4 Seconds	4 Seconds	40 Seconds
Periodic Current Reversal, Reverse CD	4.84 A/dm^2	6.45 A/dm^2	4.84 A/dm^2
Electrolyte Agitation Code (Page 13)	CN-4	CN-4	CN-4
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	30.0	48.5	71.0
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	49.21	50.26	33.97
Yield Strength, ksi	26.36	29.74	25.30
Elongation, % in 5.08 cm	21.0	26.5	4.0
Hardness, Vickers 100 g Load	112	114	105
Thickness, cm	0.089	0.199	0.140

Microstructures (Magnification 100X)



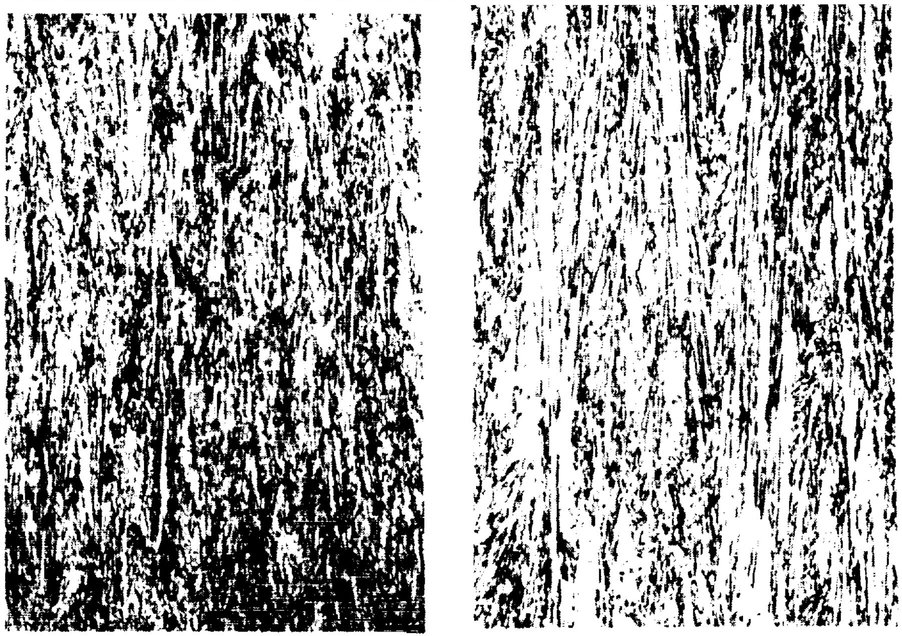
Sample 3-SE-02 Sample 3-SE-07 Sample 3-SE-08

Figure 9b. Data for Acid Copper Sulfate Deposits from Electrolytes with 50 to 100 PPM Chloride Ion and 0.00015 g/l of Selenium Dioxide Using Periodic Current Reversal.

EFFECT OF SELENIUM DIOXIDE ADDITIONS ON MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS FROM ELECTROLYTES WITH 50 TO 100 PPM BY WEIGHT CHLORIDE ION

Chemistry	**Sample 3-SE-03**	**Sample 3-SE-04**
$CuSO_4 \cdot 5H_2O$	216.4 g/l	213.4 g/l
H_2SO_4	69.6 g/l	68.1 g/l
Chloride Ion, By Weight	71 ppm	71 ppm
Selenium Dioxide	0.00015 g/l	0.00015 g/l
Operating Parameters		
Bath Temperature	32.2°C	32.2°C
Periodic Current Reversal, Forward Time	8 Seconds	12 Seconds
Periodic Current Reversal, Forward CD	4.84 A/dm^2	4.84 A/dm
Periodic Current Reversal, Reverse Time	4 Seconds	4 Seconds
Periodic Current Reversal, Reverse CD	4.84 A/dm^2	6.45 A/dm^2
Electrolyte Agitation Code (Page 13)	CN-4	CN-4
Continuous Filtration	20 Microns	20 Microns
Deposition Time, Hours	53.0	48.0
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	42.25	49.02
Yield Strength, ksi	22.50	25.91
Elongation, % in 5.08 cm	8.5	25.0
Hardness, Vickers 100 g Load	109	116
Thickness, cm	0.109	0.144

Microstructures (Magnification 100X)



Sample 3-SE-03

Sample 3-SE-04

Figure 9c. Data for Acid Copper Sulfate Deposits from Electrolytes with 50 to 100 PPM Chloride Ion and 0.00015 g/l of Selenium Dioxide Using Periodic Current Reversal.

columnar grain structures, much finer than that seen in the conventional specimens electrodeposited with periodic current reversal, but without selenium dioxide in the bath. Although the columnar grain structures of deposits from selenium containing baths (Figures 9a, 9b, and 9c) appear finer than those of specimens from comparable baths without selenium dioxide (Figure 5), there was only a slight improvement in mechanical properties in the former. Increasing the current density from 4.84 to 6.45 A/dm^2 improved yield strength and ductility slightly. Further increases in current density led to brittleness in the deposits with internal fissures forming. Increasing bath temperature did not improve mechanical properties.

2.3.2 Acid Copper Sulfate Baths With Selenium, 50 to 100 By Weight PPM Chloride Ion, and Triisopropanolamine (TIPA)

Before committing the acid copper bath containing selenium dioxide to other studies, various amounts of triisopropanolamine were added and a series of specimens were electroformed for mechanical property evaluation. Deposition parameters and test results are summarized in Table XXI. From the data in Table XXI it appears that combining TIPA and selenium dioxide in the same bath results in an improvement in mechanical properties over those found for selenium containing baths without TIPA. However, it will later be shown that the mechanical properties in Table XXI actually reflect the effects of TIPA, and these mechanical properties are no better than those for baths with TIPA as the only additive.

TABLE XXI - MECHANICAL PROPERTIES OF DEPOSITS FROM AN ACID COPPER SULFATE BATH CONTAINING SELENIUM DIOXIDE, 50 TO 100 PPM BY WEIGHT CHLORIDE ION, AND TRIISOPROPANOLAMINE (TIPA)

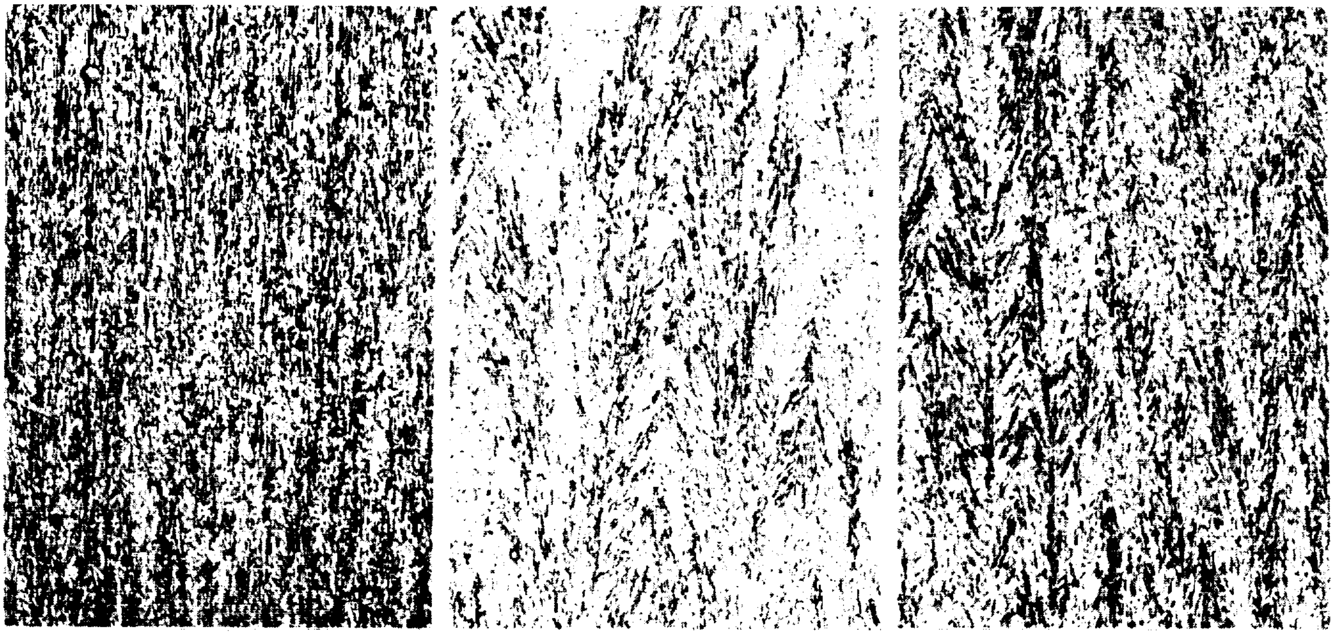
ENI Sample Number	Selenium Dioxide (g/l)	TIPA Conc. (g/l)	Bath Temp. (°C)	Current Density (A/dm^2)	Accum. Amp-Hrs Per Liter	Deposit Thickness (Cm)	Mechanical Properties Ult. Str. Ksi	Yield Str. Ksi	Elongation % in 5.08 Cm	Vickers Hardness Number 100 g Load
3-TSe-1	0.00015	2.0	26.7	2.15	3.00	0.128	54.70	37.24	18.5	119
3-TSe-2	0.00015	2.0	26.7	4.84	13.35	0.482	58.91	46.93	5.5	128
3-TSe-3	0.00015	2.0	26.7	4.84	17.44	0.177	63.84	46.08	4.5	132
3-TSe-4	0.00015	5.0	26.7	2.15	20.51	0.132	58.76	42.56	20.0	113
3-TSe-5	0.00015	5.0	26.7	3.23	23.04	0.107	61.62	41.99	12.5	128
3-TSe-6	0.00015	5.0	26.7	3.23	25.64	0.107	62.38	35.85	8.0	128
3-TSe-7	0.00015	5.0	26.7	3.23	28.27	0.110	65.84	45.27	9.0	132
3-TSe-8	0.00015	5.0	26.7	3.23	30.86	0.111	64.22	42.50	9.0	132

Use of selenium dioxide with TIPA provides useful mechanical properties but not the high strengths and ductility being sought. There appears to be a fairly stable ultimate strength and yield strength value as a function of accumulated ampere-hours per liter of bath. It is noteworthy that ductility is closely related to current density with lowest elongations observed in samples deposited at the highest current densities. Grain size was fine and columnar in all specimens as can be observed in Figures 10a, 10b, and 10c. Samples 3-TSe-2 and 3-TSe-3 had grain structures having a "herringbone" pattern. This is probably current density related, since both occurrances were on samples with the highest current densities.

EFFECT OF SeO_2 AND TIPA ADDITIONS ON MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS FROM ELECTROLYTES WITH 50 TO 100 PPM BY WEIGHT CHLORIDE ION

Chemistry	**Sample 3-TSE-1**	**Sample 3-TSE-2**	**Sample 3-TSE-3**
$CuSO_4 \cdot 5H_2O$	209.7 g/l	210.4 g/l	213.4 g/l
H_2SO_4	59.9 g/l	59.9 g/l	68.1 g/l
Chloride Ion, By Weight	71 ppm	71 ppm	71 ppm
Selenium Dioxide	0.00015 g/l	0.00015 g/l	0.00015 g/l
Triisopropanolamine (TIPA)	2.0 g/l	2.0 g/l	2.0 g/l
Operating Parameters			
Bath Temperature	26.7°C	26.7°C	26.7°C
Current Density	2.15 A/dm^2	4.84 A/dm^2	4.84 A/dm^2
Electrolyte Agitation Code (Page 13)	CN-4	CN-4	CN-4
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	48.0	73.25	29.0
Accumulated Ampere-Hours Per Liter	3.00	13.35	17.44
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	54.70	58.91	63.84
Yield Strength, ksi	37.24	46.93	46.08
Elongation, % in 5.08 cm	18.5	5.5	4.5
Hardness, Vickers 100 g Load	119	128	132
Thickness, cm	0.128	0.482	0.177

Microstructures (Magnification 100X)



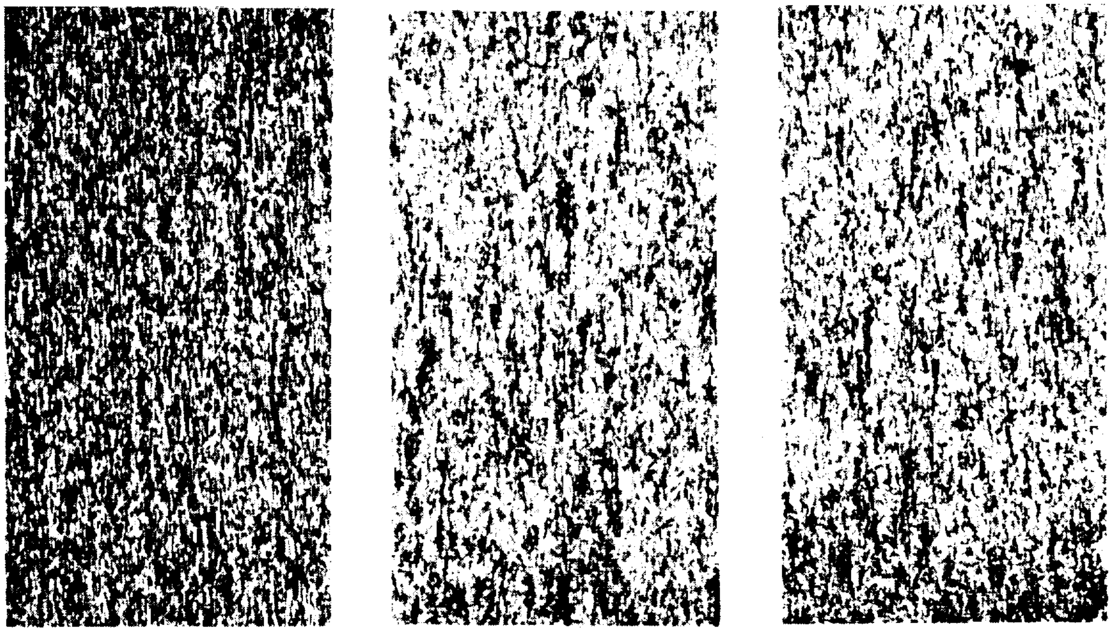
Sample 3-TSE-1 Sample 3-TSE-2 Sample 3-TSE-3

Figure 10a. Data for Acid Copper Sulfate Deposits from Electrolytes with 50 to 100 PPM Chloride Ion, 2 g/l TIPA, and 0.00015 g/l of Selenium Dioxide.

EFFECT OF SeO_2 AND TIPA ADDITIONS ON MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS FROM ELECTROLYTES WITH 50 TO 100 PPM BY WEIGHT CHLORIDE ION

Chemistry	**Sample 3-TSE-4**	**Sample 3-TSE-5**	**Sample 3-TSE-6**
$CuSO_4 \cdot 5H_2O$	214.9 g/l	220.2 g/l	214.9 g/l
H_2SO_4	68.9 g/l	68.9 g/l	67.4 g/l
Chloride Ion, By Weight	71 ppm	71 ppm	71 ppm
Selenium Dioxide	0.00015 g/l	0.00015 g/l	0.00015 g/l
Triisopropanolamine (TIPA)	5.0 g/l	5.0 g/l	5.0 g/l
Operating Parameters			
Bath Temperature	26.7°C	26.7°C	26.7°C
Current Density	2.15 A/dm^2	3.23 A/dm^2	3.23 A/dm^2
Electrolyte Agitation Code (Page 13)	CN-4	CN-4	CN-4
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	48.75	27.25	27.67
Accumulated Ampere-Hours Per Liter	20.51	23.04	25.64
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	58.76	61.62	62.38
Yield Strength, ksi	42.56	41.99	35.85
Elongation, % in 5.08 cm	20.0	12.5	8.0
Hardness, Vickers 100 g Load	113	128	128
Thickness, cm	0.132	0.107	0.107

Microstructures (Magnification 100X)



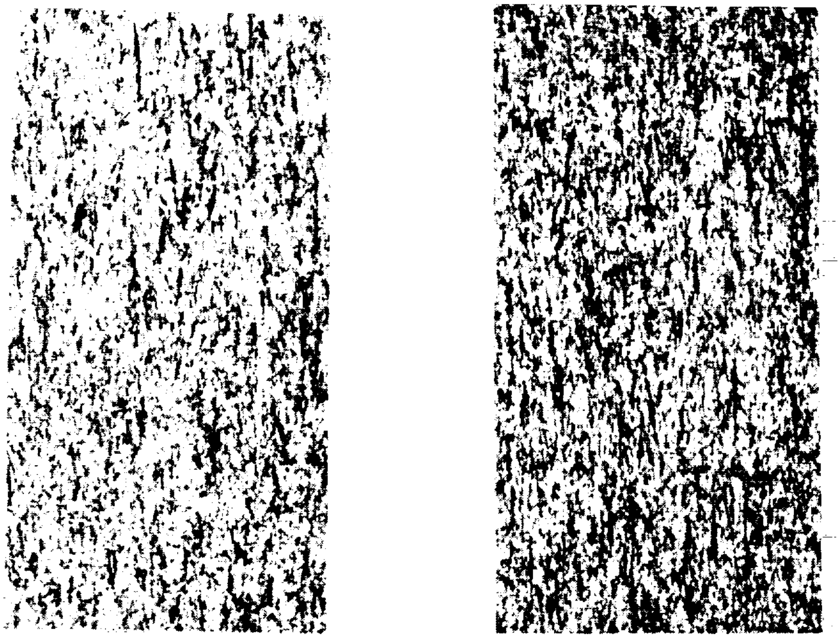
Sample 3-TSE-4 Sample 3-TSE-5 Sample 3-TSE-6

Figure 10b. Data for Acid Copper Sulfate Deposits from Electrolytes with 50 to 100 PPM Chloride Ion, 5 g/l TIPA, and 0.00015 g/l of Selenium Dioxide.

EFFECT OF SeO_2 AND TIPA ADDITIONS ON MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS FROM ELECTROLYTES WITH 50 TO 100 PPM BY WEIGHT CHLORIDE ION

Chemistry	**Sample 3-TSE-7**	**Sample 3-TSE-8**
$CuSO_4$ $5H_2O$	216.4 g/l	217.2 g/l
H_2SO_4	67.4 g/l	68.9 g/l
Chloride Ion, By Weight	71 ppm	71 ppm
Selenium Dioxide	0.00015 g/l	0.00015 g/l
Triisopropanolamine	5.0 g/l	5.0 g/l
Operating Parameters		
Bath Temperature	26.7°C	26.7°C
Current Density	3.23	3.23
Electrolyte Agitation Code (Page 13)	CN-4	CN-4
Continuous Filtration	20 Microns	20 Microns
Deposition Time, Hours	28.0	27.5
Accumulated Ampere-Hours Per Liter	28.27	30.86
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	65.94	64.22
Yield Strength, ksi	45.27	42.50
Elongation, % in 5.08 cm	9.0	9.0
Hardness, Vickers 100 g Load	132	132
Thickness, cm	0.110	0.111

Microstructures (Magnification 100X)



Sample 3-TSE-7

Sample 3-TSE-8

Figure 10c. Data for Acid Copper Sulfate Deposits from Electrolytes with 50 to 100 PPM Chloride Ion, 5 g/l TIPA, and 0.00015 g/l of Selenium Dioxide.

There appears to be a fairly stable ultimate strength and yield strength value as a function of accumulated ampere-hours per liter of bath. An examination of the photomicrographs in Figures 10a, 10b, and 10c show that all grains are fibrous columnar in nature. Good yield strengths are shown in all samples. However, as the deposition current density was increased from 2.15 A/dm^2, the elongation became progressively poor.

2.4 Task II Studies Using Organic Amines in Acid Copper Sulfate Electrolytes

According to Indira and Udupa(8), the amines and quarternary ammonium salts constitute the largest groups of cationic surface active agents. Surface active compounds have been added to plating baths to achieve a variety of effects. An important effect, of interest in this program, is the modification of the crystal size and orientation in the metal being deposited. To achieve a true strengthening of copper electrodeposits, it is expected that the grain size must be made much finer and must be of an equi-axed configuration. Although use of selenium dioxide with TIPA provided useful mechanical properties, they were not as good as those being sought in these studies. However, TIPA demonstrated that amines as additives in acid copper sulfate baths can significantly improve mechanical properties over those of similar non-additive baths. This resulted in the study of a wide variety of amines in this task to determine if further enhancement of mechanical properties might be achieved.

2.4.1 Studies Using Isopropanolamine (IPA) as an Acid Copper Sulfate Bath Additive

Isopropanolamine (IPA), a primary amine, was evaluated in a 100 liter acid copper sulfate bath containing less than 50 ppm by weight chloride ion. From prior experience with lower than normal chloride concentrations, it was expected that these samples would exhibit low yield strengths. This was not the case as shown in Table XXII. The mechanical properties of these specimens were equal to, or better than, those found for similar baths with over 50 ppm by weight chloride ion and periodically reversed current, Figure 5. Microstructures of the deposits from baths with IPA are found in Figures 11a and 11b. There is a significant difference in microstructures for those samples produced in the two different electrolytes. The initial two deposits from the bath with 1.5 g/l of IPA had very fine columnar grains perpendicular to the stainless mandrel. The deposits from the 2.0 g/l IPA bath had "spangled" grains of varied directionality. This effect was likely related to agitation of

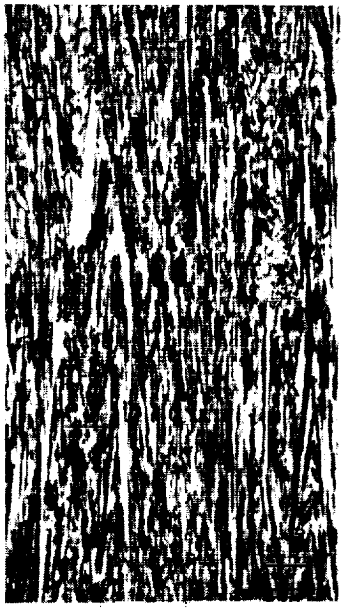
TABLE XXII - MECHANICAL PROPERTY PERFORMANCE OF ACID COPPER SULFATE DEPOSITS FROM SEPARATE ELECTROLYTES CONTAINING 1.5 G/L AND 2.0 G/L ISOPROPANOLAMINE (IPA)

ENI Sample Number	IPA Conc. (g/l)	Current Density (A/dm^2)	Bath Temp. (°C)	Accumulated Ampere-Hours Per Liter	Deposit Thickness (Cm)	Mechanical Properties Ult Str. (Ksi)	Yield Str. (Ksi)	Elongation % in 5.08 Cm	Vickers Hardness Number 100 g Load
3-IPA-01	1.5	2.15	29.4	3.02	0.135	44.80	27.56	23.0	Not Determined
3-IPA-02	1.5	3.23	29.4	7.12	0.191	48.95	30.98	22.0	Not Determined
3-IPA-10	2.0	2.15	26.7	3.31	Sample invalidated because of shield failure.				
3-IPA-11	2.0	2.15	26.7	9.47	0.241	53.68	37.68	20.0	116
3-IPA-12	2.0	2.15	26.7	15.75	0.254	51.50	33.80	18.0	116
3-IPA-13	2.0	2.15	26.7	22.16	0.254	47.80	30.14	12.5	108

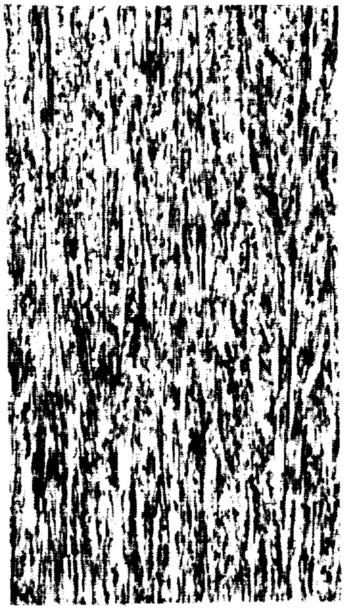
EFFECT OF ISOPROPANOLAMINE ADDITIONS ON MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS FROM ELECTROLYTES WITH LESS THAN 50 PPM BY WEIGHT CHLORIDE ION

Chemistry	**Sample 3-IPA-01**	**Sample 3-IPA-02**
$CuSO_4 \cdot 5H_2O$	226.2 g/l	232.2 g/l
H_2SO_4	68.9 g/l	68.9 g/l
Chloride Ion, By Weight	37 ppm	37 ppm
Isopropanolamine	1.5 g/l	1.5 g/l
Operating Parameters		
Bath Temperature	29.4°C	29.4°C
Current Density	2.15 A/dm^2	3.23 A/dm^2
Electrolyte Agitation Code (Page 13)	CO-1	CO-1
Continuous Filtration	20 Microns	20 Microns
Deposition Time, Hours	48.0	45.0
Accumulated Ampere-Hours Per Liter	3.02	7.12
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	44.80	48.95
Yield Strength, ksi	27.56	30.98
Elongation, % in 5.08 cm	23.0	22.0
Hardness, Vickers 100 g Load	Not Determined	Not Determined
Thickness, cm	0.135	0.191

Microstructures (Magnification 100X)



Sample 3-IPA-01



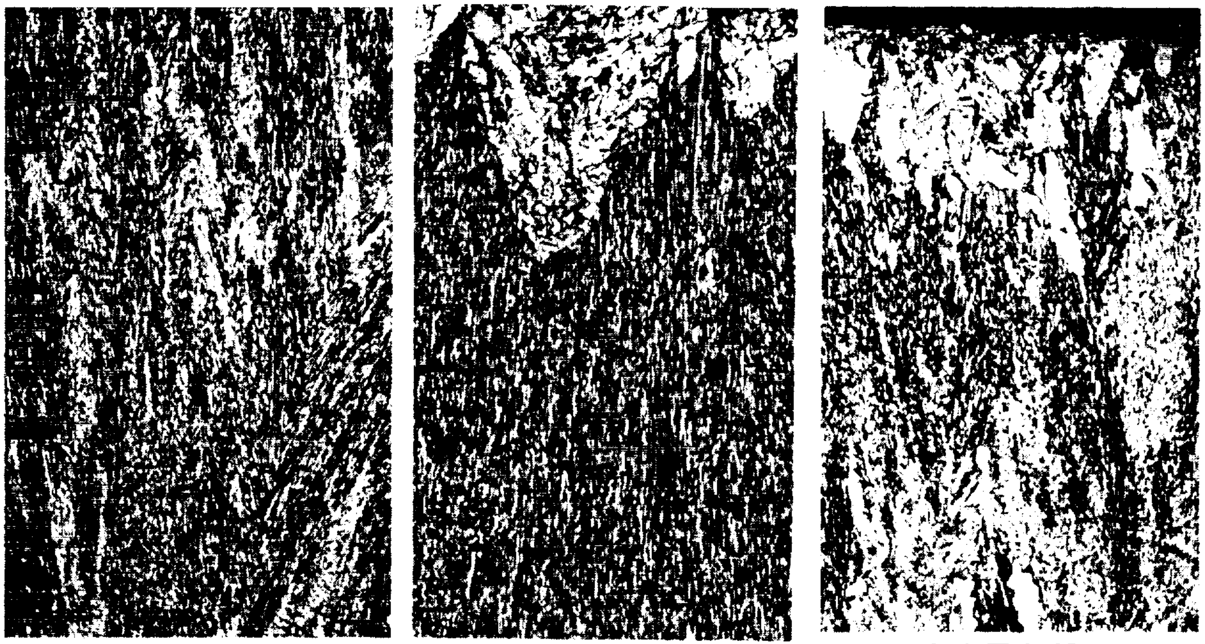
Sample 3-IPA-02

Figure 11a. Data for Acid Copper Sulfate Deposits from Electrolytes with Less Than 50 PPM by Weight of Chloride Ion and 1.5 g/l IPA.

EFFECT OF ISOPROPANOLAMINE ADDITIONS ON MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS FROM ELECTROLYTES WITH LESS THAN 50 PPM BY WEIGHT CHLORIDE ION

Chemistry	**Sample 3-IPA-11**	**Sample 3-IPA-12**	**Sample 3-IPA-13**
$CuSO_4$ $5H_2O$	232.2 g/l	226.9 g/l	220.2 g/l
H_2SO_4	67.4 g/l	75.6 g/l	73.4 g/l
Chloride Ion, By Weight	37 ppm	37 ppm	37 ppm
Isopropanolamine	2.0 g/l	2.0 g/l	2.0 g/l
Operating Parameters			
Bath Temperature	26.7°C	26.7°C	26.7°C
Current Density	2.15 A/Dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation Code (Page 13)	CO-1	CO-1	CO-1
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	97.75	99.67	101.75
Accumulated Ampere-Hours Per Liter	9.47	15.75	22.02
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	53.68	51.50	47.80
Yield Strength, ksi	37.69	33.80	30.14
Elongation, % in 5.08 cm	20.0	18.0	12.5
Hardness, Vickers 100 g Load	116	116	108
Thickness, cm	0.241	0.254	0.254

Microstructures (Magnification 100X)



Sample 3-IPA-11 Sample 3-IPA-12 Sample 3-IPA-13

Figure 11b. Data for Acid Copper Sulfate Deposits from Electrolytes with Less Than 50 PPM by Weight of Chloride Ion and 2 g/l IPA.

the solution at the cathode surface which may have been different from that on the initial panels. The latter samples also exhibited very large grains at the final surface electroformed. This might be a sign of IPA depletion below a critical level since all mechanical properties decrease sequentially from Sample 3-IPA-11 through Sample 3-IPA-13.

2.4.2 Studies Using Diisopropanolamine (DIPA) as an Acid Copper Sulfate Bath Additive

The effect of diisopropanolamine (DIPA), a secondary amine in the isopropanolamine family, on mechanical properties was evaluated in an acid copper bath containing less than 50 ppm by weight of chloride ion. The acid copper bath to which this compound was added also contained less than 50 ppm by weight of chloride ion. This particular study occurred at a time when solution agitation was still being optimized and the flow perpendicular to the cathode surface was through an open pipe about 10 cm from the flat stainless steel mandrel. The data in Table XXIII shows unexpectedly poor mechanical properties for each sample produced, even when non-optimum agitation conditions are considered. It would appear that this secondary amine does not provide grain refinement capabilities found with the primary amine (isopropanolamine) or with the tertiary amine (triisopropanolamine). The microstructures of these deposits using diisopropanolamine are found in Figure 12. Each shows an initial fine grained deposit followed by a very coarse grain such as was observed with non-additive acid copper sulfate deposits without periodic current reversal (and when chloride was under 50 ppm by weight).

TABLE XXIII - MECHANICAL PROPERTY PERFORMANCE OF ACID COPPER SULFATE DEPOSITS FROM AN ELECTROLYTE CONTAINING 1.0 G/L OR 1.5 G/L OF DIISOPROPANOLAMINE (DIPA) AND LESS THAN 50 PPM CHLORIDE ION

ENI Sample Number	IPA Conc. (g/l)	Current Density (A/dm^2)	Bath Temp. (°C)	Accumulated Ampere-Hours Per Liter	Deposit Thickness (cm)	Mechanical Properties			Vickers Hardness Number 100 g Load
						Ult Str. (Ksi)	Yield Str. (Ksi)	Elongation % in 5.08 cm	
1-DIPA-1	1.0	2.15	29.4	3.02	0.130	17.75	10.26	5.0	Not Determined
1-DIPA-2	1.5	3.23	29.4	7.48	0.092	26.53	15.54	6.0	Not Determined

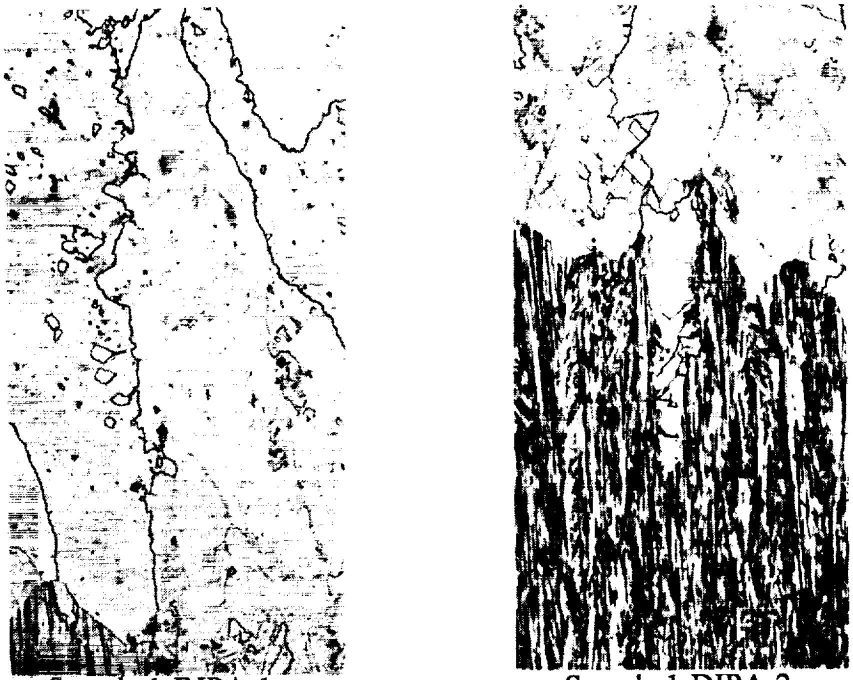
2.4.3 Studies Using Tetraethylenepentamine (TEPA) as an Acid Copper Sulfate Bath Additive

Although beaker studies at SIU using TEPA in an acid copper bath did not show significant improvement in copper deposit hardness, further studies were made at by the Principal Investigator to provide a baseline for use of this additive as a dispersion promoter in a composite deposition study required later in the program. At the time this study was conducted, electrolyte agitation effect investigations in 100 liter tanks had not been completed. For the tetraethylenepentamine (TEPA) specimens, very low levels of solution agitation were in use. This consisted of perforated electrolyte spargers from the filter pump which were aimed toward the tank bottom. This provided a slow movement of electrolyte parallel to the surface being electroformed. However, a box shield was used around the stainless steel mandrel to maintain deposit thickness uniformity. This further restricted solution flow over the cathode surface. Task IV discusses use of TEPA as a dispersion promoter for alumina particles.

EFFECT OF DIISOPROPANOLAMINE (DIPA) ADDITIONS ON MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS FROM ELECTROLYTES WITH LESS THAN 50 PPM OF CHLORIDE ION

Chemistry	**Sample 1-DIPA-1**	**Sample 1-DIPA-2**
$CuSO_4 \cdot 5H_2O$	224.7 g/l	226.2 g/l
H_2SO_4	68.1 g/l	68.9 g/l
Chloride Ion, By Weight	27 ppm	27 ppm
Diisopropanolamine	1.0 g/l	1.5 g/l
Operating Parameters		
Bath Temperature	29.4°C	29.4°C
Current Density	2.15 A/dm^2	3.23 A/dm^2
Electrolyte Agitation Code (Page 13)	CO-1	CO-1
Continuous Filtration	20 Microns	20 Microns
Deposition Time, Hours	48.0	48.0
Accumulated Ampere-Hours Per Liter	3.02	7.48
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	17.75	26.53
Yield Strength, ksi	10.26	15.54
Elongation, % in 5.08 cm	5.0	6.0
Hardness, Vickers, 100 g Load	Not Determined	Not Determined
Thickness, cm	0.130	0.092

Microstructures (Magnification 100X)



Sample 1-DIPA-1 Sample 1-DIPA-2

Figure 12. Data for Acid Copper Sulfate Deposits from Electrolytes with Less Than 50 PPM Chloride Ion and 1.0 and 1.5 g/l of Diisopropanolamine (DIPA).

TABLE XXIV - MECHANICAL PROPERTY PERFORMANCE OF ACID COPPER SULFATE DEPOSITS FROM AN ELECTROLYTE CONTAINING 0.5 G/L OF TETRAETHYLENEPENTAMINE (TEPA) AND LESS THAN 50 PPM CHLORIDE ION

ENI	TEPA	Bath	Current	PR Timing		Accumulated	Deposit	Mechanical Properties		
Sample Number	Conc. (g/l)	Temp. (°C)	Density (A/dm^2)	Forward (Sec)	Reverse (Sec)	Ampere-Hours Per Liter	Thickness (Cm)	Ult. Str. Ksi	Yield Str. Ksi	Elongation,% In 5.08 Cm
A-TEPA-1	0.5	29.4	2.15	Full*	0	4.50	0.140	35.35	18.97	14.5
A-TEPA-2	0.5	29.4	2.15	16	4	8.63	0.085	29.35	15.63	16.0
A-TEPA-3	0.5^	29.4	2.15	16	4	15.83	0.155	26.73	11.73	13.5
A-TEPA-4	0.5^	29.4	3.23	Full*	0	19.79	0.124	30.45	12.78	22.5

*Full implies that periodic current reversal was not used. ^ Indicates 0.2 g/l D$^-$ xylose also was present.

From the data in Table XXIV it is apparent that TEPA additive under poor electrolyte agitation conditions did not result in improved mechanical properties of acid copper sulfate deposits. Figures 13a and 13b show the relatively large grain sizes obtained which would account for the low yield strengths. The difference in grain size in center and edge areas (Sample A-TEPA-3, Figure 13b) would be expected to cause varied mechanical properties. These results prompted further electrolyte agitation studies under the triisopropanolamine investigation.

2.4.4 Studies Using Triisopropanolamine (TIPA) as an Acid Copper Sulfate Bath Additive

Triisopropanolamine (TIPA) was investigated in Phase I of this program and was found to cause significant grain refinement in acid copper sulfate bath deposits. Mechanical property improvements were significantly greater than found with any other additive or non-additive containing bath. In the present effort more extensive studies of this additive were made. These included (1) the effects of solution agitation on TIPA grain refinement, (2) the effects of TIPA concentration on mechanical properties, (3) the use of TIPA with other additives, and (4) life expectancies of baths with TIPA.

From the data in Table XXIV it was found that TEPA additive under low electrolyte agitation conditions would not lead to improved mechanical properties in acid copper sulfate deposits. Figures 13a and 13b show the relatively large grain sizes obtained which would account for the low yield strengths. These results prompted further electrolyte agitation studies under the triisopropanolamine investigation.

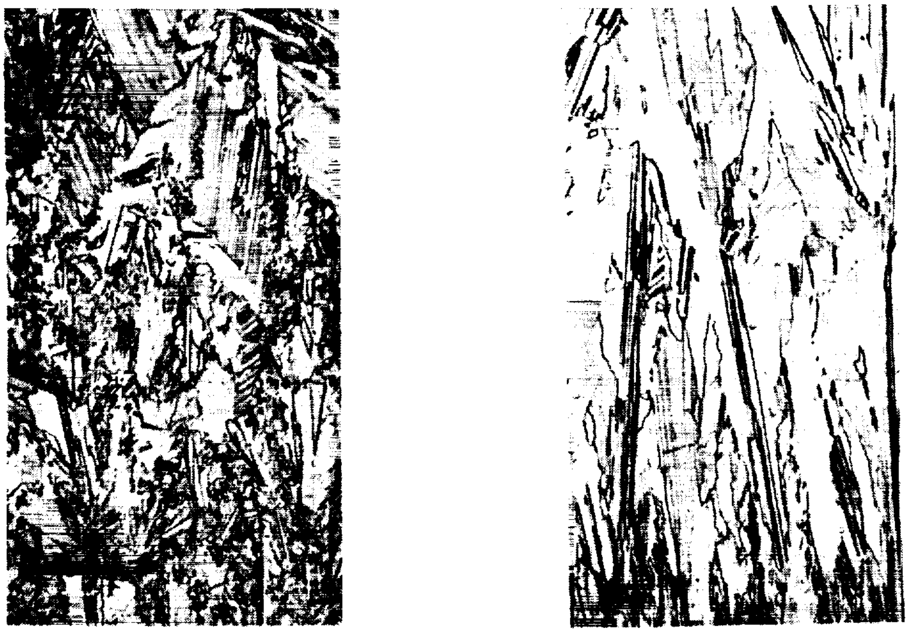
2.4.4.1 TIPA - Agitation Effects

Two 100 liter tanks, Tanks A1 and A2, were used in the initial studies on bath agitation of acid copper sulfate electrolytes with and without additives. The operating parameters and test results are summarized in Table XXV. Each tank contained less than 50 ppm by weight of chloride ion. Box shields were not used on the samples because of the remote electrolyte spray system; however, thin frame shields were applied to the mandrel to control dendrite formation. The spray system was different in each tank, Tank A1 having the least agitation. All electrolyte movement was created by the filter pump used to circulate the electrolyte through a filter in the tank weir and through a sparger

EFFECT OF TETRAETHYLENEPENTAMINE (TEPA) ADDITIONS ON MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS FROM BATHS WITH LESS THAN 50 PPM OF CHLORIDE ION

Chemistry	**Sample A-TEPA-1**	**Sample A-TEPA-2**
$CuSO_4 \cdot 5H_2O$	197.6 g/l	197.6 g/l
H_2SO_4	68.7 g/l	68.7 g/l
Chloride Ion, By Weight	37 ppm	37 ppm
Tetraethylenepentamine	0.5 g/l	0.5 g/l
Operating Parameters		
Bath Temperature	29.4°C	29.4°C
Periodic Current Reversal, Forward Time	Infinite	16 Seconds
Periodic Current Reversal, Forward CD	2.15 A/dm^2	2.15 A/dm^2
Periodic Current Reversal, Reverse Time	0 Seconds	4 Seconds
Periodic Current Reversal, Reverse CD	0.0 A/dm^2	2.15 A/dm^2
Electrolyte Agitation Code (Page 13)	B	B
Continuous Filtration	20 Microns	20 Microns
Deposition Time, Hours	72	68.85
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	35.35	29.35
Yield Strength, ksi	18.97	15.63
Elongation, % in 5.08 cm	14.5	16.0
Hardness, Vickers, 100 g Load	Not Determined	Not Determined
Thickness, cm	0.140	0.085

Microstructures (Magnification 100X)



Sample A-TEPA-1 Sample A-TEPA-2

Figure 13a. Data for Acid Copper Sulfate Deposits from Electrolytes with Less than 50 PPM Chloride Ion by Weight and 0.5 g/l of Tetraethylenepentamine (TEPA).

EFFECT OF TETRAETHYLENEPENTAMINE (TEPA) ADDITIONS ON MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS FROM BATHS WITH LESS THAN 50 PPM OF CHLORIDE ION

Chemistry	**Sample A-TEPA-3**	**Sample A-TEPA-4**
$CuSO_4 \cdot 5H_2O$	197.6 g/l	198.5 g/l
H_2SO_4	68.7 g/l	68.1 g/l
Chloride Ion, By Weight	37 ppm	37 ppm
Tetraethylenepentamine	0.5 g/l	0.5 g/l
D^- Xylose	0.2 g/l	0.2 g/l
Operating Parameters		
Bath Temperature	29.4°C	29.4°C
Periodic Current Reversal, Forward Time	16 Seconds	Infinite
Periodic Current Reversal, Forward CD	2.15 A/dm^2	3.23 A/dm^2
Periodic Current Reversal, Reverse Time	4 Seconds	0.0 Seconds
Periodic Current Reversal, Reverse CD	2.15 A/dm^2	0.0 A/dm^2
Electrolyte Agitation Code (Page 13)	B	B
Continuous Filtration	20 Microns	20 Microns
Deposition Time, Hours	72	68.85
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	26.73	30.45
Yield Strength, ksi	11.73	12.78
Elongation, % in 5.08 cm	13.5	22.5
Hardness, Vickers, 100 g Load	Not Determined	Not Determined
Thickness, cm	0.155	0.124

Microstructures (Magnification 100X)

Sample A-TEPA-3 (Center) Sample A-TEPA-3 (Edge) Sample A-TEPA-4

Figure 13b. Data for Acid Copper Sulfate Deposits from Electrolytes with Less than 50 PPM Chloride Ion by Weight, 0.2 g/l of D^- Xylose, and 0.5 g/l of Tetraethylenepentamine (TEPA).

in the bottom of each tank.

From Table XXV data only two samples had reasonably good mechanical properties when the agitation was modest and the chloride was below 50 ppm by weight. These samples were from baths with 1.5 g/l of triisopropanolamine (TIPA) or had the higher concentration of TIPA and were deposited with higher current densities, Sample A2-TIPA-I. The samples from each bath before TIPA was added had mechanical properties that were totally unacceptable. The addition of 1 g/l of TIPA improved ultimate and yield strengths significantly, but ductility remained poor. The use of periodic current reversal with TIPA present resulted in no improvements in properties. Increasing the TIPA concentration to 1.5 g/l improved mechanical properties. Increasing current density improved ultimate and yield strengths, but ductility was not significantly affected.

TABLE XXV - AGITATION EFFECTS ON MECHANICAL PROPERTIES OF ACID COPPER SULFATE DEPOSITS FROM ELECTROLYTES CONTAINING UNDER 50 PPM BY WEIGHT CHLORIDE ION AND RANGES OF TIPA FROM 0 TO 1.5 G/L

ENI Sample Number	TIPA Conc. (g/l)	Bath Temp. (°C)	Current Density (A/dm^2)	PR Timing Forward (Sec)	PR Timing Reverse (Sec)	Deposit Thickness (Cm)	Mechanical Properties Ult. Str. (Ksi)	Mechanical Properties Yield Str. (Ksi)	Mechanical Properties Elongation % in 5.08 Cm	Chloride Ion In Electrolyte PPM By Weight
Bath A1 With Sparger Pipe Containing 3 Open Holes Aimed Laterally on Bottom of Tank; No Box Shields.										
A1-NA-A	0.0	29.4	5.38	8	4	0.103	9.71	8.39	2.0	42
A1-NA-D	0.0	29.4	5.38	8	4	0.090	25.46	15.61	8.0	42
A1-TIPA-E	1.0	29.4	2.15	PR Not Used		0.174	21.35	12.80	7.0	27
A1-TIPA-F	1.0	29.4	2.15	16	4	0.079	16.60	12.71	3.5	27
A1-TIPA-G	1.0	29.4	3.23	PR Not Used		0.130	36.65	21.64	7.0	27
A1-TIPA-K	1.5	29.4	2.15	PR Not Used		0.114	45.60	27.94	16.5	27
Bath A2 With Sparger Pipe Containing 3 Spray Nozzles Aimed Laterally on Bottom of Tank; No Box Shields.										
A2-NA-A	0.0	29.4	5.38	8	4	0.103	12.61	7.43	8.5	20
A2-TIPA-F	1.0	29.4	2.15	PR Not Used		0.140	34.33	21.68	8.5	20
A2-TIPA-G	1.0	29.4	3.23	PR Not Used		0.099	33.96	18.39	10.5	20
Bath A2 With Three Nozzle Sprays (Only 1 Aimed at Panel) 17.8 Cm from Cathode Center; No Box Shields.										
A2-TIPA-H	1.5	29.4	3.23	PR Not Used		0.104	35.85	22 73	7.0	20
A2-TIPA-I	1.5	29.4	3.23	PR Not Used		0.094	43.34	28.12	22.5	20
Bath A2 With One Nozzle Spray (Aimed at Panel Center From 17.8 Cm Distance; No Box Shields.										
A2-TIPA-J	1.0	29.4	3.23	PR Not Used		0.112	25.65	16.80	5.0	20
A2-TIPA-K	2.0	29.4	2.15	PR Not Used		0.109	37.75	22.19	14.5	2 0

A comparison of mechanical properties of Samples A2-TIPA-H and A2-TIPA-I discloses a significant improvement in those of the latter specimen. With the increase of TIPA concentration there appears to be an incubation period for reaction of the additive to produce stronger deposits. This behavior was examined in subsequent studies and an "aging" period adopted before electrodepositing samples from new TIPA baths.

Microstructures of the specimens in Table XXV were examined and are shown in Figures 14a and

TANK A-1 DATA FOR MODERATE BATH AGITATION ON MECHANICAL PROPERTIES OF ACID COPPER SULFATE DEPOSITS FROM BATHS WITH LESS THAN 50 PPM BY WT. CHLORIDE ION, NO ADDITIVES, OR 1 TO 1.5 G/L TIPA

Chemistry	**Sample A1-NA-A**	**Sample A1-NA-D**	**Sample A1-TIPA-E**
$CuSO_4$ $5H_2O$	242.6 g/l	228.9 g/l	228.9 g/l
H_2SO_4	75.6 g/l	78.1 g/l	78.1 g/l
Chloride Ion, By Weight	42 ppm	42 ppm	42 ppm
Triisopropanolamine	0.0 g/l	0.0 g/l	1.0 g/l
Operating Parameters			
Bath Temperature	29.4°C	29.4°C	29.4°C
Periodic Current Reversal, Forward Time	8 Seconds	8 Seconds	Infinite
Periodic Current Reversal, Forward CD	5.38 A/dm^2	5.38 A/dm^2	2.15 A/dm^2
Periodic Current Reversal, Reverse Time	4 Seconds	4 Seconds	0 Seconds
Periodic Current Reversal, Reverse CD	5.38 A/dm^2	5.38 A/dm^2	0 A/dm^2
Electrolyte Agitation Code (Page 13)	CO-3 Indirect	CO-3 Indirect	CO-3 Indirect
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	70.3	53.0	88.0
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	9.71	25.46	21.35
Yield Strength, ksi	8.39	15.61	12.80
Elongation, % in 5.08 cm	2.0	8.0	7.0
Hardness, Vickers 100 g Load	Not Determined	Not Determined	Not Determined
Thickness, cm	0.103	0.090	0.174

Microstructures (Magnification 100X)

Not Sectioned

Not Sectioned

Sample A1-NA-A

Sample A1-NA-D

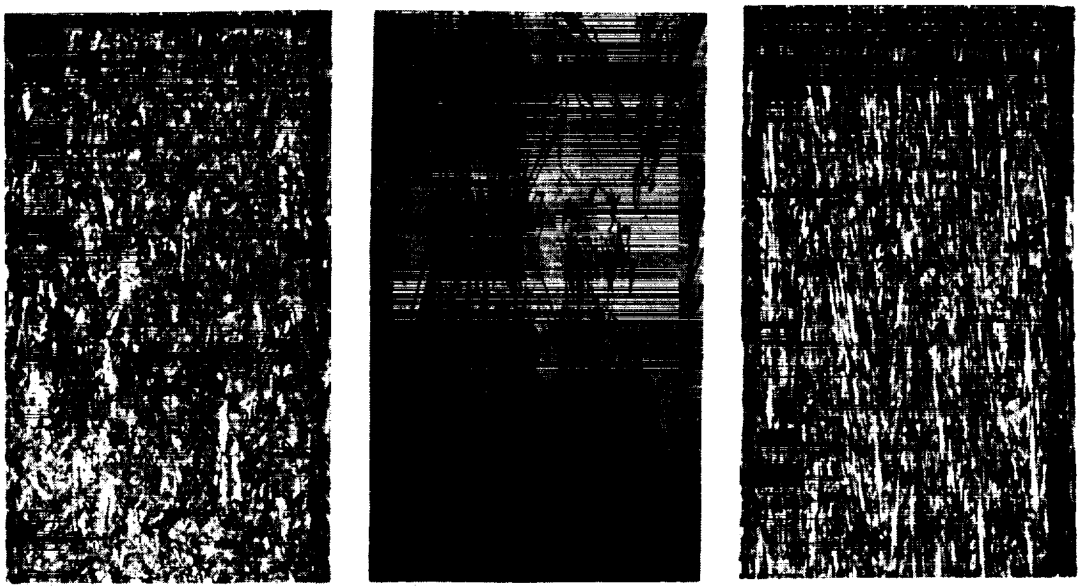
Sample A1-TIPA-E

Figure 14a. Data from Tank A-1for Acid Copper Sulfate Deposits from Moderately Agitated Baths with Less Than 50 PPM by Weight Cloride Ion, No Additions, or 1 g/l Triisopropanolamine (TIPA).

TANK A-1 DATA FOR MODERATE BATH AGITATION ON MECHANICAL PROPERTIES OF ACID COPPER SULFATE DEPOSITS FROM BATHS WITH LESS THAN 50 PPM BY WT. CHLORIDE ION, NO ADDITIVES, OR 1 TO 1.5 G/L TIPA

Chemistry	**Sample A1-TIPA-F**	**Sample A1-TIPA-G**	**Sample A1-TIPA-K**
$CuSO_4 \cdot 5H_2O$	228.4 g/l	228.4 g/l	224.7 g/l
H_2SO_4	77.1 g/l	77.1 g/l	71.9 g/l
Chloride Ion, By Weight	27 ppm	27 ppm	27 ppm
Triisopropanolamine	1.0 g/l	1.0 g/l	1.5 g/l
Operating Parameters			
Bath Temperature	29.4°C	29.4°C	29.4°C
Periodic Current Reversal, Forward Time	16 Seconds	Infinite	Infinite
Periodic Current Reversal, Forward CD	2.15 A/dm^2	3.23 A/dm^2	2.15 A/dm^2
Periodic Current Reversal, Reverse Time	4 Seconds	0 Seconds	0 Seconds
Periodic Current Reversal, Reverse CD	2.15 A/dm^2	0 A/dm^2	0 A/dm^2
Electrolyte Agitation Code (Page 13)	CO-3 Indirect	CO-3 Indirect	CO-3 Indirect
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	68.5	46.25	48.0
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	16.60	36.65	45.60
Yield Strength, ksi	12.71	21.64	27.94
Elongation, % in 5.08 cm	3.5	7.0	16.5
Hardness, Vickers 100 g Load	Not Determined	Not Determined	Not Determined
Thickness, cm	0.079	0.130	0.114

Microstructures (Magnification 100X) Note that Sample A1-TIPA-F was not sectioned.



Sample A1-TIPA-G (Center) Sample A1-TIPA-G (Edge) Sample A1-TIPA-K

Figure 14b. Data from Tank A-1 for Acid Copper Sulfate Deposits from Moderately Agitated Baths with Less Than 50 PPM by Weight Cloride Ion, No Additions, or 1 g/l. Triisopropanolamine (TIPA).

14b for Bath A1 deposits. Bath 2A deposit microstructures and deposition data are shown in Figures 15a, 15b, and 15c. Sample A1-NA-D, Figure 14a, is typical of acid copper deposits from baths with no additives and poor solution agitation. The grains become increasingly large with thickness and show indications of voids or inclusions that contribute to the poor ductility shown. With TIPA in the bath, mixed grain structures are created when agitation is poor, Figure 14b. The improved microstructure in Sample A1-TIPA-G may be due to a higher TIPA concentration which offsets some of the diffusion problems caused at the cathode surface by poor agitation. This offset of diffusion problems was best shown in Sample A1-TIPA-K, Figure 14b, where current density was lower and TIPA concentration was high. This microstructure is typical for acid copper deposits with good mechanical properties.

Microstructures for samples from Tank A2, with spray nozzles replacing the open holes in the bottom sparger, were similar to those from Tank A1. Where current densities were high, or TIPA content low, the moderate solution agitation led to mixed or large grains and low ductility. Relocation of the sprays to impinge perpendicularly onto the surface being plated, Sample A2-TIPA-I resulted in very significant improvement in mechanical properties, although grain sizes were larger than expected. Concentrating the full delivery of the pump through one spray nozzle did not result in finer grains or any improvement in mechanical properties, Sample A2-TIPA-K.

The next series of electrolyte agitation studies was performed in Tank Nos. 2 and 3 using 100 liter baths of acid copper sulfate which had been hydrogen peroxide treated and carbon filtered. Operating parameters and test results are summarized in Table XXVI. In these deposition studies, a separate in-tank solution pump was used to provide a higher volume of flow perpendicular to the cathode surface. Where concentrations of triisopropanolamine (TIPA) are given, the value includes any additions made to replace that amount estimated to have been consumed. Life expectancy of such baths had not been developed at this point in the program.

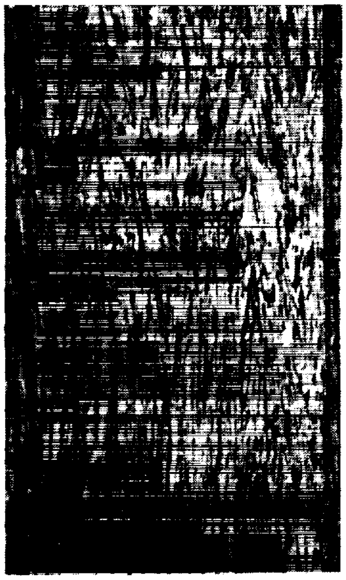
TABLE XXVI - EFFECTS OF DEDICATED ELECTROLYTE AGITATION PUMPS ON MECHANICAL PROPERTIES OF ACID COPPER SULFATE DEPOSITS FROM BATHS WITH UNDER 50 PPM BY WT. CHLORIDE ION AND 1 TO 2 G/L TIPA

ENI Sample Number	T IPA Conc. (g/l)	Current Density (A/dm^2)	Bath Temp. (°C)	Accumulated Ampere-Hours Per Liter	Deposit Thickness (Cm)	Mechanical Properties			Vickers Hardness Number 100 g Load
						Ult Str. (Ksi)	Yield Str. (Ksi)	Elongation % in 5.08 Cm	
Pump outlet with perforated one-half inch pipe located 10 cm from cathode; no box shield:									
2-TIPA-01	1.0	2.15	29.4	2.88	0.097	12.42	11.89	4.5	Not Determined
Dual open pipe sprays from pump outlet located 10 cm from cathode; no box shield:									
2-TIPA-02	1.25	2.15	29.4	4.54	0.099	17.22	12.08	5.0	Not Determined
Open pipe flow from pump outlet located 10 cm from cathode; box shield was used around cathode:									
3-TIPA-01	1.0	2.15	29.4	3.01	0.097	34.15	16.68	15.5	Not Determined
3-TIPA-02	1.25	2.15	29.4	6.03	0.102	49.05	30.38	24.0	Not Determined
Square pattern of 4 open pipes from pump outlet 15 cm from cathode; box shield was used. Bath was totally purified before adding new TIPA charge. TIPA was allowed to age 20 days in bath before plating.									
3-TIPA-03	2.0	2.15	29.4	3.09	0.135	58.96	43.93	10.0	Not Determined
3-TIPA-04	2.0	2.15	29.4	6.21	0.133	138.20	38.93	10.5	Not Determined

TANK A-2 DATA FOR MODERATE BATH AGITATION ON MECHANICAL PROPERTIES OF ACID COPPER SULFATE DEPOSITS FROM BATHS WITH LESS THAN 50 PPM BY WT. CHLORIDE ION, NO ADDITIVES, OR 1 TO 1.5 G/L TIPA

Chemistry	**Sample A2-NA-A**	**Sample A2-TIPA-F**	**Sample A2-TIPA-G**
$CuSO_4$ $5H_2O$	197.6 g/l	194.7 g/l	196.2 g/l
H_2SO_4	68.7 g/l	73.4 g/l	74.1 g/l
Chloride Ion, By Weight	20 ppm	20 ppm	20 ppm
Triisopropanolamine	0.0 g/l	1.0 g/l	1.0 g/l
Operating Parameters			
Bath Temperature	29.4°C	29.4°C	29.4°C
Periodic Current Reversal, Forward Time	8 Seconds	Infinite	Infinite
Periodic Current Reversal, Forward CD	5.38 A/dm^2	2.15 A/dm^2	3.23 A/dm^2
Periodic Current Reversal, Reverse Time	4 Seconds	0 Seconds	0 Seconds
Periodic Current Reversal, Reverse CD	5.38 A/dm^2	0 A/dm^2	0 A/dm^2
Electrolyte Agitation Code (Page 13)	CN-3 Indirect	CN-3 Indirect	CN-3 Indirect
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	65.0	61.0	33.25
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	12.61	34.33	33.96
Yield Strength, ksi	7.43	21.68	18.39
Elongation, % in 5.08 cm	8.5	8.5	10.5
Hardness, Vickers 100 g Load	Not Determined	Not Determined	Not Determined
Thickness, cm	0.103	0.140	0.099

Microstructures (Magnification 100X)



Sample A2-TIPA-F (Center)

(Magnification 50X)
Sample A2-TIPA-G (Center)

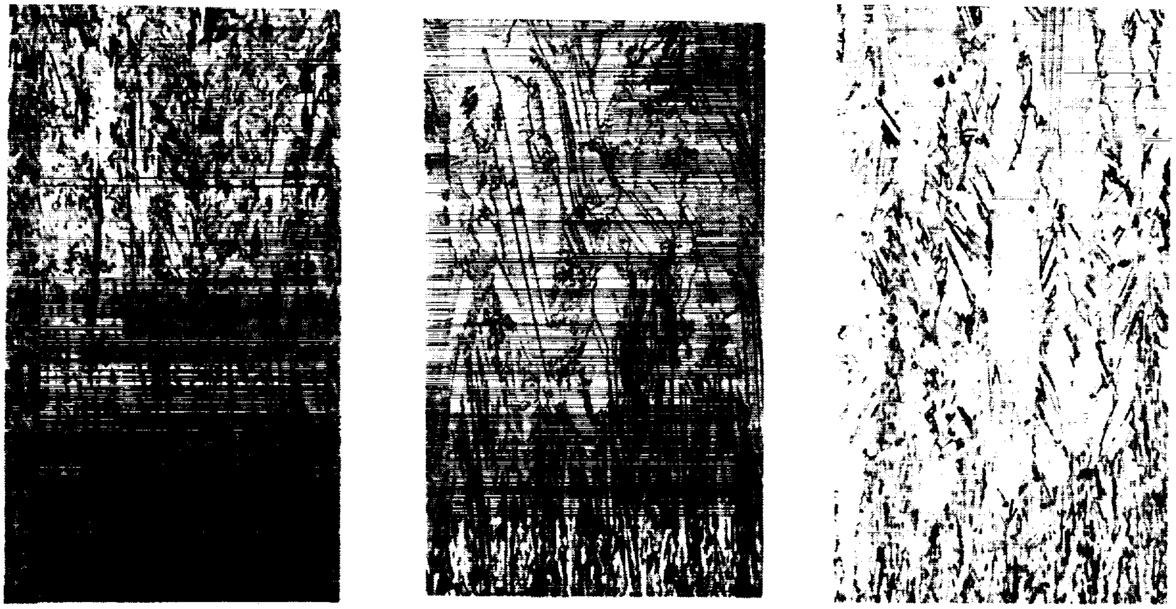
Sample A2-TIPA-G(Edge)

Figure 15a. Data from Tank A-2 for Acid Copper Sulfate Deposits from Moderately Agitated Baths with Less Than 50 PPM by Weight Cloride Ion, No Additions, or 1 g/l Triisopropanolamine (TIPA).

TANK A-2 DATA FOR MODERATE BATH AGITATION ON MECHANICAL PROPERTIES OF ACID COPPER SULFATE DEPOSITS FROM BATHS WITH LESS THAN 50 PPM BY WT. CHLORIDE ION, NO ADDITIVES, OR 1 TO 1.5 G/L TIPA

Chemistry	**Sample A2-TIPA-H**	**Sample A2-TIPA-I**
$CuSO_4 \cdot 5H_2O$	200.7 g/l	209.7 g/l
H_2SO_4	68.1 g/l	68.1 g/l
Chloride Ion, By Weight	20 ppm	20 ppm
Triisopropanolamine	1.5 g/l	1.5 g/l
Operating Parameters		
Bath Temperature	29.4°C	29.4°C
Periodic Current Reversal, Forward Time	Infinite	Infinite
Periodic Current Reversal, Forward CD	3.23 A/dm^2	3.23 A/dm^2
Periodic Current Reversal, Reverse Time	0 Seconds	0 Seconds
Periodic Current Reversal, Reverse CD	0 A/dm^2	0 A/dm^2
Electrolyte Agitation Code (Page 13)	CN-3	CN-3
Continuous Filtration	20 Microns	20 Microns
Deposition Time, Hours	48	34.75
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	35.85	43.34
Yield Strength, ksi	22.73	28.12
Elongation, % in 5.08 cm	7.0	22.5
Hardness, Vickers, 100 g Load	Not Determined	Not Determined
Thickness, cm	0.104	0.094

Microstructures (Magnification 100X)



Sample A2-TIPA-H (Center) Sample A2-TIPA-H (Edge) Sample A2-TIPA-I

Figure 15b. Data from Tank A-2 for Acid Copper Sulfate Deposits from Moderately Agitated Baths with Less Than 50 PPM by Weight Cloride Ion, No Additions, or 1.5 G/L Triisopropanolamine (TIPA).

TANK A-2 DATA FOR MODERATE BATH AGITATION ON MECHANICAL PROPERTIES OF ACID COPPER SULFATE DEPOSITS FROM BATHS WITH LESS THAN 50 PPM BY WT. CHLORIDE ION, NO ADDITIVES, OR 1 TO 1.5 G/L TIPA

Chemistry	**Sample A2-TIPA-J**	**Sample A2-TIPA-K**
$CuSO_4 \cdot 5H_2O$	217.2 g/l	224.7 g/l
H_2SO_4	68.1 g/l	68.1 g/l
Chloride Ion, By Weight	20 ppm	20 ppm
Triisopropanolamine	1.0 g/l	2.0 g/l
Operating Parameters		
Bath Temperature	29.4°C	29.4°C
Periodic Current Reversal, Forward Time	Infinite	Infinite
Periodic Current Reversal, Forward CD	3.23 A/dm^2	2.15 A/dm^2
Periodic Current Reversal, Reverse Time	0 Seconds	0 Seconds
Periodic Current Reversal, Reverse CD	0 A/dm^2	0 A/dm^2
Electrolyte Agitation Code (Page 13)	CN-1	CN-1
Continuous Filtration	20 Microns	20 Microns
Deposition Time, Hours	45	69.9
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	25.65	37.75
Yield Strength, ksi	16.80	22.19
Elongation, % in 5.08 cm	5.0	14.5
Hardness, Vickers, 100 g Load	Not Determined	Not Determined
Thickness, cm	0.112	0.109

Microstructures (Magnification 100X)

Sample A2-TIPA-J

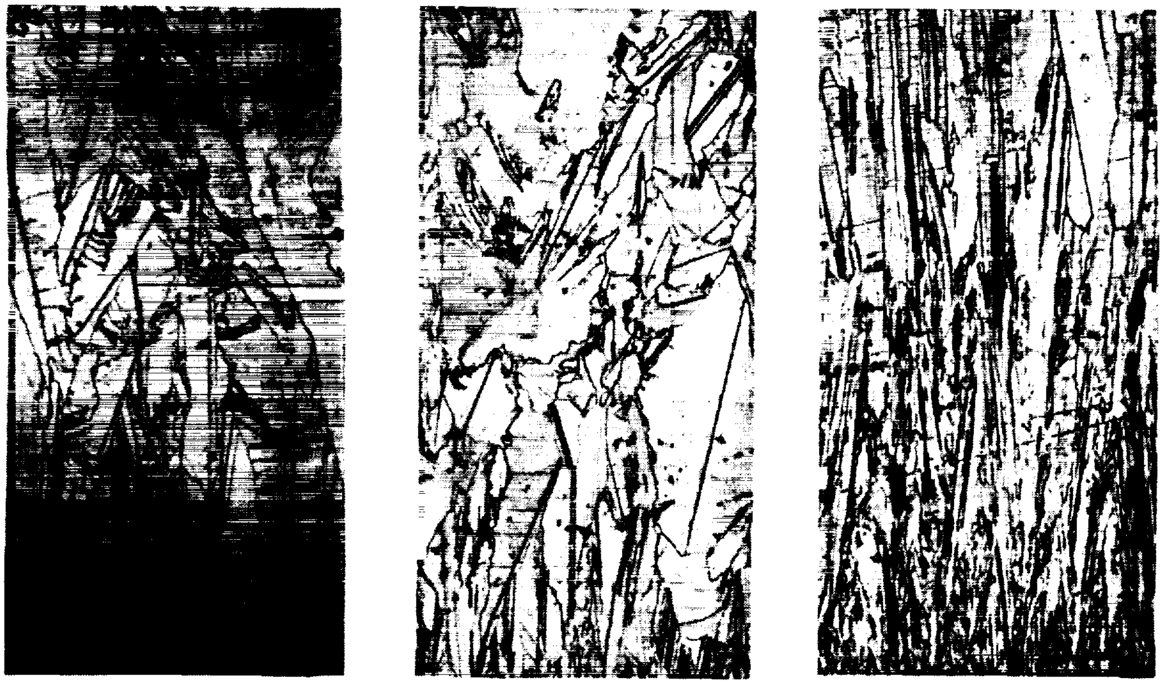
Sample A2-TIPA-K

Figure 15c. Data for Tank A-2 for Acid Copper Sulfate Deposits from Moderately Agitated Baths with Less Than 50 PPM by Weight Cloride Ion, No Additions, or 1 to 2 g/l Triisopropanolamine (TIPA).

MECHANICAL PROPERTIES OF ACID COPPER SULFATE DEPOSITS FROM BATHS WITH UNDER 50 PPM BY WT. CHLORIDE ION AND 1 TO 2 G/L TIPA WHEN CATHODE AGITATION IS SUPPLIED FROM DEDICATED IN-TANK PUMPS

Chemistry	**Sample 2-TIPA-01**	**Sample 2-TIPA-02**	**Sample 3-TIPA-01**
$CuSO_4$ $5H_2O$	224.7 g/l	217.2 g/l	239.6 g/l
H_2SO_4	68.1 g/l	68.9 g/l	72.6 g/l
Chloride Ion, By Weight	20 ppm	20 ppm	37 ppm
Triisopropanolamine	1.0 g/l	1.25 g/l	1.0 g/l
Operating Parameters			
Bath Temperature	29.4°C	29.4°C	29.4°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation Code (Page 13)	CO-Perforated	CO-2	CO-1-Box Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	45.0	26.4	47.0
Accumulated Ampere-Hours Per Liter	2.88	4.54	3.01
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	12.42	17.22	34.15
Yield Strength, ksi	11.89	12.08	16.68
Elongation, % in 5.08 cm	4.5	5.0	15.5
Hardness, Vickers, 100 g Load	Not Determined	Not Determined	Not Determined
Thickness, cm	0.097	0.099	0.097

Microstructures (Magnification 100X)



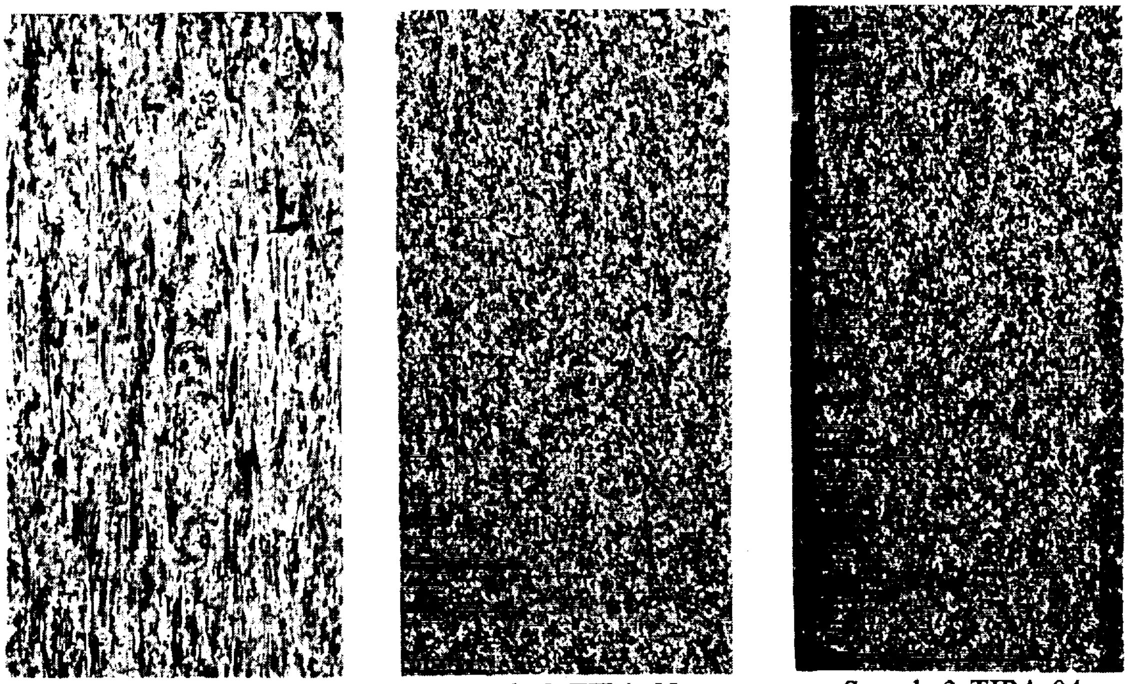
Sample 2-TIPA-01 Sample 2-TIPA-02 Sample 3-TIPA-01

Figure 16a. Data for Acid Copper Sulfate Deposits from Baths Agitated with Dedicated In-tank Pumps and Containing under 50 PPM by Wt. Chloride Ion and 1 to 1.25 g/l TIPA.

MECHANICAL PROPERTIES OF ACID COPPER SULFATE DEPOSITS FROM BATHS WITH UNDER 50 PPM BY WT. CHLORIDE ION AND 1 TO 2 G/L TIPA WHEN CATHODE AGITATION IS SUPPLIED FROM DEDICATED IN-TANK PUMPS

Chemistry	**Sample 3-TIPA-02**	**Sample 3-TIPA-03**	**Sample 3-TIPA-04**
$CuSO_4 \cdot 5H_2O$	224.7 g/l	224.7 g/l	221.7 g/l
H_2SO_4	68.1 g/l	56.2 g/l	62.9 g/l
Chloride Ion, By Weight	37 ppm	37 ppm	37 ppm
Triisopropanolamine	1.25 g/l	2.0 g/l	2.0 g/l
Operating Parameters			
Bath Temperature	29.4°C	29.4°C	29.4°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-1-Box Shield	CO-4-Box Shield	CO-4-Box Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	48.0	49.0	49.5
Accumulated Ampere-Hours Per Liter	6.03	3.09	6.21
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	49.05	58.96	138.20
Yield Strength, ksi	30.38	43.93	38.93
Elongation, % in 5.08 cm	24.0	10.0	10.5
Hardness, Vickers, 100 g Load	Not Determined	Not Determined	Not Determined
Thickness, cm	0.102	0.135	0.133

Microstructures (Magnification 100X)



Sample 3-TIPA-02 Sample 3-TIPA-03 Sample 3-TIPA-04

Figure 16b. Data for Acid Copper Sulfate Deposits from Baths Agitated with Dedicated In-tank Pumps and Containing under 50 PPM by Wt. Chloride Ion and 1.25 to 2.0 g/l TIPA.

Use of the separate in-tank pump dedicated to direct agitation of acid copper electrolyte over the entire surface of the cathode resulted in significant improvements in mechanical properties. When this was combined with box shields around the cathode, very high solution replenishment rates were obtained in a fully contained region. Box shields are simply what they imply, the cathode is the base of a four sided box having an opening at the face opposite the cathode. Such shields are constructed from PVC or acrylic sheet stock and assembled with PVC fasteners. The sidewalls of the box are usually about one-half the length of the longest side of the cathode sheet, but they may be made shorter without significantly losing their effectiveness.

As would be expected, microstructures play a dominant role in creating the mechanical properties found in Table XXVI. Figures 16a and 16b summarize deposition parameters, bath chemistries, and show microstructures and mechanical properties for the specimens listed in Table XXVI. When box shields were not used and when sprays were directed to a particular region of the cathode, the resulting microstructures showed large grains, Samples 2-TIPA-01 and -02. With the use of box shields and multiple spray heads to rapidly recirculate electrolyte over the entire cathode surface, the grain sizes were refined to extremely small (near equi-axed) sizes. The outstanding ultimate strength observed in Sample 3-TIPA-04 is rather unique and difficult to reproduce on a continuous basis. A possible explanation for this remarkable strength will be given later.

2.4.4.2 TIPA - Concentration Investigations

Different concentrations of triisopropanolamine (TIPA) ranging from 1 to 5 g/l were used in the three 100 liter tanks of acid copper sulfate employed in this task. Data was also obtained on TIPA concentration effects in a 100 liter tank and a large production tank in which D^+ xylose was present for minimizing oxygen content in the copper deposits. Care was taken to obtain data from test samples electrodeposited under similar electrolyte agitation conditions and at bath temperatures within the range of 26.7 to 29.4°C. All specimens included in this study were produced using box shields to more closely control deposit thickness and agitation uniformity. Where renewal or initial TIPA additions were made, the bath was allowed to age prior to deposition of specimens. Bath chemistry, operating parameters, and deposit test results are summarized in Table XXVII.

From the data in Table XXVII it appears that there is a slight increase in ultimate and yield strengths for acid copper sulfate bath deposits with higher triisopropanolamine concentrations in the electrolyte. Increasing the concentration of this additive beyond 3.0 g/l does not provide any mechanical property benefits. This table indicates that adding TIPA to baths with cloride ion content below 50 ppm by weight results in slightly higher ultimate and yield strengths than found in deposits from baths with similar TIPA concentrations and chloride ion above 50 ppm by weight. Bath temperature variations for the specimens in this table were not diverse enough to arrive at any conclusion as to effects on mechanical properties.

Several specimens were observed to have unusually high tensile strengths. These were Sample Nos. Phase I-AA, 3-TIPA-04, and 3-TIPA-05. Sample 3-TIPA-03 did not exhibit this high strength. Since the 3-TIPA-03 sample was the first electrodeposited after the first addition of TIPA to the acid

TABLE XXVII - EFFECTS OF TRIISOPROPANOLAMINE (TIPA) CONCENTRATION ON MECHANICAL PROPERTIES OF ACID COPPER SULFATE BATH DEPOSITS PRODUCED UNDER SIMILAR ELECTROLYTE OPERATING CONDITIONS

ENI	Concentrations			Bath	Current	Deposit	Accum.	Mechanical Properties			Vickers
Sample	TIPA	D^+Xylose	Cl^-	Temp.	Density	Thick.	Amp-Hrs	Ult. Str.	Yield Str.	Elongation, %	Hardness
Number	(g/l)	(g/l)	(ppm)	(°C)	(A/dm^2)	(Cm)	Per Liter	Ksi	Ksi	In 5.08 Cm	100 g Load
Phase I	0.1	0.2	<50	28.3	4.31(1)	0.191	?	57.30	37.25	29.0	Not Determ.
(1) Periodic Current Reversal 12 Sec. Forward; 6 Sec. Reverse											
Phase I	1.0	0.0	<50	26.7	1.79(2)	0.112	?	59.09	43.18	12.0	Not Determ.
(2) High Acid, Low Copper Deep Throw Bath											
Phase I-AA	1.0	0.0	<50	25.6	2.15	0.470	?	88.98	70.49	13.0	Not Determ.
Phase I-AD	1.0	0.0	<50	26.1	2.15	0.112	?	47.08	32.59	24.0	Not Determ.
TIPA-01	1.0	0.0	37	29.4	2.15	0.097	3.09	34.15	16.68	15.5	Not Determ.
B-Tank-01	1.0	0.6	16	26.7	2.36	0.172	0.56	51.51	34.64	21.0	116
3-TIPA-03	2.0	0.0	37	29.4	2.15	0.135	3.09	58.96	43.93	10.0	Not Determ.
3-TIPA-04	2.0	0.0	37	29.4	2.15	0.133	6.21	138.20	38.93	10.5	Not Determ.
3-TIPA-05	2.0	0.0	37	29.4	2.15	0.130	9.34	133.00	38.27	10.5	Not Determ.
3-TIPA-06	2.0	0.0	37	29.4	2.15	0.195	13.89	55.05	43.05	9.5	Not Determ.
2-TIPA-07	2.0	0.0	20	26.7	2.15	0.125	3.09	54.66	35.83	13.5	119
4-TIPA-04	2.0	0.7	81	26.7	2.15	0.138	3.21	47.35	28.67	24.5	110
B-Tank-02	2.0	0.6	16	26.7	2.15	0.141	0.50	59.40	44.86	15.0	116
B-Tank-03	2.0	0.6	16	25.6	2.15	0.157	?	65.29	48.32	11.5	128
2-TIPA-08	3.0	0.0	20	26.7	2.15	0.139	6.37	61.54	44.09	18.0	119
2-TIPA-15	3.0	0.0	30	26.7	2.15	0.137	29.60	66.20	51.00	11.0	132
4-TIPA-05	3.0	0.7	81	26.7	2.15	0.141	3.26	53.64	34.18	19.0	113
4-TIPA-06	3.0	0.7	81	26.7	2.15	0.142	6.54	64.76	47.98	18.0	105
With 0.00015 g/l Selenium Dioxide Present:											
3-TSe-01	2.0	0.0	71	26.7	2.15	0.128	3.02	54.70	37.24	18.5	119
3-TSe-04	5.0	0.0	71	26.7	2.15	0.132	3.07	58.76	42.56	20.0	113
3-TSe-05	5.0	0.0	71	26.7	3.23	0.107	5.60	61.62	41.99	12.5	128
3-TSe-06	5.0	0.0	71	26.7	3.23	0.107	8.20	62.38	35.85	8.0	128

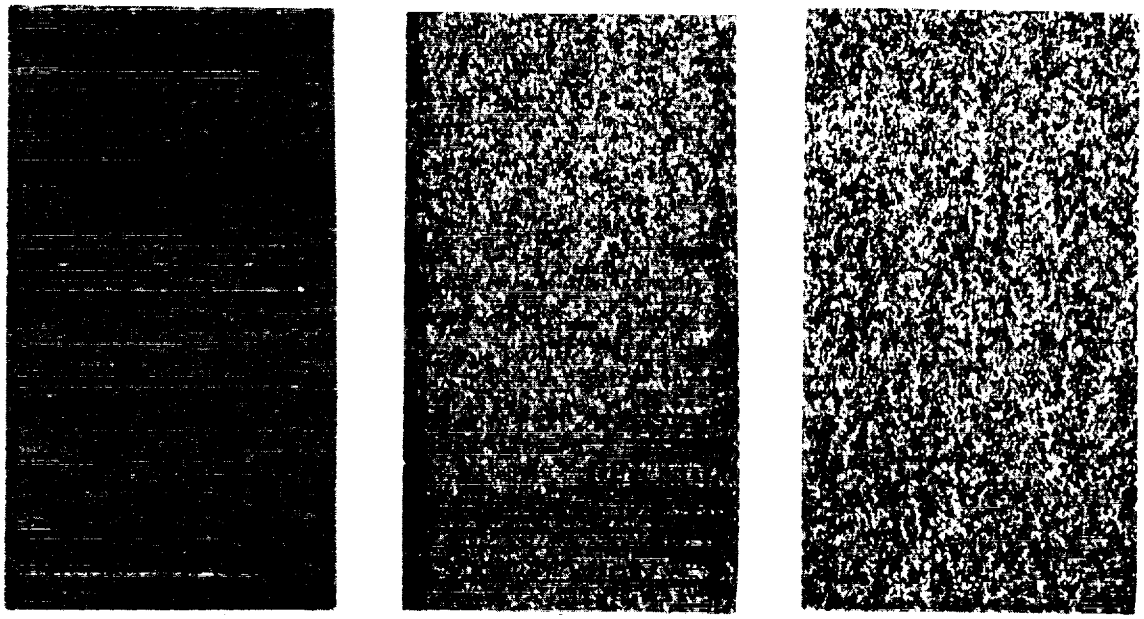
bath, it was thought that an aging period was needed after introducing the additive in order to produce very fine grain sizes for high mechanical strength such as encountered in Samples 3-TIPA-04 and 3-TIPA-05. In Phase I the production copper bath had been inactive for several weeks before Sample Phase I-AA was electroformed. This bath contained only 1 g/l of TIPA. However, data in Table XXVII did not disclose high tensile strengths when the TIPA content was increased from 2 to 3 g/l. This led to a questioning of the hypothesis that TIPA was acting directly at the cathode surface to nucleate the extremely fine grain sizes causing the very high copper strength.

As shown in Figure 17a, the very high strength deposits always had extremely fine (almost equi-axed) grains. Other moderate strength deposits from TIPA containing baths always exhibited columnar grains, Figure 17b. It was next considered that chloride ion might affect nucleation of very fine grains. Nagy, Blaudeau, Hung, Curtiss, and Zurawski(9) demonstrated that chloride ion catalyzed the reaction $Cu^{+2} + e^- = Cu^+$ at the cathode. Since CuCl has very limited solubility, it appeared possible for colloidal cuprous chloride to be generated and the surface charge to be enhanced by TIPA chemisorption. This would provide a high zeta potential for such particles in a voltage field which would

MECHANICAL PROPERTIES OF ACID COPPER SULFATE DEPOSITS FROM BATHS WITH 0.1 TO 5 G/L TIPA, 0 TO 0.7 G/L OF D^+ XYLOSE, AND VARIOUS LEVELS OF CHLORIDE ION

Chemistry	**Sample Phase I-AA**	**Sample 3-TIPA-04**	**Sample 3-TIPA-05**
$CuSO_4 \cdot 5H_2O$	195.5 g/l	221.7 g/l	224.7 g/l
H_2SO_4	65.9 g/l	62.9 g/l	62.9 g/l
Chloride Ion, By Weight	< 50 ppm	37 ppm	37 ppm
D^+ Xylose	0.0 g/l	0.0 g/l	0.0 g/l
Triisopropanolamine	1.0 g/l	2.0 g/l	2.0 g/l
Operating Parameters			
Bath Temperature	25.6°C	29.4°C	29.4°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CN-2-Box Shield	CO-4-Box Shield	CO-4-Box Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	?	49.5	49.6
Accumulated Ampere-Hours Per Liter	?	6.21	9.34
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	88.98	138.20	133.00
Yield Strength, ksi	70.49	38.93	38.27
Elongation, % in 5.08 cm	13.0	10.5	10.5
Hardness, Vickers, 100 g Load	Not Determined	Not Determined	Not Determined
Thickness, cm	0.470	0.133	0.130

Microstructures (Magnification 100X)



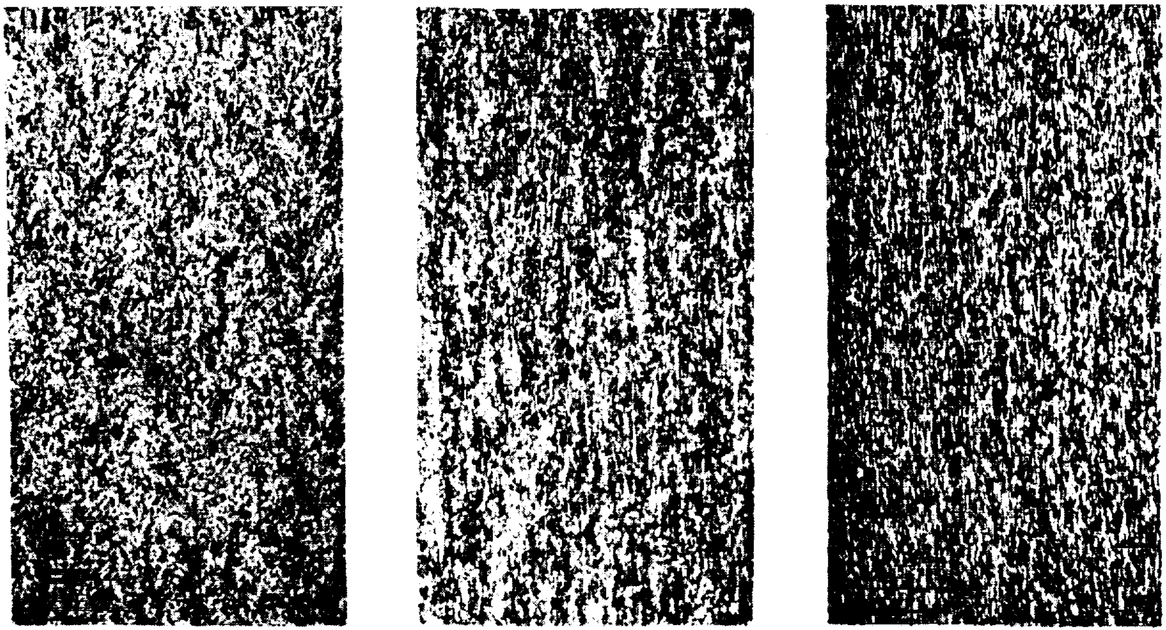
Sample Phase I-AA   Sample 3-TIPA-04   Sample 3-TIPA-05

Figure 17a. Data for Acid Copper Sulfate Deposits from Baths with TIPA and Exhibiting Very Fine Grain Structures and High Tensile Strengths.

MECHANICAL PROPERTIES OF ACID COPPER SULFATE DEPOSITS FROM BATHS WITH 0.1 TO 5 G/L TIPA, 0 TO 0.7 G/L OF D$^+$ XYLOSE, AND VARIOUS LEVELS OF CHLORIDE ION

Chemistry	**Sample 3-TIPA-06**	**Sample 4-TIPA-06**	**Sample 3-TSe-04**
$CuSO_4 \cdot 5H_2O$	217.9 g/l	233.7 g/l	224.7 g/l
H_2SO_4	63.7 g/l	75.6 g/l	62.9 g/l
Chloride Ion, By Weight	37 ppm	81 ppm	71 ppm
Selenium Dioxide	0.0 g/l	0.0 g/l	0.00015 g/l
D$^+$ Xylose	0.0 g/l	0.7 g/l	0.0 g/l
Triisopropanolamine	2.0 g/l	3.0 g/l	5.0 g/l
Operating Parameters			
Bath Temperature	29.4°C	26.7°C	26.7°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4-Box Shield	CO-4-Box Shield	CO-4-Box Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	72.2	52.0	48.75
Accumulated Ampere-Hours Per Liter	13.89	6.54	20.5
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	55.05	64.76	58.76
Yield Strength, ksi	43.05	47.98	42.56
Elongation, % in 5.08 cm	9.5	18.0	20.0
Hardness, Vickers, 100 g Load	Not Determined	105	113
Thickness, cm	0.195	0.142	0.132

Microstructures (Magnification 100X)



Sample 3-TIPA-06 Sample 4-TIPA-06 Sample 3-TSe-04

Figure 17b. Data for Acid Copper Sulfate Deposits from Baths with TIPA and Exhibiting Fine Columnar Grain Structures and Moderate Tensile Strengths.

cause codeposition with the copper (the basis for dispersion strengthening by electrodeposition). However, the specimens deposited from baths with the higher chloride ion contents did not show improvement in ultimate or yield strengths or refinement of grain size, so the cuprous chloride mechanism could not be demonstrated as valid.

Tomaszewski(10) received a patent on the use of amine additives in nickel and acid copper baths for the purpose of promoting surface charging of inert particles for composite plating. It is suspected that TIPA acts as a charge promoter. ENI experience with such systems has shown that the surface charging is time dependent. At low pH values the charging is usually weak due to a high concentration of protons which tend to suppress ionization of the amine. The source of the colloid on which this charging might occur is not well understood at this time. However, the charging time and weakness of the charge might explain why the nucleation of very fine grains is delayed and why the phenomenon is short lived. Tomaszewski listed teraethylenepentamine (TEPA) as one of the more promising amine promoters; however, studies in this program under Section 2.4.3 did not show any significant effect on mechanical properties. It should also be noted that the only amine in this program which produced the high strength copper was TIPA which is a tertiary amine.

2.4.4.3 TIPA - Bath Longevity Studies of Acid Copper Sulfate Solutions with TIPA

Electroforming aerospace hardware and other engineering structural components often requires very long deposition periods. It is thus important that mechanical properties created as a result of bath additions must be obtainable over the full deposition time span. The work presented here is believed be the first such investigation which associates mechanical properties and microstructures of acid copper deposits with accumulated passage of current for a given unit of volume of the bath containing a strength enhancing additive. 100 liter baths were used in these studies. The standard test specimen size previously described was used to enable cutting ASTM E-8 specified tensile strips from the panel center.

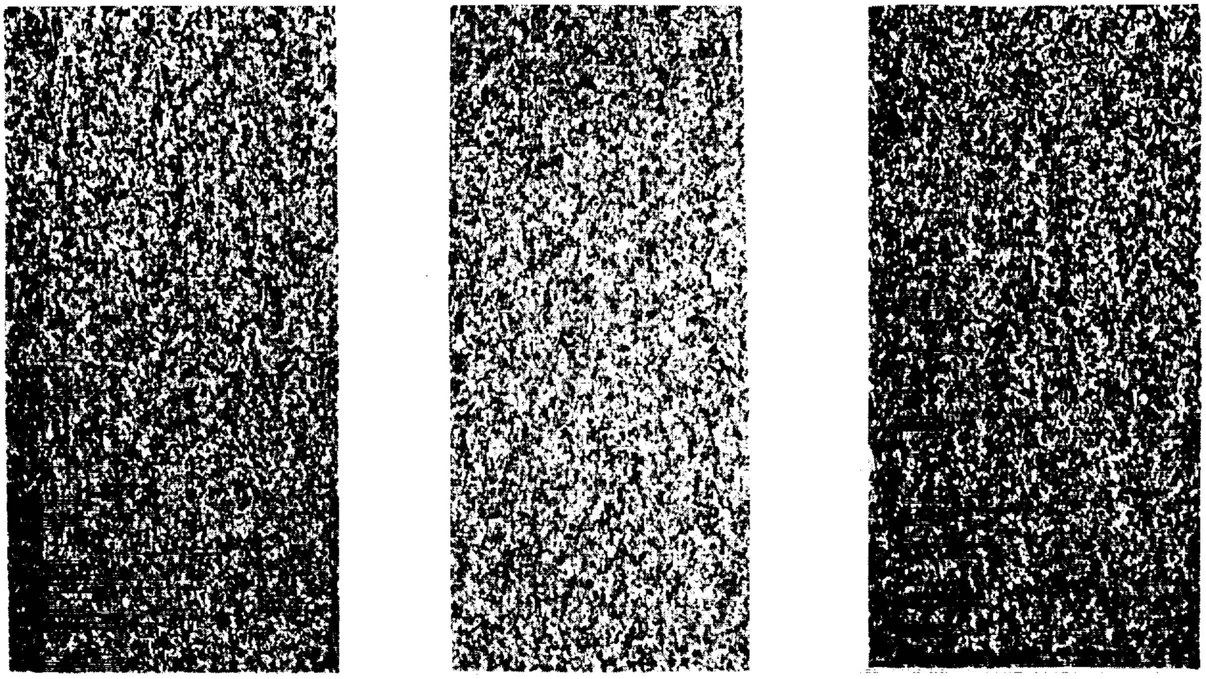
Tank No. 3 was purified by hydrogen peroxide destruction of organic contaminants followed by two consecutive carbon treatments. To this bath was added two grams per liter (2 g/l) of reagent grade triisopropanolamine (TIPA). The bath was allowed to age for twenty (20) days prior to depositing consecutive specimens. Test results and deposition data for this series of specimens is found in Table XXVIII. From this table it will be noted that there was an extremely unusual increase in ultimate strength which was not accompanied by a similar response in yield strength. This was a short lived phenomenon which occurred between 3.1 and 9.3 ampere-hours per liter of accrued electrolysis of the bath. Figure 18a shows microstructures of consecutive deposits produced during this period. All appear similar in that very fine, almost equi-axed, grains exist. From these photomicrographs it is difficult to determine why Sample 3-TIPA-03 has a much lower ultimate strength than is shown in the next two specimens.

During the next 9 ampere-hours per liter of bath operation the ultimate and yield strengths appear to stabilize with a gradual loss in ductility. The two specimens deposited during this period, Figure 18b, show a fine grain which is no longer equi-axed but has become distinctly columnar. As about 22 to

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED SEQUENTIALLY IN A BATH CONTAINING 2 G/L OF TIPA

Chemistry	**Sample 3-TIPA-03**	**Sample 3-TIPA-04**	**Sample 3-TIPA-05**
$CuSO_4\ 5H_2O$	224.7 g/l	221.7 g/l	220.2 g/l
H_2SO_4	56.2 g/l	62.9 g/l	62.2 g/l
Chloride Ion, By Weight	37 ppm	37 ppm	37 ppm
Triisopropanolamine	2.0 g/l	2.0 g/l	2.0 g/l
Operating Parameters			
Bath Temperature	29.4°C	29.4°C	29.4°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4 Box Shield	CO-4 Box Shield	CO-4 Box Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	49.0	49.5	49.6
Accumulated Ampere-Hours Per Liter	3.09	6.21	9.34
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	58.96	138.20	133.00
Yield Strength, ksi	43.93	38.93	38.27
Elongation, % in 5.08 cm	10.0	10.5	10.5
Hardness, Vickers, 100 g Load	Not Determined	Not Determined	Not Determined
Thickness, cm	0.135	0.133	0.130

Microstructures (Magnification 100X)



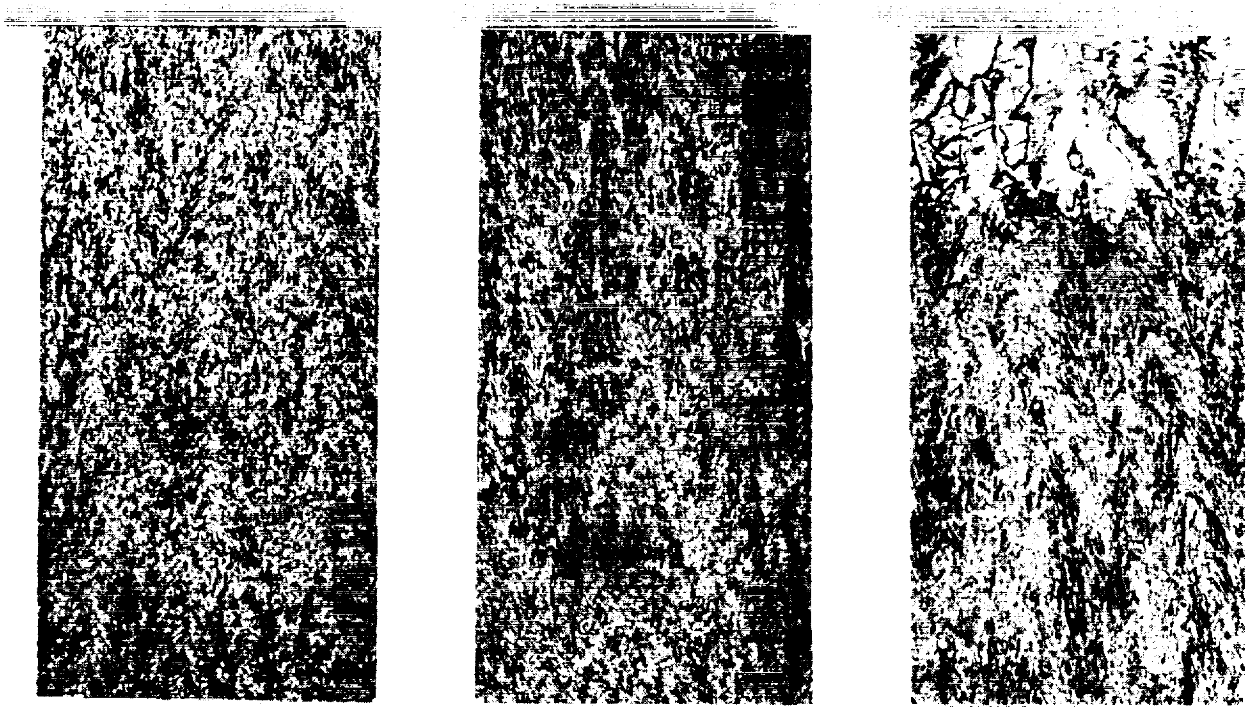
Sample 3-TIPA-03 Sample 3-TIPA-04 Sample 3-TIPA-05

Figure 18a. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 2.0 g/l of TIPA During the Initial 9.34 Ampere-Hours Per Liter Use Period.

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED SEQUENTIALLY IN A BATH CONTAINING 2 G/L OF TIPA

Chemistry	**Sample 3-TIPA-06**	**Sample 3-TIPA-07**	**Sample 3-TIPA-08**
$CuSO_4 \cdot 5H_2O$	217.9 g/l	227.7 g/l	226.2 g/l
H_2SO_4	63.7 g/l	65.9 g/l	63.7 g/l
Chloride Ion, By Weight	37 ppm	37 ppm	37 ppm
Triisopropanolamine	2.0 g/l	2.0 g/l	2.0 g/l
Operating Parameters			
Bath Temperature	29.4°C	29.4°C	29.4°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4 Box Shield	CO-4 Box Shield	CO-4 Box Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	72.17	72.25	72.0
Accumulated Ampere-Hours Per Liter	13.89	18.44	22.98
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	55.06	55.48	47.55
Yield Strength, ksi	43.05	43.15	33.71
Elongation, % in 5.08 cm	9.5	6.0	10.0
Hardness, Vickers, 100 g Load	127	128	127
Thickness, cm	0.195	0.187	0.195

Microstructures (Magnification 100X)

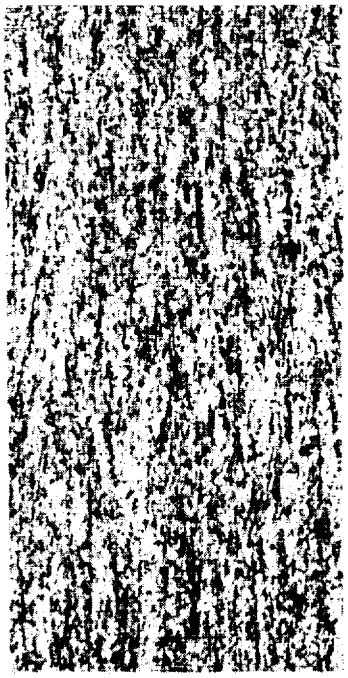


Sample 3-TIPA-06 Sample 3-TIPA-07 Sample 3-TIPA-08

Figure 18b. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 2.0 g/l of TIPA During the 9 to 23 Ampere-Hours Per Liter Use Period.

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED SEQUENTIALLY IN A BATH CONTAINING 2 G/L OF TIPA

Chemistry	**Sample 3-TIPA-09**
$CuSO_4 \cdot 5H_2O$	226.2 g/l
H_2SO_4	63.7 g/l
Chloride Ion, By Weight	37 ppm
Triisopropanolamine	> 2.0 G/L (Added 1 G/L as Replenishment)
Operating Parameters	
Bath Temperature	29.4°C
Current Density	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4 Box Shield
Continuous Filtration	20 Microns
Deposition Time, Hours	72.0
Accumulated Ampere-Hours Per Liter	22.98
Mechanical Properties and Deposit Thickness	
Ultimate Strength, ksi	60.73
Yield Strength, ksi	44.70
Elongation, % in 5.08 cm	11.0
Hardness, Vickers, 100 g Load	119
Thickness, cm	0.156
Microstructures (Magnification 100X)	



Sample 3-TIPA-09

Figure 18c. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 2.0 G/L of TIPA During the 23 to 26.3 Ampere-Hours Per Liter Use Period.

TABLE XXVIII - MECHANICAL PROPERTY DATA AND DEPOSITION PARAMETERS FOR CONSECUTIVE ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 2 G/L OF TIPA AND 37 PPM BY WT. Cl^-

ENI Sample Number	Bath Temperature (°C)	Current Density (A/dm^2)	Deposit Thickness (Cm)	Accumulated Ampere-Hours Per Liter	Mechanical Properties Ult. Str. Ksi	Yield Str. Ksi	Elongation,% In 5.08 Cm	Vickers Hardness 100 g Load
3-TIPA-03	29.4	2.15	0.135	3.09	58.96	43.93	10.0	Not Determ.
3-TIPA-04	29.4	2.15	0.133	6.21	138.20	38.93	10.5	Not Determ.
3-TIPA-05	29.4	2.15	0.130	9.34	133.00	38.27	10.5	Not Determ.
3-TIPA-06	29.4	2.15	0.195	13.89	55.05	43.05	9.5	127
3-TIPA-07	29.4	2.15	0.187	18.44	55.48	43.15	6.0	128
3-TIPA-08	29.4	2.15	0.195	22.98	47.55	33.71	10.0	127
Replenished TIPA at 1 g/l two weeks prior to deposition of next specimen.								
3-TIPA-09	29.4	2.15	0.156	26.34	60.73	44.70	11.0	119

23 ampere-hours per liter of bath is accrued, the ultimate and yield strengths significantly decrease as a result of formation of larger, more columnar grains as observed for Sample No. 3-TIPA-08 in Figure 18b. At this point the deposit surface was visibly roughened, a factor which led to the addition of more TIPA to the bath. The next specimen in the series, Sample 3-TIPA-09, Figure 18c, still contained some columnar grain structure, but the grains were very fine, Figure 18c. This specimen also exhibited higher ultimate and yield strengths with better ductility than Sample Nos. 3-TIPA-06, 3-TIPA-07, and 3-TIPA-08. This is likely due to the replenishment of TIPA resulting in a concentration of additive exceeding 2.0 g/l. Mechanical property data for this series of deposits is graphically presented in Figure 19.

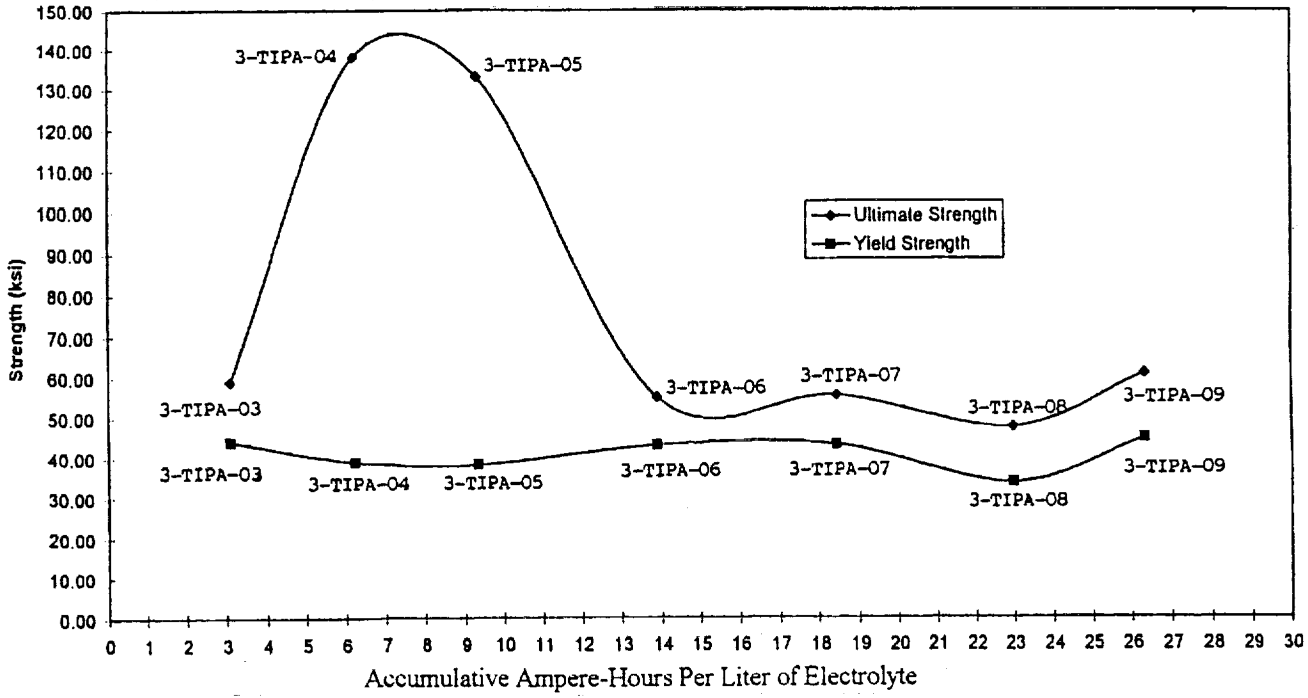


Figure 19. Graphic Presentation of Mechanical Property Data for Acid Copper Deposits Sequentially Produced from an Electrolyte with 2 g/l of TIPA.

A similar study was conducted in Tank No. 2 using 3 g/l triisopropanolamine (TIPA). Like the bath in Tank No. 3, this electrolyte also contained less than 50 ppm by weight of chloride ion. Test results and deposition parameters are summarized in Table XXIX. Reagent grade TIPA was used and the bath was only allowed to age for 4 days. At this level of TIPA concentration, the mechanical properties were very consistant for a very long duration of plating time. Upon separation of the test specimen from the stainless steel mandrel, a small amount of distortion was observed which was indicative of the presence of tensile stress. In all specimens the ductility was above the 10 percent in 5.08 cm considered to be the minimum value sought. Hardness appeared to level at about Vickers Number 132 shortly into the study.

TABLE XXIX - MECHANICAL PROPERTY DATA AND DEPOSITION PARAMETERS FOR CONSECUTIVE ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 3 G/L OF TIPA AND 20 PPM BY WT. Cl^-

ENI Sample Number	Bath Temperature (°C)	Current Density (A/dm²)	Deposit Thickness (Cm)	Accumulated Ampere-Hours Per Liter	Mechanical Properties Ult. Str. Ksi	Yield Str. Ksi	Elongation,% In 5.08 Cm	Vickers Hardness 100 g Load
2-TIPA-08	26.7	2.15	0.139	3.29	61.54	44.09	18.0	119
2-TIPA-09	26.7	2.15	0.139	6.60	64.03	43.47	15.0	126
2-TIPA-10	26.7	2.15	0.136	9.88	65.47	48.69	15.0	116
2-TIPA-11	26.7	2.15	0.138	13.17	64.02	43.06	14.5	135
2-TIPA-12	26.7	2.15	0.138	16.46	66.18	45.59	14.5	132
2-TIPA-13	26.7	2.15	0.144	19.95	Not tested due to nodules.			
2-TIPA-14	26.7	2.15	0.138	23.22	63.81	42.79	14.5	132
2-TIPA-15	26.7	2.15	0.137	26.47	66.20	51.00	11.0	132
2-TIPA-16	26.7	2.15	0.135	29.82	66.10	49.34	17.5	132
Comparison Sample from Tank No. 2 With 2 G/L TIPA:								
2-TIPA-07	26.7	2.15	0.125	3.09	54.66	35.83	13.5	119

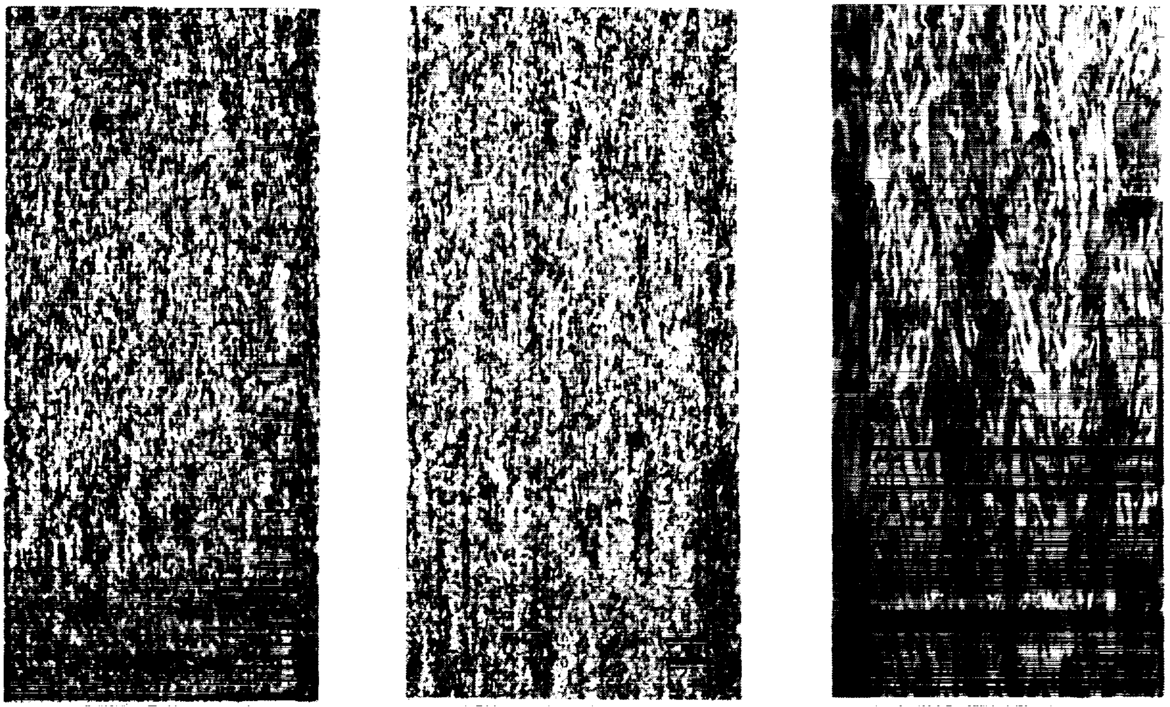
Microstructural examinations of many of the samples summarized in Table XXIX are shown in Figures 20a, 20b, and 20c. The grain sizes appeared to be consistently fine and columnar in all photomicrographs. No material was found to have the exceptionally high ultimate strengths observed for Sample Nos. 3-TIPA-04 and 3-TIPA-05 in the prior study. Whether this is related to the much briefer aging period given this electrolyte (in comparison to the bath in Tank No. 3) is not known at this time. Prior to depositing this series of specimens, this tank (Tank No. 2) contained 2 g/l of TIPA. Sample 2-TIPA-07 was the only specimen deposited from the 2 g/l TIPA bath before it was purified and the 3 g/l TIPA bath formulated. Data for this sample has been included in Table XXIX for comparison purposes. Mechanical properties for Sample 2-TIPA-07 are in general agreement with those obtained at a similar TIPA concentration in Tank No. 3.

Tank No. 2 specimens with 3 g/l TIPA in the bath show appreciably improved mechanical properties over those from the prior study with 2 g/l TIPA in the electrolyte in this same tank. Mechanical property data for these sequentially deposited samples at the higher TIPA concentration is graphically displayed in Figure 21. The improved mechanical properties in the samples in Table XXIX over those in Table XXVIII is a result of finer (more fibrous) columnar grains caused by the increased amount

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED SEQUENTIALLY IN A BATH CONTAINING 3 G/L OF TIPA

Chemistry	**Sample 2-TIPA-08**	**Sample 2-TIPA-09**	**Sample 2-TIPA-10**
$CuSO_4$ $5H_2O$	192.5 g/l	191.0 g/l	202.2 g/l
H_2SO_4	68.9 g/l	69.6 g/l	68.9 g/l
Chloride Ion, By Weight	20 ppm	20 ppm	20 ppm
Triisopropanolamine	3.0 g/l	3.0 g/l	3.0 g/l
Operating Parameters			
Bath Temperature	26.7°C	26.7°C	26.7°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4 Box Shield	CO-4 Box Shield	CO-4 Box Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	52.0	52.5	52.0
Accumulated Ampere-Hours Per Liter	3.28	6.58	9.89
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	61.54	64.03	65.47
Yield Strength, ksi	44.09	43.47	48.69
Elongation, % in 5.08 cm	18.05	15.0	15.0
Hardness, Vickers, 100 g Load	119	126	116
Thickness, cm	0.139	0.139	0.136

Microstructures (Magnification 100X)



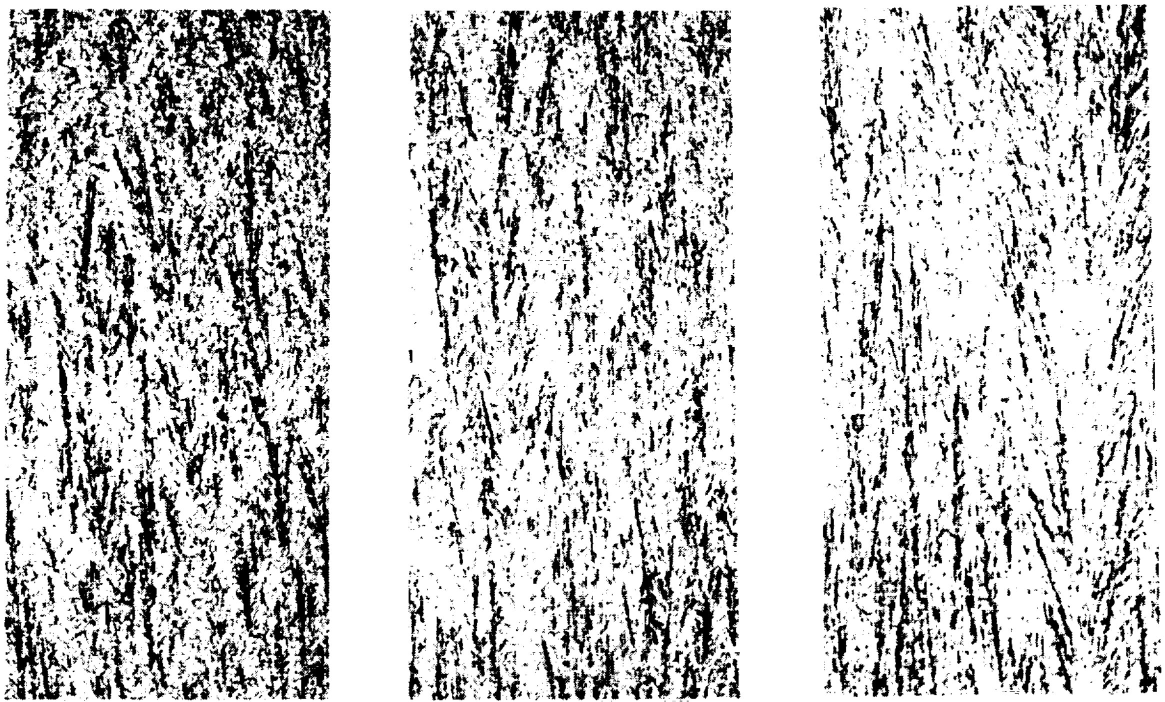
Sample 2-TIPA-08 Sample 2-TIPA-09 Sample 2-TIPA-10

Figure 20a. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 3.0 g/l of TIPA During the Initial 9.9 Ampere-Hours Per Liter Use Period.

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED SEQUENTIALLY IN A BATH CONTAINING 3 G/L OF TIPA

Chemistry	**Sample 2-TIPA-11**	**Sample 2-TIPA-12**	**Sample 2-TIPA-14**
$CuSO_4$ $5H_2O$	197.7 g/l	200.0 g/l	199.2 g/l
H_2SO_4	69.6 g/l	71.9 g/l	68.9 g/l
Chloride Ion, By Weight	20 ppm	20 ppm	20 ppm
Triisopropanolamine	3.0 g/l	3.0 g/l	3.0 g/l
Operating Parameters			
Bath Temperature	26.7°C	26.7°C	26.7°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4 Box Shield	CO-4 Box Shield	CO-4 Box Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	52.25	52.17	52.17
Accumulated Ampere-Hours Per Liter	13.17	16.46	23.22
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	64.02	66.18	63.81
Yield Strength, ksi	43.06	45.59	42.79
Elongation, % in 5.08 cm	14.5	14.5	14.5
Hardness, Vickers, 100 g Load	135	132	132
Thickness, cm	0.138	0.138	0.138

Microstructures (Magnification 100X)



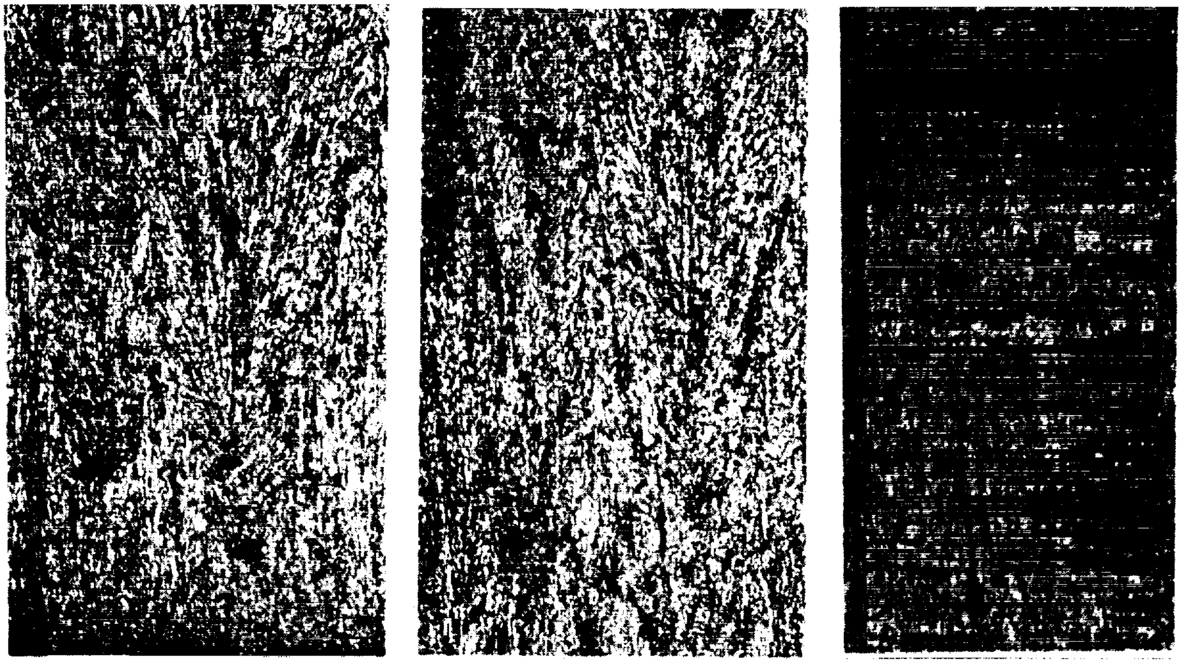
Sample 2-TIPA-11 Sample 2-TIPA-12 Sample 2-TIPA-14

Figure 20b. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 3.0 g/l of TIPA During the 9.9 to 23.2 Ampere-Hours Per Liter Use Period.

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED SEQUENTIALLY IN A BATH CONTAINING 3 G/L OF TIPA

Chemistry	**Sample 2-TIPA-15**	**Sample 2-TIPA-16**	**Sample 2-TIPA-07**
$CuSO_4 \cdot 5H_2O$	200.0 g/l	200.0 g/l	183.5 g/l
H_2SO_4	71.9 g/l	70.4 g/l	65.2 g/l
Chloride Ion, By Weight	20 ppm	20 ppm	20 ppm
Triisopropanolamine	3.0 g/l	3.0 g/l	**2.0 g/l**
Operating Parameters			
Bath Temperature	26.7°C	26.7°C	26.7°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4 Box Shield	CO-4 Box Shield	CO-4 Box Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	51.58	53.16	49.08
Accumulated Ampere-Hours Per Liter	26.47	29.82	3.09
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	66.20	66.10	54.66
Yield Strength, ksi	51.00	49.34	35.83
Elongation, % in 5.08 cm	11.0	17.5	13.5
Hardness, Vickers, 100 g Load	132	132	119
Thickness, cm	0.138	0.135	0.125

Microstructures (Magnification 100X)



Sample 2-TIPA-15 Sample 2-TIPA-16 Sample 2-TIPA-07 (2 g/l)

Figure 20c. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 3.0 g/l of TIPA During the 23.2 to 29.8 Ampere-Hours Per Liter Use Period.

of TIPA in the bath. This would suggest use of higher TIPA concentrations. However, the data in Table XXI shows no further increase in strength with 5 g/l of TIPA in the bath, whereas ductility is rapidly dimenished.

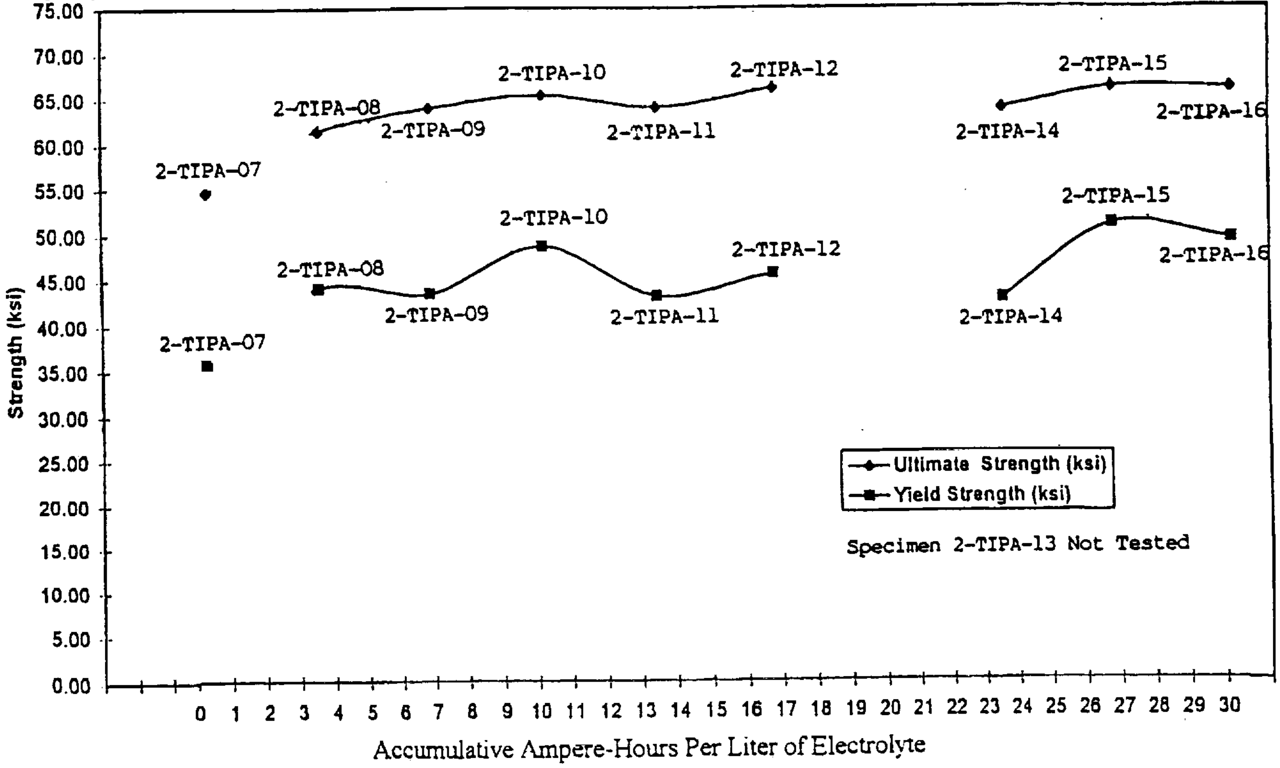


Figure 21. Graphic Presentation of Mechanical Property Data for Acid Copper Deposits Sequentially Produced from an Electrolyte with 3 g/l of TIPA.

Elevated temperature performance of the deposits from acid copper sulfate baths with TIPA was investigated and discussed under a later section of Task II. Ductility decreased with elevated temperature, even with various heat treatments applied prior to testing. It is of interest to compare the room temperature (24°C) mechanical properties of copper deposits from baths with TIPA to those of annealed wrought nickel reported by Jenkins, Digges, and Johnson(11). Their test results for high purity ***annealed*** nickel were:

Ultimate Strength, Ksi	52.7
Yield Strength, Ksi	12.5
Elongation in 5.08 Cm, %	56

Comparing test results for electrodeposited copper from acid sulfate baths containing 2 or 3 g/l of TIPA (Figures 19 and 21), the ultimate strength of the copper nearly always met or exceeded that for the nickel while yield strengths of the copper were multiples of the annealed nickel. The annealed nickel exhibited far better ductility, but the ductility of the copper was (in most cases) quite acceptable. Heat treatments at 149°C or 260°C significantly improved ductility in those copper deposits having low ductility in the as-deposited condition. This is discussed later in this task.

2.4.5 Studies Using 4-Acetamidophenol as an Acid Copper Sulfate Bath Additive

4-Acetamidophenol, also known as acetaminophen, was evaluated by SIU in beaker studies with high hardnesses being recorded on deposits from acid copper sulfate baths with 1 g/l of the additive present and high current densities being used. This was the only amine type compound used which contained an aryl (aromatic ring structure) as a radical component. Dissolving the material in the 100 liter acid copper sulfate bath required considerable time. Table XXX summarizes test results and deposition data for specimens from this bath. The extremely poor ductility of this material prevents further consideration of 4-acetamidophenol as an additive for mechanical property enhancement.

TABLE XXX - MECHANICAL PROPERTY DATA AND DEPOSITION PARAMETERS FOR ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 1 G/L OF 4-ACETAMIDOPHENOL AND 27 PPM BY WT. Cl^-

ENI Sample Number	Bath Temperature (°C)	Current Density (A/dm²)	Deposit Thickness (Cm)	Accumulated Ampere-Hours Per Liter	Mechanical Properties Ult. Str. Ksi	 Yield Str. Ksi	 Elongation,% In 5.08 Cm	Vickers Hardness 100 g Load
A-Acet-01	29.4	2.15	0.127	4.06	11.11	10.47	2.0	Not Determ.
A-Acet-02	29.4	2.15	0.109	6.90	Not tested because of brittleness.			

2.5 Studies Using Organic Additives Other Than Amines in Acid Copper Baths

Lamb, Johnson, and Valentine(3) used several non-amine organic additives in their acid copper sufate bath studies. Among these were thiourea, gelatin, molasses, lactic acid, and phenolsulfonic acid. A review of their mechanical property test results for these additives indicated that gelatin promoted the best improvements in ultimate and yield strengths. From various patent reviews, the Principal Investigator included several of the polyethylene glycol derivatives used for brightening and leveling of deposits in these studies. 2-Butyne-1,4-diol, an additive occasionally used in nickel electrolytes as a levelling agent and grain refiner, was included in the investigation.

2.5.1 Studies Using 2-Butene-1,4-diol in Acid Copper Sulfate Electrolytes

2-Butene-1,4-diol was added in the amount of 0.5 g/l to one of the purified 100 liter acid copper sulfate baths being used in this program. Three consecutive panels were electroformed and tested for mechanical properties and microstructures. Although box shields were not used in electroforming these panels, deposit thicknesses were fairly uniform. This additive did not improve mechanical properties in any way. Samples showed progressively lower elongation when tested for mechanical properties. Test data, electrolyte chemistry, and deposition parameters are summarized in Table XXXI. Metallographic examinations were made and photomicrographs are found in Figure 22.

2.5.2 ENI Studies Using Gelatin

40 mg per liter of gelatin, a nitrogenous organic compound produced from animal tissues and bone, was added to 100 liters of acid copper sulfate solution in Tank No. 1 and allowed to age for one week. Five specimens were deposited and tested for mechanical properties. After the fifth specimen

TABLE XXXI - MECHANICAL PROPERTY DATA AND DEPOSITION PARAMETERS FOR ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 0.5 G/L OF 2-BUTENE-1,4-DIOL AND 37 PPM BY WT. Cl⁻

ENI Sample Number	Bath Temperature (°C)	Current Density (A/dm²)	Deposit Thickness (Cm)	Accumulated Ampere-Hours Per Liter	Mechanical Properties Ult. Str. Ksi	Yield Str. Ksi	Elongation,% In 5.08 Cm	Vickers Hardness 100 g Load
2-But-01	29.4	2.15	0.097	2.80	26.32	14.74	11.0	Not Determ.
2-But-02	29.4	2.15	0.081	5.65	18.72	13.04	6.0	Not Determ.
2-But-03	29.4	2.15	0.081	8.50	20.59	13.95	4.5	Not Determ.

was plated and tested, the bath was purified and the concentration of gelatin was changed to 80 mg per liter. Two panels were produced at this additive level. Electrolyte chemistry, operating parameters, and test results are shown in Table XXXII.

TABLE XXXII - MECHANICAL PROPERTY DATA AND DEPOSITION PARAMETERS FOR ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 4 TO 8 MG/L OF GELATIN AND 27 PPM BY WT. Cl⁻

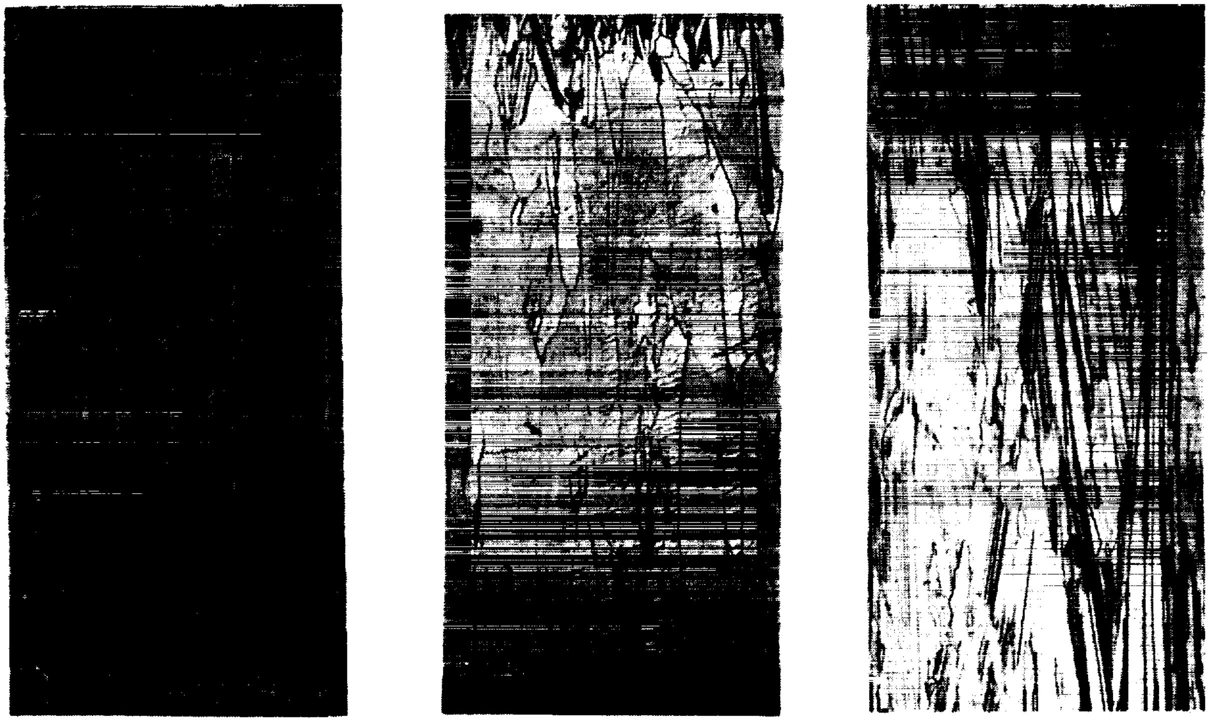
ENI Sample Number	Bath Temperature (°C)	Current Density (A/dm²)	Deposit Thickness (Cm)	Accumulated Ampere-Hours Per Liter	Mechanical Properties Ult. Str. Ksi	Yield Str. Ksi	Elongation,% In 5.08 Cm	Vickers Hardness 100 g Load
Gelatin Concentration of 40 mg/l:								
1-GEL-01	26.7	2.15	0.136	3.30	60.99	46.29	5.0	128
1-GEL-02	26.7	2.15	0.136	6.59	57.22	48.89	7.0	135
1-GEL-03	26.7	2.15	0.138	9.87	36.97	26.25	30.0	89
1-GEL-04	26.7	2.15	0.138	13.13	36.85	22.96	35.0	100
1-GEL-05	26.7	2.15	0.144	16.41	40.02	24.90	35.0	92
Gelatin Concentration of 80 mg/l:								
1-GEL-06	26.7	2.15	0.113	3.49	56.44	42.05	8.5	125
1-GEL-07	26.7	2.15	0.134	6.77	49.89	34.51	15.0	116

Microstructures of the deposits in Table XXXII are shown in Figures 23a, 23b, and 23c. It appears that the concentration of gelatine in any production bath would be difficult to control. The deposits start out with reasonably high strength value but have limited ductility. As deposition progresses, the strength decreases while the ductility improves greatly. This seems to take place in a short time span as measured by accumulated ampere-hours per liter of electrolyte. This indicates that the gelatin is consumed fairly rapidly. This conclusion is supported by the microstructural changes where small, columnar grains are replaced by large columnar grains as deposition progresses. Increasing the gelatin concentration did not improve strength, nor did it significantly delay the decay of mechanical strength and rapid increase in ductility as noted in Samples 1-GEL-06 and 1-GEL-07. Since box shields and identical agitation conditions were used on these samples and previously discussed TIPA samples, a direct comparison can be made. Using TIPA as the additive, equivalent ultimate and yield strengths to those using gelatin can be achieved while maintaining better ductility. These improvements can be maintained over a much longer plating time than found with the gelatin addition bath. Since electroforming of large thicknesses often requires days, or even weeks, it would very labor intensive to maintain proper gelatin concentration.

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 0.5G/L OF 2-BUTENE-1,4-DIOL

Chemistry	**Sample 2-BUT-01**	**Sample 2-BUT-02**	**Sample 2-BUT-03**
$CuSO_4 \cdot 5H_2O$	243.4 g/l	243.4 g/l	243.4 g/l
H_2SO_4	68.9 g/l	68.9 g/l	68.9 g/l
Chloride Ion, By Weight	37 ppm	37 ppm	37 ppm
2-Butene-1,4-diol	0.5 g/l	0.5 g/l	0.5 g/l
Operating Parameters			
Bath Temperature	29.4°C	29.4°C	29.4°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-1, Frame Shield	CO-1, Frame Shield	CO-1, Frame Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	44.5	45.3	112.4
Accumulated Ampere-Hours Per Liter	2.80	5.66	12.74
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	26.32	18.72	20.59
Yield Strength, ksi	14.74	13.04	13.95
Elongation, % in 5.08 cm	11.0	6.0	13.5
Hardness, Vickers, 100 g Load	Not Determined	Not Determined	Not Determined
Thickness, cm	0.097	0.081	0.201

Microstructures (Magnification 100X)



Sample 2-BUT-01

Sample 2-BUT-02

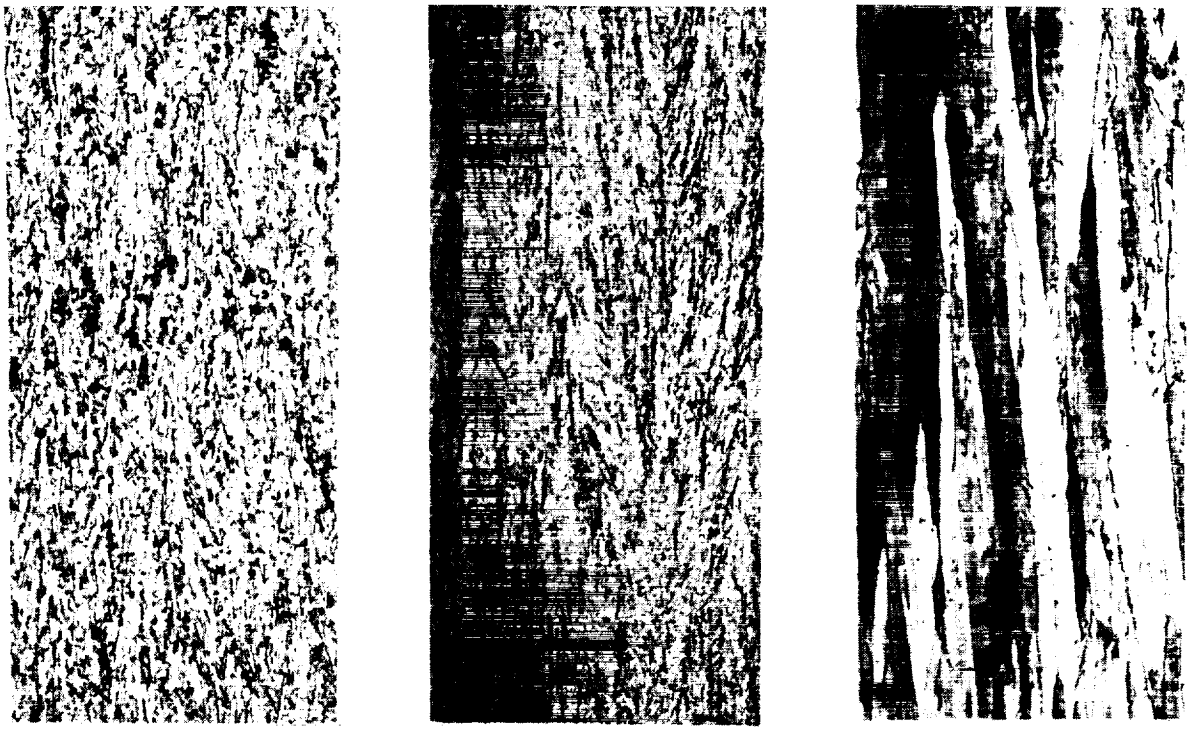
Sample 2-BUT-03

Figure 22. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 0.5 g/l of 2-Butene-1,4-diol During the Initial 12.7 Ampere-Hours Per Liter Use Period.

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 40 MG/L OF GELATIN

Chemistry	**Sample 1-GEL-01**	**Sample 1-GEL-02**	**Sample 1-GEL-03**
$CuSO_4 \cdot 5H_2O$	200.0 g/l	200.0 g/l	196.2 g/l
H_2SO_4	68.1 g/l	71.1 g/l	71.1 g/l
Chloride Ion, By Weight	27 ppm	27 ppm	27 ppm
Gelatin	40 mg/l	40 mg/l	40 mg/l
Operating Parameters			
Bath Temperature	26.7°C	26.7°C	26.7°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4, Box Shield	CO-4, Box Shield	CO-4, Box Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	52.33	52.25	52.0
Accumulated Ampere-Hours Per Liter	3.30	6.59	9.87
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	60.99	57.22	36.97
Yield Strength, ksi	46.29	48.89	26.25
Elongation, % in 5.08 cm	5.0	7.0	30.0
Hardness, Vickers, 100 g Load	128	135	89
Thickness, cm	0.136	0.136	0.138

Microstructures (Magnification 100X)



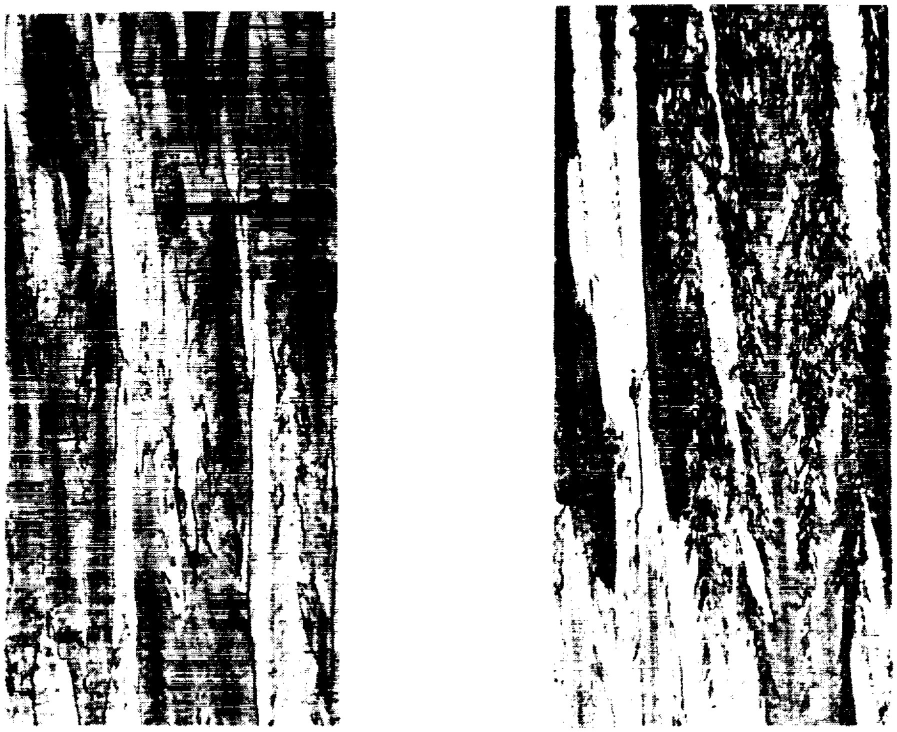
Sample 1-GEL-01 Sample 1-GEL-02 Sample 1-GEL-03

Figure 23a. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 40 mg/l of Gelatin During the Initial 9.9 Ampere-Hours Per Liter Use Period.

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 40 MG/L OF GELATIN

Chemistry	**Sample 1-GEL-04**	**Sample 1-GEL-05**
$CuSO_4 \cdot 5H_2O$	191.0 g/l	201.5 g/l
H_2SO_4	68.1 g/l	67.4 g/l
Chloride Ion, By Weight	27 ppm	27 ppm
Gelatin	40 mg/l	40 mg/l
Operating Parameters		
Bath Temperature	26.7°C	26.7°C
Current Density	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4, Box Shield	CO-4, Box Shield
Continuous Filtration	20 Microns	20 Microns
Deposition Time, Hours	51.5	52.0
Accumulated Ampere-Hours Per Liter	13.13	6.41
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	36.85	40.02
Yield Strength, ksi	22.96	24.90
Elongation, % in 5.08 cm	35.0	5.0
Hardness, Vickers, 100 g Load	100	92
Thickness, cm	0.138	0.144

Microstructures (Magnification 100X)



Sample 1-GEL-04

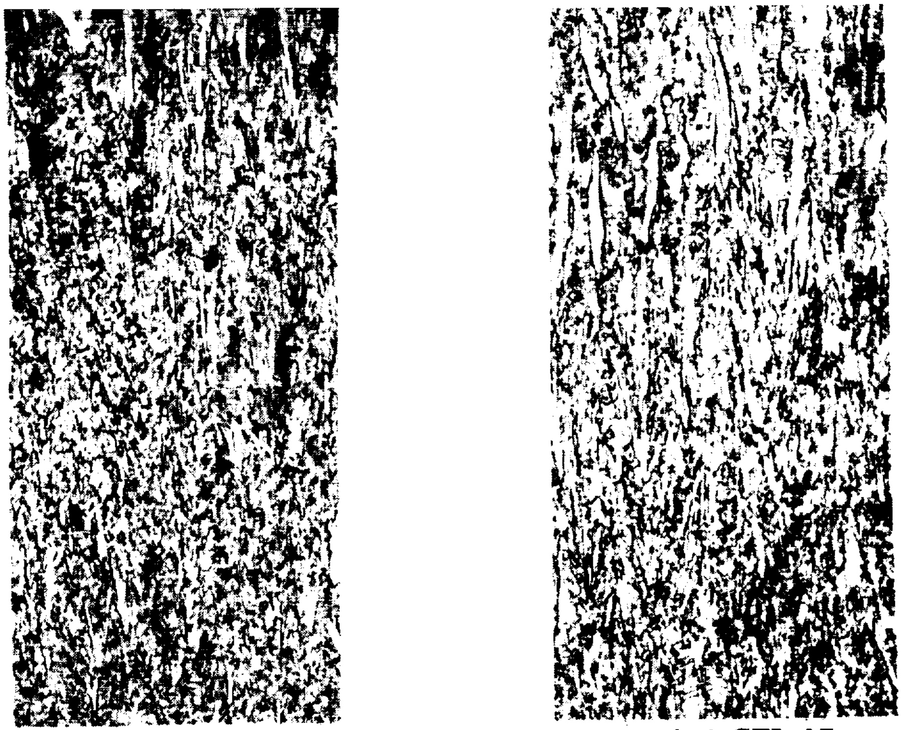
Sample 1-GEL-05

Figure 23b. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 40 mg/l of Gelatin During the 13.1 to 16.4 Ampere-Hours Per Liter Use Period.

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 40 MG/L OF GELATIN

Chemistry	**Sample 1-GEL-06**	**Sample 1-GEL-07**
$CuSO_4 \cdot 5H_2O$	195.5 g/l	196.2 g/l
H_2SO_4	68.9g/l	68.9 g/l
Chloride Ion, By Weight	27 ppm	27 ppm
Gelatin	80 mg/l	80 mg/l
Operating Parameters		
Bath Temperature	26.7°C	26.7°C
Current Density	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4, Box Shield	CO-4, Box Shield
Continuous Filtration	20 Microns	20 Microns
Deposition Time, Hours	55.4	52.08
Accumulated Ampere-Hours Per Liter	3.49	6.77
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	56.44	49.89
Yield Strength, ksi	42.05	34.51
Elongation, % in 5.08 cm	8.5	15.0
Hardness, Vickers, 100 g Load	125	116
Thickness, cm	0.113	0.134

Microstructures (Magnification 100X)



Sample 1-GEL-06

Sample 1-GEL-07

Figure 23c. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 80 mg/l of Gelatin During the Initial 6.8 Ampere-Hours Per Liter Use Period.

2.5.3 Studies Using High Molecular Weight Organic Polymer Based Additives

Reviews of patent literature have shown that high molecular weight organic polymer additives have beneficial effects in acid copper deposition. The application of such organic additives in these baths has been in the areas of thin deposits, mainly for printed circuit boards where levelling, brightness, and reasonably good ductility have been sought. They have been used independently, or with other additives to accomplish these benefits. No work has been previously reported on electroformforming thick deposits from such baths for the purpose of improving mechanical properties, in particular, ultimate and yield strengths. Such additives were investigated in this program, and the two showing most promise in production use are reported. Since these compounds are currently considered proprietary, they shall be called PEG-A and PEG-B.

2.5.3.1 Investigation of PEG-A as an Additive for Acid Copper Sulfate Baths

The initial study of this compound was made in a 100 liter acid copper bath, Tank No. 5 using 0.5 g/l of PEG-A as the only additive in the electrolyte. The next study was made with an increase of PEG-A concentration to 1 g/l. Mechanical property test results are shown in Table XXXIII. From these results it appears that significantly better mechanical properties were obtained with only 0.5 g/l of PEG-A in the bath rather than 1.0 g/l. These results represent a large improvement over those for triisopropanolamine (TIPA). The Vickers Hardness was unexpectedly high, and ductility was satisfactory.

TABLE XXXIII - MECHANICAL PROPERTY DATA AND DEPOSITION PARAMETERS FOR ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 0.5 OR 1.0 G/L PEG-A AND 61 PPM BY WEIGHT CHLORIDE ION

ENI Sample Number	Bath Temperature (°C)	Current Density (A/dm^2)	Deposit Thickness (Cm)	Accumulated Ampere-Hours Per Liter	Mechanical Properties			Vickers Hardness 100 g Load
					Ult. Str. Ksi	Yield Str. Ksi	Elongation,% In 5.08 Cm	
PEG-A Concentration of 0.5 G/L:								
5-PEGA-01	26.7	2.15	0.084	1.96	80.95	65.73	9.0	161
5-PEGA-02	26.7	2.15	0.084	4.15	80.76	64.43	11.0	161
5-PEGA-03	26.7	2.15	0.109	6.63	78.76	63.53	10.0	161
PEG-A Concentration of 1.0 G/L:								
5-PEGA-08	26.7	2.15	0.208	4.64	73.92	54.44	12.5	137
5-PEGA-09	26.7	2.15	0.124	7.59	73.74	54.75	9.0	159
5-PEGA-10	26.7	2.15	0.122	10.32	76.89	55.81	7.0	156

The microstructure of these deposits is quite different from the columnar grain structures seen in most of the acid copper sulfate deposits examined to this point. The PEG-A appears to promote formation of a very fine equiaxed grain as illustrated in Figures 24a and 24b. Finer grains were found in the specimens from the TIPA containing electrolyte illustrated in Figure 17a; however, the TIPA refined grains could not be maintained over prolonged deposition cycles.

The effects of PEG-A and a second additive on mechanical properties were investigated when triisopropanolamine (TIPA) was included in the acid copper sulfate bath. Table XXXIV lists plating parameters and test results for a series of specimens deposited from the bath with both additives. TIPA was used in concentrations of 1 and 2 grams per liter in this study. Noting only the test results

TABLE XXXIV - MECHANICAL PROPERTIES AND DEPOSITION PARAMETERS **FOR** ACID COPPER SULFATE DEPOSITS FROM AN ELECTROLYTE CONTAINING 0.5 G/L OF PEG-A, 1 OR 2 G/L OF TIPA, AND 61 PPM BY WT. OF CHLORIDE ION

ENI Sample Number	Bath Temperature (°C)	Current Density (A/dm^2)	Deposit Thickness (Cm)	Accumulated Ampere-Hours Per Liter	Mechanical Properties			Vickers Hardness 100 g Load
					Ult. Str. Ksi	Yield Str. Ksi	Elongation,% In 5.08 Cm	
PEG-A Concentration of 0.5 G/L; TIPA Concentration of 1 G/L:								
5-PATI-04	26.7	1.84	0.104	2.43	74.10	55.88	13.0	162
5-PATI-05	26.7	2.15	0.119	5.32	73.55	56.59	7.5	160
5-PATI-06	26.7	2.15	0.130	8.30	71.37	54.31	9.0	160
5-PATI-07	26.7	2.15	0.114	11.09	70.67	53.43	9.0	160
PEG-A Concentration of 0.5 G/L; TIPA Concentration of 2 G/L:								
5-PATI-01	26.7	2.15	0.191	4.40	78.22	61.36	10.0	157
5-PATI-02	26.7	2.15	0.127	7.19	77.49	57.37	10.0	162
5-PATI-03	26.7	2.15	0.127	10.69	82.31	62.62	8.5	151

for the samples produced with TIPA present at only 1 g/l, there is an unexpected decrease in ultimate and yield strengths to levels below those where only the PEG-A was present at 0.5 g/l. Increasing the TIPA to 2 g/l, with 0.5 g/l of PEG-A present, restored the mechanical properties to the range found with 0.5 g/l of PEG-A alone (Table XXXIII). Vickers hardness values were much higher than experienced for TIPA additive deposits.

Microstructures of the deposites summarized in Table XXXIV are illustrated in Figures 25a, 25b, and 25c. The grains are extremely fine in all examples and there are no signs of columnarity typical with most deposits from baths with only TIPA as the additive. It should be mentioned that the 2 g/l specimens were produced before purifying the bath by peroxide and carbon treatments and making fresh additions of 0.5 g/l of PEG-A and 1 g/l of TIPA. A bath aging period was not used between making samples from these baths. From the mechanical property test results and the microstructures observed, it is concluded that the PEG-A additive exerts a much greater influence on mechanical properties, hardness, and microstructure than does TIPA.

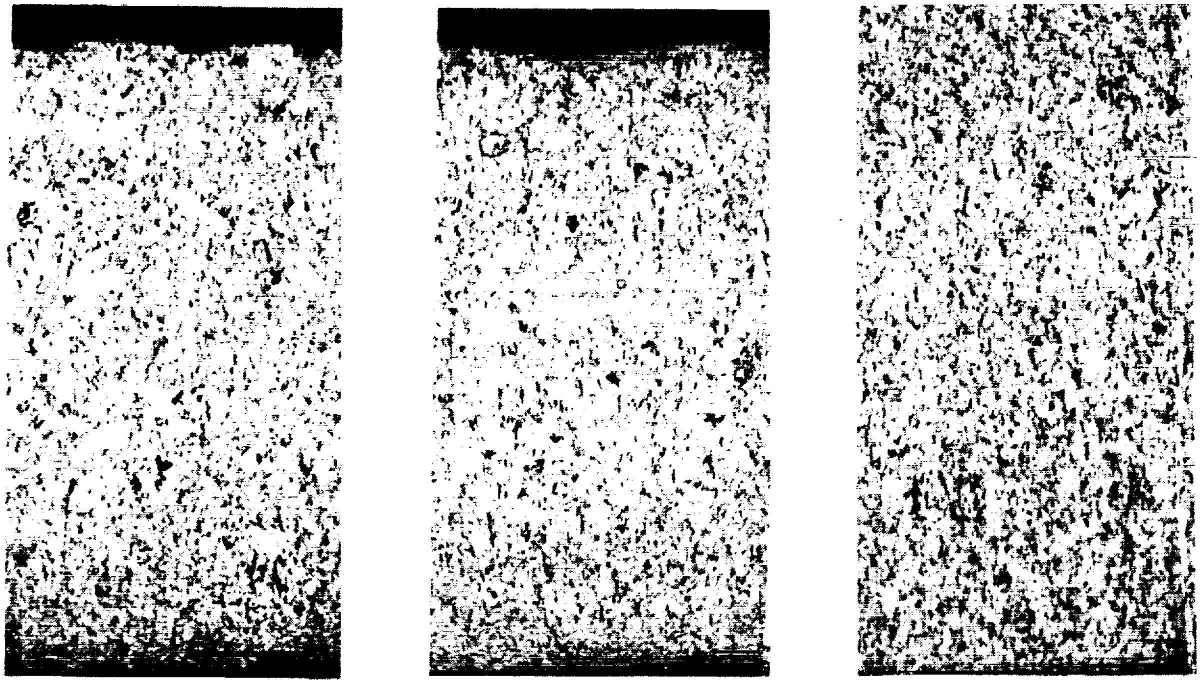
2.5.3.2 Investigation of PEG-B as an Additive for Acid Copper Sulfate Baths

Another long chain organic polymer additive, refered to as PEG-B in this study, was investigated in Tank No. 3, a 100 liter acid copper sulfate facility. This bath had at one time contained 0.00015 g/l of selenium dioxide. This was believed to be fairly depleted and hence of no influence on mechanical properties in subsequent studies. Initial PEG-B concentration was 0.5 g/l with no other additives. PEG-B concentration was later increased to 1.5 g/l after purification of the bath by hydrogen peroxide destruction of the organic additive and double carbon treating. Test data and electrodeposition parameters for the specimens produced at the two PEG-B concentrations are shown in Table XXXV. Although the ultimate and yield strengths of these deposits at ambient temperature were generally lower than those for deposits from acid copper sulfate baths with PEG-A, the ductility was

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 0.5 G/L OF PEG-A

Chemistry	**Sample 5-PEGA-01**	**Sample 5-PEGA-02**	**Sample 5-PEGA-03**
$CuSO_4 \cdot 5H_2O$	223.2 g/l	223.2 g/l	223.2 g/l
H_2SO_4	75.6 g/l	75.6 g/l	75.6 g/l
Chloride Ion, By Weight	61 ppm	61 ppm	61 ppm
PEG-A	0.5 g/l	0.5 g/l	0.5 g/l
Operating Parameters			
Bath Temperature	26.7°C	26.7°C	26.7°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4, Box Shield	CO-4, Box Shield	CO-4, Box Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	31.67	35.25	40.0
Accumulated Ampere-Hours Per Liter	1.96	4.15	6.63
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	80.95	80.76	78.76
Yield Strength, ksi	65.73	64.43	63.53
Elongation, % in 5.08 cm	9.0	11.0	10.0
Hardness, Vickers, 100 g Load	161	161	161
Thickness, cm	0.084	0.084	0.109

Microstructures (Magnification 100X)



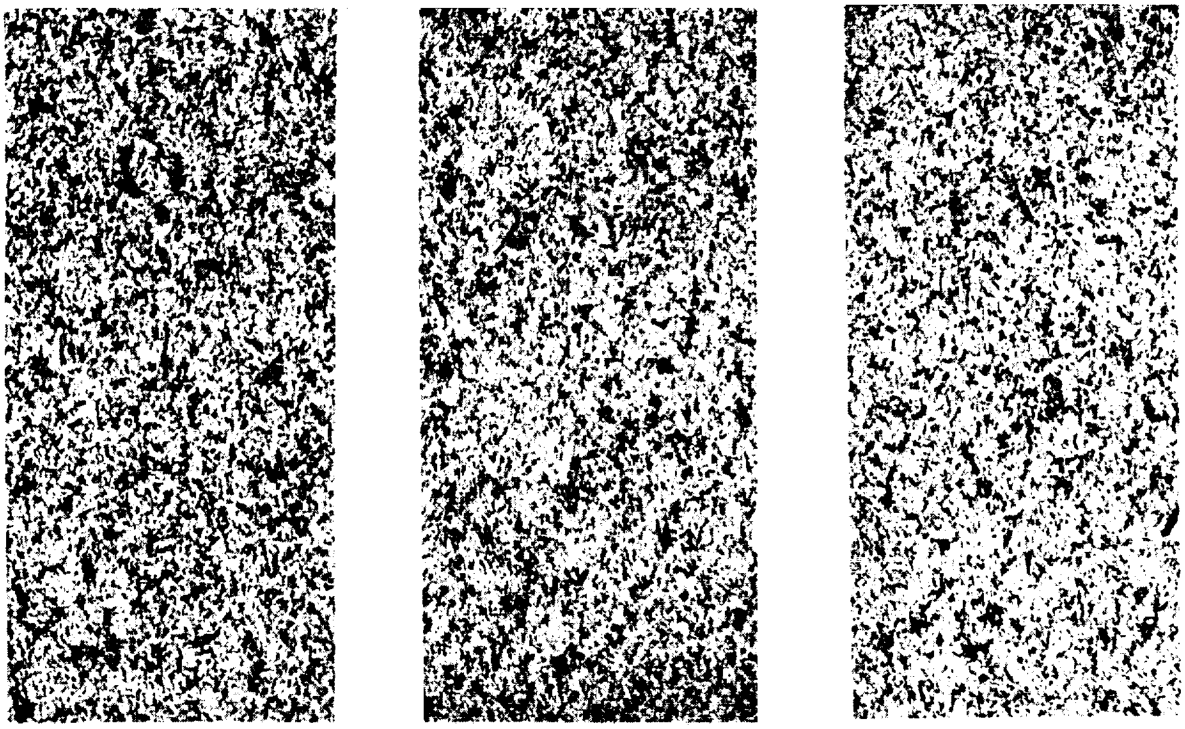
Sample 5-PEGA-01 Sample 5-PEGA-02 Sample 5-PEGA-03

Figure 24a. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 0.5 g/l of PEG-A During the Initial 6.6 Ampere-Hours Per Liter Use Period.

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 1.0 G/L OF PEG-A

Chemistry	Sample 5-PEGA-08	Sample 5-PEGA-09	Sample 5-PEGA-10
$CuSO_4 \cdot 5H_2O$	217.2 g/l	220.2 g/l	218.7 g/l
H_2SO_4	75.6 g/l	74.1 g/l	74.1 g/l
Chloride Ion, By Weight	61 ppm	61 ppm	61 ppm
PEG-A	1.0 g/l	1.0 g/l	1.0 g/l
Operating Parameters			
Bath Temperature	26.7°C	26.7°C	26.7°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4, Box Shield	CO-4, Box Shield	CO-4, Box Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	74.8	47.5	44.0
Accumulated Ampere-Hours Per Liter	4.64	7.59	10.32
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	73.92	73.74	76.89
Yield Strength, ksi	65.73	54.75	55.81
Elongation, % in 5.08 cm	9.0	9.0	7.0
Hardness, Vickers, 100 g Load	137	159	156
Thickness, cm	0.208	0.124	0.122

Microstructures (Magnification 100X)



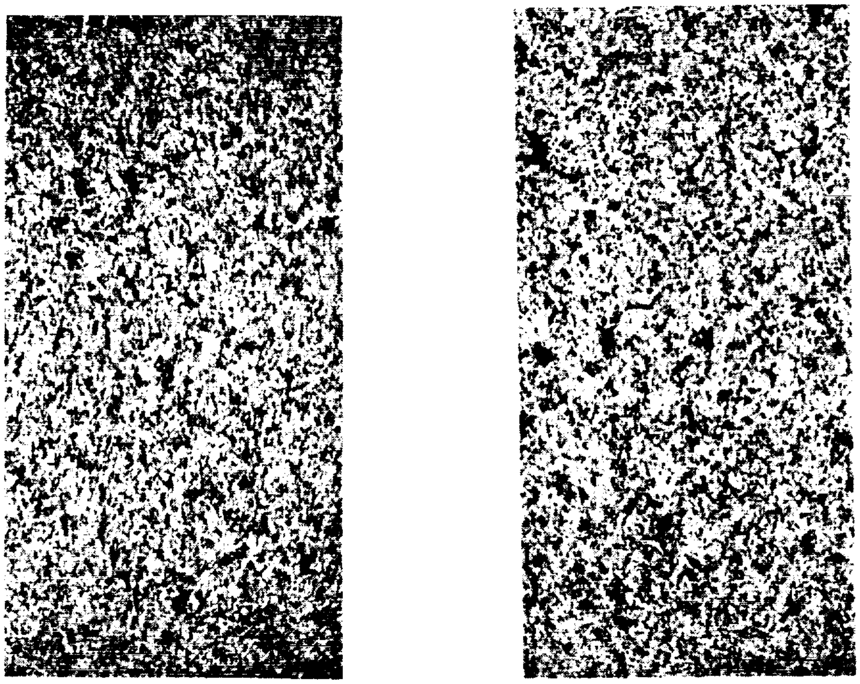
Sample 5-PEGA-08 Sample 5-PEGA-09 Sample 5-PEGA-10

Figure 24b. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 1.0 g/l of PEG-A During the Initial 10.3 Ampere-Hours Per Liter Use Period.

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 0.5 G/L PEG-A AND 1 G/L TIPA

Chemistry	**Sample 5-PATI-04**	**Sample 5-PATI-05**
$CuSO_4 \cdot 5H_2O$	228.4 g/l	224.7 g/l
H_2SO_4	68.1 g/l	69.6 g/l
Chloride Ion, By Weight	61 ppm	61 ppm
PEG-A	0.5 g/l	0.5 g/l
Triisopropanolamine	1.0 g/l	1.0 g/l
Operating Parameters		
Bath Temperature	26.7°C	26.7°C
Current Density	1.84 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4, Box Shield	CO-4, Box Shield
Continuous Filtration	20 Microns	20 Microns
Deposition Time, Hours	45.0	46.67
Accumulated Ampere-Hours Per Liter	2.43	5.32
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	74.10	73.55
Yield Strength, ksi	55.88	56.59
Elongation, % in 5.08 cm	13.0	7.5
Hardness, Vickers, 100 g Load	162	160
Thickness, cm	0.104	0.119

Microstructures (Magnification 100X)



Sample 5-PATI-04

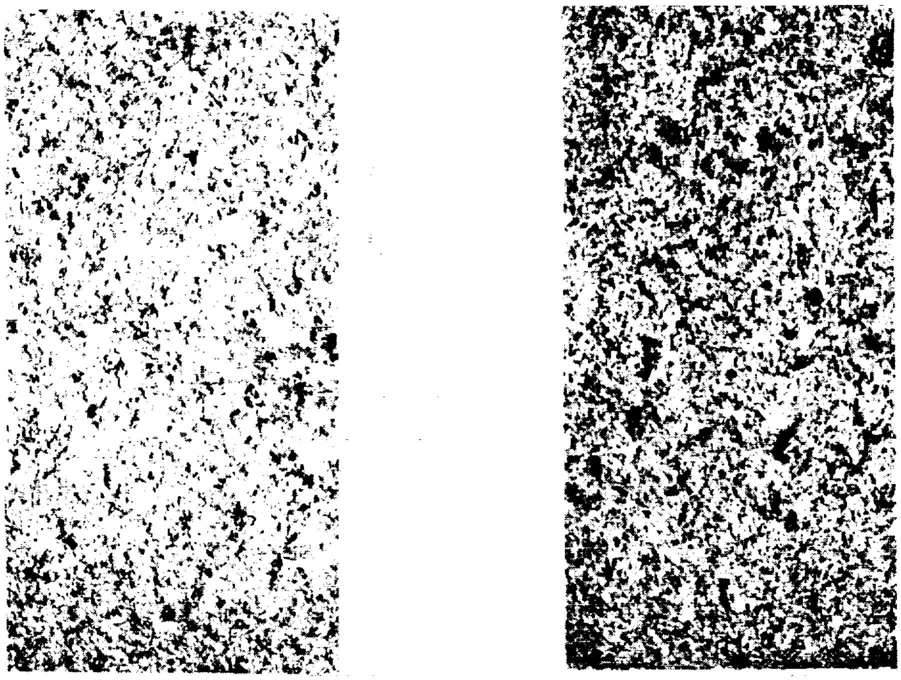
Sample 5-PATI-05

Figure 25a. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 0.5 g/l PEG-A and 1 g/l TIPA During the Initial 5.3 Ampere-Hours Per Liter Use Period.

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 0.5 G/L PEG-A AND 1 G/L TIPA

Chemistry	**Sample 5-PATI-06**	**Sample 5-PATI-07**
$CuSO_4 \cdot 5H_2O$	223.9 g/l	223.9 g/l
H_2SO_4	68.9 g/l	68.9 g/l
Chloride Ion, By Weight	61 ppm	61 ppm
PEG-A	0.5 g/l	0.5 g/l
Triisopropanolamine	1.0 g/l	1.0 g/l
Operating Parameters		
Bath Temperature	26.7°C	26.7°C
Current Density	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4, Box Shield	CO-4, Box Shield
Continuous Filtration	20 Microns	20 Microns
Deposition Time, Hours	48.0	45.0
Accumulated Ampere-Hours Per Liter	8.30	11.09
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	71.37	70.67
Yield Strength, ksi	54.31	53.43
Elongation, % in 5.08 cm	9.0	9.0
Hardness, Vickers, 100 g Load	160	160
Thickness, cm	0.130	0.114

Microstructures (Magnification 100X)



Sample 5-PATI-06

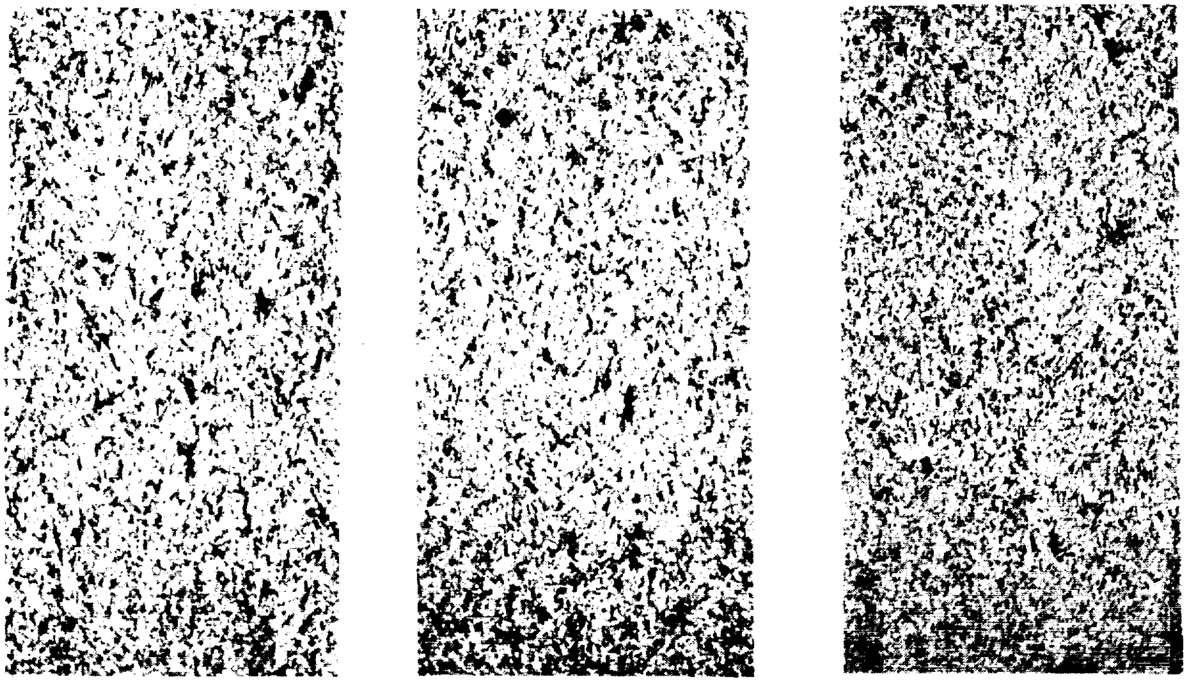
Sample 5-PATI-07

Figure 25b. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 0.5 g/l PEG-A and 1 g/l TIPA During the 5.3 to 11.1 Ampere-Hours Per Liter Use Period.

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 0.5 G/L PEG-A AND 2 G/L TIPA

Chemistry	**Sample 5-PATI-01**	**Sample 5-PATI-02**	**Sample 5-PATI-03**
$CuSO_4$ $5H_2O$	222.4 g/l	223.2 g/l	224.7 g/l
H_2SO_4	74.9 g/l	68.1 g/l	69.6 g/l
Chloride Ion, By Weight	61 ppm	61 ppm	61 ppm
PEG-A	0.5 g/l	0.5 g/l	0.5 g/l
Triisopropanolamine	2.0 g/l	2.0 g/l	2.0 g/l
Operating Parameters			
Bath Temperature	26.7°C	26.7°C	26.7°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4, Box Shield	CO-4, Box Shield	CO-4, Box Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	71.0	45.0	45.0
Accumulated Ampere-Hours Per Liter	4.40	7.19	10.69
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	78.22	77.49	82.31
Yield Strength, ksi	61.36	57.37	62.62
Elongation, % in 5.08 cm	10.0	10.0	8.5
Hardness, Vickers, 100 g Load	157	162	151
Thickness, cm	0.191	0.127	0.122

Microstructures (Magnification 100X)



Sample 5-PATI-01 Sample 5-PATI-02 Sample 5-PATI-03

Figure 25c. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 0.5 g/l of PEG-A and 2 g/l of TIPA During the Initial 10.7 Ampere-Hours Per Liter Use Period.

better. Vickers hardness values for the deposits with PEG-B are lower than those for material from the bath with PEG-A, and this is reflected in the improved ductility of the PEG-B specimens. Microstructures of the samples in Table XXXV are found in Figures 26a and 26b. All of the PEG-B samples contained fine, equi-axed grains as was noted in the PEG-A deposits.

TABLE XXXV - MECHANICAL PROPERTIES AND DEPOSITION PARAMETERS FOR ACID COPPER SULFATE DEPOSITS FROM AN ELECTROLYTE CONTAINING 0.5 OR 1.5 G/L OF PEG-B AND 60 PPM BY WT. OF CHLORIDE ION

ENI Sample Number	Bath Temperature (°C)	Current Density (A/dm^2)	Deposit Thickness (Cm)	Accumulated Ampere-Hours Per Liter	Mechanical Properties			Vickers Hardness 100 g Load
					Ult. Str. Ksi	Yield Str. Ksi	Elongation,% In 5.08 Cm	
PEG-B Concentration of 0.5 G/L:								
3-PEGB-01	26.7	2.15	0.109	2.85	64.15	45.39	12.5	135
3-PEGB-02	26.7	2.15	0.107	5.63	61.52	43.35	9.0	128
3-PEGB-03	26.7	2.15	0.102	8.37	61.73	41.75	14.0	132
3-PEGB-04	26.7	2.15	0.112	11.16	58.62	43.23	11.5	125
PEG-B Concentration of 1.5 G/L:								
3-PEGB-05	26.7	2.15	0.119	2.79	71.40	53.50	11.5	138
3-PEGB-06	26.7	2.15	0.061	4.34	68.07	48.68	12.0	140

2.6 Elevated Temperature Performance of Wrought Copper and Electrodeposited Copper

2.6.1 Background Information

Lamb, Johnson, and Valentine(3) investigated effects of heat treatment and temperature on the mechanical properties of copper deposits from various electrolytes. Their "annealing" was performed in vacuum or argon. They concluded that heat treating caused decrease in tensile strength and increase in ductility. However, the changes were small for deposits that were initially soft and ductile such as those from non-addition agent acid sulfate baths, the fluoborate bath, and the pyrophosphate bath. They claimed that acid sulfate deposits from baths with triisopropanolamine resisted change to a fairly high heat treating temperature of 325°- 400°C, then abruptly lost strength and gained ductility.

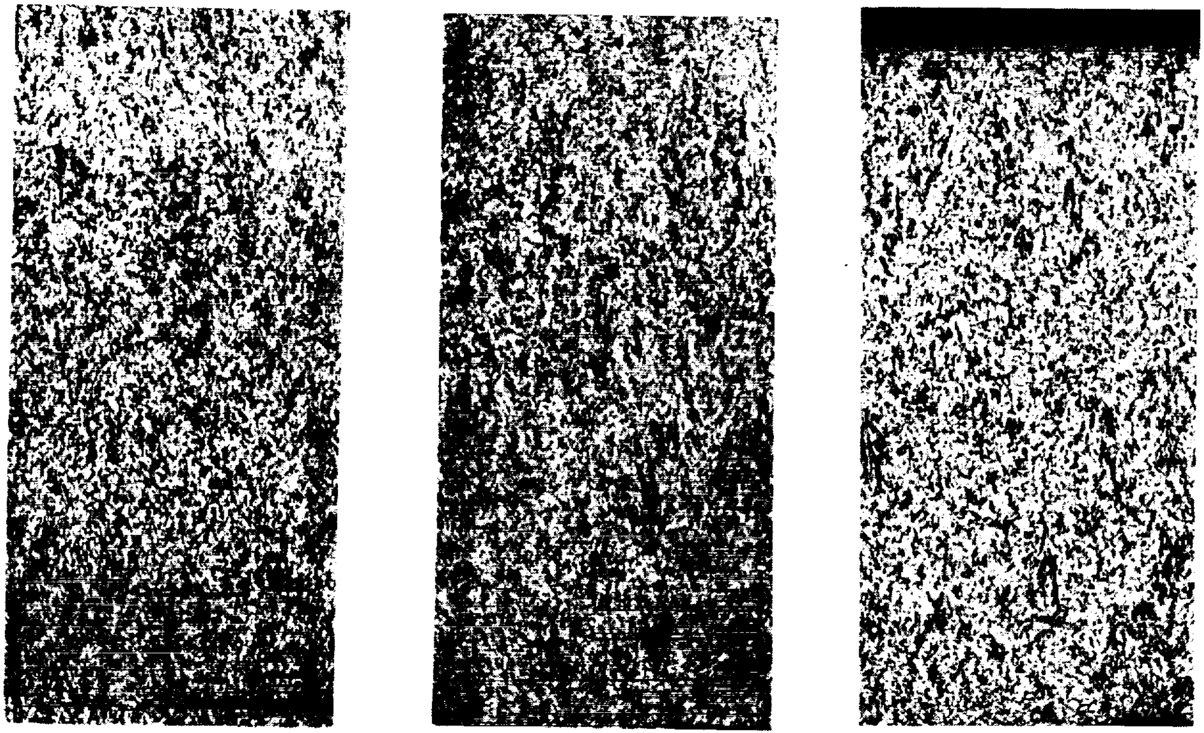
They noted that the effect of heat treating on hardness was similar to its effect on tensile strength. The deposits that were initially soft or fairly soft (non-addition agent baths) undergo minor additional softening. Yield strength was found to decrease with heat treatment for all of the deposits, reaching the extremely low value of 3,000 ksi for fluoborate deposits annealed at 500°C. Their test results are shown in Table XXXVI. It will be noted that as-deposited mechanical properties are reported for all general types of electrolytes studied. The heat treated samples were all tested at ambient (20°C) temperature.

Examples of the microstructures of the "as plated" and heat treated specimens from Lamb, Johnson, and Valentine studies are shown in Figures 27a through 27d. The grain structure of conventionally deposited acid sulfate copper is typically coarse and columnar as illustrated in Figure 27a. The initial thickness is composed of very fine columnar grains followed by a coarsening structure. The 325°C

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED IN A BATH CONTAINING 0.5 G/L PEG-B

Chemistry	**Sample 3-PEGB-01**	**Sample 3-PEGB-02**	**Sample 3-PEGB-03**
$CuSO_4 \cdot 5H_2O$	188.0 g/l	196.2 g/l	188.0 g/l
H_2SO_4	82.4 g/l	83.1 g/l	82.4 g/l
Chloride Ion, By Weight	60 ppm	60 ppm	60 ppm
PEG-B	0.5 g/l	0.5 g/l	0.5 g/l
Operating Parameters			
Bath Temperature	26.7°C	26.7°C	26.7°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4, Box Shield	CO-4, Box Shield	CO-4, Box Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	46.0	44.75	44.25
Accumulated Ampere-Hours Per Liter	2.85	5.63	8.37
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	64.15	61.52	61.73
Yield Strength, ksi	45.39	43.35	41.75
Elongation, % in 5.08 cm	12.5	9.0	14.0
Hardness, Vickers, 100 g Load	135	128	132
Thickness, cm	0.109	0.107	0.102

Microstructures (Magnification 100X)



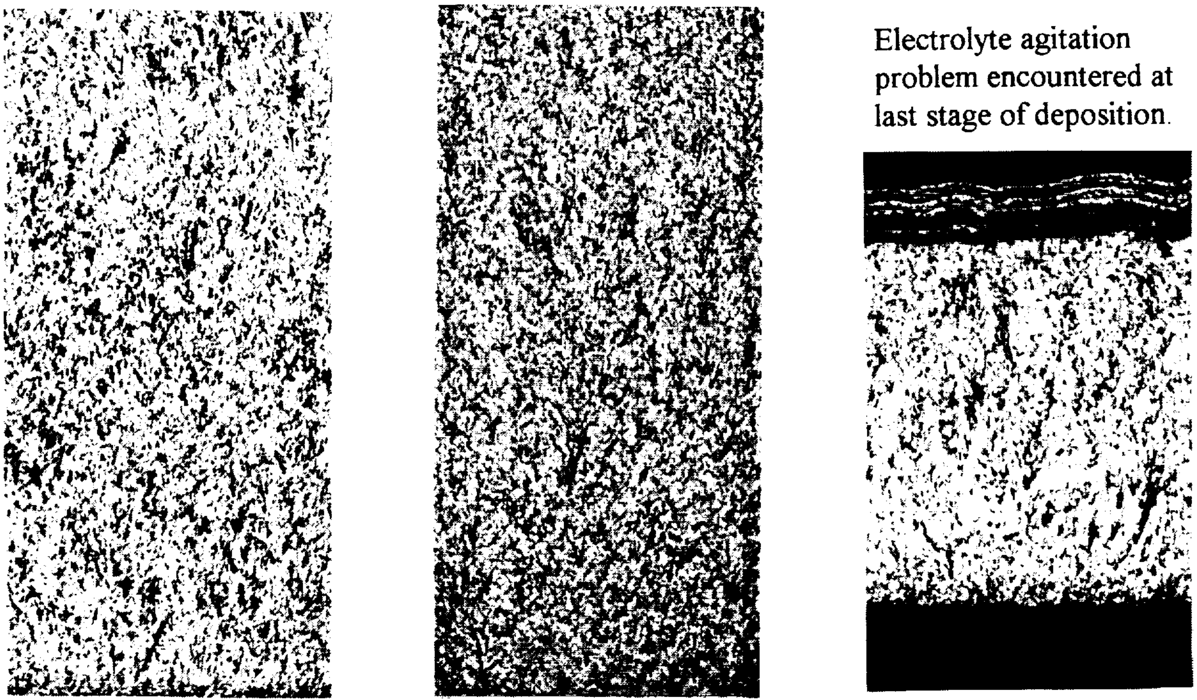
Sample 3-PEGB-01 Sample 3-PEGB-02 Sample 3-PEGB-03

Figure 26a. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 0.5 /l of PEG-B During the Initial 8.4 Ampere-Hours Per Liter Use Period.

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF ACID COPPER SULFATE DEPOSITS PRODUCED IN BATHS CONTAINING 0.5 OR 1.5G/L PEG-B

Chemistry	**Sample 3-PEGB-04**	**Sample 3-PEGB-05**	**Sample 3-PEGB-06**
$CuSO_4 \cdot 5H_2O$	188.0 g/l	188.7 g/l	188.7 g/l
H_2SO_4	82.4 g/l	83.1 g/l	83.1 g/l
Chloride Ion, By Weight	60 ppm	60 ppm	60 ppm
PEG-B	0.5 g/l	1.5 g/l	1.5 g/l
Operating Parameters			
Bath Temperature	26.7°C	26.7°C	26.7°C
Current Density	2.15 A/dm^2	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	CO-4, Box Shield	CO-4, Box Shield	CO-4, Box Shield
Continuous Filtration	20 Microns	20 Microns	20 Microns
Deposition Time, Hours	45.0	45.0	25.0
Accumulated Ampere-Hours Per Liter	11.16	2.79	4.34
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	58.62	71.40	68.07
Yield Strength, ksi	43.23	53.50	48.68
Elongation, % in 5.08 cm	11.5	11.5	12.0
Hardness, Vickers, 100 g Load	125	138	140
Thickness, cm	0.112	0.119	0.061

Microstructures (Magnification 100X)



Electrolyte agitation problem encountered at last stage of deposition.

Sample 3-PEGB-04 Sample 3-PEGB-05 Sample 3-PEGB-06

Figure 26b. Data and Microstructures of Deposits from an Acid Copper Sulfate Bath with 0.5 g/l of PEG-B During the 8.4 to 11.2 Ampere-Hours Per Liter Use Period and 1.5 g/l of PEG-B During the Initial 4.3 Ampere-Hours Per Liter Use Period.

TABLE XXXVI - EFFECTS OF HEAT TREATING ON PROPERTIES OF ELECTRO-DEPOSITED COPPER AND PROPERTIES AT LOW AND HIGH TEMPERATURES(3)

Test Panel Number	Bath Symbol (Page 5)	Addition Agent Name	Addition Agent (g/l)	Bath Temp. (°C)	Current Density (A/dm^2)	Heat Treat Temp. (°C)	Heat Treat Time (Hrs)	Test Temp. (°C)	Mechnaical Properties Ult. Str. Ksi	Mechnaical Properties Yield Str. Ksi	Mechnaical Properties Elongation, % In 5.08 Cm
Acid Copper Sulfate Baths:											
322-4	Cu2-H2	None		30	2.0	None		Ambient	32	11	39
						150	2.00	Ambient	31	9	41
						325	0.25	Ambient	31	10	40
						500	0.25	Ambient	30	5	44
						None		-78	38	Not Determ.	41
						None		150	20	Not Determ.	13
						None		325	11	Not Determ.	7
337-41	Cu2-H3	TIPA	3.5	30	5.0	None		Ambient	71	43	7
						150	2.00	Ambient	62	34	8
						325	0.25	Ambient	62	34	11
						500	0.25	Ambient	32	11	32
						None		-78	78	Not Determ.	14
						None		150	39	Not Determ.	3
						None		325	12	Not Determ.	4
Acid Copper Fluoborate Baths:											
342-45	F-1	None		30	8.0	None		Ambient	37	16	31
						150	2.00	Ambient	35	14	33
						325	0.25	Ambient	33	13	29
						500	0.25	Ambient	28	14	3
						None		-78	44	Not Determ.	33
						None		150	28	Not Determ.	22
						None		325	14	Not Determ.	8
Pyrophosphate Baths:											
317-20	Pyrophosphate	None		50	2.0	None		Ambient	38	20	39
						150	2.00	Ambient	38	18	42
						325	0.25	Ambient	36	15	46
						500	0.25	Ambient	31	8	56
						None		-78	49	Not Determ.	39
						None		150	29	Not Determ.	47
						None		325	16	Not Determ.	25

heat treatment resulted in recrystallization mainly of the fine grain region. After the 500°C treatment, the entire cross-section showed recrystallization to large columnar grains. From Table XXXVI it is noted that very little mechanical property change occured as a result of these heat treatments, although a significant amount of recrystallization took place.

The fine grained acid copper sulfate deposits shown in Figure 27b were produced from baths containing TIPA at either 2 or 3.5 g/l. The deposit from the bath containing 2 g/l of TIPA has equiaxed grains of medium size after annealing at 500°C, while the deposit from the 3.5 g/l bath also has equiaxed grains but with many voids (black areas). These investigators did not mention the current density used during deposition of the sample from the 2 g/l bath; it is assumed that it was 5 A/dm^2 as was used for the sample from the 3.5 g/l bath. They concluded that the black voids were due to gas from additive entrapment during deposition. Since the problem was not noted on the 2 g/l TIPA sample, it may be due to a combination of high additive concentration and high current density.

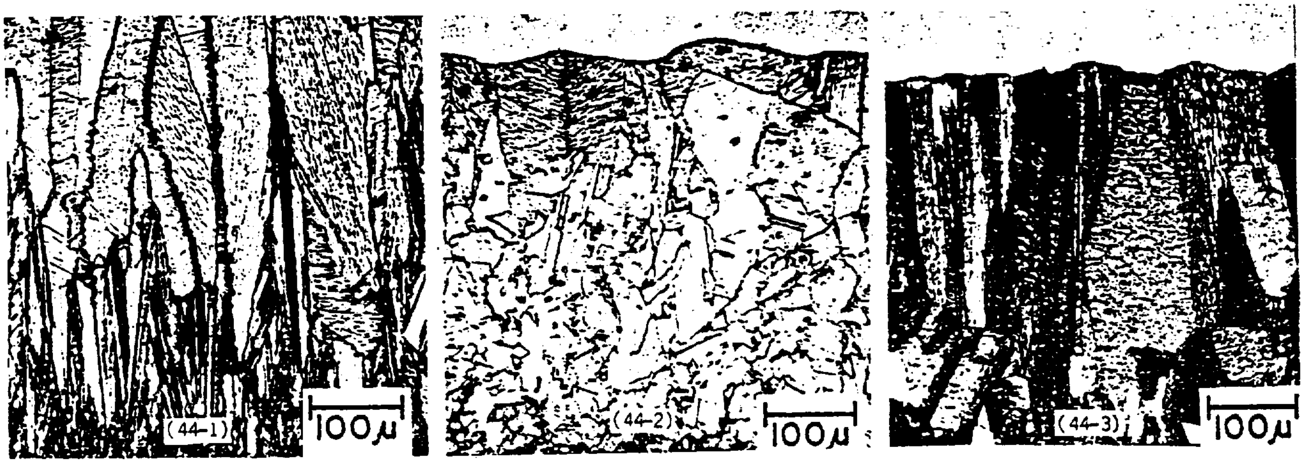


Figure 27a. Effect of Heat Treating on Structure of a Coarse Grained Acid Copper Sulfate Deposit Plated at 30°C and 2 A/dm^2 from Bath Cu2-H2: As Deposited (Left), Annealed 15 Minutes at 325°C (Center), and Annealed 15 Minutes at 500°C (Right).
(Reproduced by permission of The Electrochemical Society, Pennington, NJ)

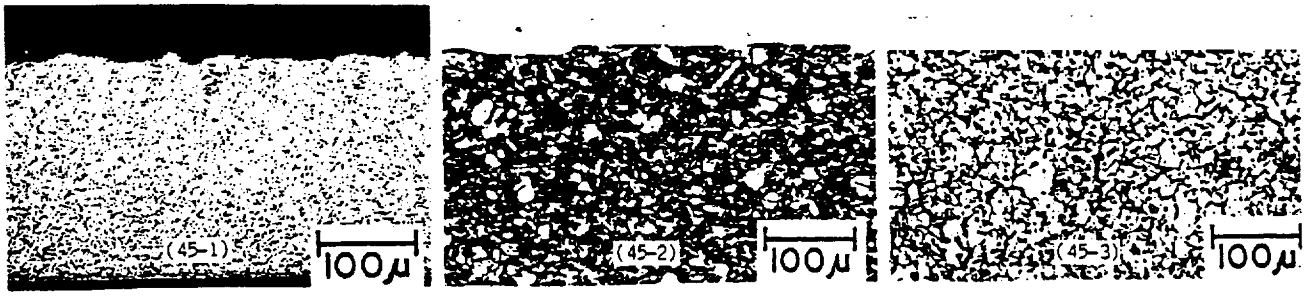


Figure 27b. Effect of Heat Treating on Structure of a Fine Grained Acid Copper Sulfate Deposit Plated at 30°C and 5 A/dm^2 from Bath Cu2-H3 Containing Triisopropanolamine (TIPA): As Deposited from 2 G/L TIPA Bath (Left), 2 G/L TIPA Deposit Annealed 15 Minutes at 500°C (Center), and 3.5 G/L Deposit Annealed 15 Minutes at 500°C (Right).
(Reproduced by permission of The Electrochemical Society, Pennington, NJ)

These investigators reported the effects of annealing on the structure of copper fluoborate deposits, Figure 27c, to be similar to those for non-addition agent acid copper sulfate deposits. However, they noted a larger difference in grain size before and after annealing at 500°C, which correlates with a slightly larger effect on properties than occurred in the case of the acid sulfate deposits. They stated that there was hardly any effect from heat treating pyrophosphate copper deposits at 150°C and only a small effect at 325°C, Figure 27d. However this same figure shows that annealing at 500°C produces a marked grain growth. Large columnar grains containing a fine substructure are evident.

The specimens tested at 150°C were heat treated at this same temperature for one hour, while the

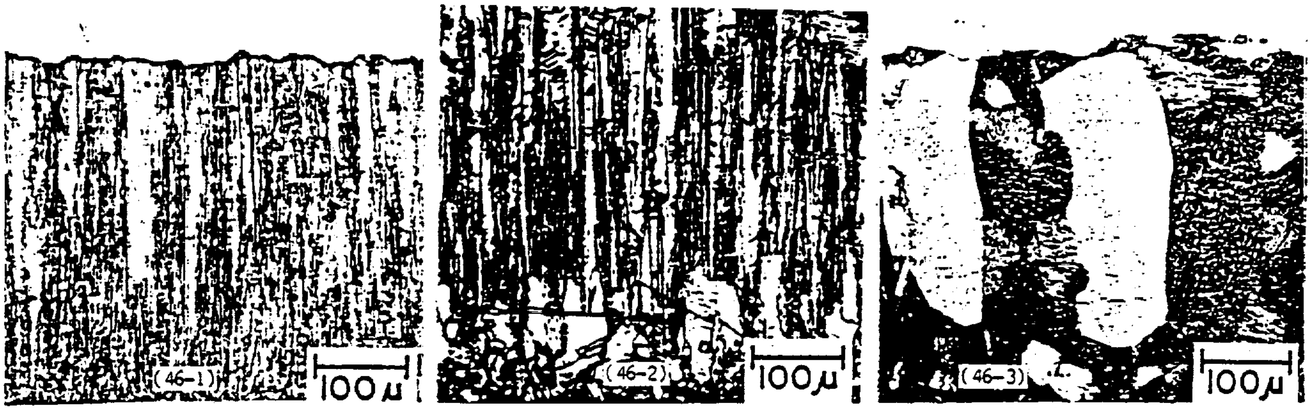


Figure 27c. Effect of Heat Treating on Structure of a Fluoborate Copper Deposit Plated at 30°C and 8 A/dm^2: As Deposited (Left), Heat Treated 15 Minutes at 325°C (Center), and Annealed 15 Minutes at 500°C (Right). (Reprinted by Permission of The Electrochemical Society)

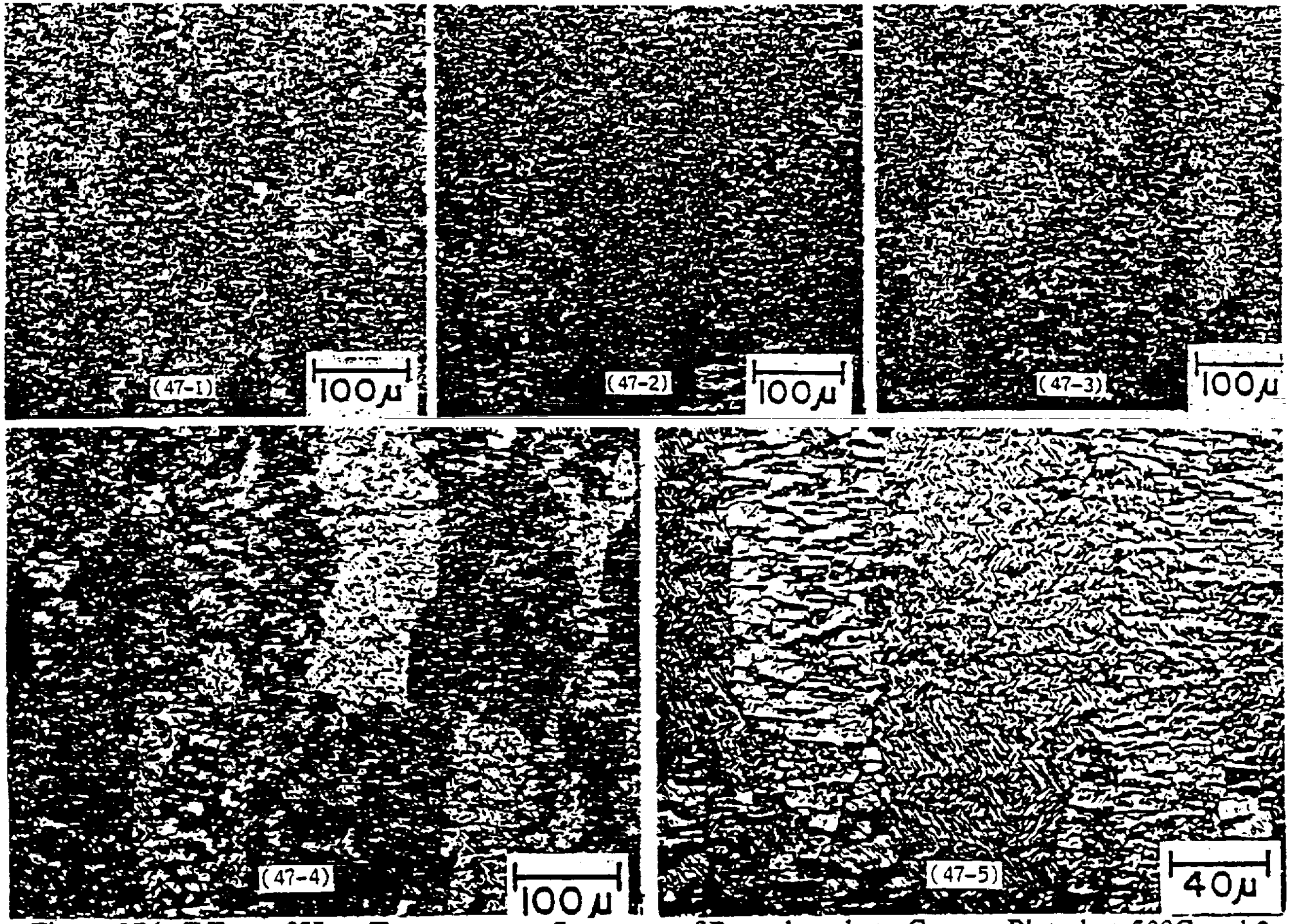


Figure 27d. Effect of Heat Treatment on Structure of Pyrophosphate Copper Plated at 50°C and 2 A/dm^2: As Deposited (Top Left), Heat Treated at 150°C for 2 Hours (Top Center), Heat Treated at 325°C for 15 Minutes (Top Right), Annealed at 500°C for 15 Minutes (Bottom Left and Right). (Reprinted by Permission of The Electrochemical Society)

ones tested at 350°C were held at this temperature for 15 minutes before pulling. Specimens tested at -78°C were pulled immediately once this temperature was obtained using absolute alcohol and dry ice. From Table XXXVI it was noted that tensile strength increased for all deposits as test temperature decreased from 325°C to -78°C. The soft sulfate, fluoborate, and pyrophosphate deposits remained close together in strength with parallel decreases with increase in temperature. The TIPA deposits exhibited higher strengths at room temperature, but they lost strength more rapidly with increase in test temperature. However, all deposits (including the TIPA) approached similar strengths at 325°C. They also noted that the soft type deposits (which at low test temperatures have markedly higher ductility) decrease in ductility more rapidly with increase in temperature so that, at 325°C, all but the pyrophosphate deposit have very low and nearly equal elongations. This very low elongation was also true for the TIPA bath specimen.

The deviation in elongation for the pyrophosphate deposit is large enough to indicate a microstructural difference which would account for the exceptional ductility. It is the author's opinion that this uniqueness is related to the very fine subgrains present in this deposit.

2.6.2 Effects of Heat Treating on Cryogenic, Room, and Elevated Temperature Test Results for Copper Deposits

Mechanical property testing at various temperatures was performed by the Principal Investigator on standard periodic reverse plated acid sulfate copper deposits, as well as those from standard acid copper sulfate baths containing TIPA, PEG-A, and PEG-B. The latter three copper deposits were selected on the basis of outstanding room temperature mechanical properties. The samples to be tested at cryogenic, ambient (room), and elevated temperatures were heat treated at 149°C for 30 minutes, or at 260°C for 24 minutes, or at 371°C for one hour prior to testing for mechanical properties at the various temperatures. 260°C and 371°C heat treatments were performed by wrapping the samples in stain-less foil and placing them in an alumina crucible in a top loading furnace having an argon gas feed to reduce oxygen exposure. 149°C heat treatments were conducted in an oven with the samples foil wrapped but no special atmospheric controls.. Samples thus treated did not exhibit significant surface oxidation. All mechanical property testing was subcontracted.

Table XXXVII summarizes fabrication data and mechanical property test results for ambient (room temperature), cryogenic, and elevated temperature conditions. It should be noted that the TIPA bath samples were produced under much different conditions than those of Lamb, Johnson, and Valentine reported in Table XXXVI. The samples from acid copper sulfate baths with TIPA in this study were deposited at slightly lower bath temperatures from electrolytes with lower TIPA concentrations using a current density of 2.15 A/dm^2. Lamb, Johnson, and Valentine used a much higher current density of 5 A/dm^2. From the observations of Lamb, Johnson, and Valentine, it was suspected that higher current densities and TIPA concentrations were leading to excessive codeposition of organic contaminants, either by oxidation at the anodes, or by reduction at the cathode. These milder deposition conditions were used to minimize impurities in the deposits that might lead to void formation after heat treating or during the elevated temperature testing.

TABLE XXXVII - EFFECTS OF VARIOUS HEAT TREATMENTS ON THE MECHANICAL PROPERTIES OF ELECTRODEPOSITED COPPERS AT CRYOGENIC, STANDARD, AND ELEVATED TEMPERATURES

Test Panel Number	Addition Agent Name	Addition Agent (g/l)	Chloride Wt. Conc. (PPM)	Bath Temp. (°C)	Current Density (A/dm^2)	Heat Treat Temp. (°C)	Heat Treat Time (Hrs)	Test Temp. (°C)	Mechanical Properties Ult. Str. Ksi	Mechanical Properties Yield Str. Ksi	Mechanical Properties Elongation, % In 5.08 Cm
Acid Copper Sulfate Baths using PR Current (8 seconds forward, 4 seconds reverse):											
4-NA-02	None		81	26.7	4.84	None	0.0	20	46.30	27.59	22.0
						None	0.0	371	10.95	7.93	9.5
5-NA-02	None		61	26.7	4.84	None	0.0	20	43.16	24.78	15.0
						149	0.5	20	40.70	19.17	22.5
						149	0.5	149	32.19	19.59	10.0
						260	0.4	20	39.63	16.53	26.5
						260	0.4	149	31.00	15.43	14.5
5-NA-03	D$^+$Xylose	0.7	61	26.7	4.84	None	0.0	20	44.39	23.76	27.5
						149	0.5	20	44.74	21.93	26.0
						149	0.5	149	34.29	17.36	7.5
Acid Copper Sulfate Baths Containing 0.00015 G/L Selenium Dioxide and Triisopropanolamine (TIPA):											
3-SEL-05	None	0.0	71	26.7	6.45	None	0.0	20	51.32	30.65	26.5
						149	0.5	20	32.27	27.27	3.5
						149	0.5	149	21.41	21.41	3.5
						260	0.4	20	46.66	27.92	9.0
						260	0.4	149	38.52	29.64	6.0
3-TISE-01	TIPA	2.0	71	26.7	2.15	None	0.0	20	54.70	37.24	18.5
						149	0.5	20	52.70	34.03	17.0
						149	0.5	149	40.28	31.86	3.5
3-TISE-04	TIPA	5.0	71	26.7	2.15	None	0.0	20	58.76	42.56	20.0
						149	0.5	20	56.07	35.78	21.5
						149	0.5	149	44.92	38.63	4.5
Acid Copper Sulfate Baths Containing Triisopropanolamine (TIPA):											
3-TIPA-06	TIPA	2.0	37	29.4	2.15	None	0.0	20	55.05	43.05	9.5
						149	0.5	20	52.54	34.65	13.5
						149	0.5	149	40.20	32.68	4.5
						260	0.4	20	44.75	27.15	21.0
						260	0.4	149	31.84	20.74	5.5
2-TIPA-08	TIPA	3.0	20	26.7	2.15	None	0.0	20	61.54	44.09	18.0
						149	0.5	20	61.82	41.34	17.0
2-TIPA-09	TIPA	3.0	20	26.7	2.15	None	0.0	20	64.03	43.47	15.0
						149	0.5	149	45.82	34.77	4.0
2-TIPA-10	TIPA	3.0	20	26.7	2.15	None	0.0	20	65.47	48.69	15.0
						149	0.5	20	64.43	44.55	16.5
						149	0.5	149	45.74	35.27	3.5
2-TIPA-16	TIPA	3.0	20	26.7	2.15	None	0.0	20	66.10	49.34	17.5
						149	0.5	20	65.22	43.48	15.5
2-TIPA-12	TIPA	3.0	20	26.7	2.15	149	0.5	149	46.54	34.77	4.0
Acid Copper Sulfate Baths Containing Triisopropanolamine (TIPA) and 0.6 to 0.7 G/L D$^+$Xylose:											
4-TIPA-04	TIPA	2.0	81	26.7	2.15	None	0.0	20	47.35	28.67	24.5
						149	0.5	20	47.32	28.84	26.5
						149	0.5	149	36.89	28.03	8.0

Table is continued on next page.

TABLE XXXVII - EFFECTS OF VARIOUS HEAT TREATMENTS ON THE MECHANICAL PROPERTIES OF ELECTRODEPOSITED COPPERS AT CRYOGENIC, STANDARD, AND ELEVATED TEMPERATURES (CONTINUED)

Test Panel Number	Addition Agent Name	Addition Agent (g/l)	Chloride Wt. Conc. (PPM)	Bath Temp. (°C)	Current Density (A/dm^2)	Heat Treat Temp. (°C)	Heat Treat Time (Hrs)	Test Temp. (°C)	Mechanical Properties Ult. Str. Ksi	Mechanical Properties Yield Str. Ksi	Mechanical Properties Elongation, % In 5.08 Cm
Acid Copper Sulfate Baths Containing Triisopropanolamine (TIPA) and 0.6 to 7.0 G/L D$^+$Xylose (Continued):											
						260	0.4	20	46.39	27.49	23.0
						260	0.4	149	35.42	26.92	8.0
B-Tank-02	TIPA	2.0	44	26.7	2.15	None	0.0	20	59.40	44.86	15.0
						149	0.5	20	58.42	41.73	15.5
						149	0.5	149	41.55	33.75	5.0
						149	0.5	-196	71.71	41.53	18.0
4-TIPA-08	TIPA	3.0	81	26.7	2.15	None	0.0	20	65.09	41.77	22.5
						149	0.5	20	54.07	35.22	23.0
4-TIPA-06	TIPA	3.0	81	26.7	2.15	149	0.5	149	40.40	30.84	5.0
Acid Copper Sulfate Baths Containing Additive PEG-A:											
5-PEGA-02	PEG-A	0.5	61	26.7	2.15	None	0.0	20	80.76	64.43	11.0
						149	0.5	20	79.22	60.24	10.5
5-PEGA-03	PEG-A	0.5	61	26.7	2.15	149	0.5	149	37.57	32.82	1.0
5-PEGA-08	PEG-A	1.0	61	26.7	2.15	None	0.0	20	73.92	54.44	12.5
						149	0.5	20	72.81	51.19	14.0
						149	0.5	149	45.25	40.46	2.0
						260	0.4	20	69.85	51.26	13.0
						260	0.4	149	39.84	35.74	2.0
Acid Copper Sulfate Baths Containing Additive PEG-A and 2 G/L Triisopropanolamine (TIPA):											
5-PEGT-02	PEG-A	0.5	61	26.7	2.15	None	0.0	20	77.49	57.37	10.0
						149	0.5	149	39.64	30.95	2.0
Acid Copper Sulfate Baths Containing Additive PEG-B:											
3-PEGB-01	PEG-B	0.5	60	26.7	2.15	None	0.0	20	64.15	45.39	12.5
						149	0.5	20	72.39	51.86	12.5
						None	0.0	-196	90.76	57.57	23.0
						149	0.5	-196	83.26	46.51	22.5
3-PEGB-02	PEG-B	0.5	60	26.7	2.15	None	0.0	20	61.52	43.35	9.0
						371	1.0	20	37.98	26.31	25.0
						371	1.0	371	19.92	16.03	9.5
3-PEGB-03	PEG-B	0.5	60	26.7	2.15	None	0.0	20	61.73	41.75	14.0
						149	0.5	149	42.66	27.78	24.5
(Retest of 3-PEGB-03 sample at 149°C)						149	0.5	149	42.35	27.83	22.5
						149	0.5	-196	79.86	40.17	21.0
						371	1.0	20	37.00	24.76	36.0
						371	1.0	371	18.60	15.48	10.5
B-Tank-03	PEG-B	1.0	88	26.7	2.15	None	0.0	20	65.29	48.32	11.5
						149	0.5	20	65.93	45.59	15.5
3-PEGB-05	PEG-B	1.5	60	26.7	2.15	None	0.0	20	71.40	53.50	11.5
						149	0.5	20	57.57	37.51	12.5
						149	0.5	149	42.93	34.63	16.0
						None	0.0	-196	85.43	57.60	18.0
						149	0.5	-196	84.91	68.34	29.5

Table is continued on next page.

TABLE XXXVII - EFFECTS OF VARIOUS HEAT TREATMENTS ON THE MECHANICAL PROPERTIES OF ELECTRODEPOSITED COPPERS AT CRYOGENIC, STANDARD, AND ELEVATED TEMPERATURES (CONTINUED)

Test Panel Number	Addition Agent Name	(g/l)	Chloride Wt. Conc. (PPM)	Bath Temp. (°C)	Current Density (A/dm²)	Heat Treat Temp. (°C)	Heat Treat Time (Hrs)	Test Temp. (°C)	Mechanical Properties Ult. Str. Ksi	Mechanical Properties Yield Str. Ksi	Mechanical Properties Elongation, % In 5.08 Cm
Acid Copper Sulfate Baths Containing Additive PEG-B:											
						260	0.4	20	46.60	36.06	18.0
						260	0.4	149	37.85	29.88	22.5
Wrought Fine-Grained OFHC Grade Copper[11]:											
Annealed								24	31.90	12.20	51.0
								149	25.85	7.00	62.5
								-196	51.60	8.10	72.0
Cold Drawn, 40% Reduction								24	51.10	50.30	11.0
								149	44.45	42.40	14.0

2.6.2.1 Effect of Heat Treatment on Room Temperature Mechanical Properties

A comparison of room temperature mechanical properties for acid copper sulfate deposits plated with periodically reversed current from baths with no grain refining additives (Sample Nos. 4-NA-02, 5-NA-02, and 5-NA-03) and in the as-deposited state, show little difference from those of companion samples heat treated at 149°C for 30 minutes and tested at room temperature. Those deposits heat treated at 260°C for 24 minutes exhibited improved room temperature ductility with some sacrifice of yield strength. This is typical for acid copper sulfate deposits having columnar grain structures. These same comments are applicable to most of the deposits from acid copper sulfate baths containing additives with the exception of those from electrolytes with PEG-B added. Room temperature mechanical properties of deposits from baths with selenium and heat treated at 149°C were signif-icantly improved when TIPA was also used as an additive. Heat treating a sample from a selenium containing bath at 260°C (Sample 3-SEL-05) improved room temperature ductility while also improving ultimate strength. However, sought properties were not achieved in this material.

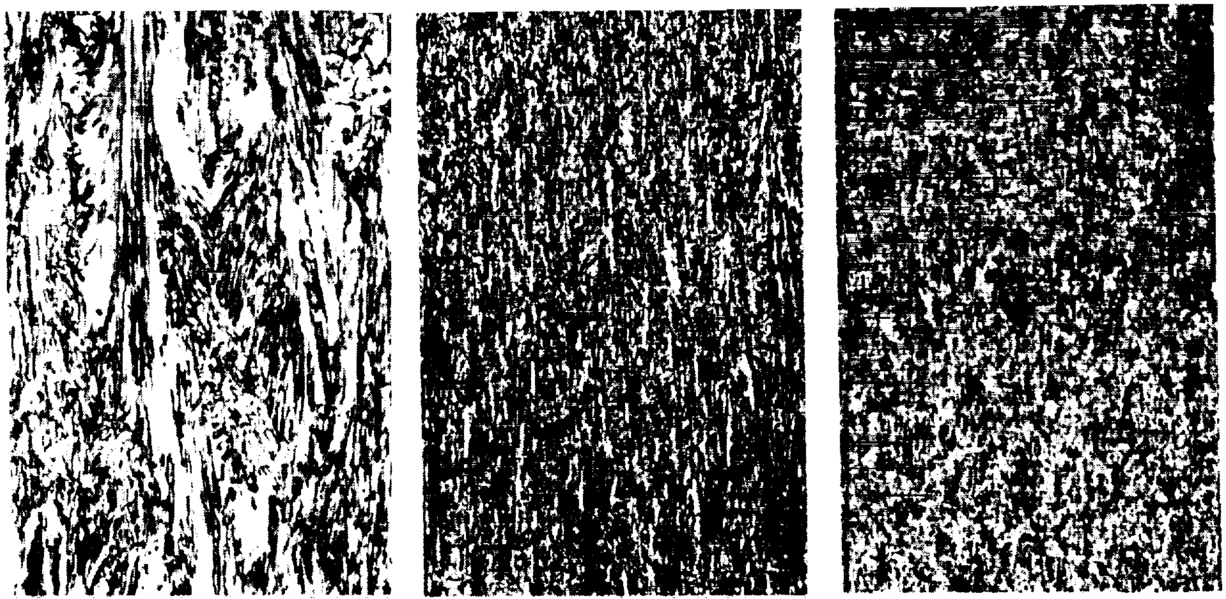
Deposits from baths containing various amounts of TIPA as the only additive did not show significant mechanical property differences between as-deposited and 149°C heat treated materials when tested at room temperature. A comparison of data for Sample Nos. 3-TIPA-06 and 4-TIPA-04 show that for baths with identical concentrations of TIPA, those containing over 50 ppm of chloride produce deposits of much better ductility than is obtained from baths with less than 50 ppm of chloride ion (although tensile and yield strengths are not as high). Heat treatment of these same materials at 260°C for 24 minutes and testing at room temperature showed an equalization of mechanical properties (particularly ductility) from the two electrolytes. Room temperature tensile and yield strengths were not compromised by the 260°C heat treatment.

Increasing PEG-A additive in acid copper sulfate baths decreased ultimate and yield strengths at room temperature in both the as-deposited and 149°C heat treated samples. Heat treating a companion sample at 260°C for 24 minutes did not significantly alter room temperature mechanical properties.

Room temperature properties of these samples were among the highest found in this investigation.

The PEG-B bath deposits heat treated at 149°C exhibited insignificant change in mechanical properties from those of the as-deposited companion samples when tested at room temperature. Comparing the 149°C performance of the PEG-B deposits and results of the Lamb, Johnson, and Valentine studies, Table XXXVI, it was found that the PEG-B mechnical properties were far superior. The ultimate strength of the PEG-B deposits at room temperature (after the 149°C heat treatment) was far better than that of pyrophosphate copper. Heat treating of Specimen 3-PEGB-05 at 260°C for 24 minutes reduced room temperature ultimate and yield strengths greatly but good ductility was maintained. Even so, these properties were better than those for similarly heat treated deposits from baths with no additives or from baths containing TIPA. This was not expected since the chemical analysis of a typical PEGB sample (Specimen 3-PEGB-04) revealed a carbon content of 117 ppm and an oxygen content of 43 ppm. Deposits from acid copper baths with 1 g/l of TIPA have been found to contain less than 40 ppm of carbon and less than 30 ppm of oxygen.

Figure 28a illustrates microstructures of several acid copper sulfate deposits from non-additive or TIPA containing baths which were heat treated at 149°C for 30 minutes. Although there is some evidence of recrystallization or recovery, the grain growth is not very pronounced. Microstructures of similarly heat treated deposits from PEG-B containing baths are found in Figure 28b. There are no significant changes in microstructure in these samples from those shown in prior photomicrographs of the same samples as-deposited. These show equi-axed grains with almost no columnarity. The microstructures of deposits from the non-additive, TIPA containing, and PEG-B containing baths

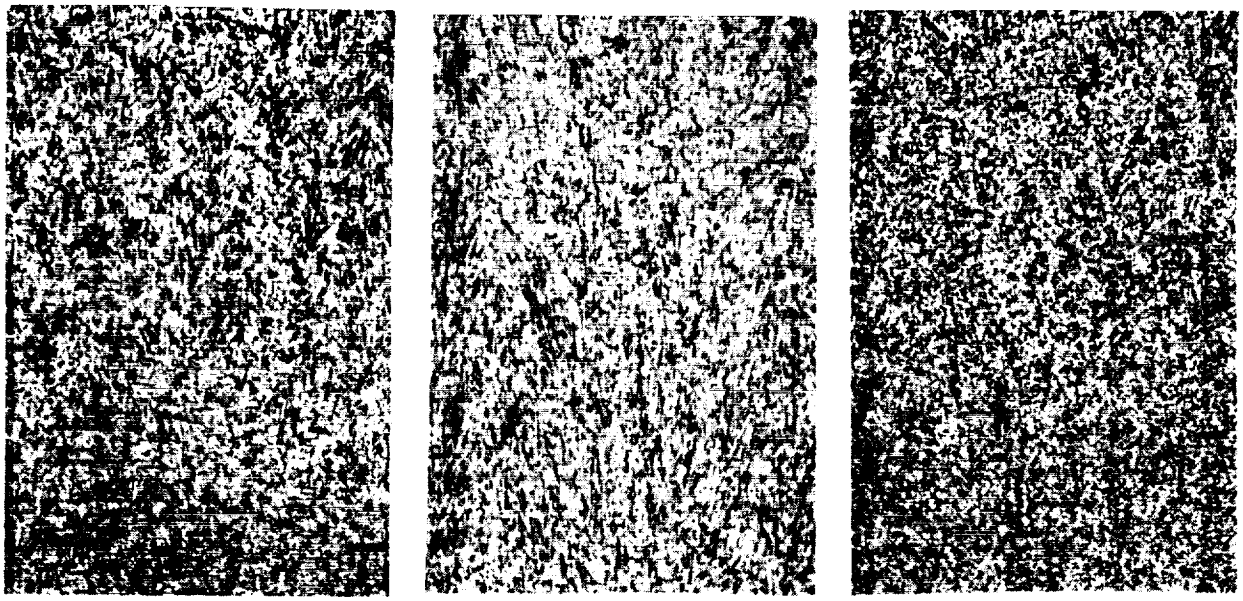


Panel 5-NA-02 (No Additive Bath). Magnification 100X.

Panel 4-TIPA-04 (2 G/L TIPA). Magnification 100X.

Panel B-Tank-02 (2 G/L TIPA). Magnification 100X.

Figure 28a. Typical Microstructures of Acid Copper Sulfate Deposits from Non-additive and TIPA Containing Baths after Heat Treating at 149°C for 30 Minutes.

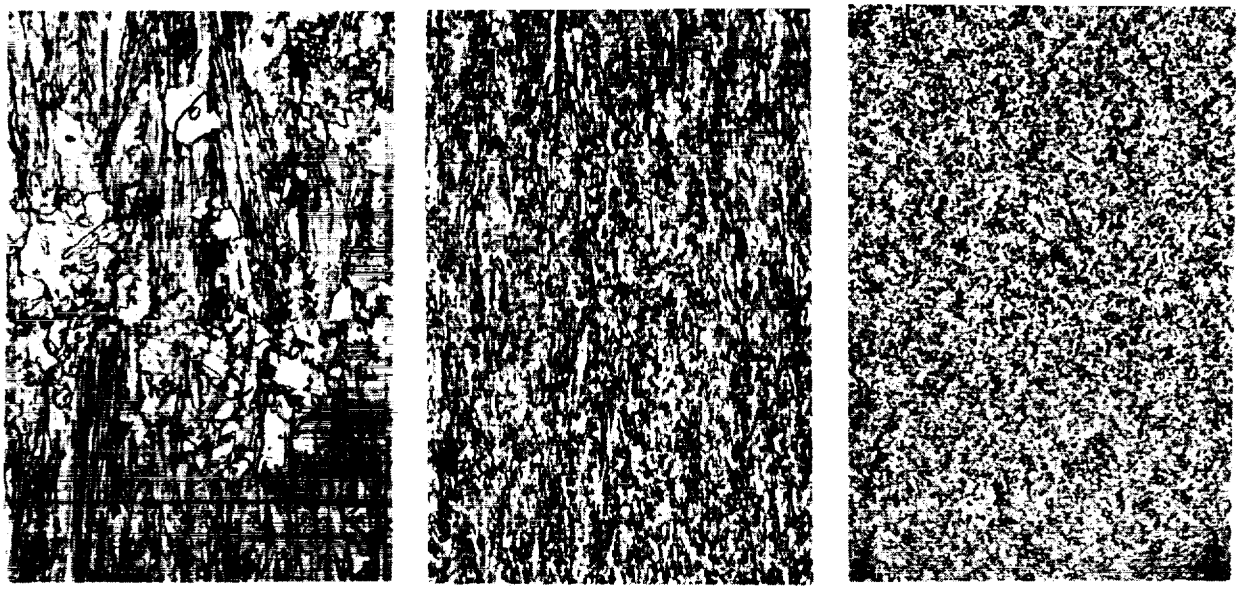


Panel 3-PEGB-01 (0.5 G/L PEGB). Magnification 100X.

Panel B-Tank-03 (1 G/L PEGB). Magnification 100X.

Panel 3-PEGB-05 (1.5 G/L PEGB). Magnification 100X.

Figure 28b. Typical Microstructures of Acid Copper Sulfate Deposits from PEG-B Containing Baths after Heat Treating at 149°C for 30 Minutes.



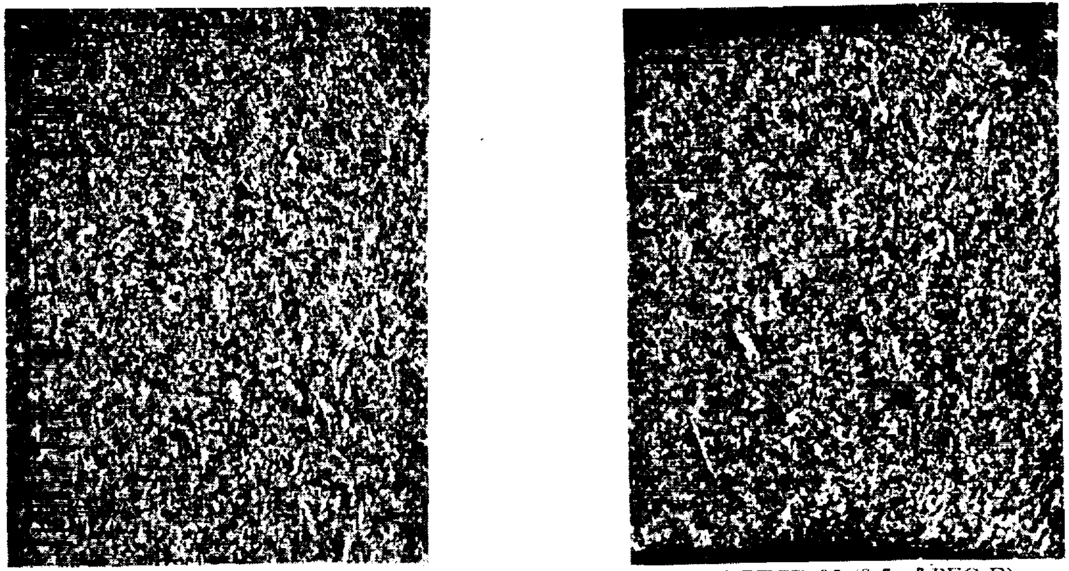
Panel 5-NA-02 (No Additive Bath). Magnification 100X.

Panel 4-TIPA-04 (2 G/L TIPA). Magnification 100X.

Panel 3-PEGB-05 (1.5 G/L PEGB). Magnification 100X.

Figure 29. Typical Microstructures of Acid Copper Sulfate Deposits from Non-additive, TIPA Containing, and PEG-B Containing Baths after Heat Treating at 260°C for 24 Minutes.

which were heat treated at 260°C for 24 minutes are shown in Figure 29. Microstructures of deposits from a PEG-B containing bath which were heat treated at 371°C for one hour are illustrated in Figure 30. Grain growth was insignificant in all of the deposits from PEG-B containing baths shown in Figure Nos. 29 and 30.



Panel 3-PEBG-02 (0.5 g/l PEG-B)
Magnification 100X.

Panel 3-PEGB-03 (0.5 g/l PEG-B)
Magnification 100X.

Figure 30. Typical Microstructures of Acid Copper Sulfate Deposits from PEG-B Containing Baths after Heat Treating at 371°C for One Hour.

Comparing the properties of 149°F heat treated wrought OFHC grade copper (at the end of Table XXXVII) with those of similarly heat treated electrodeposited counterparts, it is noted that all of the latter show vastly superior ultimate and yield strengths to those of the former. The wrought material has far greater ductility, but this is far in excess of the 10 percent minimum elongation desired in most structural components.

The deposits from the electrolyte containing PEG-B additive were outstanding when compared to wrought OFHC grade material. Even PEG-B bath deposits heat treated at 260°C exhibited 400 to 500 percent greater yield strength than found in annealed wrought copper while maintaining excellent ductility. This is a major technological achievement.

2.6.2.2 Effect of Heat Treatment on Elevated Temperature Mechanical Properties

All elevated temperature testing was performed on specimens that had been heat treated at either 149°C or 260°C, the purpose being to permit removal of gaseous impurities and allow recovery of lattice imperfections that might otherwise be time dependent at the temperature of testing. Since experience has shown that acid copper sulfate deposits show degradation of ductility at elevated temperatures, the 260°C heat treatment was applied to certain specimens to determine if sufficient annealing would occur to improve ductility at elevated temperature. These specimens were tested for mechanical properties at 20°C and 149°C and reported in Table XXXVII.

Copper from the non-additive bath containing only 61 ppm chloride and from the same bath modified with .7 g/l D^+ xylose exhibited much higher ultimate and yield strengths compared to annealed OFHC grade wrought copper. Ductility was much less, as expected. The marginal ductility noted at 149°C in the sample from the D^+ xylose containing bath may have been due to a higher than normal amount of xylose which may have created codeposited impurities in the deposit. Deposits from selenium con-taining baths did not show acceptable ductility at 149°C, although ultimate and yield strengths were high. Heat treating these specimens at 260°C resulted in improved ductility but not to the levels sought. Deposits from TIPA containing baths having less than 50 ppm of chloride exhibited good mechanical strength at 149°C, but in all cases the ductility was very poor, even after a treatment at 260°C. Similar deposits from baths containing 2 g/l TIPA (with chloride over 50 ppm) had good ultimate and yield strengths at 149°C, and ductility was improved, but still below 10 percent in 5.08 cm gauge lengths. Higher concentrations of TIPA were detrimental to ductility. Samples from a bath containing the PEG-A additive exhibited outstanding ultimate and yield strengths at 149°C, but the ductility was extremely poor, even after a heat treatment at 260°C.

All samples from the bath containing various concentrations of PEG-B additive exhibited outstanding mechanical properties at a test temperature of 149°C. At this test temperature, these deposits had yield strengths of four times that of annealed OFHC, the wrought counterpart. Ultimate strengths at 149°C were at least 68 percent higher in the electrodeposited material. Ductility well exceeded the sought value of 10 percent. Heat treatment at 260°C resulted in a decrease in strength and an increase in ductility at 149°C as would be expected. However, at this test temperature, the ultimate strength was fifty (50) percent higher and the yield strength three hundred (300) percent higher than annealed wrought OFHC copper at this test temperature. A sample of copper from the PEG-B containing bath heat treated at 371°C and tested at this same temperature had superior yield strength to wrought copper tested at 371°C, but just achieved the minimal elongation sought.

2.6.2.3 Effect of Heat Treatment on Cryogenic Mechanical Properties

Cryogenic testing for mechanical properties was only performed on one TIPA bath sample and on several PEG-B bath samples, since it is prior knowledge that properties at cryogenic temperatures are improved in copper electrodeposits. This was demonstrated on all samples tested. Comparing as-deposited and 149°C heat treated mechanical properties at liquid nitrogen temperature (-196°C), there was no significant difference in ultimate strengths for 1.5 g/l PEG-B deposits, but an 0.5 g/l PEG-B sample had about 10 percent less tensile strength resulting from the heat treatment. Although yield strengths of as-deposited PEG-B samples at both PEG-B concentrations were equal, heat treatment resulted in test data showing the 1.5 g/l PEG-B material to retain a much higher yield. Ductilities were good in all cases. ***Compared to wrought annealed OFHC, the PEG-B samples showed a 75 percent increase in ultimate strength and almost a six fold increase in yield strength at liquid nitrogen temperature while maintaining excellent ductility.***

2.7 Copper Deposited from Sulfamate Baths

2.7.1 Background Information

Copper Development Association Publication No. 62(12) cites several non-conventional copper plating baths of which the copper sulfamate electrolyte was of interest because of the very fine grain sizes illustrated in the reference. The bath was originally developed by Piontelli(12) but was not well received by industry (probably due to the cost of preparation chemicals). A bath was proposed which contained 250-500 g/l copper sulfamate and 50-60 g/l free sulfamic acid. A current density range of 4.9 to 9.7 A/dm^2 (38 to 56 A/ft^2) was claimed to provide a 92 percent cathode efficiency, while the efficiency decreased to about 80 percent at 3.23 A/dm^2 (30 A/ft^2). No mechanical property data was furnished.

2.7.2 Investigation of Acid Copper Sulfamate Deposits

Since no source of copper sulfamate salts or liquid concentrates could be located, it was necessary to manufacture the bath from a solution of copper sulfate. Barium carbonate was reacted with sulfamic acid to form barium sulfamate according to the following mechanism:

$$BaCO_3 + 2HSO_3{\cdot}NH_2 = Ba(SO_3{\cdot}NH_2)_2 + CO_2\ (g) + H_2O$$

The barium sulfamate was then combined with copper sulfate solution to cause the following reaction:

$$Ba(SO_3{\cdot}NH_2)_2 + CuSO_4 = Cu(SO_3{\cdot}NH_2)_2 + BaSO_4\ \text{(precipitate)}$$

This is a slow process since the barium carbonate reaction with sulfamic acid formed some hydrous barium oxide which had to be carefully filtered out. The copper concentration was recommended at 75 to 100 g/l, and it took numerous reaction cycles to achieve this range. Boric acid was added as a buffer, and the pH was maintained at 2 or less as recommended. The bath volume was about 24 liters for the initial trials. Agitation was furnished by an in-tank pump. Bath temperatures ranged from 18.3° to 35°C. A comparison of specimen electroforming parameters and mechanical property test results is found in Table XXXVIII. Bath compositions, microstructures and mechanical property test results are shown in Figures 31a and 31b.

The microstructure of Specimen 6-SFAM-01, using a current density of 3.23 A/dm^2 and indirect solution sprays for agitation, show a very coarse structure similar to that found in acid copper sulfate deposits where no additives are employed and where no periodic current reversal is used. Use of a direct agitation spray on the cathode surface resulted in a much improved microstructure on Specimen 6-SFAM-02. This resulted in greatly improved mechanical properties. Allowing the pH to increase significantly in producing Specimen 6-SFAM-03 appeared to increase grain size while reducing mechanical properties. Efforts using periodic current reversal met with no success due to extremely rough deposits which could not be tested. Significant deposit roughness was encountered throughout this particular study. This was believed to be related to anode corrosion problems and containment of copper sludge which appeared to be more prevalent in the sulfamate baths. Anode bagging helped considerably on the last sample, Specimen 6-SFA-08; however, the mechanical

TABLE XXXVIII - MECHANICAL PROPERTIES OF ELECTRODEPOSITED COPPER FROM ACID SULFAMATE BATHS AT CRYOGENIC AND STANDARD TEST TEMPERATURES

Test	Addition				Bath	Current	Heat Treat		Test	Mechanical Properties		
Panel	Agent		pH		Temp.	Density	Temp.	Time	Temp.	Ult. Str.	Yield Str.	Elongation, %
Number	Name	(g/l)	Start	End	(°C)	(A/dm^2)	(°C)	(Hrs)	(°C)	Ksi	Ksi	In 5.08 Cm
6-SFA-01	None	0.0	1.8	1.7	18.3	3.23	None	0.0	20	16.67	7.88	12.0
6-SFA-02	None	0.0	2.1	2.4	35.0	3.23	None	0.0	20	36.63	16.89	35.0
6-SFA-02	None	0.0	2.1	2.4	35.0	3.23	149	0.5	20	34.92	16.91	38.0
6-SFA-02	None	0.0	2.1	2.4	35.0	3.23	149	0.5	-196	49.90	15.76	37.5
6-SFA-03	None	0.0	2.3	4.5	35.0	3.23	None	0.0	20	27.44	13.50	22.0
6-SFA-04	None	0.0	2.0	2.1	35.0	3.25	None	0.0	20	Not Determined		
6-SFA-05	None	0.0	2.1	2.2	25.0	4.30	None	0.0	20	Not Determined		
6-SFA-06	None	0.0	2.1	2.2	25.0	4.30	None	0.0	20	Not Determined		
6-SFA-07	None	0.0	2.2	2.0	25.0	2.15	None	0.0	20	29.81	20.10	5.5
6-SFA-08	NH_4Sulf.	20.0	2.2	2.0	25.0	2.15	None	0.0	20	36.49	17.03	33.5

properties were not improved over those of acid copper sulfate deposits. Chloride was not added to the sulfamate bath. Addition of chloride, as was done in the sulfate bath, might improve grain structures and mechanical properties. This was not pursued since the deposits showed no improvement over the acid copper sulfate material.

2.8 Task II Conclusions

The objective to produce an unalloyed copper electrodeposit that would be competitive with electroformed nickel such as used on the Space Shuttle Main Combustion Chamber closeout was met by acid copper sulfate deposits from baths containing PEG-B additive. The Rocketdyne specification for these nickel deposits (stress relieved) calls for a minimum of 65 ksi tensile strength, 39 ksi yield strength, and 10 percent elongation in 5.08 cm. As deposited and 149°C PEG-B bath deposits met or exceeded these values for room temperature testing.

From the studies of this task it was found that:

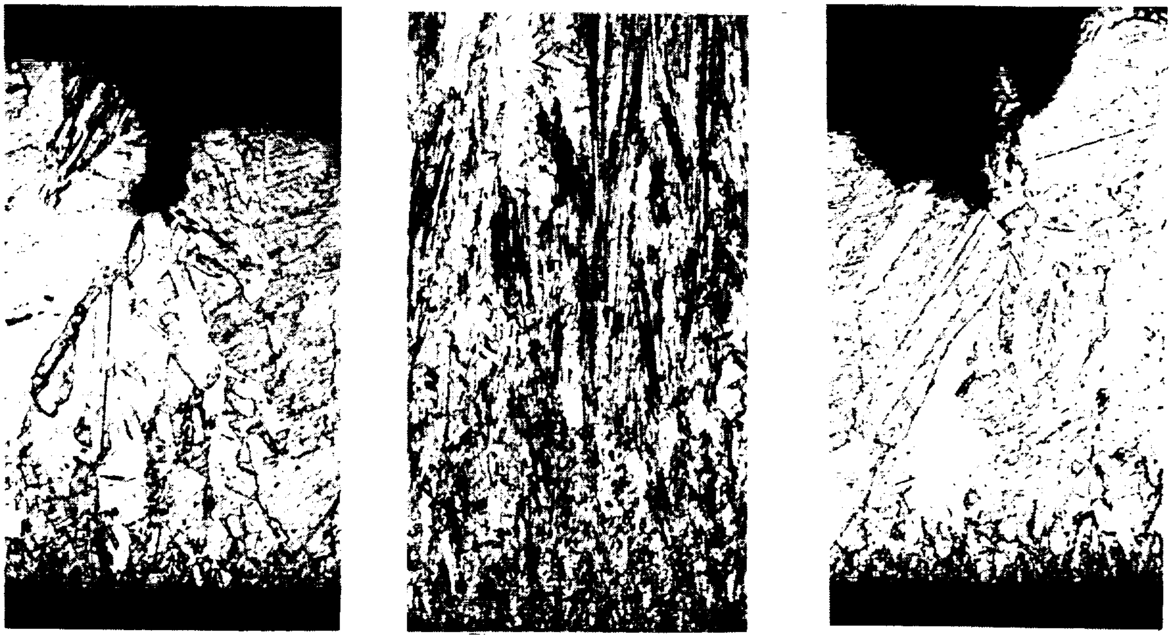
- Selenium as an additive promoted a slightly finer grain structure than obtained with conventional acid sulfate copper using periodic current reversal, but the deposits showed poor ductility at elevated temperature. Addition of TIPA improved strength but not elevated temperature ductility.

- Isopropanolamine (IPA), as an additive to acid copper sulfate baths, promotes improved mechanical properties (including elongation) at room temperature. It appears to have a shorter bath life than TIPA and ductility decreases sharply with use. Gelatin as an additive appears to have the same mechanical property performance shortcomings as IPA.

- Diisopropanolamine (DIPA), tetraethylenepentamine (TEPA), 4-acetamidophenol, and 2-butene-1,4-diol appear to exert no improvements in mechanical property performance of acid

MECHANICAL PROPERTIES, DEPOSITION PARAMETERS, AND MICROSTRUCTURES OF ACID COPPER SULFAMATE DEPOSITS

Chemistry	**Sample 6-SFAM-01**	**Sample 6-SFAM-02**	**Sample 6-SFAM0-03**
Copper Sulfamate	172.5 g/l	172.5 g/l	172.5 g/l
Boric Acid	30.1 g/l	30.1 g/l	30.1 g/l
Ammonium Sulfamate	0.0 g/l	0.0 g/l	0.0 g/l
Acidity (pH)	1.7 to 1.8	2.1 to 2.4	2.3 to 4.5
Operating Parameters			
Bath Temperature	18.3°C	35.0°C	35.0°C
Current Density	3.23 A/dm^2	3.23 A/dm^2	3.23 A/dm^2
Electrolyte Agitation (Page 13)	Short Box Shield	Short Box Shield	Short Box Shield
Continuous Filtration	None	None	None
Deposition Time, Hours	23.5	26.2	41.2
Accumulated Ampere-Hours Per Liter	12.24	22.49	38.61
Mechanical Properties and Deposit Thickness			
Ultimate Strength, ksi	6.67	36.63	27.44
Yield Strength, ksi	7.88	16.89	13.50
Elongation, % in 5.08 cm	12.0	35.0	22.0
Hardness, Vickers, 100 g Load	70.5	76.0	68.5
Thickness, cm	0.084	0.089	0.058
Microstructures (Magnification 100X)			



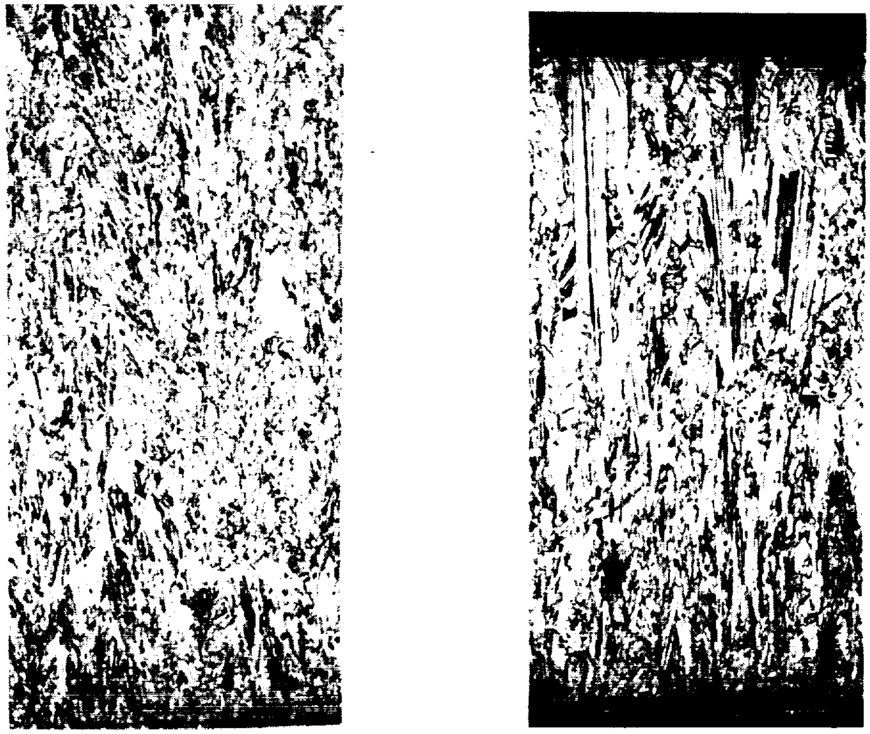
Sample 6-SFA-01 Sample 6-SFA-02 Sample 6-SFA-03

Figure 31a. Data and Microstructures of Non-heat Treated Deposits from an Acid Copper Sulfamate Bath Without Chloride Ion During the Use Period of 38.6 Ampere-Hours Per Liter.

MECHANICAL PROPERTIES, DEPOSITION PARAMETERS, AND MICROSTRUCTURES OF ACID COPPER SULFAMATE DEPOSIT

Chemistry	**Sample 6-SFAM-07**	**Sample 6-SFAM-08**
Copper Sulfamate	188.1 g/l	188.1 g/l
Boric Acid	30.0 g/l	30.0 g/l
Ammonium Sulfamate	0.0 g/l	20.0 g/l
Acidity (pH)	2.0 to 2.2	2.0 to 2.2
Operating Parameters		
Bath Temperature	25.0°C	25.0°C
Current Density	2.15 A/dm^2	2.15 A/dm^2
Electrolyte Agitation (Page 13)	Short Box Shield	Short Box Shield
Continuous Filtration	None (Anodes Bagged)	None (Anodes Bagged)
Deposition Time, Hours	46.0	43.0
Accumulated Ampere-Hours Per Liter	57.69	62.71
Mechanical Properties and Deposit Thickness		
Ultimate Strength, ksi	29.81	36.49
Yield Strength, ksi	20.10	17.03
Elongation, % in 5.08 cm	5.5	33.5
Hardness, Vickers, 100 g Load	83.5	82.0
Thickness, cm	0.114	0.094

Microstructures (Magnification 100X)



Sample 6-SFA-07

Sample 6-SFA-08

Figure 31b. Data and Microstructures of Non-heat Treated Deposits from an Acid Copper Sulfamate Bath Without Chloride Ion During Final Use Period to 62.7 Ampere-Hours Per Liter.

sulfate deposits when used individually as additives in the baths. Some of these agents actually result in deposits with greatly degraded mechanical properties.

- Tensile strengths of 100 ksi, or greater, were achieved in certain acid copper sulfate deposits from baths with triisopropanolamine (TIPA) additive; however, this strength could not be maintained in prototype production baths. Of the amine additives, only baths with TIPA produced a combination of good tensile strength and high ductility at room temperature. This was also true for specimens receiving moderate heat treatments. However, all specimens from baths with TIPA and tested at elevated temperature exhibited poor ductility (whether heat treated or not). A nearly identical performance using PEG-A, a long chain organic polymer, in acid copper sulfate baths was observed. Room temperature mechanical properties were excellent, but elevated temperature ductility was very poor.

- ***Use of another long chain organic polymer, PEG-B, in acid copper sulfate baths led to very good mechanical properties (including excellent ductility) in copper deposits tested at cryogenic, ambient (room), and elevated temperatures (to 371°C). These deposits could be heat treated to 371°C with retention of good ductility.***

- Acid copper sulfamate deposits were more difficult to deposit in great thicknesses and did not exhibit better mechanical properties than conventional acid copper sulfate deposits.

3. TASK III - DEPOSITION OF COPPER ALLOY DEPOSITS

3.0 Background

Application of a copper alloy to aerospace rocket engines will require that the metal have excellent strength and ductility at cryogenic and elevated temperatures, high thermal conductivity, good thermal fatigue strength, and be economically and commercially practical. Most electrodeposited copper alloys developed to date are of the brass or bronze types and of little value for the above requirements. Based on current wrought alloy technology, it is recognized that improved elevated temperature performance is achieved by alloying copper with modest amounts of zirconium and silver. This is the basis for the successfully applied NASA-Z (or NARalloy Z) alloys. Such alloys are costly to make due to extensive mechanical working and thermal treatments required in the manufacture. An electroformed counterpart would decrease cost and simplify fabrication by producing the net shape during the deposition process.

Selection of candidate metals to alloy with copper was based on (1) ease of electrodepositing the element from electrolytes in which copper could be plated, (2) the ability to maintain adequate melting temperature of the resulting binary alloy, (3) having good thermal conductivity as a physical property, and (4) the possibility of codepositing the alloying elements in sufficient ratios so as to form phases or lattice structures that would retard recrystallization and retain significant yield strength at elevated temperatures. From Hanson's Constitution of Binary Alloys(13), binary alloy diagrams and associated crystal structures descriptions were examined. It appeared that silver, palladium, and platinum would be the most logical alloying elements.

According to Hanson, silver and copper form a series of solid solutions, all of which are composed of face-centered-cubic lattice cells. However, these cells will have lattice parameters that will vary based on the ratio of copper to silver. It was anticipated that these differences would result in a crowding or distortion structure that would interrupt slip planes to some degree and aid in yield strength retention at elevated temperatures. Brenner(14) reviewed work prior to 1963 on depositing alloys of copper and silver. He stated that there were no practical processes (through 1962) for depositing commercially acceptable copper-silver alloys and only one detailed study had been made using a cyanide bath. He also noted that the difference between the standard electrode potentials of copper and silver is about 0.45 volt, which is too great to permit satisfactory codeposition of the two metals from simple salt baths. By complexing the copper and silver with cyanide, the reduction potential difference could be reduced to about 0.15 volt. However, deposits from such electrolytes were of poor quality.

Brenner mentioned deposition of copper-silver alloys from complexes formed in strong solutions of halides. In this same reference is described the work of Graham and his associates to deposit alloys of copper and silver from baths containing high concentrations of lithium chloride or sodium iodide. Alloys of good appearance were deposited at current densities below 1.5 A/dm^2 with anode and cathode efficiencies approaching 100 percent. The process was difficult to control to maintain any specific alloy composition. Ahuja and Banerjee(15) reported copper-silver alloy deposits with copper ranging from 0.92 to 94.93 percent.

Domnikov(16) reported work in the former Soviet Union by Burkat and his coworkers to deposit silver and copper simultaneously from a pyrophosphate bath. The bath was prepared by dissolving copper sulfate and silver nitrate in excess potassium pyrophosphate. Ammonia was added to the silver complex. It was found that silver concentration in the alloy increased with total metal concentration in the electrolyte, and the solution became unstable at total metal concentrations above 20 g/l. Use of solution agitation enabled deposition of alloys with wider ranges of composition. Increasing the current density increased silver content of the alloy; however, increasing current density resulted in a decrease in cathode current efficiency. Increasing bath temperature led to increased silver content in the alloy. Operating the bath at pH of 9 resulted in low silver in the deposit of about 30% by weight, while raising the pH above 10 increased the silver to over 60 percent by weight.

Reksc and Mrugalski(17) were unable to obtain useful alloy deposits from the weak ammonium pyrophosphate complexes used by the Soviet investigators. They found that deposition potentials for silver and copper were nearly equal in iodide solutions. Their alloys were in the 1 to 30 weight percent copper range, and X-ray diffraction data revealed a mixture of alpha and beta solid solutions. Low current densities were necessary when operating this bath, but good quality deposits were obtained.

Prior investigations to electrodeposit copper-palladium and copper-platinum alloys were almost non-existent. No commercially successful baths have been reported. In Phase I it was demonstrated that copper and platinum could be codeposited from a molten cyanide bath operated at 600°C, but the deposits from such baths were soft due to annealing caused by the high deposition temperature.

3.1 Deposition of Low Alloyed Copper from Molten Salt Baths - Current Studies

3.1.1 Deposition from Molten Eutectic Cyanide Baths

Initial studies were conducted with a three liter molten salt bath composed of 30 percent by weight potassium cyanide and 70 percent by weight sodium cyanide which form an eutectic mixture melting at about 540°C. The bath (previously used for iridium deposition) contained about 20 g/l of iridium metal. Copper was added to the melt as Cupralite which is a sodium cuprous cyanide salt. The melt temperature for operation was 580°C, and stainless steel and copper cathodes were used.

The first trial to deposit an alloy was made on a stainless steel strip measuring 16.5 cm long by 4.1 cm wide. A single copper anode was suspended in the melt. The plating duration was 3 hours using a current density of 1.07 A/dm^2. Significant dendrites (tree-like growths) were experienced, hence the current mode was switched to periodic current reversal using a forward plating time of 12 seconds and a reversal time of 4 seconds, both at 1.07 A/dm^2. Slow rotation of the cathode was used to provide melt agitation. After another 18 hours the panel was removed and found to contain a rough surface with many long nodules. These could be brushed off easily. Deposits were poorly bonded to the substrate, the coating being soft and porous. Cohesion was poor in the alloy deposit. Testing was not performed on this sample.

A second test plating was made on the same stainless steel strip (after removal of the previous deposit) using a pulsed periodic current reversal mode (pulsed PR) with a peak current density of 2.69 A/dm^2 and a duty cycle of 66.7 percent. The deposit obtained was similar to the first whereby much metal was deposited, but the coating was soft and spongy. A third trial was conducted on a copper substrate of the same dimensions as the previous cathode. The cathode was slowly rotated during plating with a peak pulse current current density of 2.69 A/dm^2 and a periodic reverse duty cycle of 70 percent. After 15 hours of plating, the panel was found to have a soft, spongy deposit of no engineering value.

A fourth attempt was made to deposit coherent iridium-copper alloy from the molten salt bath using a copper cathode and two iridiu anodes (rather than the copper anode previously used). A high copper content remained in the melt from the use of the copper anodes in prior runs. The panel was plated for 2 hours at 2.15 A/dm^2 current density (conventional dc) and was found to have the same soft, spongy deposits as previously encountered. No further work was performed with this system.

3.1.2 Molten Acetate Baths

Several low melting temperature salts are available from which electrolytes for depositing copper, silver, and platinum can be prepared. Such salts are lithium acetate (M.P. 70°C), ammonium acetate (M.P. 114°C), silver acetate (decomposes ?), copper acetate (M.P. 115°C), and dihydrogen hexachloroplatinate (M.P. 60°C). An attemt was made to deposit a copper-silver alloy from a melt composed of 150 ml of ammonium acetate containing 29.95 grams of copper acetate and 5.01 grams of silver acetate. The melt was operated at 121.1°C, no agitation, and a current density of 1.07 A/dm^2. The bath container was a 250 ml glass beaker. The anodes were OFHC copper, and the cathode was a chromium plated molybdenum tube. The sample was plated for four hours during which time nearly all of the anodes dissolved. The deposit was rough and of poor quality. In some areas it appeared that mostly silver had deposited. The thickness of the coating was about 0.0051 cm.

A new molten salt electrolyte was prepared for copper-platinum deposition. This melt contained 150 ml of ammonium acetate, 29.95 grams of copper acetate and 15.54 grams of dihydrogen hexachloroplatinate. The plating container was a 250 ml glass beaker and the melt temperature was 121.1°C. No agitation was employed. Initially the anodes were copper, but they dissolved midway in the run and were replaced by platinized niobium mesh. This deposit also was of poor quality and was rough. The deposit thickness was about the same as the copper-silver sample.

Suspecting that the ammonium salt might be unstable as an electrolyte solvent, a new bath was formulated with lithium acetate. A 150 ml glass beaker was used as a molten salt container. The experiment was conducted on a stirrer-hotplate using a Teflon coated stir bar to provide agitation. The melt temperature was 110°C. About 3.3 grams of copper acetate was added to the melt. The anode was a strip of electrodeposited copper. After one hour of plating at 2.15 A/dm^2 it was observed that copper was being deposited, but it was non-coherent. There was no evidence of corrosion of the anode. It is believed that the copper in the melt simply was removed by deposition and not replenished. Addition of cetyltriammonium bromide to aid in anode corrosion was not effective. As the acetate melts showed no promise for commercial deposition of copper alloys, further work with them was abandoned.

3.2 Deposition of Low Alloyed Copper from Non-aqueous (Organic) Electrolytes

3.2.1 Studies at Southern Illinois University at Carbondale (SIU)

At the request of ENI, SIU performed hardness studies on deposits from a non-aqueous bath formulated from dimethyl sulfoxide (DMSO) and n,n-dimethylformamide (DMF). The bath contained 750 ml of DMSO, 120 ml of DMF, 32 grams of cuprous chloride, and 32 grams of ammonium chloride as a conducting salt. Such a bath was described by Wakefield(18). It was the intent of this work to deposit only copper in the initial studies. If successful, attempts would be made to codeposit other elements with the copper. Four trial platings were made, some with additives, as summarized in Table XXXIX. Deposits appeared to be smooth and bright.

TABLE XXXIX - RESULTS OF SIU STUDIES OF COPPER DEPOSITION FROM DMSO-DMF ELECTROLYTES OPERATED AT 80°C

Sample Number	Additive Data Name	g/l	Current Density (A/dm^2)	Deposit Thickness (µm)	Knoop Hardness (Normalized) 25 g Load	50 g Load
DMF-01	None		0.5	205	173	271
DMF-02	TIPA	1.0	0.5	106	147	204
DMF-03	D$^+$Xylose	1.0	0.5	Not Determined	Not Determined (Thin Sample)	
DMF-04	D$^+$Xylose	0.2				
	TIPA	1.0	0.5	119	184	228

Note: TIPA = Triisopropanolamine

3.2.2 Investigations of Copper Deposition from Organic Baths at ENI

Investigations at ENI were initiated with solubility determinations for various copper and silver salts in candidate organic electrolyte systems such as methanesulfonic acid (MSA), dimethylsulfoxide and dimethylformamide mixtures (50% DMSO/50% DMF), dimethylesulfoxide and methanesulfonic acid mixtures (50% DMSO/50% MSA), and toluene-ethylbenzene mixtures (80% TOL/20% ETBZ). For the solubility determinations, about 1 gram of each salt was added to 10 ml of the solvent or solvent system. Each sample was agitated and heated in an ultrasonic bath at 57.2°C. Upon removal from the ultrasonic bath, the DMSO/MSA samples were allowed to stand in a water bath at a temperature of 82.2°C. The TOL/ETBZ samples were placed in a water bath at 65.6°C. Solubility of each salt in each solvent is described in Table XL.

From Table XL it appeared that best solubility of both silver and copper salts would be obtained in the 50% DMSA/50% DMF solvent mixture. The bath was prepared in a 500 ml beaker and operated on a stirrer-hotplate using a magnetic stir bar and a bath temperature of 38.9°C. To the 500 ml of solvent was added 53.5 grams of copper (II) bromide along with 28 grams of lithium chloride as a conducting salt. OFHC copper was used as the anode, and cathodes were 2.54 cm wide stainless steel strips with about 9.144 cm of length submerged in the bath. No shielding was used on the strips. The side facing the anode was labled "A" while the other side was designated "B". The initial run was made with the stir bar rotating at 400 rpm. Subsequent runs were made at a higher bath temperature of 71.1°C and no electrolyte agitation. For all deposition trials, the voltage was maintained between 1.3 and 1.5 volts to minimize oxidation of the solvent at the anode. This resulted in very low

TABLE XL - RESULTS FOR SOLUBILITY TRIALS OF COPPER AND SILVER SALTS IN NON-AQUEOUS BATHS

	Methanesulfonic Acid at 57.2°C		**50% DMSO/50% DMF at 57.2°C**	
Metal Salt	Solubility	Appearance	Solubility	Appearance
Copper (I) Bromide	Insoluble	No change	Soluble	Brownish green
Copper (II) Bromide	Sparingly sol.	Solvent darker brown	Soluble	Black and murky
Copper (II) Acetate Monohydrate	Insoluble	No change	Soluble	Dark green
Silver Acetate	Soluble	No change	Slightly soluble	Foamed (decomposition?)
Copper (I) Iodide	Sparingly sol.	Solvent darker brown	Soluble	Brown
Silver Iodide	Sparingly sol.	Solvent darker brown	Sparingly soluble	Light yellow
Copper (II) Chloride	Insoluble	No change	Slightly soluble	Brown, green, yellow, and orange colored layers
Silver Chloride	Insoluble	No change	Insoluble	No change
Copper Sulfate	Insoluble	No change	Sparingly soluble	Light green
	50% DMSO/50% MSA at 82.2°C		**80% Toluene/20% Ethylbenzene at 65.6°C**	
Metal Salt	Solubility	Appearance	Solubility	Appearance
Copper (I) Bromide	Soluble	Black	Insoluble	No change
Copper (II) Bromide	Soluble	Black	Insoluble	No change
Copper (II) Acetate Monohydrate	Slightly soluble	Blue-green	Slightly soluble	Blue
Silver Acetate	Sparingly sol.	Light yel. (foaming)	Insoluble	No change
Copper (I) Iodide	Soluble	Brown	Soluble	Pink
Silver Iodide	Sparingly sol.	Yellow	Sparingly soluble	Light yellow
Copper (II) Chloride	Slightly soluble	Light green	Sparingly soluble	Light green
Silver Chloride	Insoluble	No change	Insoluble	No change
Copper Sulfate	Slightly soluble	Bluish green	Sparingly soluble	Light blue

TABLE XLI - SUMMARY OF PLATING CONDITIONS FOR DMSO/DMF BATH SPECIMENS

Sample No.	Copper Content of Bath (g/l)	Silver Content of Bath (g/l)	Plating Temperature (°C)	Agitation of Bath	Length of Plating Run (Hours)	Weight of Deposit (g)	Average Current Density (A/dm^2)
ORG-1A	113	0	48.9	Yes	94	7.9	0.129
ORD-2A	113	0	71.1	No	93	23.2	0.409
ORD-2B	113	0	71.1	No	93	11.0	0.194
ORD-3A	116	5.5	71.1	No	56	12.2	0.355
ORD-3B	116	5.5	71.1	No	56	7.8	0.215

current densities. Plating conditions for all runs are found in Table XLI.

The average current density for each side of the cathode strip was determined from the weight of each deposit and the time of the plating run. Since copper in the +2 state was added to the bath, the initial valence state from which the copper was deposited was assumed to be +2. However, the necessary current to deposit copper from the +2 state was twice as great as the actual current noted during the experiments. Therefore, even though copper (II) bromide was added to the bath, the copper deposited as though in the +1 valence. The reason for this was not known; however, complexes formed in this solvent from anode dissolution may favor oxidation to the monovalent copper cation.

Of the three cathode strips plated in this bath, the first two were intentionally "pure" copper to establish bath parameters of temperature and current density. The remainng two samples from the third cathode strip were produced after an addition of silver acetate for alloying. Chemical and mechanical property testing was performed on selected deposits from each side of the plated strips. The results are shown in Table XLII. Samples ORG-3A and ORG-3B were high in silver content with the low current density side being the highest. Both silver containing samples were brittle and meaningful mechanical property results could not be obtained. A remedy for this condition might exist with a suitable heat treatment before testing.

TABLE XLII - SUMMARY OF CHEMICAL ANALYSES AND MECHANICAL PROPERTIES FOR COPPER AND COPPER-SILVER ALLOY DEPOSITS FROM 50% DMSO/50% DMF ELECTROLYTES

Sample No.	Current Density (A/dm^2)	Copper In Deposit (Weight %)	Silver In Deposit (Weight %)	Ultimate Strength (Ksi)	Yield Strength (Ksi)	Elongation in 5.08 Cm (%)	Vickers Hardness (100 g Load)
ORG-1A	0.129	Not Tested	Not Tested	29.47	28.68	3.0	116
ORG-2A	0.409	99.9	0.1	32.30	26.58	10.0	88
ORG-2B	0.194	99.9	0.1	46.03	36.34	8.0	130
ORG-3A	0.355	90.8	9.2	24.76	-	-	258
ORG-3B	0.215	74.0	26.0	6.65	-	-	162

3.3 Deposition of Low Alloyed Copper from Aqueous or Mixed Electrolytes

3.3.1 Southern Illinois University Studies of Copper Alloy Deposition

Initial alloying studies at SIU were conducted with the system of copper and chromium. Room temperature deposition was carried out on a copper cathode rotated at a speed of 150 rpm. The anode was a platinum mesh placed on the bottom of the cell. The plating bath consisted of copper sulfate (200 g/l), sulfuric acid (75 g/l), chromium (II) sulfate (45 g/l), and formic acid (5 ml/l) dissolved in sufficient distilled water to make one liter of electrolyte. Plating was conducted at various current densities ranging from 30 to 88 A/cm^2 to assure a potential more negative than -1.0 volt (versus the standard calomel electrode) at the cathode. Lower current densities led to no chromium in the deposit. The deposits obtained were brittle, but one sample contained 5.3 weight percent chromium. Additional attempts were made to deposit copper-chromium alloy using pulse plating, but the deposits obtained were not of good quality.

SIU investigated using silver nitrate in standard acid copper sulfate baths to deposit copper-silver alloys. Plating parameters and deposit appearances are described in Table XLIII. It appeared that very low silver concentrations were required to facilitate Cu-Ag codeposits. Energy dispersive X-ray spectroscopy indicated weight percentages of silver in Samples 200, 201, and 202 to be 8.75, 0.37, and 0.62 respectively.

TABLE XLIII - OBSERVATIONS OF DEPOSITS FROM STANDARD ACID COPPER SULFATE BATHS CONTAINING SILVER NITRATE

Sample Number	Silver Nitrate Concentration (g/l)	Current Density (A/dm^2)	Plating Time (Hours)	Bath pH	Remarks
194	8.0	7.5	Not Determined	0.71	Dendrites and powdery deposits obtained.
195	1.0	5.0	1.58	Not Det.	Dendrites and powdery deposits obtained.
196	1.0	7.5	0.55	0.40	Dendrites and powdery deposits obtained.
197	0.5	2.5	1.58	0.25	Dendrites and powdery deposits obtained.
198	0.2	5.0	2.08	0.38	Dendrites and powdery deposits obtained.
199	0.2	5.0	0.78	0.59	Dendrites and powdery deposits obtained.
200	0.2	7.5	0.55	Not Det.	Run stopped periodically to wash deposits with tap water and methanol rinse to remove powdery deposit.
201	0.2	7.5	1.33	0.4 to 0.1	Run stopped periodically to wash deposits with tap water and methanol rinse to remove powdery deposit.
202	0.2	7.5	1.42	0.13	Run stopped periodically to wash deposits with tap water and methanol rinse to remove powdery deposit.

Explorations were also made at SIU to deposit copper-platinum alloys using 2.0 g/l of hexachloroplatinic acid in a standard acid copper sulfate bath. Current densities ranged from 2.5 to 7.5 A/dm^2. Either no deposits or burnt deposits were obtained. They next evaluated deposition of copper-silver alloys from a pyrophosphate bath prepared by dissolving 67 g/l of copper sulfate and 4 g/l of silver nitrate in excess potassium pyrophosphate (300 g/l) to produce pyrophosphate complexes of copper and silver. Four deposition trials were made with this bath, including one with ammonium sulfate as an additive. Current density ranged from 0.25 to 1.5 A/dm^2; pH ranged from 9.35 to 10.8. Either no deposit or black powdery deposits were obtained having no engineering value.

Based on extensive experience with platinum electrolytes using hexachloroplatinic acid, it was suggested a copper-platinum alloy plating bath might best operate at a pH in the range of 7.0 to 7.8 for sound deposits. ENI recommended a continuation of investigations using the pyrophosphate bath with operation at a pH near 7.5, a bath temperature of 55° to 60°C, and use of vigorous agitation. SIU prepared a new bath composed of copper pyrophosphate (70 g/l), potassium pyrophosphate (250 g/l), potassium nitrate (5 g/l), ammonium hydroxide (8 ml/l), and hexachloroplatinic acid (1 g/l). As mixed, and after dissolving all of the platinum salts, the pH was 11.5. It was lowered to a value between 7.5 and 8 by use of phosphoric acid. ENI recommended the use of pyrophosphoric acid for future adjustments to minimize phosphate buildup. Four plating runs were made with this bath as summarized in Table XLIV.

TABLE XLIV - DEPOSITION PARAMETERS AND CHEMICAL ANALYSES FOR COPPER-PLATINUM ALLOYS FROM A PYROPHOSPHATE BATH AT SIU

Sample Number	Electrolyte Temp. (°C	Current Density (A/dm^2)	Analyses of Alloy: Copper (Weight %)	Platinum (Weight %)	Potassium (Weight %)
B10	20°C	1.0	88.95	6.46	4.59
B11	20°C	2.0	97.49	1.54	0.98
B12	50°C	5.0	86.50	8.97	4.53
B13	20°C	5.0	98.21	1.37	0.43

Deposits in Table XLIV were analyzed using EDS. The deposits resembled copper in appearance. The data also indicates that the amount of platinum present can be increased by lowering the current density or raising the bath temperature. These were very encouraging results which prompted formulation of a similar, but larger, bath at ENI.

3.3.2 ENI Studies to Deposit Low Alloyed Copper from Aqueous or Mixed Electrolytes

3.3.2.1 Copper-Platinum Alloys

A three liter pyrophosphate bath was prepared containing copper pyrophosphate (70 g/l), potassium pyrophosphate (250 g/l), potassium nitrate (5 g/l), ammonium hydroxide (8 ml/l), and hexachloroplatinic acid (1 g/l). The copper pyrophosphate, potassium pyrophosphate, and potassium nitrate were dissolved in two liters of deionized water at 52°C. Ammonium hydroxide was then added. The hexachloroplatinic acid was dissolved in a small amount of deionized water at room temperature and this was slowly added to the bath. Deionized water was added to bring the final volume to three liters. The bath was stirred for two hours at 52°C to assure that all salts were dissolved and well mixed. The initial pH of the bath was about 10.5 and was lowered to about 8.0 by adding pyrophosphoric acid. Sodium hydroxide was used to raise pH where required.

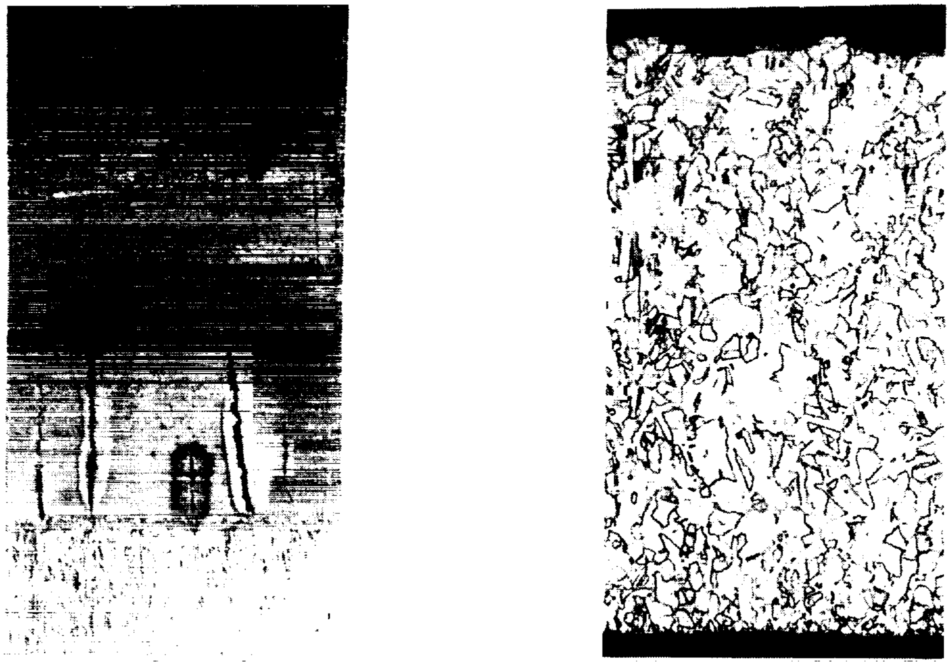
The experimental parameters for the deposition runs were: pH 8.0, bath temperature 52°C, current density 2.15 A/dm^2, and vigorous agitation of the solution. Agitation during deposition of the first two samples was by means of vigorous bubbling of argon through the solution. Agitation was more vigorous in the deposition of Sample 2 in comparison with Sample 1. More bubble impinge-ment was on the cathode in the Sample 2 run. Sample 2 was smoother than Sample 1 as a result of the increased agitation at the cathode surface. The argon supply was replaced by a small vacuum pump that was attached in reverse to the bubbler to act as a low pressure air blower. This permitted longer plating times without the problem of an argon bottle becoming empty. Sample 3 was fairly smooth. Table XLV shows the analytical results for the first three alloy samples deposited. EDS was used to determine the analyses. Significant amounts of potassium and phosphorous were found in Sample No. 1, possibly due to poor solution agitation (not directed at the cathode). No phosphorous was reported for Sample Nos. 2 and 3, but potassium was found. All samples experienced problems with constant and continuous electrolyte agitation, and this is likely responsible for the impurities found.

Thicker samples were needed for mechanical property testing, so a fourth sample was electroformed

TABLE XLV - ANALYSES OF COPPER-PLATINUM ALLOY DEPOSITS FROM A 3 LITER PYROPHOSPHATE ELECTROLYTE AT ENI

Sample Number	Weight Percent of Element:				Atomic Percent of Element:			
	Cu	Pt	P	K	Cu	Pt	P	K
1	95.38	1.95	0.94	3.17	92.52	0.62	1.87	4.99
2	95.00	4.86	0.00	0.31	97.85	1.63	0.00	0.52
3	95.57	3.05	0.00	1.96	95.82	1.00	0.00	3.19

Thicker samples were needed for mechanical property testing, so a fourth sample was electroformed from the 3 liter bath over a three day period using the pumped air for agitation of the electrolyte. No changes were made in plating parameters. The deposit was cut into four samples of which three were vacuum heat treated for one hour. One sample was treated at 260°C, another at 371°C, and the third at 482.2°C. Each heat treated sample was tested for Vickers (100 g load) hardness and examination of microstructure. Small as-deposited coupons were examined for comparison. The sample heat treated at 260°C had a Vickers hardness of 30 to 32. Photomicrographs, Figure 32, show an odd microstructure in the as-deposited alloy where a significant change in grain structure occurred which is indicative of poor bath agitation in the vicinity of the cathode. The as-deposited microstructure contains a region best described as amorphous like that of many electroless deposits, while the heat treated structure is more characteristic of that of most pyrophosphate deposits. The degree of recrystallization occurring at 260°C was greater than expected.



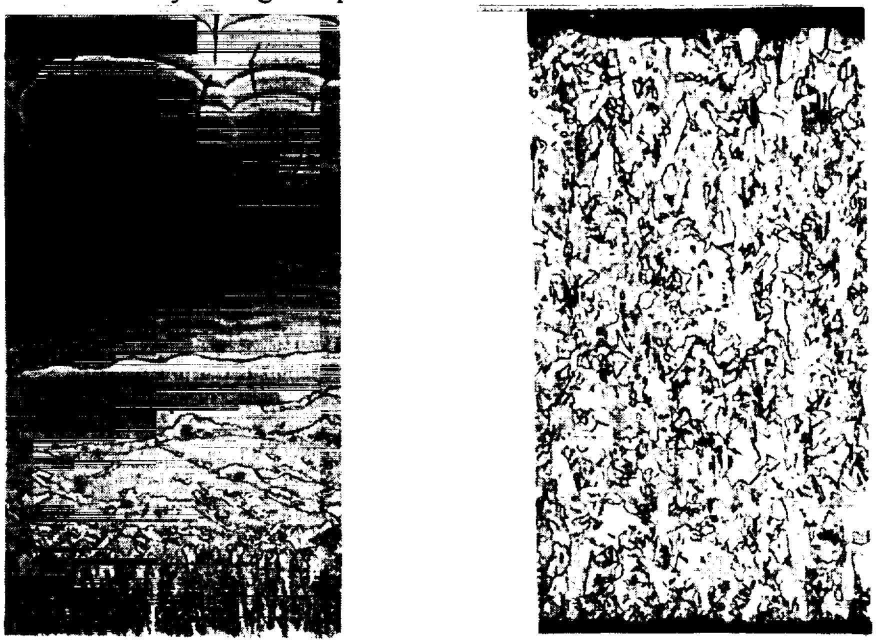
"As-deposited" Cross-section. Magnification 100X.

Cross-section of 260°C Heat Treated Sample

Figure 32. Microstructures of Copper-platinum Alloy from a Pyrophosphate Bath Before and After Vacuum Heat Treating at 260°C.

Photomicrographs of a companion piece of the same sample, before and after heat treatment at

371.1°C, are found in Figure 33. This specimen had a post heat treatment Vickers hardness of 122 to 151. The sample is possibly from the panel center where current density was probably lowest, and based on SIU conclusions, the silver content should be highest. This might account for the higher hardness and slightly smaller grain sizes than observed with the 260°C heat treated sample. If true, this would support the supposition that alloying copper with platinum retards recrystallization and probably leads to mechanically stronger deposits.

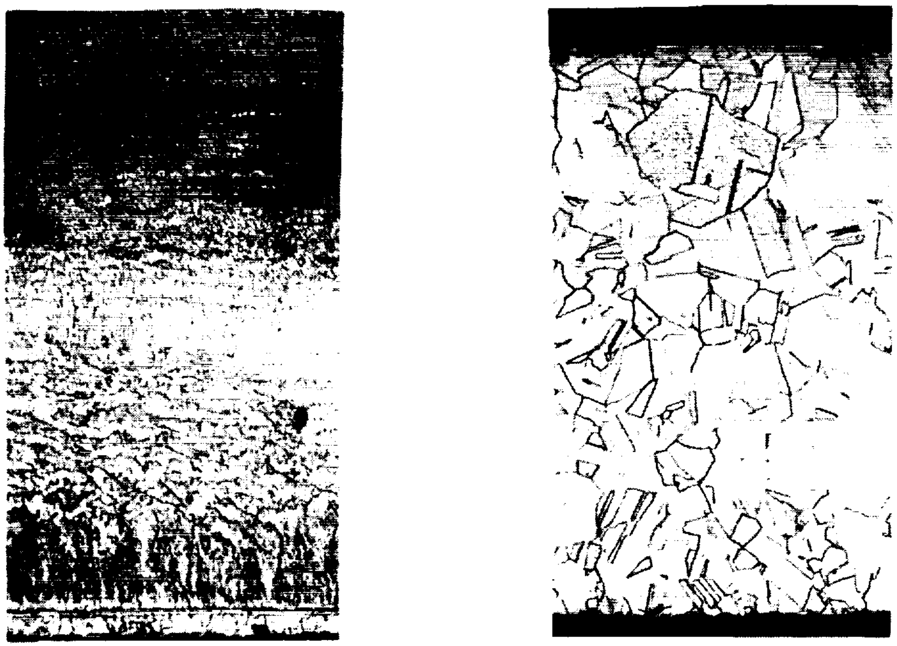


"As Deposited" Cross-section. Magnification 100X. Cross-section of 371.1°C Heat Treated Sample.

Figure 33. Microstructures of Copper-platinum Alloy from a Pyrophosphate Bath Before and After Vacuum Heat Treating at 371.1°C.

The sample heat treated at 482.2°C showed a high degree of recrystallization as shown in the photomicrographs in Figure 34. The heat treated material had a Vickers hardness (100 g load) of 39 to 41. Recrystallization at this temperature is to be expected, even with platinum present as an alloying ingredient. However, even larger grains might be expected from this heat treating temperature if platinum were not present. According to Hanson's Constitution of Binary Alloys(13), order-disorder transformations in the copper-platinum system take place in a very wide range of compositions and at relatively low annealing temperatures. Platinum rich layers capable of producing 1:1 ratios of platinum to copper in lattice cells are claimed to distort diagonally to form a trigonal structure. This makes the copper-platinum system interesting for further development in an effort to improve elevated temperature strength of electrodeposited copper.

Observations from prior studies of the copper-platinum system have shown a need for better control of the pyrophosphate bath, particularly in the areas of contamination control, current density uniformity, and better bath agitation at the cathode surface. To meet these needs, a 20 liter pyrophosphate bath was established. This permited use of an in-tank heater with thermostatic control and an in-tank



"As Deposited" Cross-section. Magnification 100X. Cross-section of 482.2°C Heat Treated Sample.

Figure 34. Microstructures of Copper-platinum Alloy from a Pyrophosphate Bath Before and After Vacuum Heat Treating at 482.2°C.

filter pump to keep the bath clean and provide an electrolyte spray for directing fresh electrolyte perpendicular to the cathode surface plane for more complete coverage. The cathode holding fixtures were redesigned to incorporate a small "shadow box" shield around the area to be electroformed. The electrolyte composition was the same as previously used, except the hexachloroplatinic acid content was slightly under 1 g/l.

Three consecutive samples were electroformed at a bath temperature of 52°C with the pH maintained between 8.2 and 8.5. A current density Of2.15 A/dm^2 was used on all samples. The first sample had a center roughness deteremined to be a result of an angular solution spray. This was corrected for the second and third samples. These samples were wrapped in stainless steel foil for oxidation protection during heat treating at ENI. A top-loading furnace was heated to 371°C and purged with argon for 30 minutes prior to loading the samples into the heating zone. Heat treating time was one hour, and the furnace was allowed to cool to 50°C before removal of the deposits. The furnace was argon purged during heat treating and the cooling period. Alloy composition and mech-anical property data for these specimens are shown in Table XLVI.

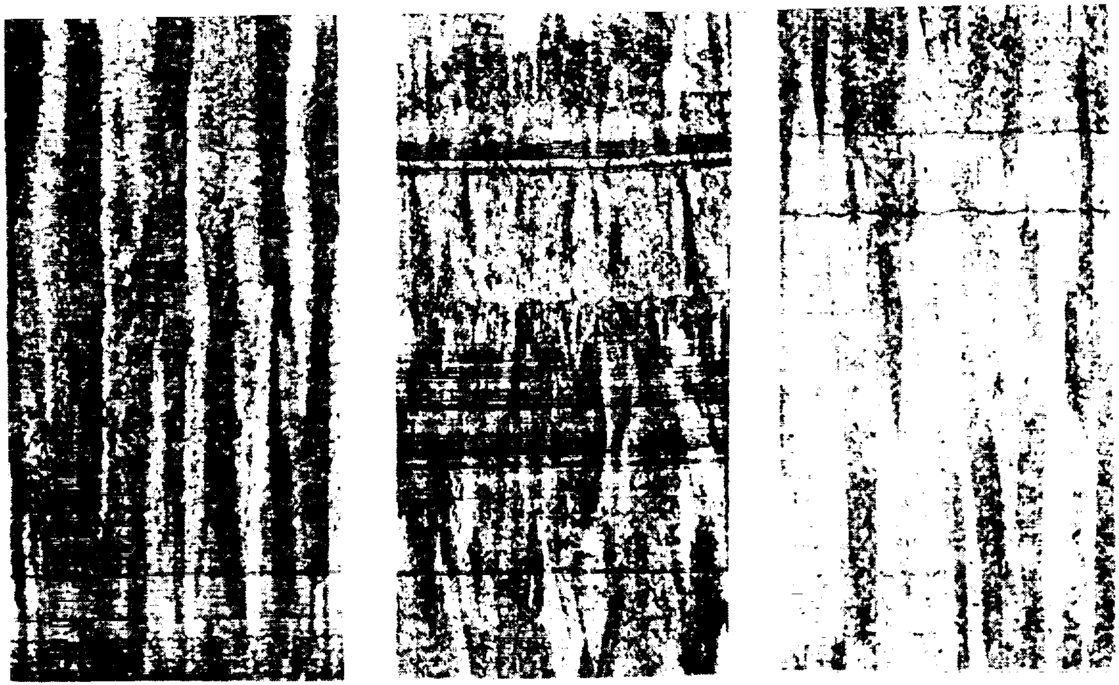
Photomicrographs of these heat treated specimens disclose a columnar grain structure such as observed in conventional acid copper sulfate deposits, or in copper pyrophosphate deposits with less than optimum solution agitation during deposition. However, a close examination indicates that the large columnar grains may contain finer sub-grains. Illustrations are found in Figure 35. There is also a banding found in all specimens. This is typical in electrodeposited alloys and may be due to layered variations in compositional content of the alloying element, in this case, platinum.

TABLE XLVI - TEST DATA FOR COPPER-PLATINUM ALLOYS DEPOSITED FROM A PYROPHOSPHATE BATH OPERATED AT 52°C AND 2.15 A/DM^2 CURRENT DENSITY (ANNEALED 1 HOUR AT 371°C)

			Mechanical Properties			Vickers Hardness
Sample Number	Thickness (Cm)	Platinum (Weight %)	Ultimate Str. (Ksi)	Yield Str. (Ksi)	Elongation % in 5.08 Cm	Value (100 g Load)
CuPt-01	0.191	1.95	38.21	28.59	38.5	82
CuPt-02	0.175	4.86*	39.50	29.04	32.5	82
CuPt-03	0.234	3.05	38.70	27.83	35.0	76

* Denotes platinum replenishment addition made.

The mechanical properties at 20°C of the alloys shown in Table XLVI are greatly superior to those of deposits from conventional acid copper sulfate baths using periodic reverse (PR) current, Table XXXVII. Yield strengths and ductility in combination are significantly better than the non-alloyed copper deposits. These alloys also show much better ultimate and yield strengths than found in wrought annealed OFHC grade copper. These remarkable properties led to an inclusion of this alloy in dispersion strengthening investigations discussed later in this report. It is recommended that future work with this alloy be conducted to further define the influence of platinum content on mechanical properties at ambient and elevated temperatures. Means should be explored to better control the uniformity of platinum in the deposits and to establish platinum salt replenishment rates. Use of periodic current reversal and pulsed current deposition (or combinations) should be examined.



Sample CuPt-01 Sample CuPt-02 Sample CuPt-03

Figure 35. Microstructures of Copper-Platinum Alloy Deposits from a Pyrophosphate Bath After Heat Treating One Hour at 371.1°C. Magnification 100X.

3.3.2.2 Copper-Silver Alloys

Based on the poor quality copper-silver alloy deposits obtained by SIU from acid copper sulfate and copper pyrophosphate baths, and the inability of other investigators to electrodeposit commercially useful copper-silver alloys, ENI determined that the greatest probability for producing a successful alloy would be from the iodide bath investigated by Reksc and Mrugalski(17). They noted that deposition potentials for copper and silver were very close together in iodide solution and the complex ions had advantageous stability constants in such solutions. Their work demonstrated good quality alloy deposits with 1 to 30 weight percent copper. In the present work, good quality deposits with over 90 weight percent copper are sought.

An aqueous solution composed of potassium iodide (996 g/l), copper (I) iodide (76.2 g/l), and silver iodide (9.4 g/l) was prepared as a primary electrolyte. For this study, a Hull type cell was used as the plating container to evaluate deposits over a broad range of current densities. All deposition trials were conducted at 29.4°C, and pH was allowed to vary for each run. The cell was equipped to provide air agitation for electrolyte circulation. The anode was copper and the cathode panel was stainless steel. Since the Hull cell cathode is angled to be close to the anode at one end and far away at the other, a wide range of current densities will simultaneously exist during plating. This allows one to examine resulting deposits for appearance which can be immediately related to current density.

Table XLVII summarizes Hull cell panel plating conditions and appearance of the deposits. Areas defined as “A”, “B”, and “C” represent high, intermediate, and low current densities, respectively.

TABLE XLVII - HULL CELL DATA AND DEPOSIT DESCRIPTIONS FOR COPPER-SILVER ALLOYS FROM AN IODIDE SOLUTION OPERATED AT 29.4°C

Plating Run No.	Aveerage C.D. (A/dm^2)	Electrolyte pH	Plating Time (Minutes)	Current Density Area A (High CD)	 B (Intermediate CD)	 C (Low CD)
01	1.935	7.46	5.0	Dark gray.	Mostly dark gray.	Copper-orange.
02	1.451	4.30	5.5	Dark gray.	Narrow mixed band.	Copper-orange.
03	0.968	4.24	5.0	Silver gray/gray.	Gray-orange/prange.	Copper-orange.
04	0.484	4.08	5.0	Light orange.	Light orange	Silver-orange/silver
05	0.484	4.60	10.0	Dark orange.	Orange.	Light orange/silver
New Solution:						
06	0.484	7.16	10.0	Dark orange to orange.	Orange to light orange.	Light orange to Orange-silver.
07	0.484	4.34	8.0	Dark orange	Orange.	Light orange.

From each Hull cell panel, three coupons were cut for alloy chemical analysis. Coupon “A” represented the high current density end of the specimen, Coupon “B” was from the intermediate current density area, and Coupon “C” was the section of low current density. The samples were examined by SEM and EDX methods to determine the concentration of copper and silver. The EDX system is capable of detecting all elements from boron to uranium on the periodic table. However, it can not quantify elements below sodium. The actual analyses consisted of using SEM EDX to determine the ratio of copper to silver in the center of each coupon. Only selected coupons were examined. Complete scans of these coupons were furnished to include relative K values, weight percents, and atomic percents. Table XLVIII summarizes the analytical results for the coupons examined. Figure 36 illustrates a typical analytical scan for the alloy elements. Iron is present from the Hull panel substrate. Plating Run Nos. 1-3 were not analyzed based on poorer visual quality of these particular deposits.

TABLE XLVIII - ANALYTICAL RESULTS FOR COPPER-SILVER ALLOY DEPOSITS FROM THE IODIDE ELECTROLYTE AT 29.4°C

Plating Run No.	Average C.D. (A/dm^2)	Electrolyte pH	Coupon Region	Analytical Results: Cu Wt. %	Cu Atomic %	Ag Wt. %	Ag Atomic %
04	0.484	4.08	A (High C.D.)	98.01	98.82	1.99	1.18
05	0.484	4.60	B (Intermed. C.D.)	98.59	99.16	1.41	0.84
06	0.484	7.16	A (High C.D.)	97.98	98.80	2.02	1.20
			B (Intermed. C.D.)	97.66	98.61	2.34	1.39
			C (Low C.D.)	96.62	97.98	3.38	2.02
07	0.484	4.34	B (Intermed. C.D.)	97.63	98.59	2.37	1.41

From Table XLVIII it appears that lower current densities lead to higher silver content in the alloys. Since a two percent by weight silver content was sought in the alloy (to simulate the silver content of NASA-Z alloy), these experiments were extremely successful.

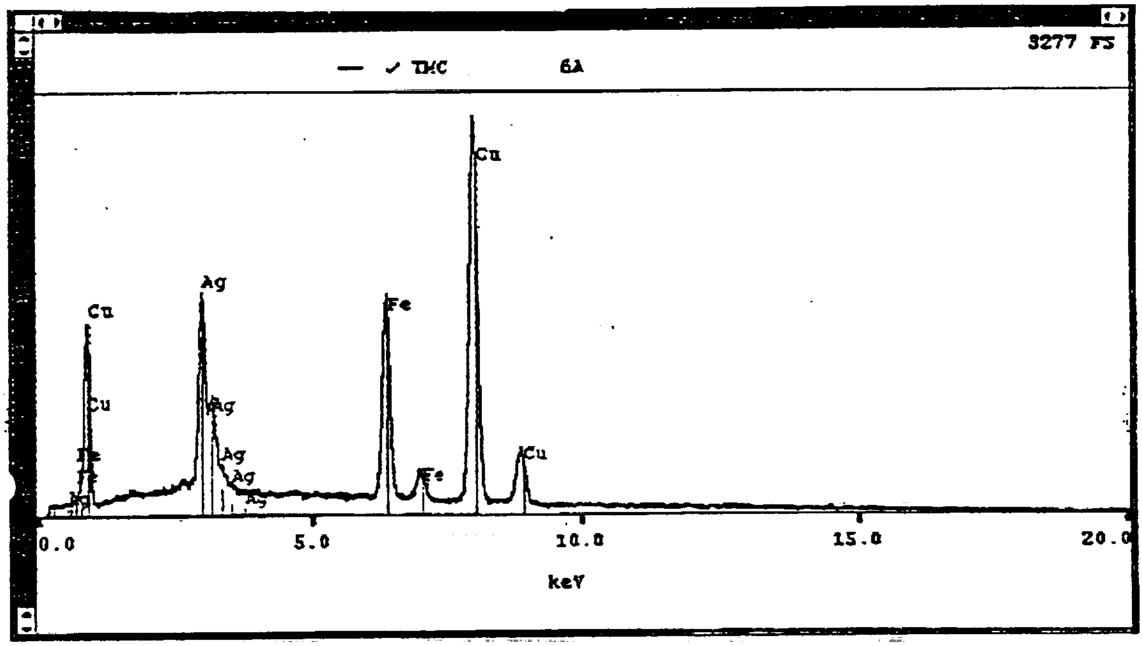


Figure 36. SEM EDX Scan of Copper-Silver Alloy Coupon No. 6A.

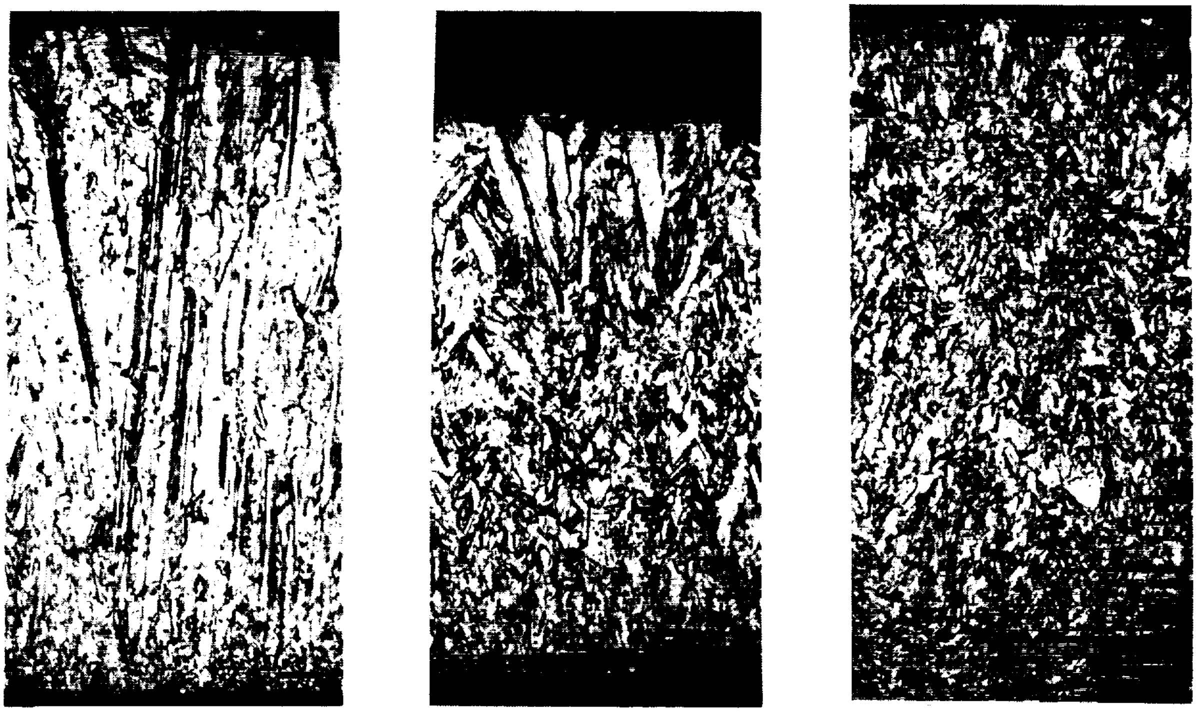
3.3.3 Mixed Electrolytes - Water and Phenolsulfonic Acid

Many organic acids are soluble in water, and the combination of these solvents can sometimes result in improved solvent systems with better deposit levelling capability. The water and phenolsulfonic acid (PSA) electrolyte has been used for many years in high speed acid tin plating and with great success. A 3.5 liter bath was prepared by heating 2 liters of deionized water to 50°C and heating a quantity of PSA to cause melting. One liter of liquid PSA was added to the water and mixed thoroughly on a hotplate-stirrer. Copper sulfate was added to a concentration of about 190 g/l. The bath was heated to 35°C as an operating temperature. OFHC grade copper slugs were used as an anode and a stainless steel shielded cathode was the substrate for deposition. Three consecutive samples were deposited from this bath before 1 g/l of dihydroxydiphenol sulfone (DHDPS) was added as a levelling agent. One additional sample was produced from the modified bath using the same bath temperature and current density of 2.15 A/dm^2 as employed on the prior samples. Table XLIX summarizes property test data for these samples.

TABLE XLIX - MECHANICAL PROPERTY AND HARDNESS TEST DATA FOR COPPER DEPOSITS FROM A WATER-PHENOLSULFONIC ACID BATH AT 35°C

	Additives		Current Density	Deposit Thickness	Mechanical Properties			
Sample Number	Name	g/l	(A/dm^2)	(Cm)	Ultimate Str. (Ksi)	Yield Str. (Ksi)	Elongation in 5.08 Cm, %	Vickers Hradness (100 g Load)
PSA-01	None	0.0	2.15	0.094	25.73	16.15	13.0	69
PSA-02	None	0.0	2.15	0.086	28.37	14.77	20.0	74
PSA-03	None	0.0	2.15	0.094	32.11	20.32	10.0	71
PSA-04	DHDPS	1.0	2.15	0.048	40.34	23.36	22.0	91.5

Microstructures of these deposits are shown in Figure 37a and 37b. Columnar grain structures were



Sample PSA-01 (Magnif. 100X). Sample PSA-02 (Magnif. 100X). Sample PSA-03 (Magnif. 100X).

Figure 37a. Microstructures of Acid Copper Deposits from Water-Phenolsulfonic Acid Baths With No Additives.

Figure 37b. Microstructure of Acid Copper Deposit from Water-Phenolsulfonic Acid Bath Containing 1.0 G/L of Dihydroxydiphenol Sulfone.

evident in all samples. Addition of dihydroxydiphenol sulfone greatly improved mechanical properties. Response of this material to heat treatments is not known, nor are the elevated temperature properties. However the bath may provide an acid electrolyte for copper alloy deposition for future studies.

3.4 Conclusions and Recommendations

Alloys of copper with silver or platinum were successfully electrodeposited in aqueous and organic electrolytes. High and low temperature molten salt baths were not found to yield commercially useful copper alloy deposits.

- Attempts to codeposit copper and iridium from a molten cyanide eutectic mixture were not successful. Deposits were soft and spongy.

- Investigation of molten acetate electrolytes operated at 110°C to 125°C and containing copper and silver salts yielded deposits having little coherency. They were of no commercial value.

- Copper-silver alloys could be deposited from DMSO/DMF and aqueous iodide electrolytes, but only at low deposition rates. Silver contents to about 3.4 weight percent were obtained in the aqueous iodide bath. As with most electroformed alloys, the as-deposited metal has low ductility due to crystalline disorientation and other anomalies. Heat treating offers a potential remedy for the poor ductility. Investigations disclosed that useful copper-silver alloys could not be obtained from acid copper sulfate baths containing silver as a nitrate. Commercialization of these alloys would require development of improved deposition rates.

- Alloying platinum with copper was very successful using the pyrophosphate bath and adding platinum in the form of hexachloroplatinic acid. This bath provides a moderate pH range in which both metals can be readily codeposited in a wide range of compositions. The deposits respond well to heat treatment and after such treatments show excellent mechanical properties. Specimens containing 2 to 5 weight percent platinum and heat treated at 371°C for one hour were found to have room temperature mechanical properties of over 38 ksi ultimate strength, over 27 ksi yield strength, and over 32 percent elongation in 5.08 cm. This alloy has great potential for intermediate temperature service.

- Studies to deposit copper from phenolsulfonic acid electrolytes as a possible media for alloy deposition indicated that this bath offered no advantages over conventional acid sulfate baths.

4. TASK IV - ALTERNATE STRENGTHENING TECHNIQUES FOR ELECTRODEPOSITED COPPER

4.0 Background

Other means for strengthening copper electrodeposits exist whereby the deposit can be dispersion strengthened or composite strengthened. Dispersion strengthening requires the inclusion of submicron particles in the metal matrix. These particles are usually refractory metal oxides having high temperature stability. They serve to block, or at least delay, dislocation movement in the metal. This promotes retention of yield strength at elevated temperature, since they introduce an interference to primary slip planes. The smaller the particles are, the more efficient the strengthening because of the increased population density for a given weight percent of the dispersant material. Composite strengthening might be in the form of metal matrix composites or layered composites. Wire wrapping between layers of the deposited metal or alloy can impart directional strength based on the properties of the wire. Codeposition of high modulus whiskers of such materials as silicon carbide or tungsten cabide can impart three dimensional strength to the deposit dependent on ratios of bulk volumes of the matrix metal and the high strength fibers or whiskers.

Dispersion strengthened copper is produced commercially by powder compaction techniques and is available as Glidcop® (SCM Corporation) Al-10, Al-35, and Al-60. Mechanical properties reported for these alloys are shown in Table L(19). These properties are achieved through severe mechanical working of the metal and heat treating. It is not considered possible to duplicate these properties in an electrodeposited counterpart. However, the principles of dispersion strengthening can be applied to electrodeposition to create copper having enhanced elevated temp-erature mechanical properties.

TABLE L - ROOM TEMPERATURE MECHANICAL PROPERTIES OF AS EXTRUDED OR COLD WORKED AND ANNEALED GLIDCOP ALLOYS(19)

				Mechanical Properties			Thermal Conductivity
Product	Glidcop Grade	Al_2O_3 Weight %	Condition	Ultimate Str. Ksi	Yield Str. Ksi	Elongation In 5.08 Cm, %	At 20°C Cal/Cm²/Cm/Sec/°C
Rod and Bar	AL-10	0.2	As Extruded	64.0	52.0	22	0.86
	AL-35	0.7	As Extruded	70.0	59.0	16	0.81
	AL-60	1.1	As Extruded	80.0	68.0	7	0.77
Strip (0.038 Cm Thick)	AL-10	0.2	Cold Worked 88%: Annealed @ 927°C	58.0	49.0	7	
	AL-35	0.7	Cold Worked 96%: Annealed @ 927°C	69.0	64.0	7	

In 1971, Chen, Lakshminaranan, and Sautter(20) investigated codeposition of alumina and titania with copper using an acid sulfate bath. They examined the effects of solution pH, particle concentration in the electrolyte, addition agents, and the nature of the crystalline phase of the oxide particles. They found that the crystalline form of aluminum oxide is a critical parameter in codeposition in the acid copper plating system. The most stable oxide forms, α-Al_2O_3 and rutile TiO_2, were the ones most favorably codeposited. They found that addition agents did not promote the codeposition of the γ form of alumina. However such agents improved the amount of α-Al_2O_3 deposited. They observed that in freshly prepared suspensions of the oxide particles, the pH has little effect on the amount of oxide codeposited. However, on aging, the effectiveness of oxide incorporation dimenished for solutions with pH maintained at 1.0 while solutions at pH 2.0 and 3.0 showed no aging effect after a period of two weeks. By controlled heat treating they were able to convert the outer surfaces of the γ form to the α form for more favorable codeposition.

In a later study, Chen, Lakshminaranan, and Sautter(21) examined mechanical properties of copper deposits dispersion strengthened with alumina. They found that the codeposition of Al_2O_3 copper increases room temperature yield strength, ultimate tensile strength, hardness, electrical resistivity and decreases the ductility of the as plated deposits. They noted that annealed Cu-Al_2O_3 deposits retain higher strength up to 425°C, after which strength properties decreased. Unlike copper deposits, annealing at temperatures over 315°C decreased the ductility of the dispersion strengthened specimens. Cold rolling these deposits appeared to increase strength while promoting embrittlement.

Tomaszewski(22) examined codeposition of non-conducting fine particles in acidic copper plating baths He claimed that many of these particles will not codeposit readily unless aliphatic amines are present in the bath. Tomaszewski, et al(23) also claimed that certain monovalent cations would improve the codeposition of dispersion particles. Celis and Roos(24) investigated the kinetics of the deposition of alumina particles from copper sulfate plating baths. They proposed a deposition mechanism based on a two step adsorption process.

4.1 Dispersion Strengthening Studies at Southern Illinois University

Initial studies at SIU involved codeposition of one micron sized particles of α-SiC, β-SiC, α-Al_2O_3, and TiO_2 with copper from the acid sulfate bath. They observed, as did other investigators, that the α-Al_2O_3 was difficult to codeposit. The copper sulfate bath was operated at room temperature using a current density of 5 A/dm^2 for each plating run. Table LI summarizes deposition and hardness data for the copper samples containing the one micron particles of various compounds.

TABLE LI - PRODUCTION AND HARDNESS TEST DATA FOR DISPERSION STRENGTHENED ACID COPPER SULFATE DEPOSITS FROM ELECTROLYTES WITHOUT DISPERSION PROMOTERS

	Particle Information:			Additives:		Current	Sample	Knoop Hardness (Normalized Values)	
Sample Number	Type	Size (µm)	Conc. (g/l)	Name	Conc. (g/l)	Density (A/dm^2)	Thickness (µm)	10 g Load	25 g Load
110	α-SiC	1	3	None		5	220	100	133
114		1	3	TIPA	1.0	5	170	117	143
116		1	3	D^+Xylose	0.2	5	250	130	134
118		1	3	D^-Xylose	0.2	5	210	123	146
124		1	3	TIPA	1.0				
				D^+Xylose	0.2	5	150	123	127
125		1	3	TIPA	1.0				
				D^-Xylose	0.2	5	220	118	126

Normalized hardness values are corrections for surface finish.

TABLE LI - PRODUCTION AND HARDNESS TEST DATA FOR DISPERSION STRENGTHENED ACID COPPER SULFATE DEPOSITS FROM ELECTROLYTES WITHOUT DISPERSION PROMOTERS (CONTINUED)

Sample Number	Particle Information: Type	Size (µm)	Conc. (g/l)	Additives: Name	Conc. (g/l)	Current Density (A/dm^2)	Sample Thickness (µm)	Knoop Hardness (Normalized Values) 10 g Load	25 g Load
101	β-SiC	1	3	None		5	170	115	144
103		1	10	None		5	140	99	113
105		1	3	TIPA	1.0	5	130	117	130
109		1	3	D^+Xylose	0.2	5	180	99	127
113		1	3	D^-Xylose	0.2	5	210	107	110
102	α-Al_2O_3	1	10	None		5	190	68	86
104		1	30	None		5	180	77	102
106		1	30	TIPA	1.0	5	230	120	135
108		1	30	D^+Xylose	0.2	5	200	92	117
112		1	30	D^-Xylose	0.2	5	230	119	148
120		1	30	TIPA	1.0				
				D^+Xylose	0.2	5	260	115	122
121		1	30	TIPA	1.0				
				D^-Xylose	0.2	5	280	98	122
115	TiO_2	0.3	3	None		5	240	132	147
126		0.3	10	None		5	200	137	144
107		0.3	30	None		5	220	92	112
111		0.3	3	TIPA	1.0	5	240	107	137
117		0.3	3	D^+Xylose	0.2	5	290	122	133
119		0.3	3	D^-Xylose	0.2	5	220	112	137
122		0.3	3	TIPA	1.0				
				D^+Xylose	0.2	5	170	124	130
123		0.3	3	TIPA	1.0				
				D^-Xylose	0.2	5	230	131	130

From the data in Table LI it appears that α-Al_2O_3 was not codeposited in any significant amount becasue of the low hardness values experienced when no additives were present in the bath other than the alumina particles themselves. The highest hardnesses in the α-alumina group were undoubtedly due to the grain refinement in the copper caused by the organic additives. Hardening in samples containing the α-SiC and β-SiC was probably due to codeposited particles, since the samples from similar baths with organic additives not show significant changes in hardness. Samples containing TiO_2 exhibited hardening as a result of the inclusion of particles. It was noted that the hardest samples with TiO_2 were found in late runs where TIPA had an opportunity to affect the$_2$TiO particles. Such was not apparent with the α-SiC particles which were much larger in size.

SIU performed a second set of deposition experiments using tetraethylenepentamine (TEPA) as a dispersion codeposition promoter based on the recommendations of Tomaszewski(22). Initial deposits were made from the acid copper sulfate bath with only the TEPA as an additive; no dispersion particles were present. Hardness measurements on the deposits disclosed a very large increase over conventional deposits from non-additive acid copper baths. This indicated that this amine exerted a significant crystal texturing influence, even at concentrations as low as 0.4 g/l. This was of interest because the SIU bath did not contain chloride ion. A similar bath at ENI with chloride ion and 0.5

g/l TEPA produced soft, ductile deposits with good (but not remarkable) mechanical properties. The SIU bath was also operated at higher current densities. Table LII summarizes bath compositions and hardness test results for these samples.

TABLE LII - PRODUCTION AND HARDNESS TEST DATA FOR ACID COPPER AND DISPERSION STRENGTHENED ACID COPPER SULFATE DEPOSITS FROM ELECTROLYTES WITH A DISPERSION PROMOTER

Sample Number	Particle Information: Type	Size (μm)	Conc. (g/l)	Additives: Name	Conc. (g/l)	Current Density (A/dm^2)	pH Change Start	pH Change End	Knoop Hardness (Normalized Values) 10 g Load	25 g Load
178	None			TEPA	0.4	2.5	0.27	0.11	150	137
176	None			TEPA	0.4	5.0	0.34	0.15	157	170
177	None			TEPA	0.4	7.5	0.30	0.10	152	152
163	α-SiC	1	3.0	TEPA	0.4	5.0	0.25	0.10	108	123
166	α-SiC	1	3.0	TEPA	0.4	7.5	0.29	0.17	120	129
165	α-SiC	1	3.0	TEPA	0.4					
				D^{+}Xylose	0.2	5.0	0.27	0.12	115	122
168	α-SiC	1	3.0	TEPA	0.4					
				D^{+}Xylose	0.2	7.5	0.22	0.07	127	122
164	α-SiC	1	3.0	TEPA	0.4					
				D^{-}Xylose	0.2	5.0	0.23	0.11	123	134
167	α-SiC	1	3.0	TEPA	0.4					
				D^{-}Xylose	0.2	7.5	0.24	0.10	112	116
169	β-SiC	1	3.0	TEPA	0.4	5.0	0.26	0.12	117	120
172	β-SiC	1	3.0	TEPA	0.4	7.5	0.30	0.12	130	134
171	β-SiC	1	3.0	TEPA	0.4					
				D^{+}Xylose	0.2	5.0	0.23	0.07	126	131
174	β-SiC	1	3.0	TEPA	0.4					
				D^{+}Xylose	0.2	7.5	0.22	0.08	101	105
170	β-SiC	1	3.0	TEPA	0.4					
				D^{-}Xylose	0.2	5.0	0.29	0.10	120	122
173	β-SiC	1	3.0	TEPA	0.4					
				D^{-}Xylose	0.2	7.5	0.26	0.10	146	142

From Table LII it was observed that pH of the electrolyte decreased with each plating run. This was also true for the runs in Table LI, except for the α-alumina runs where little change was noted. In other studies involving acid copper baths, with or without organic additives, the pH was observed to increase. This phenomenon is probably exaggerated by the small beaker sized baths used. However, fine particles, particularly colloidal in size, are believed my many to acquire a double charge layer about their surfaces. The nature of the particle and the pH of the electrolyte media dictates the charge of the inner layer which is opposite that of the outer layer. The strength of this charge is also related to the pH of the media (i.e., strongly acid media will weaken the charge). If one assumes that a neutral colloidal material (or one capable of chemisorption) is introduced to the acidic electrolyte, it follows that chemisorption through an aging process will draw protons from the acid solution to form a positively charged layer. This charging causes like charged particles to repel one another to create a suspension. The creation of proton layers on these particles with very large surafec areas leads to a reduction of protons in the acid solution, hence the pH rises slightly. Conversely, when the particle is codeposited on the negative cathode, a discharge takes place which gives protons back to the electrolyte, and the pH is slightly decreased. The magnitude of this pH change is a crude measure of the effectiveness of the dispersion system in codeposition.

This pH decrease was also noted on the samples in Table LII where no dispersion particles had been added, but the promoter, TEPA, was present. These were new electrolytes into which were placed filmed copper anodes. It is possible that colloidal fines were introduced which reacted in the same way as the dispersion particles. Once plated out this effect might be ended.

4.2 Dispersion Strengthening Studies at ENI Using the Copper-Al_2O_3 System

Copper Experimental Tank No. 4, a 100 liter facility was modified for dispersion plating. A standard acid copper sulfate electrolyte was peroxide treated to destroy prior organic additives and carbon treated twice to restore original purity. The filter was removed from the primary circulation system in the tank weir so that pumped solution could be sprayed through two sparger pipes to asist in suspension of the dispersion particles. A second in-tank pump was provided in the main plating chamber to direct fresh electrolyte onto the surface of the stainless steel cathode on which deposits would be made. The cathode was positioned in a vertical attitude with a surrounding box shield to promote uniformity of thickness in the deposit. It would have been desireable to use Cabot Alon C® as the form of alumina to be dispersion deposited. This material has an average particle diameter of 0.03 microns, and was produced in Australia by a fuming process. It was discovered that this material was no longer available. A substitute was obtained from Alpha Aesar in the form of a mixed powder of α (20%) and γ (80%) aluminum oxide with particle diameters ranging from 0.01 to 0.02 microns.

In the initial plating, Sample 4-Al_2O_3-1, pulsed current deposition was used since intermittent high voltages are introduced which aid the electrophoretic deposition of surface charged oxide particles. The alumina concentration in the bath was 5 g/l. The pulse duty cycle was 50 percent with an average current density of only 1.08 A/dm^2 and a peak current density of 2.15 A/dm^2. Under these conditions the copper matrix contained large grain sizes which would account for the low tensile and yield strengths found in Table LIII. The microstructure of Sample 4-Al_2O_3-1 is found in Figure 37a. To refine grain size in the copper matrix, triisopropanolamine (TIPA) was added to the same bath and plated with pulsed current on the first sample and conventional direct current on the next two specimens. Mechanical properties for these samples are included in Table LIII. Properties typical for acid copper from TIPA baths were found for current densities of 2.15 A/dm^2.

To the same electrolyte was added an amine dispersion promoter, tetraethylenepentamine (TEPA). Five days of aging was allowed before depositing Sample 4-Al_2O_3-TITE-1. This deposit was rough and grainy and had poor mechanical properties. This was believed due to a problem with the in-tank pump used to supply sulution agitation at the cathode surface. Another eleven days of aging was allowed before depositing Sample 4-Al_2O_3-TITE-2. Mechanical properties of this sample were similar to those of acid copper sulfate deposits produced with this current density and from a bath containing TEPA only (see page 40). In each of these samples the strengthening typical for deposits from acid sulfate baths with TIPA was lost. This would suggest that TEPA suppresses the effects

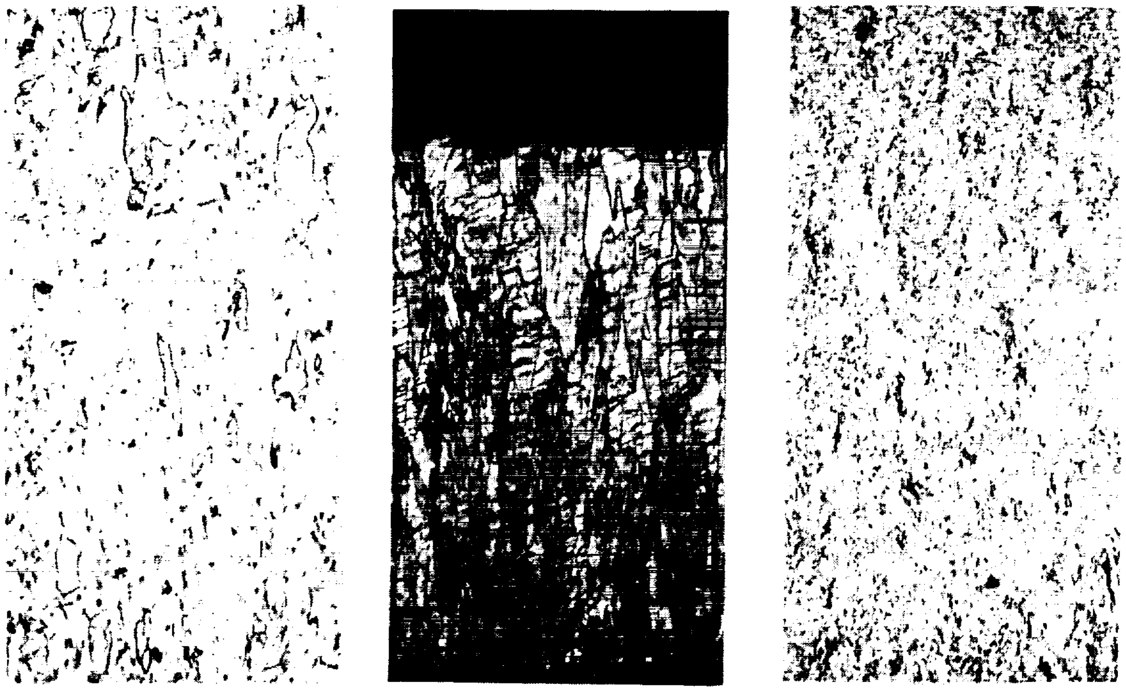
TABLE LIII - MECHANICAL PROPERTY DATA FOR ACID COPPER SULFATE DEPOSITS FROM ELECTROLYTES CONTAINING ALUMINUM OXIDE PARTICLES (20% α AND 80% γ FORMS) AND CHLORIDE ION (81 PPM)

Sample Number	Current Density (A/dm^2)	Bath Temp. (°C)	Additives: Mixed Al_2O_3 (g/l)	Other Name	(g/l)	Mechanical Properties Ulttimate Str. Ksi	Yield Str. Ksi	Elongation % in 5.08 Cm	Hardness Vickers (100 g Load)
4-Al_2O_3-1	1.08*	26.7	5.0	None		17.68	8.51	10.0	68
4-Al_2O_3-TIPA-1	1.08*	26.7	5.0	TIPA	2.0	15.13	13.28	2.0	72
4-Al_2O_3-TIPA-2	2.15	26.7	5.0	TIPA	2.0	56.81	41.47	10.0	118
4-Al_2O_3-TIPA-3	2.15	26.7	5.0	TIPA	2.0	56.97	39.39	13.5	112
4-Al_2O_3-TITE-1	2.15	26.7	5.0	TIPA	2.0				
				TEPA	0.5	11.98	6.79	6.0	78
4-Al_2O_3-TITE-2	2.15	26.7	5.0	TIPA	2.0				
				TEPA	0.5	36.31	17.83	24.0	78

* indicates deposits were pulse deposited at a 50% duty cycle, 20 msec on and 20 msec off, with a peak C.D. of 2.15 A/dm^2.

of TIPA. Microstructures appear to be coarse columnar initially but become finer columnar as bath use and aging progresses.

Analyses for carbon, aluminum, and oxygen were performed on one of the samples described in TABLE LIII using the combustion and inert gas fusion method. Sample 4-Al_2O_3-TIPA-2 contained 29 ppm carbon, 100 ppm aluminum, and 191 ppm oxygen (all percent by weight).

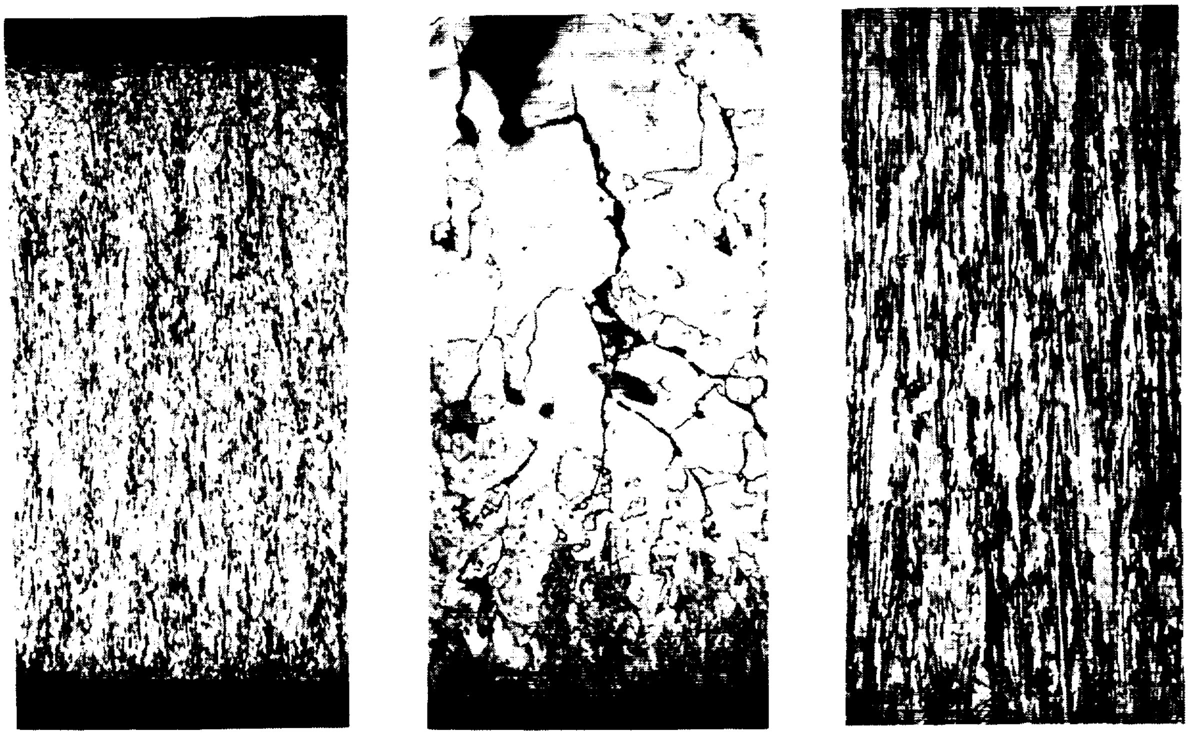


Sample 4-Al_2O_3-1
Magnification 100X.

Sample 4-Al_2O_3-TIPA-1
Magnification 100X.

Sample 4-Al_2O_3-TIPA-2
Magnification 100X.

Figure 38a. Microstructures of Acid Copper Sulfate Deposits from an Electrolyte Containg 5 g/l of Mixed α and γ Alumina With 0.01 to 0.02 Micron Particle Size.



Sample 4-Al_2O_3-TIPA-3
Magnification 100X.

Sample 4-Al_2O_3-TITE-1
Magnification 100X.

Sample 4-Al_2O_3-TITE-2
Magnification 100X.

Figure 38b. Microstructures of Acid Copper Sulfate Deposits from an Electrolyte Containing 5 g/l of Mixed α and γ Alumina With 0.01 to 0.02 Micron Particle Size.

TABLE LIV - MECHANICAL PROPERTIES AT 371.1°C FOR AS-DEPOSITED ACID COPPER SULFATE DEPOSITS FROM NON-ADDITIVE, ADDITIVE, AND DISPERSION BATHS

Sample Number	$CuSO_4$ (g/l)	H_2SO_4 (g/l)	Additions: Name	g/l	Bath Temp. (°C)	Current Density (A/dm^2)	Mechanical Properties at 371.1°C		
							Ultimate Str. Ksi	Yield Str. Ksi	Elongation % in 5.08 Cm
4-NA-02	239.6	74.1	Chloride	81 ppm	26.7	4.84 Fwd			
(PR at 8 sec forward; 4 sec reverse)						4.84 Rev	10.95	7.93	9.5
B-Tank-01	217.9	69.6	Chloride	16 ppm	26.7	2.36			
			D^+Xylose	0.6					
			TIPA	1.0			12.85	7.97	14.0
4-Al_2O_3-TITE-2			Chloride	81 ppm	26.7	2.15			
	225.4	73.4	TEPA	0.5					
			TIPA	2.0					
			α/γ Alumina	5.0			12.15	11.04	5.5
4-Al_2O_3-TIPA-2			Chloride	81 ppm	26.7	2.15			
	214.9	66.7	TIPA	2.0					
			α/γ Alumina	5.0			Broke before 2% offset achieved.		

Several specimens, including two containing alumina as a dispersent were submitted to mechanical property testing at 371.1°C in the as-deposited condition. The test results are summarized in Table LIV.

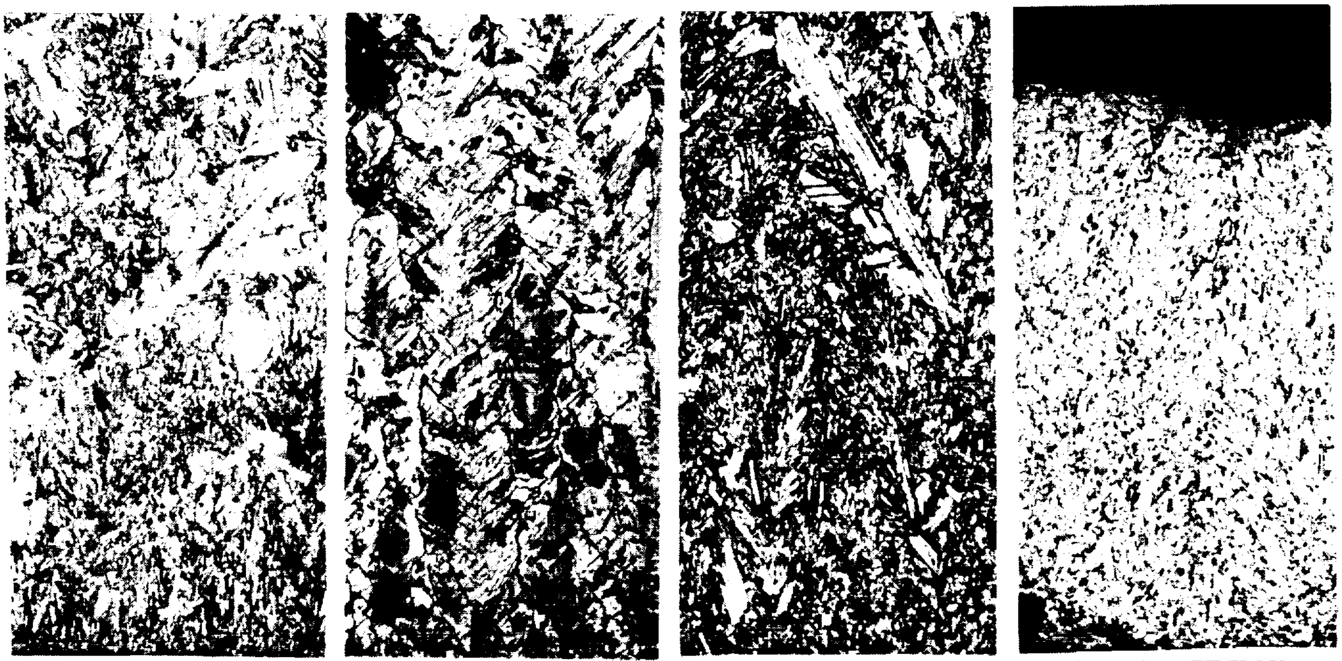
Since the previous trials were with an alumina containing only 20 percent α form and very little of the dispersoid was found in the deposit from an anaysis, it was necessary to substitute a dispersion material containing all α-alumina. This was obtained with Ceralox® Type APA-0.2. It was reported that most of this material was in the 0.1 to 0.4 micron size range. Four samples were produced with and without additives other than the α-alumina. Production data and mechanical property test data for all specimens are summarized in Table LV.

TABLE LV - MECHANICAL PROPERTIES AT 20°C FOR AS-DEPOSITED ACID COPPER SULFATE DEPOSITS FROM NON-ADDITIVE AND ADDITIVE α-ALUMINA DISPERSION BATHS WITH 81 PPM OF CHLORIDE ION

Sample Number	$CuSO_4$ (g/l)	H_2SO_4 (g/l)	Additives: Name	(g/l)	Bath Temp. (°C)	Current Density (A/dm²)	Mechanical Properties Ultimate Str. Ksi	Yield Str. Ksi	Elongation % in 5.08 Cm	Vickers Hardness (100 g Load)
4-Al_2O_3-N1										
	221.7	73.4	α-Alumina	5.0	26.7	2.15	17.82	13.36	3.0	77
4-Al_2O_3-TEPA-N1			TEPA	0.5						
	224.7	74.9	α-Alumina	5.0	26.7	2.15	14.91	10.91	3.0	71
4-Al_2O_3-TEPA-N2			TEPA	0.5						
	224.7	73.4	α-Alumina	5.0	26.7	2.15	21.60	19.11	1.5	80
4-Al_2O_3-TETI-N3			TEPA	0.5						
	220.9	75.6	TIPA	1.0						
			α-Alumina	5.0	26.7	2.15	59.24	43.35	5.5	135

Sample 4-Al_2O_3-TETI-N3 was analyzed by the combustion and inert gas diffusion method and found to contain 89 ppm carbon, 100 ppm aluminum, and 137 ppm oxygen (all by weight). The aluminum content (as alumina) was less than expected but about the same as encountered on the sample in which the α/γ-alumina was dispersion codeposited. This would indicate that a higher concentration of α-alumina and higher deposition voltage may be required to increase the alumina to the desired concentration of 2000 ppm or higher in the deposit.

As-deposited microstructures of the deposits in Table LV are shown in Figure 38. With only the dispersoid present in the bath, the grains of the resulting deposit, Sample 4-Al_2O_3-N1, are rather coarse and columnar. With the addition of TEPA and very little aging, the grains remained coarse and columnar. With about two weeks of aging, Sample 4-Al_2O_3-TEPA-N2 showed significant grain refinement, although some columnar appearance was still evident. When TIPA was added to the same bath and Sample 4-Al_2O_3-TETI-N3 was deposited with no aging period, grain sizes were greatly refined and became almost equi-axed, as reflected in the high yield strength and slightly improved ductility. However, all samples showed sufficiently poor elongation as to require ductility improvement by means of heat treating. With the low alumina content of these samples, elevated temperature testing was not considered justified. Sedimentation of the particulate was allowed to occur in order to recover the copper sulfate electrolyte and dispose of the particulate material.



Sample 4-Al_2O_3-N1
Magnification 100X.

Sample 4-Al_2O_3-TEPA-N1
Magnification 100X.

Sample 4-Al_2O_3-TEPA-N2
Magnification 100X.

Sample 4-Al_2O_3-TETI-N3
Magnification 100X.

Figure 39. Microstructures of Acid Copper Sulfate Deposits from an Electrolyte Containing 5 g/l of α-Alumina with Predominantly 0.1 to 0.5 Micron Particles.

4.3 Dispersion Strengthening Studies at ENI Using the Copper-Platinum-Alumina System

The pyrophosphate bath previously used to develop and electrodeposited copper-platinum alloy was employed in this investigation to produce a dispersion strengthened product with an alloy matrix. The bath used throughout the study contained 70 g/l of copper pyrophosphate, 250 g/l of potassium pyrophosphate, 5 g/l of potassium nitrate, and 8 ml/l of ammonium hydroxide. For the initial plating trial, 5 g/l of mixed α and γ alumina and slightly less than 1 g/l of hexachloroplatinic acid was added to the bath. The pH was adjusted to 8.03 and the bath temperature was 52°C. Agitation of the bath was performed by use of small in-tank pump with no filter. The pump outlet was directed at the tank bottom to keep the alumina in suspension. Since all prior experience with the alumina particles was in an acid copper bath, it was not known what the reaction of this mildly alkaline bath on the particles might be over a long plating period. The current density was 2.15 A/dm^2 for this and all subsequent sample platings. The first specimen surface varied from extremely smooth and bright to dull and rough, an indication of widely varient flow across the cathode surface. This sample was not tested.

With no further additions of alumina or platinum salts, a second panel was electroformed. The in-tank pump outlet was modified to incorporate a tee with one leg having a perforated and capped tube to spray electrolyte over the cathode surface while the other end of the tee directed part of the electrolyte flow through a plastic pipe to the bottom of the tank to suspend alumina. The pH for this run was about 8.1. This specimen was bright and smooth over most of the surfaces, but edges were still rough. The deposit was machined for flatness and heat treated at 371.1°C for one hour in argon. A third panel was electroformed similarly to the second panel, but this panel was not heat treated. It had a similar appearance to the second panel.

The fourth panel differed from the previous only on the basis that platinum salt and alumina replenishments were made. This panel looked bright and smooth with the exception of a few rough areas. The fifth panel duplicated the previous panel and had less roughness than any of the other specimens. This panel was also heat treated at 371.1°C for one hour with an argon purge. The sixth panel duplicated the fifth panel but was not heat treated. Production, analytical, and mechanical property data for these samples are found in Table LVI. Microstructures of several of the deposits are found in Figure 39. The samples all exhibited banding as typical in many electrodeposited alloys. The heavy lines demarking thick layers are possibly the result of removal of the sample for visula inspection. These are not disbonds. Best mechanical properties were found in Sample CuPtAl-2 which was heat treated at 371°C for one hour. Unexpectedly high yield strength has been retained by this sample based on the thermal exposure. It was observed that the two samples showing tensile failure prior to attaining 0.2% yield offset were also compositionally low in platinum.

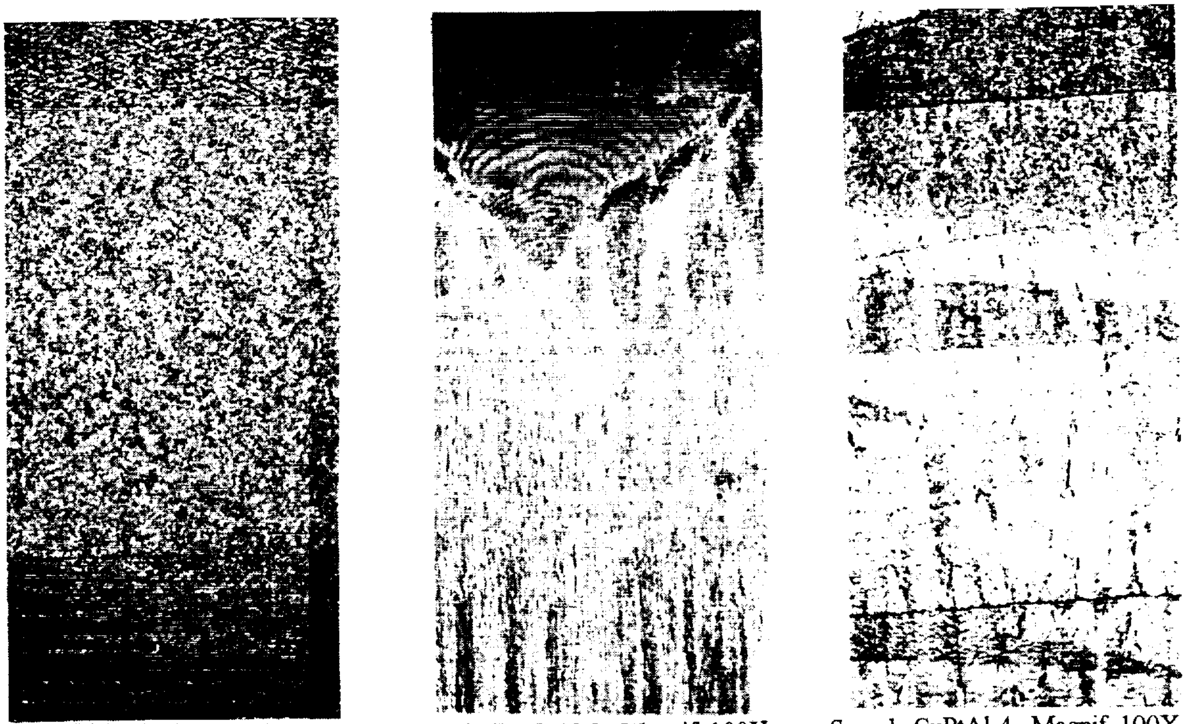
TABLE LVI - ANALYTICAL AND MECHANICAL PROPERTY TEST DATA FOR ALUMINA DISPERSION STRENGTHENED COPPER-PLATINUM ALLOY FROM A PYROPHOSPHATE BATH OPERATED AT 52°C AND 2.15 A/DM^2

	SEM/EDS Analysis:			Combustion- Inert Gas Analysis:		Mechanical Properties			
Sample Number	Cu Wt.%	Pt Wt.%	Al Wt.%	Al Wt.%	O Wt.%	Ultimate Str. Ksi	Yield Str. Ksi	Elongation % in 5.08 Cm	Vickers Hardness (100 g Load)
CuPtAl-2*	97.6	2.13	0.27	0.16	0.0531	49.22	42.11	7.5	105
CuPtAl-3	99.7	0.14	0.09	0.06	0.0462	28.20	Broke Before Yield	1.5	124
CuPtAl-4	98.3	1.60	0.10	0.09	0.0793	62.51	53.42	5.5	122
CuPtAl-5*	99.2	0.64	0.14	0.06	0.0302	40.29	Broke Before Yield	2.5	122
CuPtAl-6	98.3	1.47	0.27	Not Determined		50.10	48.14	2.0	108

Note: The lower detection limit for the SEM instrument was 3 atomic percent; Pt and Al results may be inaccurate by this method.

* Samples were heat treated at 371.1°C for 1 hour with argon purge.

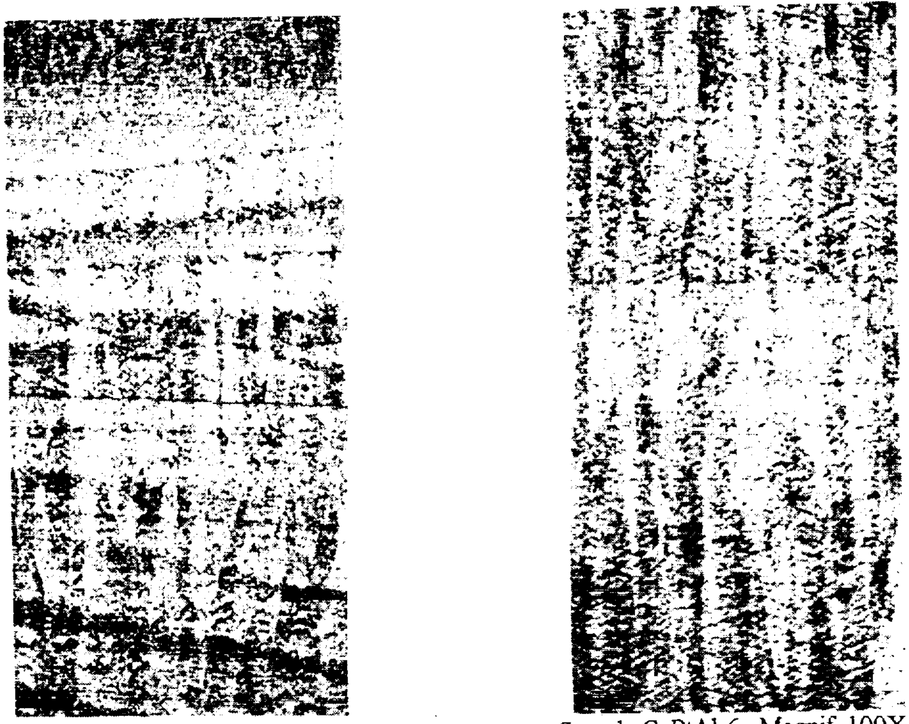
Mechanical property data for similar copper-platinum alloy deposits without alumina present were shown in Table XLVI. These samples had also been heat treated at 371.1° for one hour. The tensile and yield strengths of Sample CuPtAl-2 are much greater than those shown by the binary alloy deposits containing no alumina. The extremely fine equi-axed grains of Sample CuPtAl-2 would suggest that the alumina dispersion is exerting an inhibiting effect on dislocation movement through grain boundaries to retard coalescence of grains under normal annealing environments. This represents a significant achievement in the development of high temperature electrodeposited copper alloys. Future work with this, and similar systems, should address means to better control the com-position of the alloy. For this particular system, platinum and alumina was not replenished at an optimum rate, since little prior experience was available. Metering these ingredients might be beneficial.



Sample CuPtAl-2. Magnif. 100X.
Heat Treated at 371.1°C for 1 Hour.

Sample CuPtAl-3. Magnif. 100X.

Sample CuPtAl-4. Magnif. 100X.



Sample CuPtAl-5. Magnif. 100X.
Heat Treated at 371.1°C for 1 Hour.

Sample CuPtAl-6. Magnif. 100X.

Figure 40. Microstructures of Alumina Dispersion Strengthened Copper-Platinum Alloy Deposits from a Pyrophosphate Bath Operated at 52°C.

4.4 Studies to Codeposit Fullerenes With Electrodeposited Acid Sulfate Copper

Experiments to incorporate fullerenes into copper deposits were performed in a two liter acid copper sulfate bath. Fullerenes, commonly known as "Buckyballs", are a special form of carbon having 60 or 120 carbon atons grouped in a geodesic sphere configuration. These particles are believed to have extraordinary thermal conductivity, even greater than that of silver. This appeared to be an incent-ive for use in copper alloys which might otherwise suffer thermal conductivity losses due to the alloying element. Another reason for choosing fullerenes for this subtask was the fact that fullerenes could be obtained in submicron particle sizes which would make them useful for dispersion strengthening. A high purity form was obtained for this study. Structural configuration of a fullerene, C_{60} is shown in Figure 41.

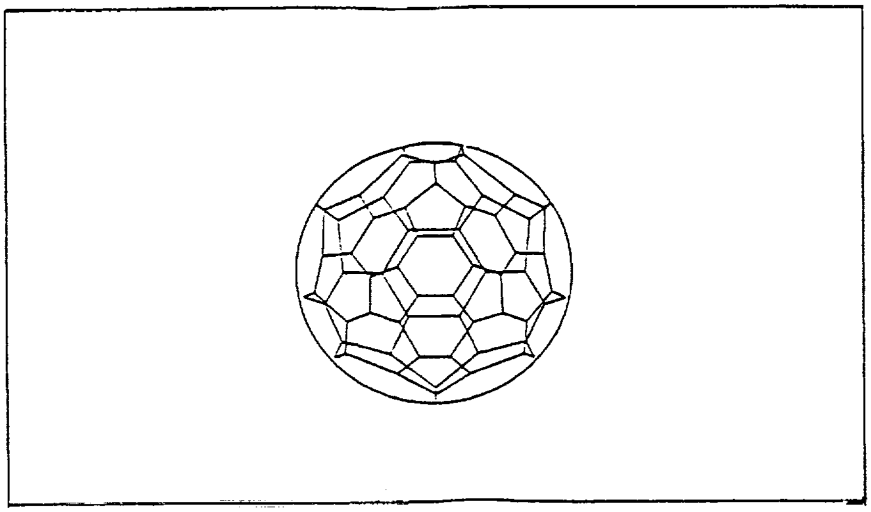


Figure 41. Structural Configuration of a Fullerene of the Type C_{60}.

Test specimens were produced by electroforming onto 12.7 cm. by 3.175 cm. stainless steel cathodes. A standard acid copper sulfate electrolyte was used in this work. A control panel, Sample CuC60-0, was deposited before any fullerenes were added to the bath in order to determine the carbon content of typical acid copper deposits from baths with no additives. Following plating of the control panel, 0.0537 grams of fullerenes were added to the solution to bring the initial C_{60} particle concentration to 26.85 mg/l. To determine the effect of pH on the deposition of fullerenes, the pH of the solution was varied by ammonium hydroxide additions. The pH of the bath was determined before and after each panel was plated. The panels were then submitted for chemical analysis to determine the carbon content of each. Four specimens were produced in this initial phase of the study. Electrodeposition data and sample carbon contents are shown in Table LVII.

As the pH of the initial phase electrolyte was increased, the fullerene particles appeared to become more dispersed such as might be expected from gel suspensions. Strength of the double layer field about these particles may account for this. In classic theory, sub-micron particles having very large surface areas tend to chemisorb anions or cations on the surface in primary adsorption sites. The choice of positive or negative charge in this first layer is dependent on the character of the particle and surface chemistry. Surrounding this inner charged layer is a layer of opposite charge. Where negatively charged anions may compose the inner layer, the outer layer will be electrically balanced by positively charged cations such as hydronium ions, H_3O^+. The strength of this double layer is greatly influenced by the acidity of the media surrounding the particles. Highly acid electrolytes present a great surplus of hydronium ions which compete for the anions adsorbed on the particle surfaces. This weakens the repelling charge between the particles and reduces the electrophoretic movement desired for uniform codeposition. If the acidity is too severe, particles can actually agglomerate and not be codeposited.

Data for the initial series of deposits, with low fullerene concentration in the electrolyte, show that fullerenes could be codeposited with copper from an acid sulfate bath. In the second phase of this study, the fullerene concentrations were increased to determine the effects of these particles on the thermal and mechanical properties of copper deposits. Plating experiments were continued in a two liter beaker of acid copper sulfate solution. Additional fullerenes were added to bring the starting concentration to 0.247 g/l. Two sets of panels were made of which 12.7 cm. by 3.175 cm. rectangular specimens, Table LVII, were for chemical analysis and mechanical property testing, while two inch diameter disk panels were for thermal conductivity testing. All samples were plated at 2.688 A/dm^2 with the starting pH being varied.

TABLE LVII - PLATING CONDITIONS AND CARBON ANALYSES FOR COPPER DEPOSITS FROM ACID SULFATE BATHS CONTAINING FULLERENES

Sample Number	Bath Temp. (°C)	Current Density (A/dm^2)	Deposit Thickness (Cm)	Bath pH Initial	Bath pH Final	Carbon Content Of Deposit (ppm)
Samples from bath with low fullerene content:						
CuC60-0	24	2.688	0.054	0.59	0.62	< 10
CuC60-1	24	2.688	0.058	0.65	0.65	90
CuC60-2	24	2.688	0.054	0.98	0.95	102
CuC60-3	24	2.688	0.048	1.56	1.43	26
Samples from bath with high starting fullerene content:						
CuC60-5	24	2.688	0.069	1.57	1.58	115
CuC60-6	24	2.688	0.093	1.58	1.63	53
CuC60-7	24	2.688	0.096	1.80	2.00	105
CuC60-8	24	2.688	0.081	1.08	1.12	69

Contrary to what was observed in the first set of specimens from the very low fullerene content bath, deposition of specimens from the high fullerene content bath resulted in pH increases. This indicated that a continuous aging process was occurring whereby surface charging of the fullerene particles was taking place. Two test pieces were cut from each rectangular specimen. This permitted heat treating one of each duplicate deposit strip for subsequent testing and comparison with "as deposited" copper from each primary specimen. Heat treatments were at 204°C or 371°C for one hour. Table LVIII summarizes properties of the deposits from the high fullerene content bath.

From Table LVIII it is apparent that codeposition of fullerenes in the copper had a very significant

TABLE LVIII - MECHANICAL PROPERTIES AND HARDNESS TEST RESULTS FOR ACID COPPER SULFATE DEPOSITS CONTAINING FULLERENES

Sample Number	Carbon Content (ppm by weight)	Heat Treatment Temperature (°C)	Heat Treatment Time (Hours)	Mechanical Properties Ultimate Str. Ksi	Mechanical Properties Yield Str. Ksi	Mechanical Properties Elongation % in 5.08 Cm	Hardness Vickers (100 g Load)
CuC60-5	115	As Deposited		61.54	34.54	14	128
		204	1	51.34	38.51	22	122
CuC60-6	53	As Deposited		64.96	40.18	10	135
		204	1	33.13	14.94	42	75
CuC60-7	105	As Deposited		65.11	42.04	4	147
		371	1	29.76	8.47	44	76
CuC60-8	69	As Deposited		61.58	34.54	17	119
		371	1	33.19	16.06	36	77

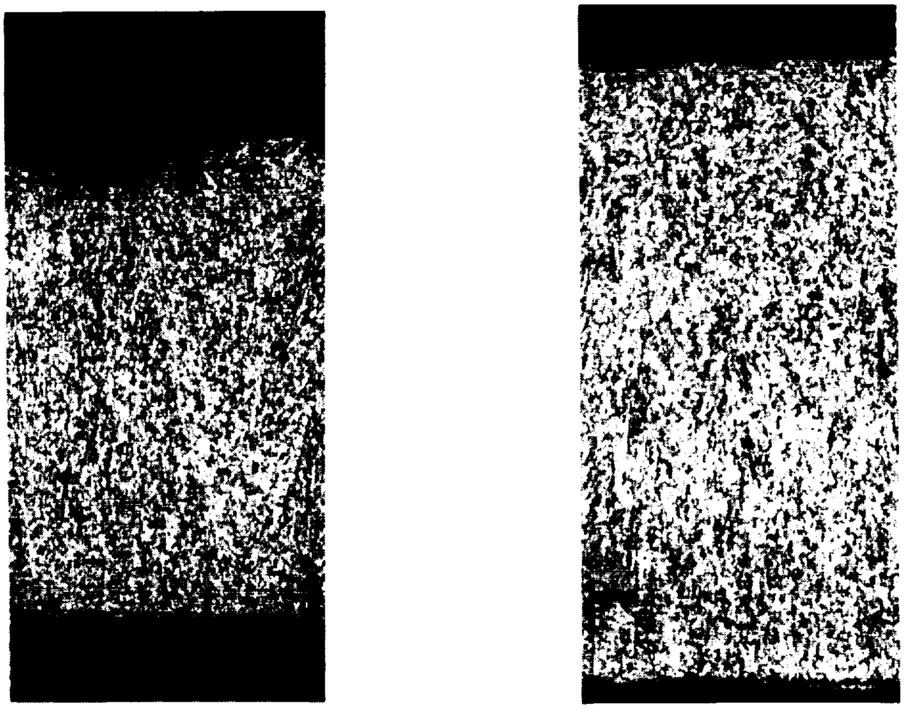
effect on as-deposited strength and hardness. Sample CuC60-5, with the highest fullerene concentration, retained much of its mechanical strength after heat treating at 204°C, a sign that dislocation movement was being retarded as would be expected in dispersion strengthened metals. However, strength retention after a similar heat treatment where only 53 ppm of carbon was found (Sample CuC60-6) was greatly reduced. Heat treating at 371°C reduced ultimate and yield strengths significantly. A higher carbon content from codeposited fullerenes is probably needed to arrest dislocation movement for these annealing temperatures. Microstructures of the as- deposited copper containing fullerenes are found in Figure 42.

Microstructures of these same specimens after heat treating at 204°C or 371°C are found in Figure 43. Grains are primarily equi-axed after heat treating. Of particular interest is the fact that the copper samples heat treated at 371°C for one hour showed almost no grain growth, a sign that the limited amount of fullerenes present is retarding climb whereby larger grains coalesce smaller grains to increase size.

Three circular flat disks of copper with varying fullerene concentrations were prepared to compare thermal conductivity properties of the deposits. Sample CuC60-T0 was produced as a baseline standard in a conventional acid copper sulfate bath with no fullerenes or other additives. Samples CuC60-T1 and CuC60-T2 were electrodeposited from the same electrolyte initially charged with 0.245 g/l of fullerenes. Plating conditions and carbon content for each sample are shown in Table LIX.

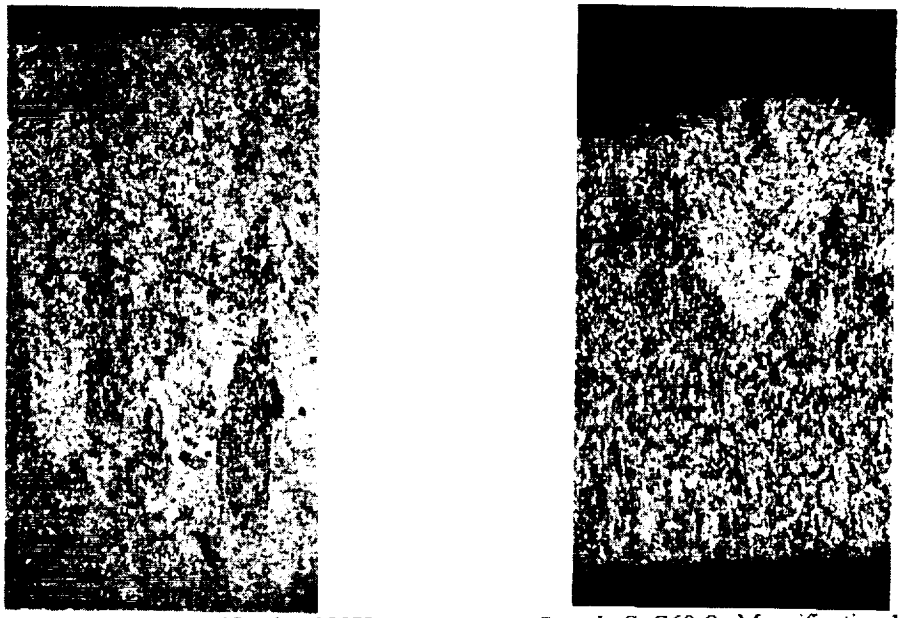
TABLE LIX - PRODUCTION DATA FOR ACID COPPER SAMPLES FROM FULLERENE CONTAINING BATH

Sample Number	Bath Temp. (°C)	Current Density (A/dm^2)	Deposit Thickness (Cm)	Bath pH Initial	Bath pH Final	Carbon Content Of Deposit (ppm)
CuC60-T0	24	2.688	0.069	0.59	0.60	<10
CuC60-T1	24	2.688	0.075	2.00	2.01	105
CuC60-T2	24	2.688	0.087	1.12	1.25	69



Sample CuC60-5. Magnification 100X.

Sample CuC60-6. Magnification 100X.

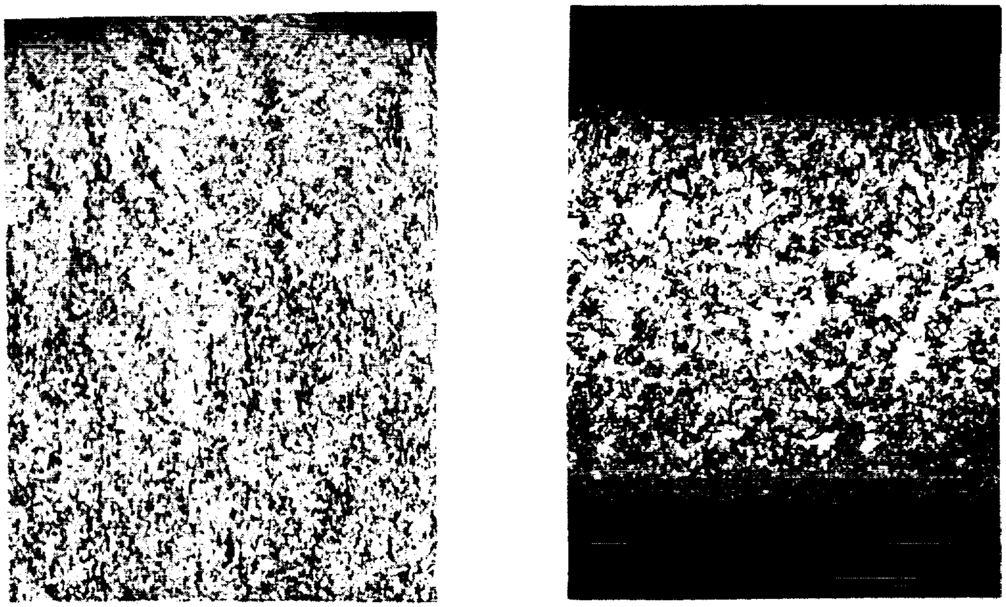


Sample CuC60-6. Magnification 100X.

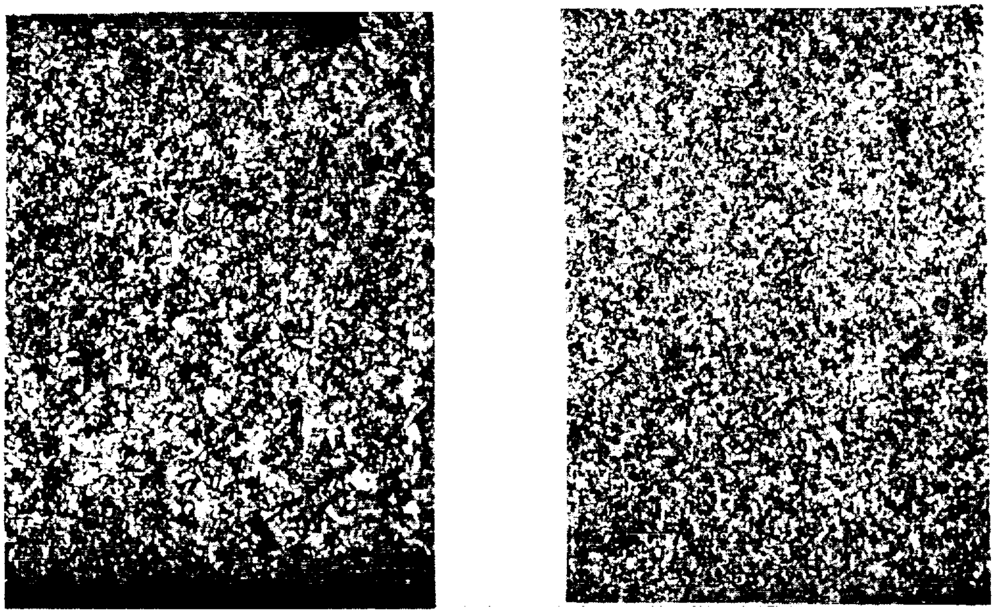
Sample CuC60-8. Magnification 100X.

Figure 42. Microstructures of Copper Deposits from Acid Sulfate Electrolytes Containing Fullerenes for Dispersion Strengthening and Thermal Conductivity Improvement.

A device in which to compare thermal conductivity of the three copper disks was fabricated from PVC. It was essentially a closed box having two compartment of which one was about three times the volume of the other. A partition between the two compartments contained a circular hole into which a copper test disk could be inserted. From the insulative nature of PVC, almost all of the heat introduced through hot water in one compartment would be transferred through the copper disk to the water reservoir in the other compartment. In each experiment the copper disk was secured into the partition and the small compartment was filled with 562 grams of deionized water. The large compartment was initially empty. The test apparatus was placed on a stirrer-hotplate with no heat applied. A magnetic stir bar was placed in the bottom of the small compartment to mix the water



Sample CuC60-5 After 204°C Heat Treatment. Sample CuC60-6 After 204°C Heat Treatment.



Sample CuC60-7 After 371°C Heat Treatment. Sample CuC60-8 After 371°C Heat Treatment.

Figure 43. Microstructures of Acid Copper Deposits Containing Fullerene Particles After Heat Treating at 204°C or 371°C for One Hour (All at 100X Magnification)

thoroughly. Thermocouples were inserted into both compartments for continuous measurement of temperature in each. On a separate hotplate, a four liter beaker of deionized water was maintained at 73.9°C (165°F).

At the start of each experiment, the hot water from the four liter beaker was pumped into the large compartment. As the compartment filled with water, it reached a second tube at the top which returned it to the heated four liter beaker. Therefore, the water was constantly circulated from the four liter reservoir to the large compartment and back to the beaker. The thermocouples in each compartment measured the temperature changes in the water in each compartment as time progressed. Results for these experiments are graphically presented in Figure 44.

From the data in Figure 44 it would appear that a steady state heat transfer is not established until about 10 minutes transpires. This is based on temperature data for the hot reservoir. Sample CuC60-T2 contained only 69 ppm by weight carbon (fullerenes) and exhibited slightly lower thermal transfer rates than the control, Sample CuC60-T0. Sample CuC60-T2 containing 105 ppm by weight carbon, transferred heat more rapidly than the control. This would indicate that fullerene codeposits may need to be above a weight percent threshold value in order to improve thermal conductivity. More testing of copper electrodeposits with greater fullerene contents would be needed to establish and

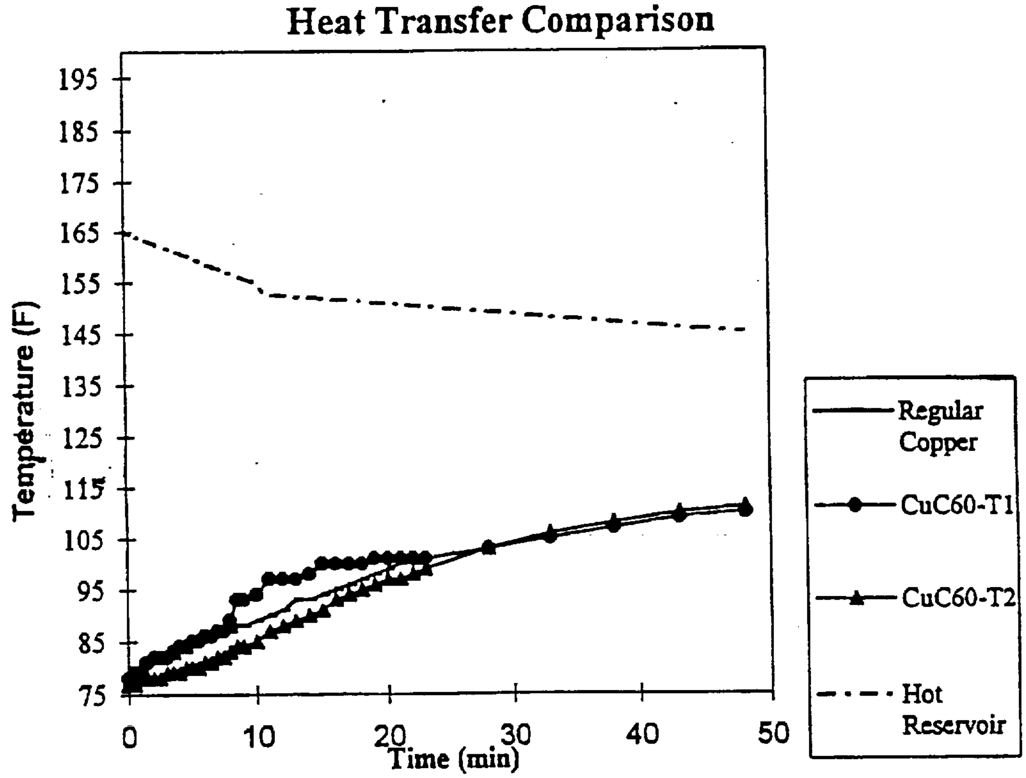


Figure 44. Comparison of Heat Transfer Characteristics of Electrodeposited Acid Sulfate Copper With and Without Codeposited Fullerenes.

verify the beneficial effects of these particles on thermal conductivity of this system. These results are very encouraging and warrant continued investigation. The use of higher fullerent contents in the deposit should also lead to improved dispersion strengthening.

4.5 Fabrication of High Strength Copper Electrocomposites

Electrocomposites as applied to this subtask refers to layering of electrodeposited metal with filament material such as wire. Little information is available in the literature on this process using copper as the electrodeposited media. However, much work has been done with electrodeposited nickel composites. McCandless and Davies(25) investigated stainless steel wire wrapping incorporated in a matrix of electrodeposited nickel. The mandrel employed was a cylinder onto which nickel was electroformed and machined to provide a surface on which wire could be uniformly wrapped. Wire wrap spacing was based on various wire diameter multiples with a schematic shown in Figure 45.

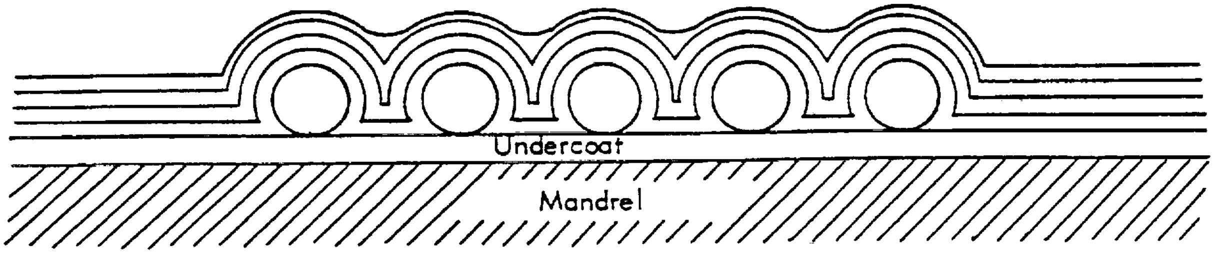


Figure 45. Schematic Representation of Electroformed Composite.

These investigators used a wire with a cross-section having a "D" shape in order to make as complete a contact as possible between the flat of the "D" and the machined layer of electrodeposited nickel. Once the subsequent layer of nickel was deposited (and subsequent wrapping and plating for multiple layers made), the mandrel was removed and the structure was pressurized to failure.

In the present study the mandrel was a solid OFHC copper bar of 5.08 cm diameter having a length of 20.32 cm. In the upper half of the bar, two channel-manifold patterns were machined 180 degrees apart from one another. The same was machined in the lower half of the copper bar. This provided four rocket engine thrust chamber coolant channel simulations in each of two bars. Machining centers were milled at each end of each bar for subsequent alignment for lathe turning after electroforming channel close-outs. Small holes were drilled axially into the bar in the channel manifold areas. These were connected at right angles to threaded holes drilled from the bar ends. This permitted attachment of pressure fittings for hydrostatic testing of the electroformed copper and electroformed composite close-outs. Each channel manifold pattern had a pressure fitting accommodation. This would permit retests where desired using the duplicate pattern located 180 degrees from the original test pattern.

The channel-manifold patterns were filled with Rigidax® WI Blue wax, a filler used in electroforming structural close-outs on the Space Shuttle Main Engine Combustion Chamber (SSME-MCC). The wax was sanded flush with the copper rod outside diameter. The wax was made conductive by burnishing silver powder onto the wax. Only patterns at one end of each rod were processed in this manner at any one time, since electroform close-outs were varied for comparison purposes. In order to hydrostatically fail the channel close-outs at a reasonably low pressure, the electrodeposited coatings and composites were made with thicknesses of only 0.127 cm.

Close-out Zone 2 was produced by electroforming with conventional (non-additive) copper using periodically reversed copper using a forward plating cycle of 8 seconds, a reverse cycle of 4 seconds, and a current density of 4.84 A/dm^2. The bath temperature was 26.7°C for all close-outs. Close-out Zone 1 was made with an electrolyte containing 1 g/l of triisopropanolamine (TIPA) using a current density of 2.15 A/dm^2. Zone 3 was closed out with copper from an electrolyte containing PEG-A, an organic polymer. Deposition was made at a current density of2.15 A/dm^2.

Zone 4 was produced from the TIPA electrolyte, but with wire wrapping between the initial and final copper electroforming operations. The initial deposit was about 0.100 cm thick and was machined to a thickness of 0.076 cm. A spiral groove was then cut in this coating in which the wrapped wire would be laid. The groove depth was about 0.013 cm with an upper width of about 0.026 cm. Groove pitch was such that two wire diameters could be measured between each groove. The wire was Inconel 718 Annealed and had a diameter of 0.025 cm. In order to secure the wire ends before and after winding, very small screws were inserted into holes adjacent to the start and termination positions of the wire. To assure that the wire would not slide in the copper layers of the composite, it was activated and preplated with copper before wrapping on the mandrel. A final copper layer was deposited over the wire wrap and machined to a total composite thickness of 0.127 cm.

Pressure testing was performed by hydrostatic means with calibrated gauges. Close-out fabrication and pressure test data are found in Table LX, while Figure 46 contains photographs of the copper test cylinders after failure.

TABLE LX - FABRICATION AND PRESSURE TEST DATA FOR COPPER AND COPPER COMPOSITE CLOSE-OUTS OF CHANNEL PATTERNS

Close-out Zone No.	Current Mode	Bath Additives	Current Density (A/dm^2)	Burst Pressure (PSI)	Failure Location and Comments
1	Conventional	TIPA (1 g/l)	2.15	9,500	End of Land No. 1 at manifold. This was a stress concentration region.
2	Periodically	None	4.84	2,500	End of Land No. 1 at manifold. This was a stress concentration region.
3	Conventional	PEG-A (1 g/l)	2.15	14,000	Copper electrodeposit failure along edge of Land No. 1.
4	Conventional	TIPA (1 g/l)	2.15	10,000	End of Land No. 3 near manifold.

4.6 Conclusions and Recommendations

It was demonstrated that incorporating electrodeposited copper into composites would result in viable means for improving structural performance. In these studies, electrodeposited copper was the matrix material on which the composites were based, while dispersion strengthening and wire wrapping were the supplemental strengthening methods applied.

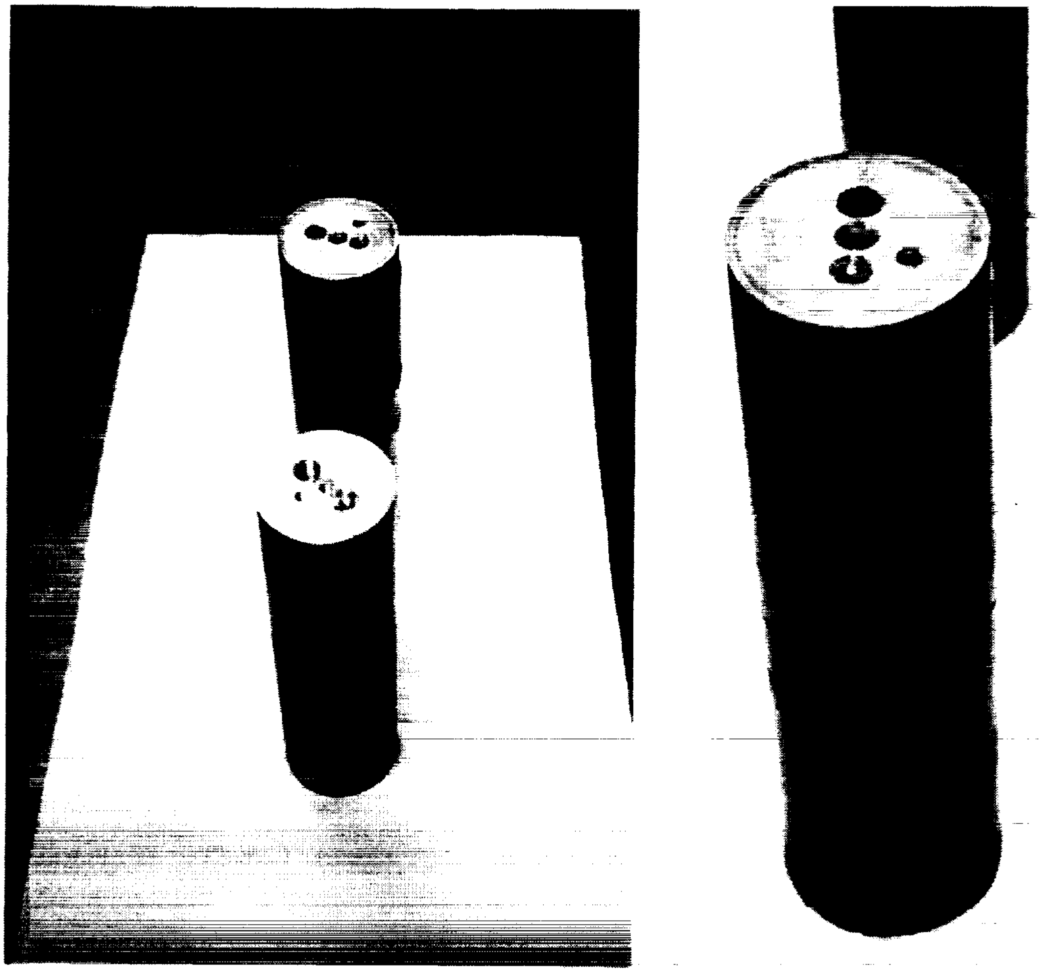


Figure 46. Illustrations of Copper Test Cylinders Containing Manifolded Coolant Passages with Copper and Copper Composite Close-outs.

- Electrodeposited copper was dispersion strengthened by codepositing with α- alumina having a sub-micron particle diameter. When these specimens were tested at room temperature, the mechanical properties were found to be representative of the properties of the copper matrix when no dispersion particles were present. However, when the same deposits were tested at 371°C, higher tensile (and in particular, higher yield) strengths were observed than would be normally encountered in conventional acid copper sulfate deposits at a similar temperature. This indicated that the dispersion phase was exerting the desired effect of retarding dislocation movement. This was especially encouraging since the amount of alumina codeposited was quite small. Yield strength improvements to about 40 percent over conventional PR copper were obtained at 371°C.

- Wrought dispersion strengthened coppers achieve high strength through a series of mechanical workings and heat treatments. Since this is not practical for electroformed shapes, it has been necessary to demonstrate an alternate means for increasing the matrix copper strength. This was accomplished by incorporating triisopropanolamine (TIPA) in the electrolyte in which the dispersion particles were being codeposited. Ductility of dispersion strengthened copper from the acid sulfate bath needs improvement. This must be explored in future work. It is recommended that more severe thermal treatments be examined together with use of copper deposits from the PEG-B containing acid bath where better elevated temperature ductility has been demonstrated.

- Copper-platinum-αalumina alloy deposits were successfully deposited. Response of these alloys to heat treatment (371°C) was good, but higher temperatures will be necessary to obtain desired ductility. This material appears to retain high yield strength after thermal treatments.

- Fullerene (Carbon 60) was successfully codeposited with copper from an acid sulfate bath. The deposits could be heat treated with excellent retention of yield strength and ductility when tested at room temperature. Thermal conductivity performance was equivalent to, if not better than, that of conventional acid copper sulfate deposits. Further development of this material with higher fullerene contents is expected to yield deposits suitable for intermediate temperature service applications.

- Circumferential wire wrapping (Zone No. 4 in Table LX) did not afford the degree of strengthening anticipated in the composite strengthening investigation. This was due to the fact that the strengthening was uni-axial only (across the width of the channels). Therefore, the failure occurrred in the weakest region, the matrix copper between the wire wraps. Even so, the pressure required for channel failure was higher than with Zone No. 1 closed out with the same copper deposit as the wire wrapped zone. In each case this deposit was from an acid sulfate bath containing 1 g/l of TIPA. The best performance was shown by the copper deposited from an acid sulfate bath containing 1 g/l of PEG-A. This is believed due to the higher yield strength of this copper which better resisted buckling of the channel closeout. In all cases, Zones 1, 3, and 4 performed better than the conventional copper standard deposited from an acid sulfate bath with periodic current reversal.

5. TASK V - FABRICATION OF ROCKET ENGINE REGENERATIVELY COOLED THRUST CHAMBER USING COPPER TUBES

5.0 Background

Kazaroff and Pavli(26) discussed rocket chamber design and fabrication over the past forty years and noted that among the most successful has been the brazed-tube construction. This method was used in regeneratively cooled flight engines such as the F-1 and J-2 (Saturn), the RL10 (Centaur), and the LR87-A and LR91-A series of engines (Titan). The RL10 is a liquid oxygen-liquid hydrogen engine using an expander-cycle to power its propellant pumps. The hydrogen, which is used as the turbine working fluid, is pressurized by the fuel pump, circulates through the cooling tubes (picking up heat in the cooling process) and is then expanded through the turbine to drive the propellant pumps. When the fuel exits the turbines it is routed to the injector and is burned in the combustor. By this means any residual energy left in the fuel is carried back into the combustion chamber, hence the name "regenerative" cooling.

A need to improve performance and decrease size has led to designs with higher chamber pressures and increases in combustion chamber heat flux. The Space Shuttle Main Engine (SSME) is an example of this advanced class of engine. It is a staged-combustion cycle engine operating with liquid hydrogen (LH_2) and liquid oxygen (LOX) propellants. With the higher chamber pressure, the heat flux is so severe that the combustion chamber can not be made from the relatively low conductivity types of alloys used in the brazed tube bundle configuration described previously, and the only materials that would adequately transfer the heat are copper or silver and some of their higher conductivity alloys. The combustion chamber wall of the SSME is made from a single billet of copper alloy (NARloy-Z) with a series of machined axial grooves in the outside surface of the chamber wall. The grooves serve as the coolant passages after they are closed out by successive layers of electrodeposited copper and nickel. While satisfactory for steady-state conditions, this design is very susceptible to thermal strains in excess of yield strength during startup and shutdown(27). A major cause of this strain level is the very rigid nature of the configuration. The relatively cold outside electroformed layer resists the thermal expansion of the hot inner copper liner resulting in plastic deformation of the copper liner. The deformation increases with each thermal cycle until the wall thickness at the center of the coolant passage (hot gas wall) is so thin that a pressure rupture occurs in the form of a crack. As increasingly severe service requirements are placed on such engines, the life expectancy of engines of this configuration becomes a matter of serious concern.

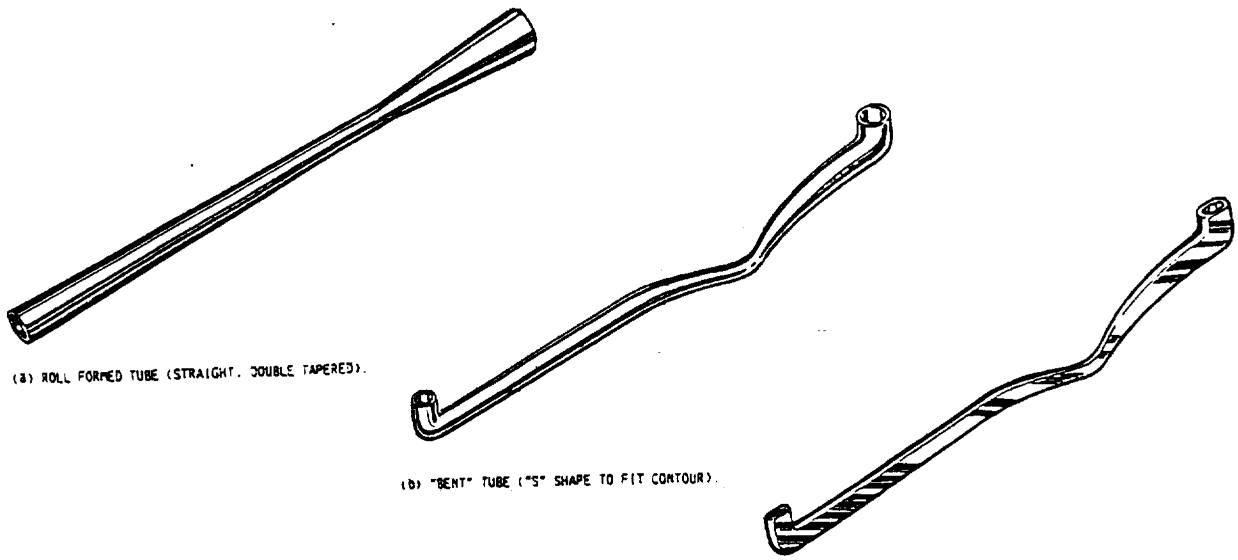
In designing future engines, needs must be addressed to include (1) space based, (2) man-rated, and (3) high performance. A strong case exists for the expander-cycle instead of the more complicated staged combustion cycle. The advanced expander cycle engine is expected to operate in the realm of 1200 to 2000 psia chamber pressure based on improvements made to the combustion cooling system and its ability to provide energy to the turbopumps. The improved pickup is being explored in several ways: (1) increased combustor length, (2) cooled combustor baffles, (3) coolant passage ribs and fins, (4) optimizing the combustor contraction ratio, (5) high aspect ratio coolant channels, and (6) using copper tube construction for the combustor (to provide increased surface area).

One of the most promising fabrication methods is the use of copper tube combustion chambers. The manufacturing processes used in producing the brazed-tube-bundle type combustion chambers has become well developed over the years. Even so, the procedure for stacking the tubes is a very labor intensive, hand operation requiring selective fit to achieve the very close tolerances between tubes to assure proper capillary wetting of the braze alloy during furnace brazing. Brazing is per-formed at high temperatures. For many metals and alloys having the high thermal conductivity desir-ed in regeneratively cooled thrust chambers, this high brazing temperature tends to degrade tensile and yield strengths through annealing and grain growth. Alloying of the tube material with the braze alloy might also be of concern.

Tube construction is expected to provide improved heat pickup and considerable life improvement. This is due to the fact that the tubes present a greater area for heat transfer. They are anchored in full length hemispherical segments furthest away from the chamber centerline. This means that they can move independently to a much higher degree during heatup or cooldown. This makes them compliant and reduces thermal strain fatigue. This task was introduced to demonstrate that such a thrust chamber could be fabricated in its entirety by electroforming with copper over wrought OFHC copper tubes without using and weld or braze joining methods that would thermally degrade the material properties of the electroformed copper.

5.1 Fabrication of Mandrel, Tube Bundle Assembly, and Initial Copper Electroform

A copper tubular thrust chamber design was furnished by NASA-Lewis Research Center. OFHC copper tubes were commercially fabricated for NASA on a separate contract and supplied for this chamber. Figure 47$^{(26)}$ shows the tube fabrication sequence whereby the raw tube stock was roll



(a) ROLL FORMED TUBE (STRAIGHT, DOUBLE TAPERED).

(b) "BENT" TUBE ("S" SHAPE TO FIT CONTOUR).

(c) "BOOKED" TUBE (FLATTENED TO WIDTH SPECIFIED).

Figure 47. Copper Tube Fabrication Sequence for Copper Tube Bundle Chamber.

formed for a double taper, bent to shape to match the chamber contour, and "booked" (partially flattened) to permit a larger population of tubes in the hot gas wall of the chamber. The mandrel was machined in two mating sections from an aluminum billet. Drilled and tapped holes in the axial direction of one segment allowed attachment of the two sections. Centers were added to each end of the mandrel for horizontal rotation of the assembly in the electroforming solution and for intermediate and final machining. Risers were left on each end of the mandrel to permit ball milling of slots for placement and spacing of the tubes. An illustration of the mandrel is found in Figure 48. Since each tube was not perfectly identical to every other tube, some selection and relocation of tubes was necessary. An end view of the tubes nestled in the ball milled slots is found in Figure 49.

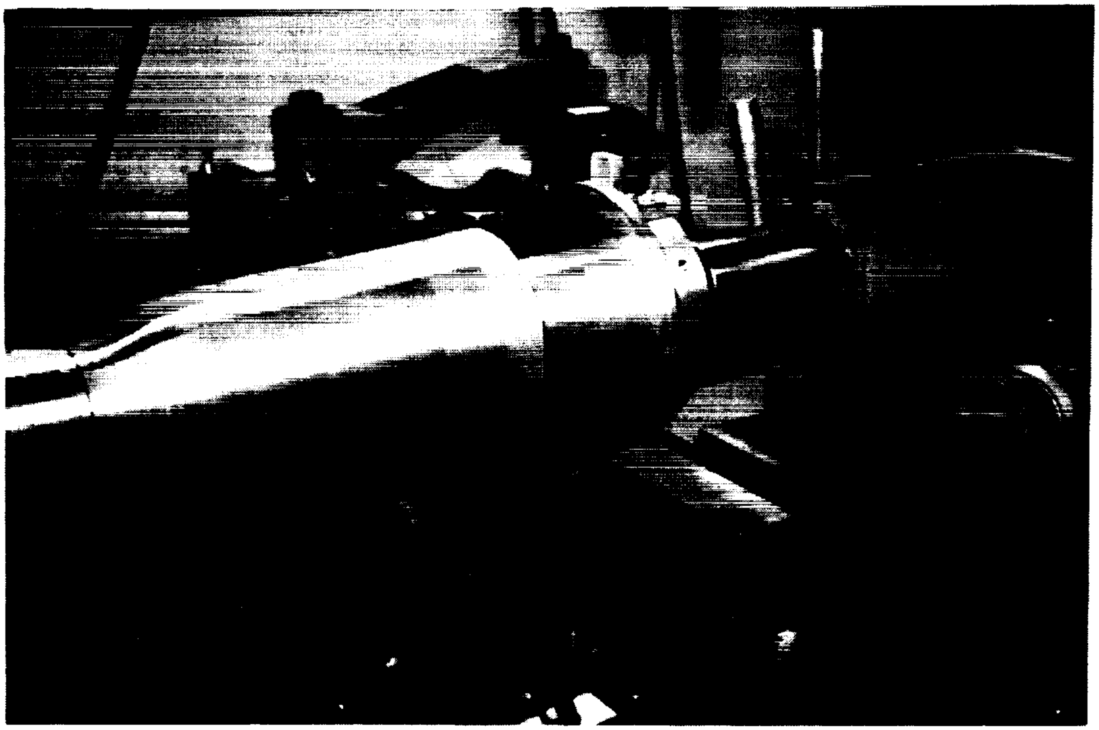


Figure 48. View of Aluminum Mandrel During Fabrication Showing Milled Slots at the Injector End of the Part.

The tube assembly was held in place by thin metal straps or wires for the wax dipping step. A soft stop-off wax was melted in a tubular aluminum container and the the assembled (and secured) tube bundle was immersed in the wax, allowed to come to the wax temperature to allow wax penetration into recesses between tubes, and withdrwn for cooling. The wax held the tubes firmly in place, so the metal straps could be removed. The excess wax was then removed from the outside surfaces of the tubes using a hot-knife (solder iron with formtool tip) to a point where copper was exposed. The surface was made smooth with fine grit sandpaper. A formtool was fabricated to scrape wax from between tubes from the outside diameter surface to the tangential contact area of adjacent tubes. A sanding with folded fine grit paper further removed wax in these areas. This left enough wax in the mandrel to tube contact region to hold the tubes in place.

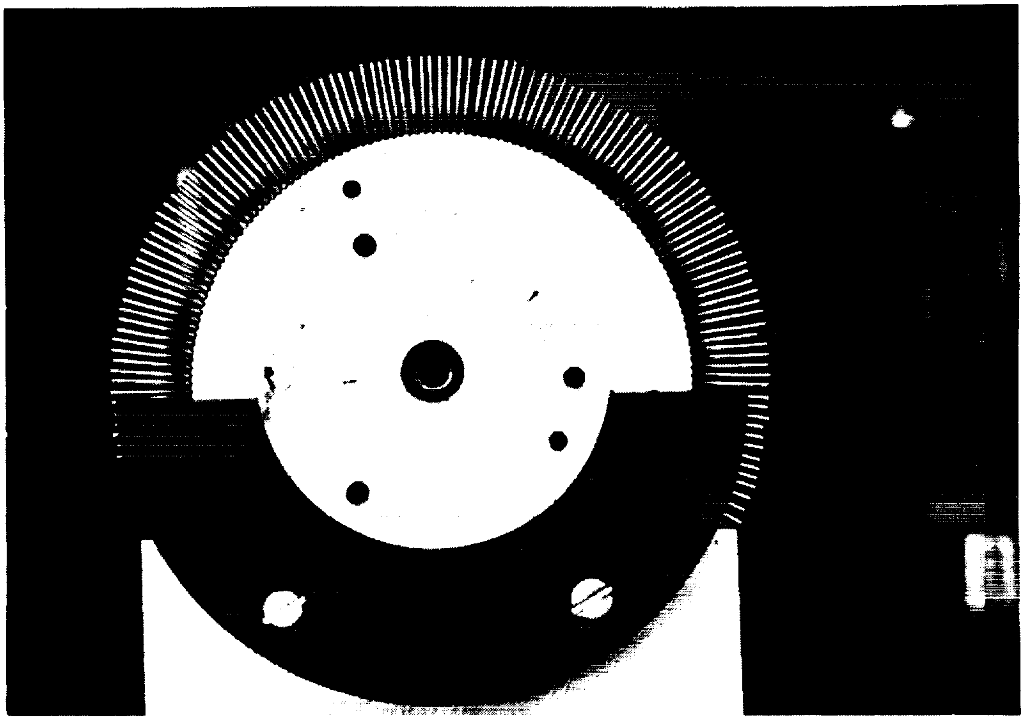


Figure 49. End View of Copper Tubes Nestled in Ball Milled Slots in End of Mandrel.

A fine silver powder was brushed between the tubes and burnished into the thin wax bridge between tubes. A special tool was required to access the fine gap between tubes for the burnishing. At this point the end shields were affixed to the mandrel to prevent copper plating of the exposed aluminum. Figure 50 illustrates the mandrel with assembled tubes prior to shielding and fixturing for electroforming. The pretreatment for activating and bonding copper to the tube bundle assembly consisted of an anodic treatment in 80 to 83 percent by volume phosphoric acid at room temperature for an amount of time needed to polish the copper tubes using an electropolishing potential of 9 volts. This was followed by a rinse and a thorough inspection for wax or silver contamination of the surfaces of each individual tube. The anodic treatment was repeatable if contamination required rework. The assembly was rotated by a gear drive during all activation and electroforming steps. After rinsing, the assembly was cathodically treated in 25 percent by volume sulfuric acid at room temperature and a current density of 10.75 to 21.5 A/dm^2. Once current was activated in this treatment, there was a brief time span in which current was nil. This was due to the time required to dissipate the film formed during the anodic treatment. This was followed by successive rinses in clean deionized water to remove any copper salts that might result in poor bonds of electrodeposited copper. The assembly and fixture were then immersed in the copper electroforming bath with low current density applied, and the current was slowly adjusted to the required precalculated value.

Prior experience with electrodeposition of copper into the open regions between the tubes has shown that a serious problem with the structural integrity can exist unless special precautions are taken. If a conventional acid copper sulfate bath is used, the radial growth of copper from each tube will result

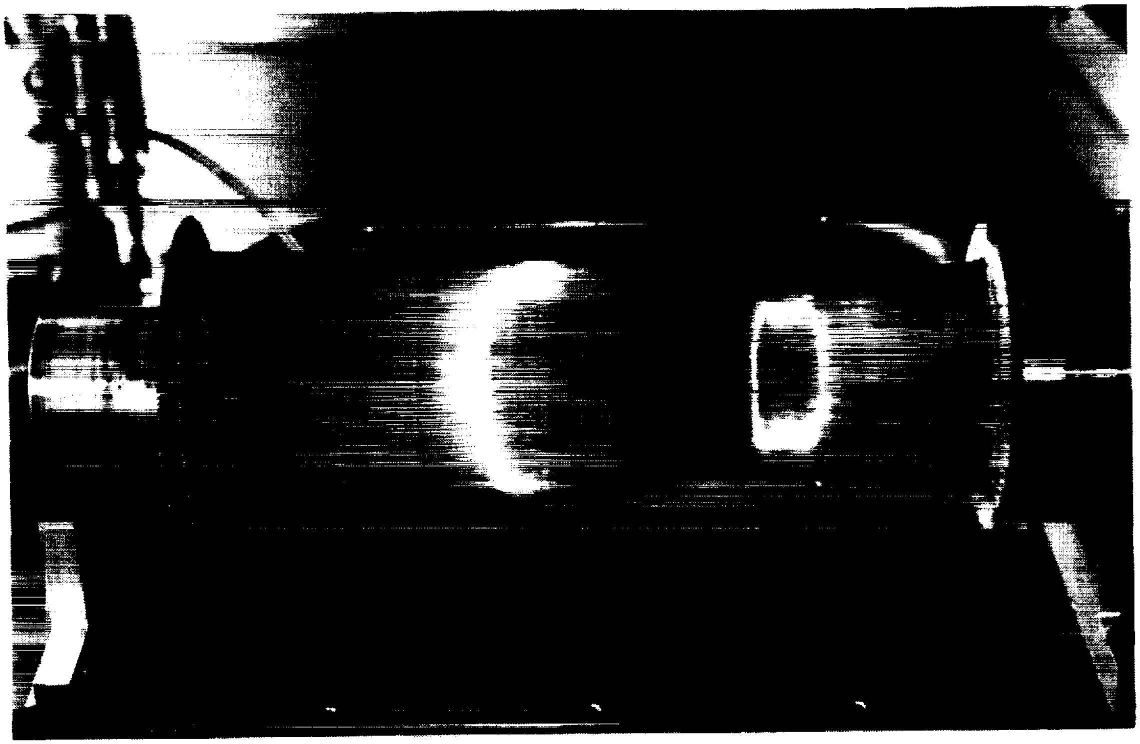


Figure 50. Mandrel with Tube Bundle Assembly Ready for Fixturing for Electroforming.

in grain intersection to form a cleavage plane having no material strength at the intersection plane. Since the tubes are firmly bonded to the electroformed "filler" metal and this material will, in turn, be bonded to an electroformed copper shell, the overall structure will have good integrity. However, the cleavage plane poses a problem in that thermal stress may open the cleavage to allow propellant byproducts (water) to become entraped. Should this water freeze, a danger exists in further expansion of the cleavage gap. Figure 51 shows a typical cleavage plane which was not terminated

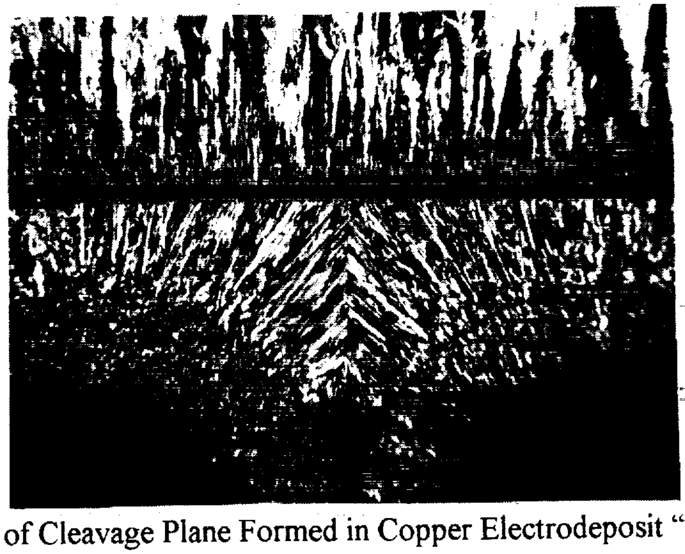


Figure 51. Example of Cleavage Plane Formed in Copper Electrodeposit "Filler" Between Tubes.

until intermediate machining was able to create a smooth surface on which a uniform outer copper shell could be deposited. To alleviate this problem, it is necessary to deposit the electrodeposit "fill" between tubes using an acid copper sulfate bath modified to produce very fine grains, preferably grains that are small and equi-axed. This was accomplished using an acid copper bath containing 0.5 g/l triisopropanolamine (TIPA) and 0.4 g/l D^+xylose. Mechanical properties for the copper deposited in this stage were obtained from an in-process test panel and found to be:

Ultimate Strength, Ksi	51.50
Yield Strength, Ksi	34.60
Elongation in 5.08 cm, %	21.0

Microstructure of the copper deposit "fill" between tubes is shown in Figure 50. It would have been preferred to deposit copper from the PEG-B bath where grains are very fine and equi-axed. However, this bath had not been developed at the time the tube chamber task was started.

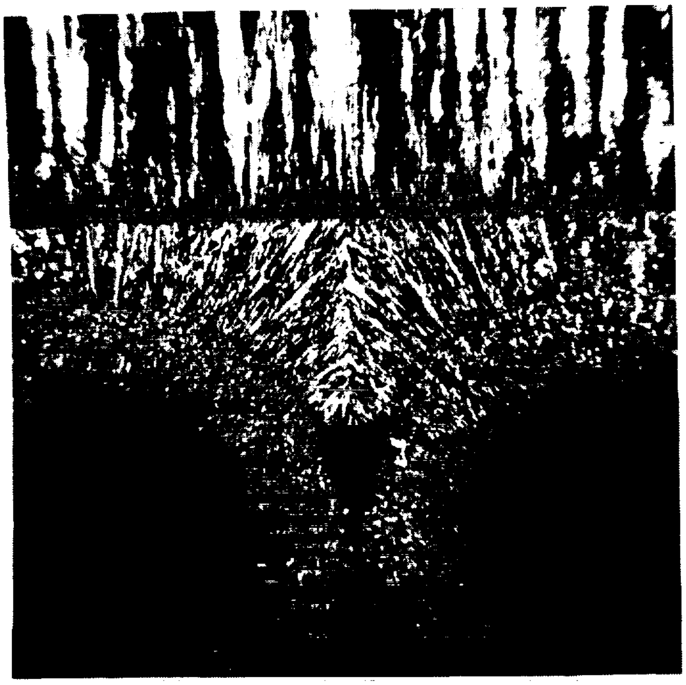


Figure 52. Cleavage Plane Correction Using Copper "Fill" From An Acid Sulfate Bath With TIPA.

Several electroplating runs were necessary to build a sufficient layer of copper between tubes to permit machining a surface suitable for electroforming the 0.762 cm thick copper structural shell. It was necessary to use light sanding and grinding between plating runs to dress tube crowns. Machining was avoided because of the possibility of damaging tube walls. It was also necessary to insert long plastic plugs in the ends of each tube to prevent electroform closeout of the passages. The tube ends after the copper "fill" task was completed appeared as shown in Figure 51. Since the tube ends were exposed everywhere but the openings, the copper growth filled in all gaps beteen the 90 degree end bends.

5.2 Inlet and Outlet Annuli and Chamber Flange Fabrication

Once sufficient copper was deposited to produce the required shell thickness, the chamber was template machined to the required thickness of 0.635 cm (0.25 in). Each of the chamber ends was also machined to produce the required length plus excess stock for future machining. Completed areas of the chamber were masked to prevent further plating. New PVC shielding and endplates were installed for electroforming the inlet and outlet manifolds. This shielding consisted primarily of two split PVC rings at each end of the chamber. Once assembled, each set of rings would permit electroform build-up to occur only in the manifold areas. Copper electroforming was continued until sufficient metal was deposited to permit machining of the annuli located at the feed and outlet ends of the tubes. The annuli were filled with wax and conductivized with silver powder to electroform a closeout. Mechanical properties of the acid copper sulfate bath containing 1 g/l TIPA were verified at this time. The ultimate strength was 59.4 ksi, the yield strength was 44.8 ksi, and the elongation in 5.08 cm was 15%. The bath was operated at 26.7°C with a current density of 2.15 to 2.36 A/dm^2. These properties were considered satisfactory based on the thermal analysis results for the design. The maximum expected chamber temperature (excluding the hot gas wall of the tubes) was 129°C. Cryogenic temperature levels were of no concern due to the improved properties of electroformed copper at these temperatures.

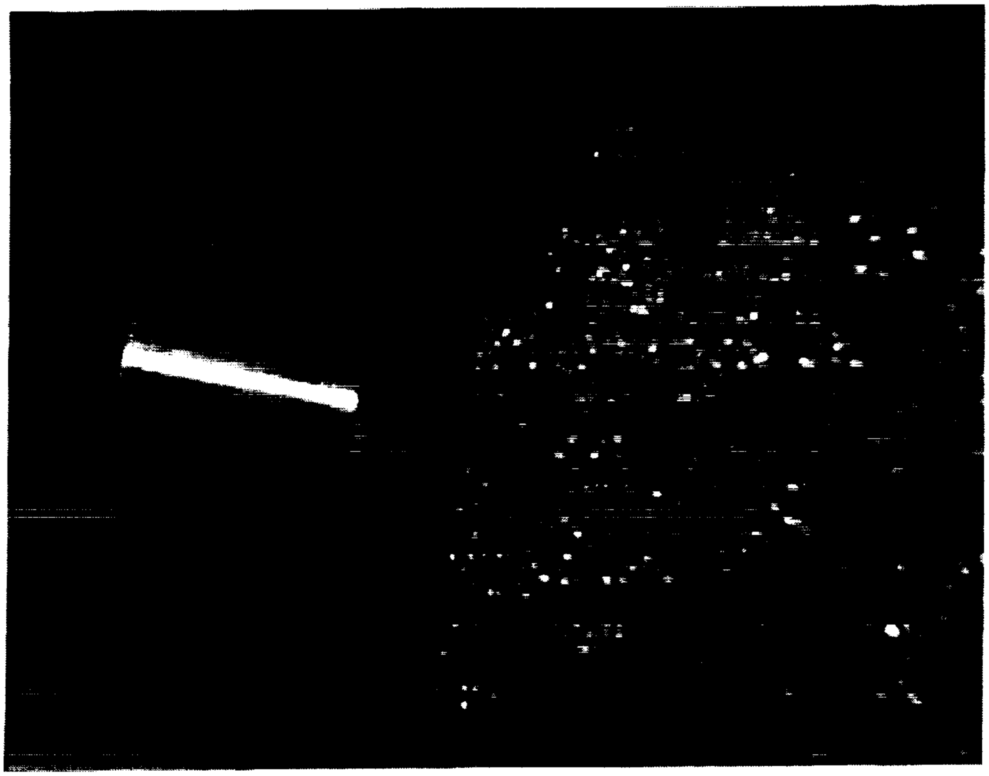


Figure 53. Appearance of Tube Ends After Electroform "Fill" of Tube Bundle Interfaces.

The inlet and outlet manifolds were also electroformed in copper as a means to circumvent any thermal joining operations which might degrade material properties.. The foreward and aft chamber flanges containing the manifolds were also electrodeposited from the same acid copper bath used to make the annuli closeout. Electroforming interruptions were made after every 0.76 cm of copper build-up for light machining operations to correct moderate roughness. Anodic etching to remove machining cold work and cathodic activation was performed before each initiation of copper electroforming. Once the thicknesses of the chamber flanges had reached those diameters approximating the center diameters of the respective manifolds, permission was obtained to change the manifold shapes from an "O" cross-section to a "D" shape of equivalent cross-sectional area. This permitted a slight reduction in the flange diameters necessary to accommodate the manifolds and simplified the wax-fill and wax sculpturing operations needed prior to final closeout of the manifolds with copper. The machining operations at this time included (1) drilling the forward and aft flange mounting bolt holes and (2) drilling angular holes to connect the manifolds to the annuli around the forward and aft tube openings.

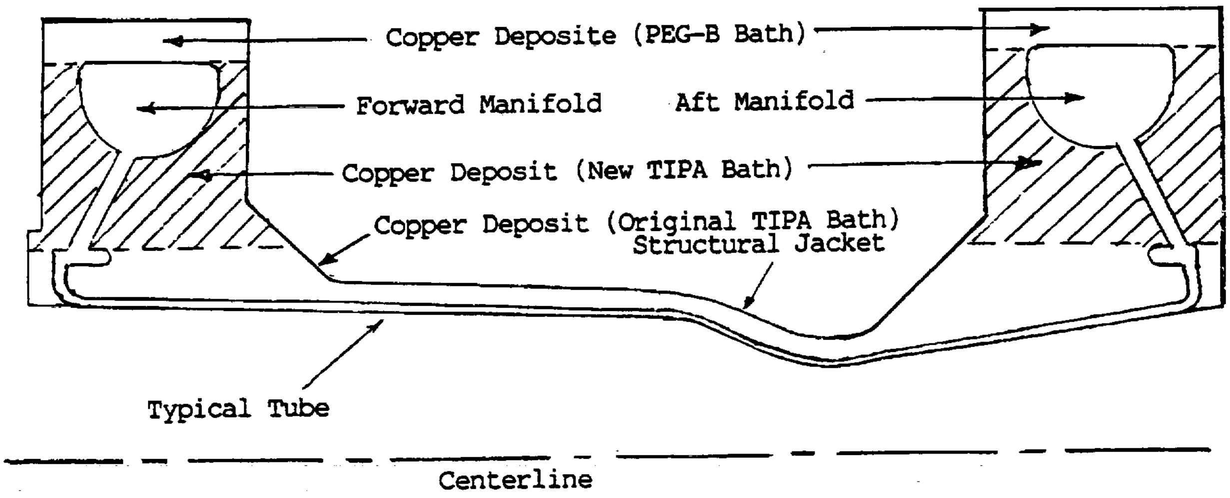


Figure 54. Copper Electroformed Tube Bundle Thrust Chamber Design.

Buildup was continued until the diameter at each end was reached where the inlet and outlet manifold passages would be contained. Mechanical properties of the copper deposits were again verified. The ultimate strength was 65.2 ksi, the yield strength was 48.3 ksi, and the elongation in 5.08 cm was 11.5 percent.

5.3 Manifold Closeouts, Final Machining, and Wax Removal

The required flange diameters for "D" shaped manifolds necessitated new drawings for datum planes to locate the coolant manifold slots and entry passages to the inlet and outlet annuli for the tubes. The machining work included fabrication of the "D" shaped channels of the foreward and aft manifolds, drilling 22 equally spaced mounting bolt holes in each end flange of the chamber, and drilling 22 angular holes from the "D" shaped channel to intersect and join the tube annulus at the forward end of the chamber, and drilling similar passages to meet the annulus of the tubes at the aft end of the chamber. All holes were visually inspected to assure that clear openings to the annuli were achieved.

At ENI the "D" shaped manifolds were filled with wax to the tops of the channels. The wax was carefully machined to provide a radius of 0.076 cm (0.030 in) at the corners of the "D" to prevent stress concentrations of the closeout when coolant was supplied under high pressure. The wax was conductivized with silver powder. Foreward and aft split ring shielding was applied to each flange. The areas of the chamber to receive no copper deposits were masked. The chamber was anodically etched to remove machining cold work, cathodically activated, and immersed in the copper bath with voltage applied. During the period in which machining was being performed, the copper bath was hydrogen peroxide and carbon treated for complete purification. The electrolyte was converted to the acid copper sulfate bath containing PEG-B, since this formulation was shown to produce the best combination of high tensile and yield strengths combined with outstanding ductility. This bath was used to electroform the close-out of both manifolds.

After at least 2.54 cm (0.5 in) of copper had been deposited over the "D" shaped manifolds, the chamber was final machined. The injector face end was machined to provide suitable match-up to the test stand injector. This included an "O" ring groove. All other flange faces were finish machined, and holes for coolant feed and exit were milled into the forward and aft manifolds. Fill and drain bosses were machined from OFHC copper round bar. They were designed and machined to have a

Figure 55. Lathe Turning Chamber Structural Shell and Manifolds.

slight interference fit to the manifold holes. These were pressed in place but not electroform cold welded. All wax and wax filler was removed by heating the chamber. Figures 55 through 58 illustrate various views of the electroformed chamber. All passages were pressure flushed with a

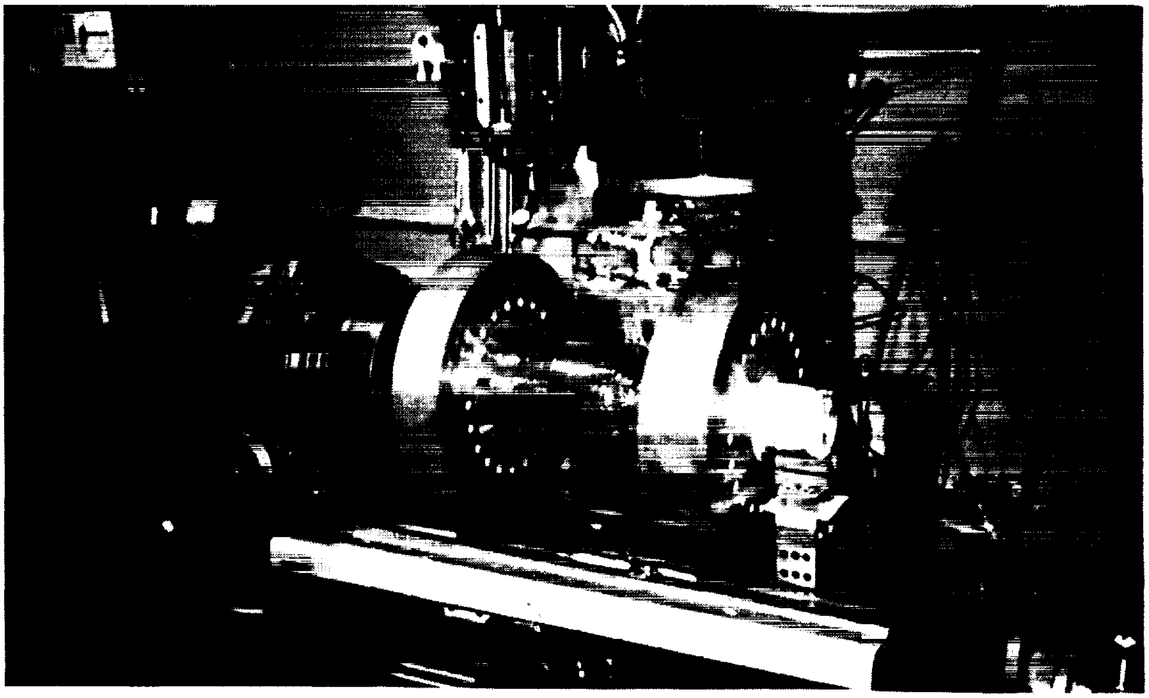


Figure 56. End Milling Inlet and Outlet Port Holes in Manifolds

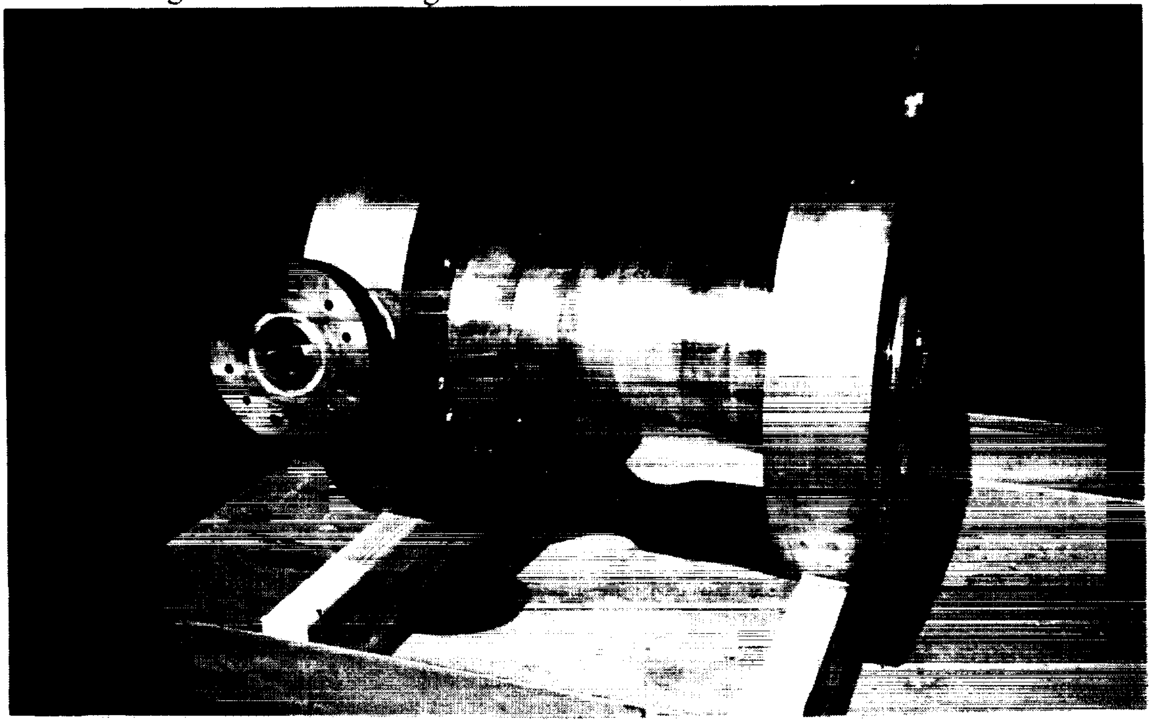


Figure 57. View of Copper Tube Bundle Chamber With Coolant Ports Installed.

suitable solvent and treated with 20% by volume glacial acetic acid to dissolve the filler material. The chamber was then rinsed and dried. No leaks were observed and the solvent was observed to flow very freely from the forward to the aft manifold, indicating that no tubes were plugged.

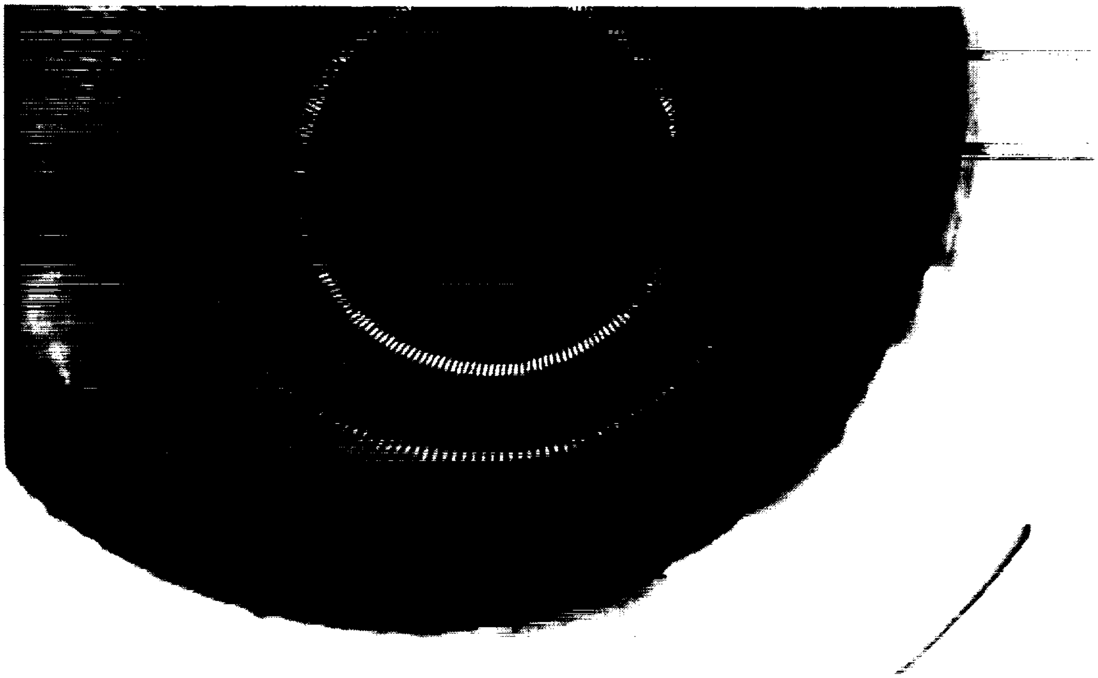


Figure 58. View of Copper Tube Bundle Chamber Interior

5.4 Conclusions and Recommendations

- It has been demonstrated that tubes of highly complex shape can be fabricated into a bundle having high strength with very uniform joints between tubes. This provides a desireable alternative to conventional joining methods such as brazing since:
  - There is no thermal processing involved which might degrade material properties of the tubes being joined.
  - Individual tube movement during the joining process is not a problem in electroforming since the process is performed at low enough temperatures to allow the wax "adhesive" to secure the position of each tube.
  - In process inspection during the electroform joining of tubes is simplified, since the entire tube bundle secured to the mandrel can be elevated for visual observation at any time. It is difficult to make such inspections when furnace brazing such hardware.
- It has been shown that entire thrust chambers can be fabricated by electroforming with only

the support of machining as a secondary operation. The only constraint on production by electroforming is the time that would be required to make an entire chamber by this process. However, production time can be greatly decreased by machining or electroforming components such as manifolds and literally "growing" them onto the chamber body by electroforming methods known as "cold welding".

- Electroforming has been shown to have a great versatility whereby metals and alloys of very different mechanical properties can be sequentially applied with metallurgical bonds and without the need for thermal joining methods.

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G.A. Malone, W. Hudson, B. Babcock, and R. Edwards

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Electroformed Nickel, Inc.
785 Martin Road
Huntsville, Alabama 35824

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13. ABSTRACT ***(Maximum 200 words)***

Electroforming offers a superior means for fabricating internally cooled heat exchangers and structures subjected to thermal environments. Copper is deposited form many such applications because of the good thermal conductivity. It suffers from mediocre yield strength as a structural material and loses mechanical strength at intermediate temperatures. Mechanical properties similar to those of electroformed nickel are desired. Phase I examined innovative means to improve deposited copper structural performance. Yield strengths as high as 483 MPa (70 ksi) were obtained with useful ductility while retaining a high level of purity essential to good thermal conductivity. Phase II represents a program to explore new additive combinations in copper electrolytes to produce a more fine, equiaxed grain which can be thermally stabilized by other techniques such as alloying in modest degrees and dispersion strengthening. Evaluation of new technology – such as the codeposition of fullerness (diamond–like) particles were made to enhance thermal conductivity in low alloys. A test fire quality tube–bundle engine was fabricated using these copper property improvement concepts to show the superiority of the new coppers and fabrications methods over competitive technologies such as brazing and plasma deposition.

14. SUBJECT TERMS

Electroforming; Copper/copper alloys; Thrust chambers; Materials properties; Copper electrodeposition; Dispersion strengthening

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