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G. A. Malone

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16. Abstract

The report contained herein constitutes a literature analysis of reports, specifications, and documented experiences with the use of electroforming to produce copper and nickel structures for aerospace and other engineering applications. The literature period covered is from 1948 to 1974. Specific effort was made to correlate mechanical property data for the electrodeposited material with known electroforming solution compositions and operating conditions. From this survey, electrolytes are suggested for selection to electroform copper and nickel outer shells on regeneratively cooled thrust chamber liners, and other devices subject to thermal and pressure exposure, based on mechanical properties obtainable, performance under various thermal environments, and ease of process control for product reproducibility. Processes of potential value in obtaining sound bonds between electrodeposited copper and nickel and copper alloy substrates are also discussed.

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I. SUMMARY

The objective of the program encompassed by Contract NAS 3-17823 is to investigate, develop and perform copper and nickel electroforming for the purpose of establishing the necessary processes and procedures for repeatable, successful fabrication of the outer structure of regeneratively cooled thrust chambers. This report describes the findings of a literature analysis performed to determine information available on processes, procedures and experiences in the industry with copper and nickel electroforming for structural applications where thermal and pressure environments are encountered.

Electroforming is essentially a fabrication technique whereby a piece of hardware is made by heavy electrodeposition on a preformed shape or mandrel. Although many metals can be electroformed, this report is concerned only with copper and nickel due to the wide variety of mechanical and thermal properties available in the electrodeposits and the vast experience existing in fabricating electroforms from these metals.

Copper is usually deposited from the cyanide, acid sulfate, fluoborate, or pyrophosphate electrolytes. Data are presented which indicate copper deposits with high purity and uniformly small grained microstructure afford the best thermal performance and mechanical strength for most engineering applications. The literature revealed that pyrophosphate, acid sulfate (with oxygen reduction additive) and acid sulfate with periodic reversal of current afforded excellent products for arduous aerospace applications.

Although nickel is deposited from many electrolytes, the sulfamate bath has evolved as the primary solution for producing deposits acceptable for aerospace and other critical structural applications. This is mainly due to the wide variety of mechanical properties which can be produced and controlled, as well as the low residual stress possible in the deposits — a factor of importance in fatigue resistance of substrate metals to which the electroform may be bonded.

Several suggested basis metal cleaning and activation procedures for bonding are discussed. It appears that solvent or vapor degreasing and alkaline cleaning are common practices—most solutions involve similar chemical ingredients. The method of bond activation varies from acid dips to electrochemical means. Some bond strength data are presented and it must be recognized that results are not always comparative due to the test method used to fail electrodeposit bonds.

Although the ASTM has attempted to establish several recommended practices for cleaning, pickling and activation of metals for plating and electroforming, there is a general lack of definitive specifications and instructions to insure an electroformer that his product will consistently meet the rigid requirements now being imposed on structural electroforms. It is anticipated that the information herein will offer a guideline for the electroforming engineer in selecting a process to meet his requirements.

II. INTRODUCTION

Electroforming has gained general acceptance as one of the primary methods of fabricating the outer shells of regeneratively cooled thrust chambers for advanced design rocket engines. Such devices consist of a combustion chamber where burning of high energy fuel and oxidizer occurs, a throat restriction to convert the high pressure gasses into high velocity vector flow, and a nozzle to increase gas velocity and amplify thrust. Figure 1 shows a schematic section of a typical chamber.

The inner member of the chamber wall structure is the liner, or hot gas side, which is usually produced by conventional spinning and machining techniques from specially selected wrought metal alloys having outstanding elevated temperature performance. Channels are machined into the liner to provide flow passages for a coolant (usually the propellant fuel) to maintain the hot gas wall at a safe operating temperature. The outer shell closes out the coolant passages and provides structural support for the liner-coolant system.

Electroforming provides the most economical means of fabricating the complex shape required in the outer shell. Properly performed, this technology can provide material properties and structural integrity required by the design engineer.

Experience required to utilize this technology to produce hardware meeting the rigid service requirements demanded is limited to a few electroforming vendors and captive aerospace shops. Processes and procedures are for the most part, proprietary. As a result, the product of one electroformer will usually differ from that of another with respect to mechanical properties, deposit quality, and bond strengths achieved between the electroformed outer shell and the chamber liner. Similar variation is possible in consecutive products from the same electroformer.

The following report is a survey of published literature concerning the procedures, practices, and specifications for electroforming hardware requiring deposits meeting specific design and environmental service requirements. The electroformed metals are restricted to copper and nickel based on current preference of these materials as outer shells for regeneratively cooled thrust chambers. Information on electroforming techniques and procedures was not limited to thrust chambers in order to present methods, data, and experiences which might prove beneficial or applicable to chamber shell electroforming.

Many references cited indicated deposits of superior mechanical properties which might warrant adoption by one inexperienced in the general fabrication sequence or service requirements of thrust chambers. Where such occurs, the literature findings have been editorially supplemented to point out the shortcomings of the deposit properties or electroforming baths as specifically related to regeneratively cooled thrust chambers.

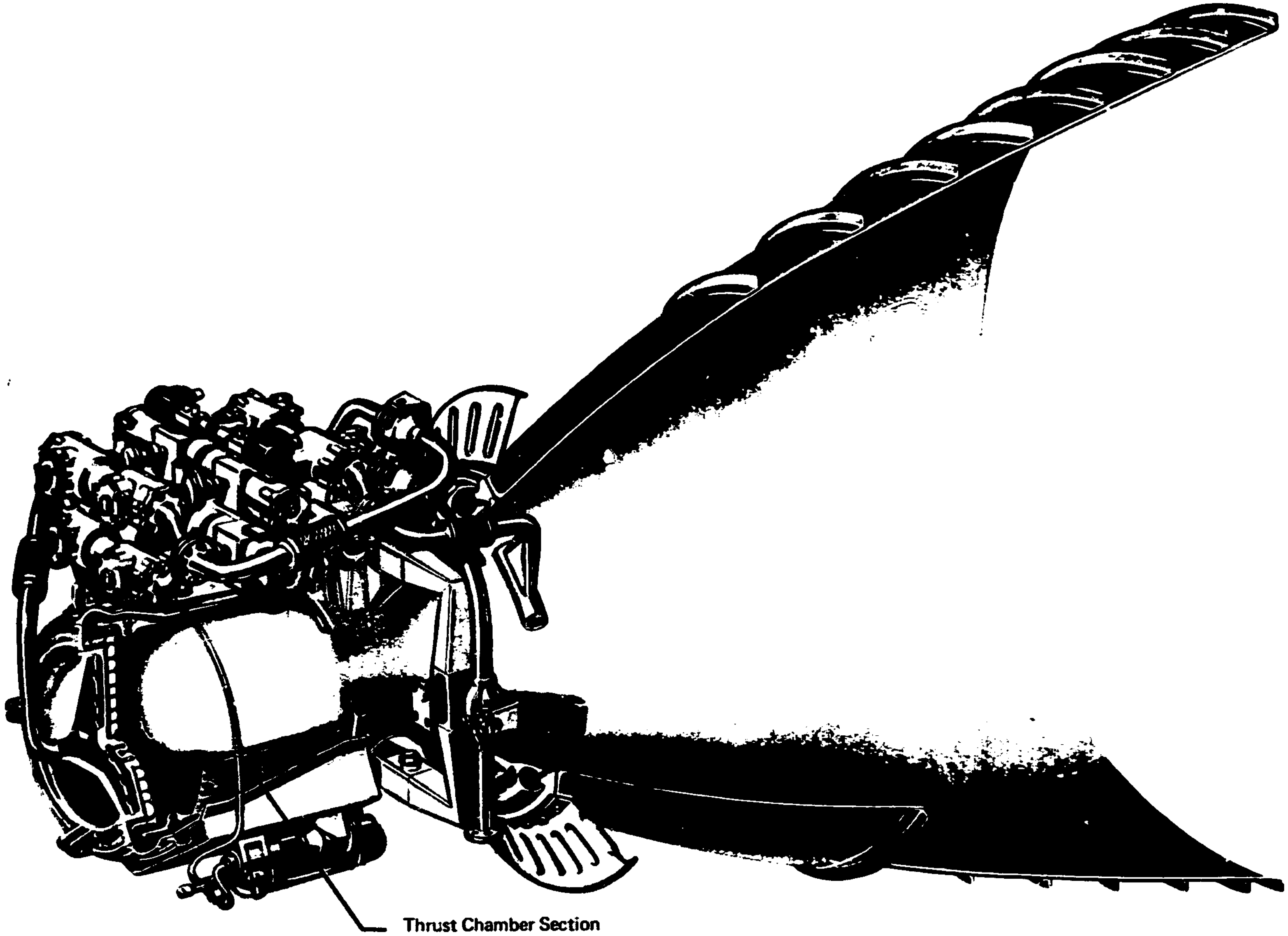

Figure 1. Schematic Section of a Typical Regeneratively Cooled Thrust Chamber

This report provides a summary of electroforming practices and property data for engineering applications of electrodeposited nickel and copper which are expected to prove useful in the manufacture of outer shells on thrust chambers or structures with similar requirements. A subsequent program is planned to direct this information and further development effort into a series of general specifications for electroforming chamber shells of more consistent deposit quality and structural integrity.

III. COPPER ELECTROLYTES

A. ELECTROLYTE TYPES AND RANGES OF PROPERTIES

Most copper is deposited from the alkaline cyanide and acid sulfate solutions (1). In recent years, the copper pyrophosphate bath has been used where high throwing power (ability to deposit metal in recesses) was required (2). There has also been an interest in depositing copper from fluoborate solutions due to the high plating rates possible (3). Most of these electrolytes are suitable for electroplating or electroforming, but the cyanide solutions are generally not used for very thick deposits due to high internal stresses and low plating efficiencies in comparison with the other available electrolytes.

Many authors have reported differing ranges of properties obtained in copper deposits from these various electrolytes. It has been shown by many investigators that the thickness of the deposit often has a significant effect on mechanical properties (4). Properties of electrodeposited metals can be varied over a wide range by varying the type and composition of the electrolyte, by the use of addition agents or alloying constituents in the bath, or by varying the operating conditions such as current density, bath temperature, agitation or current modulation (5). As with wrought metals, the properties of electrodeposited metals can be modified subsequent to formation by heat treatment or mechanical working.

Most of the property range summarization tables found in the literature were of limited value, since the conditions of deposition and effect of additives on thermal stabiltiy of the metal was not described. Many authors cite the formation of porous structures, loss of of tensile strength, and reduction in ductility of deposits produced from electrolytes with certain organic electrolyte additives (4) (7) (8). Many of such additives have a tendency to decompose or change in concentration during long periods of electroforming which makes control of composition in the electrolyte and uniform properties in the electroformed deposit difficult to achieve.

To better define the properties available for electroforming the outer structures of regeneratively cooled thrust chambers, the individual electrolytes are characterized by the following comparison criteria:

1) Bath composition and concentration range
2) Bath operating conditions
3) Properties obtained for the above conditions
4) Thermal stability of deposits
5) Elevated temperature mechanical properties
6) Ease of bath control and deposit reproducibility

B. ACID SULFATE ELECTROLYTES

Acid sulfate electrolytes are commonly used for electroforming since they are simple to operate and control. The bath is composed of copper sulfate as a source of copper metal ion, sulfuric acid to reduce electrolyte resistivity, and water. Several recommended commercial bath formulas and operating conditions were found in the literature. These are shown in Table I.

Safranek (9) points out a favorable operating characteristic of the copper sulfate bath in that anode and cathode polarization are nearly negligible in purified solutions used at low current densities. Even at 21.5 amps/dm^2 (200 amp/ft^2) cathode current density, a 6 volt current source is ample if the solution is agitated. Excessive anode polarization can occur at about 5 amp/dm^2 (49 amp/ft^2). The bath has lower throwing power than cyanide or pyrophosphate baths and good current shielding practices must be used.

Lamb, Johnson, and Valentine performed an extensive evaluation of acid sulfate deposits (5) (7). Except for a few deposits produced for thickness studies, all deposits were 0.018 - 0.020 inches (0.51 mm) thick. In the thickness studies, it was found that deposits 0.001 - 0.006 inches thick were stronger but less ductile than the thicker deposits. This change in mechanical properties with thickness conforms to expected results based on the fine grained microstructure which occurs in the initial 0.005 inch of deposit.

These investigators found that tensile strength and elongation decreased with increase in bath temperature in most cases. There was a general trend for tensile strength, and elongation to increase with increase in current density. Increasing copper concentration in the bath did not appear to affect tensile strength but did increase elongation in many cases. Increasing the concentration of sulfuric acid from an intermediate value to a high value results in an increase in tensile strength and elongation. The reverse occurs when the acid concentration is dropped to a low value. Table II presents the properties obtained from this investigation.

Bell Aerospace Company (11) investigated freshly purified copper sulfate electrolyte at various copper sulfate and sulfuric acid ratios. The current density was held constant and the temperature varied. Increasing the concentration of sulfuric acid increased tensile strength, but elongation was only slightly improved at 100°F (38°C). These results are shown in Table III.

Rocketdyne Division of North American Rockwell (12) employs the copper sulfate electrolyte to electroform channel passage closures for many thrust chambers utilizing hydrogen as a coolant. Reagent grade chemicals are used to formulate the bath. Although the bath uses an oxygen control additive (U.S. Patent 3,616,330), it is categorized in this report as a non-additive solution since the deposits retain very useful mechanical properties and metallurgical structure at temperatures to 700°F

TABLE I

RECOMMENDED ELECTROLYTES FOR ACID SULFATE COPPER ELECTRODEPOSITION

INGREDIENT OR OPERATING VARIABLE		REFERENCE (8)	REFERENCE (9)	REFERENCE (10) PLATING	REFERENCE (10) ELECTROFORMING
Copper Sulfate Pentahydrate	g/1	195 - 247	150 - 250	210	240
	oz./gal.	26 - 33	20 - 33	28	32
Sulfuric Acid	g/1	30 - 75	45 - 110	45	60 - 75
	oz./gal.	4 - 10	6 - 15	7	8 - 10
Temperature	°C	21 - 49	32 - 43	16 - 49	16 - 49
	°F	70 - 120	90 - 110	60 - 120	60 - 120
Current Density	A/dm.^{2}	2.2 - 10.8	3.7 - 22	2.2 - 21.6	2.2 - 21.6
	A/ft.^{2}	20 - 100	34 - 204	20 - 200	20 - 200
Cathode Efficiency	%	95 - 100			
Agitation	Air	Yes			
	Cathode	Yes			
Anode-Cathode Ratio		1:1			

Reference (8) - States that continuous filtration is preferred, especially for heavy deposits.

Reference (9) - Notes that soluble anodes are rolled, cast electrolytic, or phosphorized copper, operated at not more than 45 amp/ft.^{2} without agitation. Cast anodes are not recommended because they contain considerable amounts of copper oxide.

Reference (10) - States that cast anodes can be used most satisfactorily if they are OFHC copper.

TABLE II

SUMMARY OF PROPERTIES OF ACID SULFATE COPPER DEPOSITS (5)

(NO ADDITION AGENTS USED)

BATH SYMBOL	BATH TEMP., °C	CURRENT DENSITY, Amp/dm.^{2}	TENSILE STRENGTH kpsi	YIELD STRENGTH kpsi	ELONGATION IN 2 INCHES, PERCENT	HARDNESS KHN 200g. LOAD Kg/mm^2	INTERNAL STRESS psi *	DENSITY 25°C g/cm^3
Cu1-H1	20	0.5	27	8	18	56	-79	8.922
	30	2	30	8	37	49	400	8.920
	40	0.5	30	10	24	57	80	8.922
	40	4	29	8	32	46	530	8.921
Cu1-H2	20	2	31	9	28	59	3,300	8.921
	30	2	25	7	15	58	570	8.921
	40	2	24	8	13	47	370	
Cu1-H3	30	0.5	20	8	8	56	-110	8.919
	30	2	28	8	16	58	1,800	8.919
	30	4	31	11	16	77	3,800	8.925
	30	4	36	15	14	80		
Cu2-H1	30	2	30	8	32	48	580	8.922
	40	8	32	10	36	61	1,400	8.925
Cu2-H2	20	0.5	26	7	25	105	-510	8.928
	20	2	32	11	33	61	1,500	8.925
	20	2	32	10	34			
	20	4	33	12	29	67	4,300	8.920
	32	0.5	23	7	11	87	-700	8.924
	30	2	25	8	14	88	550	8.921
	30	2	26	7	19			
	30	2	32	11	39	55		8.925
	30	4	30	9	24	53	2,200	8.922
	40	2	22	7	10	85		
	45	2	21	8	10	49	-320	8.923
	45	4	24	7	14	57	190	8.924

* Positive numbers indicate a tensile internal stress. Negative numbers indicate a compressive state of stress.

TABLE II

SUMMARY OF PROPERTIES OF ACID SULFATE COPPER DEPOSITS (5)

(NO ADDITION AGENTS USED) (CONTINUED)

BATH SYMBOL	BATH TEMP., °C	CURRENT DENSITY, Amp/dm.^{2}	TENSILE STRENGTH kpsi	YIELD STRENGTH kpsi	ELONGATION IN 2 INCHES, PERCENT	HARDNESS KHN 200g. LOAD Kg/mm^2	INTERNAL STRESS psi *	DENSITY 25°C g/cm^3
Cu2-H3	20	2	37	15	41	78	2,000	8.926
	30	0.5	33	10	41	62	-90	8.926
	30	2	28	9	17	54	180	8.924
	30	2	29		21			
	30	4	34	11	46	66	1,500	8.925
	30	8	32	14	24	75	4,300	8.926
	40	8	37	15	44	80	2,600	8.926
	60	8	27	10	18	58	380	8.925
	60	20	2[illegible]	7	5	58	1,400	8.86
Cu3-H3	20	4	32	12	42	64	3,100	8.925
	30	0.5	27	8	16	57	-90	8.920
	30	2	30	9	29	55	620	8.924
	45	0.5	32	10	34	57		8.919
	45	4	26	8	15	51	1,400	8.921
	60	4	30	8	41	53		8.925
	60	4	31	8	43	57		
	60	8	31	10	33	59	620	8.925

* Positive numbers indicate a tensile internal stress. Negative numbers indicate a compressive state of stress.

Electrolyte Compositions:

	$CuSO_4 \cdot 5H_2O$ g/l	$CuSO_4 \cdot 5H_2O$ oz./gal.	H_2SO_4 g/l	H_2SO_4 oz./gal.
Cu1-H1	87	12	25	3.3
Cu1-H2	87	12	39	5.2
Cu1-H3	87	12	74	9.8
Cu2-H1	187	25	25	3.3
Cu2-H2	187	25	39	5.2
Cu2-H3	187	25	74	9.8
Cu3-H3	275	36	74	9.8

TABLE III

BELL AEROSPACE COMPANY TEST DATA FOR COPPER DEPOSITS FROM A NON-ADDITIVE SULFATE BATH (11)

COMPOSITION AND OPERATING DATA:				
Copper Sulfate, oz./gal. (g/1)	33 (247)	33 (247)	31.5 (236)	31.5 (236)
Sulfuric Acid, oz./gal. (g/1)	7.6 (57)	7.6 (57)	11.5 (86)	11.5 (86)
Temperature, °F (°C)	80 (27)	100 (38)	90 (32)	100 (38)
Current Density, A/ft.^{2} (A/dm^2)	30 3.2	30 3.2	30 3.2	30 3.2
MECHANICAL PROPERTIES:				
Ultimate Strength, kpsi (MN/m^2)	20.7 (142.8)	28.3 (195.3)	29.5 (203.6)	32.5 (224.3)
Yield Strength, kpsi (MN/m^2)	7.4 (51.1)	10.3 (71.1)	13.0 (89.7)	13.4 (92.5)
Elongation in 2 inches, %	20.6	24	16.3	26

ANODES: OFHC Cast

(371°C). The grain structure for these deposits is required to be fine columnar and it is unlike that of conventional acid sulfate deposits. This would indicate the oxygen control additive may contribute to grain refinement in the as-deposited condition. Solution composition, operating conditions and mechanical property requirements imposed by Rocketdyne on electrodeposited copper are shown in Table IV.

Schuler, Tripp, and Mullery (13) investigated the ductility of copper sulfate deposits in the 500 - 700°F (260 - 371°C) range. The object of this work was to improve properties and performance of electrodeposited copper subject to exposure to furnace brazing hydrogen atmosphere. In the first part of this investigation, the standard Rocketdyne electrolyte (with oxygen control additive) was compared to similar electrolytes with commercial brightening and leveling agents. OFHC phosphorized anodes were evaluated in each bath. Under comparable operating conditions for each bath, it was found that deposits from the bright leveling sulfate bath were stronger than the Rocketdyne bath deposits at temperatures up to 500°F (260°C). Use of phosphorized anodes in the Rocketdyne bath in place of OFHC anodes resulted in loss of ductility.

A second series of experiments was performed to determine 1) the effect OFHC anodes on the Rocketdyne electrolyte product ductility, 2) the difference in mechanical properties between deposits from old and new electrolyte, 3) the effect of increased current density and lower bath temperatures on grain size and ductility, and 4) if old electrolyte could be purified to produce a bath equivalent to new electrolyte by activated carbon treatment. Results of these tests are shown in Table V.

1) Apparent impurities in old electrolyte serve to produce deposits that have higher room temperature tensile strength than deposits from new electrolyte at 100°F and 20 A/ft^2.

2) Deposits from either new or old electrolytes at 100°F and 20 A/ft^2 have very low ductility at 700°F.

3) Electrodeposited copper with increased room temperature tensile strength and 700°F ductility can be produced at 20A/ft^2 from purified new or old electrolyte by keeping electrolyte temperature below 90°F and using electrolyte agitation.

4) Old electrolyte can be restored to new electrolyte quality and performance using a standard method of the plating industry (namely, treating with activated carbon).

5) The low-oxygen-content copper chip-titanium basket anode system is compatible with the Rocketdyne electrolyte.

6) The phosphorized-low oxygen copper chip titanium basket anode cannot be regarded as incompatible with the Rocketdyne electrolyte but appears to produce electrodeposited copper with decreased room temperature ductility when compared to deposits using low-oxygen-content copper as anodes.

TABLE IV

ROCKETDYNE COPPER SULFATE ELECTROFORMING BATH COMPOSITION, OPERATING PARAMETERS AND DEPOSIT MECHANICAL PROPERTY REQUIREMENTS (OXYGEN CONTROL ADDITIVE BATH)

Composition and Operating Conditions	Requirement
Copper Sulfate, Reagent Grade	210 - 240 grams/liter
Sulfuric Acid, Reagent Grade	60 - 75 grams/liter
Oxygen Control Additive	.25 - .75 grams/liter
Water	1 megohm/cm min. specific resistance
Anodes	ASTMB 170 Grade 1 in titanium basket covered with polypropylene bags
Temperature	82 - 90°F (28 - 32°C)
Filtration, continuous	Nominally rated 10 micron polypropylene elements
Filtration Rate	2 tank volumes/hour minimum
Current Density	40 - 50 A/ft.^{2} (4.3 - 5.4 A/dm^2)
Agitation	Cathode and electrolyte flow

Electrodeposited Copper Properties

	Room Temperature	700 ± 15°F (371 ± 8°C)
Ultimate Tensile, kpsi	40	10
MN/m^2	276	69
Yield Strength, kpsi	20	5
MN/m^2	138	35
Elongation in 0.5 inches, %	25	10

TABLE V

INVESTIGATION OF NEW AND OLD COPPER SULFATE ELECTROLYTES AT ROCKETDYNE USING OFHC ANODES AND AN OXYGEN CONTROL ADDITIVE (13)

Electrolyte Composition:

Copper Sulfate	28 to 32 oz./gallon
Sulfuric Acid	8 to 10 oz./gallon
Oxygen Control Additive	1.5 to 3.0 g/gallon

Current Density: 20 A/ft.^{2} (2.15 A/dm^2)

TEST RESULTS FOR UNTREATED ELECTROLYTES

	New Electrolyte		Old Electrolyte	
Bath Temperature	100°F (38°C)		100°F (38°C)	
Test Temperature	75°F (24°C)	700°F (371°C)	75°F (24°C)	700°F (371°C)
Ultimate Strength, kpsi	29	9	48	15
Yield Strength, kpsi	14	8	30	11
Elongation in 0.5 inch, %	21	2	30	7

TEST RESULTS FOR PEROXIDE AND CARBON TREATED ELECTROLYTES

	New Electrolyte		Old Electrolyte	
Bath Temperature	90°F (32°C)		90°F (32°C)	
Test Temperature	75°F (24°C)	700°F (371°C)	75°F (24°C)	700°F (371°C)
Ultimate Strength, kpsi	46	14	47	13
Yield Strength, kpsi	26	5	29	5
Elongation in 0.5 inch, %	30	29	27	18
Bath Temperature	100°F (38°C)		90°F (32°C)	
Test Temperature	75°F (24°C)	700°F (371°C)	75°F (24°C)	700°F (371°C)
Ultimate Strength, kpsi	33	10	42	13
Yield Strength, kpsi	14	8	26	5
Elongation in 0.5 inch, %	41	4	29	17

7) Bright acid copper while having a wide and useful commercial market does not appear to be applicable to rocket engine applications requiring high ductility at elevated temperatures.

Lamb, Johnson, and Valentine (7) have extensively investigated the thermal properties, fatigue strength, modulus, composition and structure of copper from the non-additive agent acid sulfate bath. Annealing caused decrease in tensile strength and increase in other baths containing additives. Yield strength decreased greatly upon annealing, depending on the temperature and time for recrystallization to occur. No density changes were noted due to annealing. Annealing at 325°C has the effect of recrystallizing mainly the fine grain structure of the initial deposit layer where internal stress is usually predominant. Annealing at 500°C results in complete recrystallization with large grains extending throughout the deposit. The typical columnar structure is retained. Table VI shows thermal properties for acid copper sulfate deposits.

Safranek (14) advised that copper sulfate containing no addition agents can produce a variety of tensile strengths and ductility based on solution agitation. With little or no agitation, copper is low in both strength and ductility. He stipulates that this may be due to cuprous oxide particles included in the deposit. Examples are cited in which copper tensile strengths of 39,000 to 62,000 psi (269 to 428 MN/m^2) were achieved with as much as 34 percent elongation in 2 inches. The highest tensile value was with high speed rotation of the cathode (5500 rpm). (This is not practical in electroforming the outer shells of thrust chambers, but it indicates the significance of vigorous bath agitation). In this work, Safranek reported elastic moduli for purified copper sulfate bath deposits as $14.0 \pm 0.2 \times 10^6$ psi (as plated) and $16.1 \pm 0.1 \times 10^6$ psi (as machined). From impure sulfate baths, the corresponding values were $15.9 \pm 0.3 \times 10^6$ psi and $16.9 \pm 0.1 \times 10^6$ psi, respectively.

C. BRIGHT LEVELING ACID ELECTROLYTES

The bright acid copper process has three characteristics of importance to the plating industry (15): brightness, good ductility, and exceptional leveling power. Brightness is of little concern to the electroformer, but ductility and leveling power (the ability to produce smooth deposit surfaces) is highly desirable. In contrast to the conventional acid sulfate deposits which are coarse grained and columnar in microstructure, the bright leveling copper bath deposits are fine grained without banding. Bright copper deposited from sulfate solutions is nearly stress free. The bath also has good throwing power to deposit into recessed areas.

Phosphorized anodes are recommended for use with these solutions. Other anodes may cause roughness, poor leveling and other detrimental effects. The anodes should also be covered with Dynel or polypropylene bags to minimize roughness in deposits caused by sludge. The bath temperatures range from 75 to 95°F (24 to 35°C) in practice. The cathode current density range should be within 30 to 60 A/ft^2. (3.2 to 6.5 A/dm^2) for good leveling and brightness. Anode current density should be in

TABLE VI

EFFECTS OF ANNEALING ON PROPERTIES OF COPPER SULFATE DEPOSITS FROM NO-ADDITIVE ELECTROLYTES AND PROPERTIES AT LOW AND HIGH TEMPERATURES (7)

Bath Composition and Operating Conditions:

Copper Sulfate 187 g/l, Sulfuric Acid 39 g/l, Temperature 30°C (86°F), and Cathode Current Density 2 A/dm.^{2} (18.6 A/ft.^{2})

Physical Properties Before and After Annealing:

	As Deposited	Annealed 150°C, 2 hrs.	Annealed 325°C, 15 min.	Annealed 500°C, 15 min.
Tensile Strength, kpsi (MN/m^2)	32 (221)	31 (214)	31 (214)	30 (207)
Yield Strength, kpsi (MN/m^2)	11 (75)	9 (62)	10 (69)	5 (35)
Elongation in 2 inches %	39	41	40	44
Density at 25°C (g/cm^3)	8.925	-	-	8.925
Hardness, KHN, 200g. load, kg/mm^2	55	-	62	54
Elastic Modulus (10^{-6}psi)	14	-	-	12
Linear Thermal Expansion (x 10^{-6} = parts/unit length/°C)				
Temperature Range 20 - 200°C	17.1			
Temperature Range 20 - 400°C	17.8			

Mechanical Properties at High and Low Temperatures:

	Pulled at -78°C	Pulled at 150°C	Pulled at 325°C
Tensile Strength, kpsi (MN/m^2)	38 (262)	20 (138)	11 (76)
Elongation in 2 inches, %	41	13	7

the range of 15 to 30 A/ft^2 (1.6 to 3.2 A/dm^2).

A commercial formulation and operating conditions for a bright leveling acid copper bath is given in Table VII (16). Included in this table are ranges suggested in Reference (15) which also compares mechanical properties of bright acid deposits with conventional acid sulfate deposits.

Lamb, Johnson, Valentine (5) included the investigation of proprietary and common organic additives in their investigation of the properties of acid sulfate deposits. Gelatin was seen to produce a significant effect on strength, but slightly decreased ductility and increased hardness. A maximum strength was reached at about 0.1 g/l of gelatin. Phenolsulfonic acid (PSA) increased the tensile strength of copper sulfate deposits over a wide range of operating conditions. It also slightly increased ductility. Raising bath temperature decreased the tensile strength when PSA was present. Triisopropanolamine (TIPA), selenium dioxide, and a proprietary brightener designated "A" were the most effective additives to increase tensile strength. Many of the additives depleted rapidly and were difficult to control. Data for representative deposits from acid copper sulfate baths with additives is shown in Table VIII. The bath symbols used to designate the basic sulfate and sulfuric acid concentrations are the same as in Table II.

A bright acid copper bath was used at Bell Aerospace Company to produce flat test panels for nondestructive evaluation of thrust chamber wall simulations (17). The particular bath in use at Bell requires separate brightener and leveler additions (18). To meet technical requirements for the test panels, this bath was operated at two current densities to produce mechanical properties of wide difference. The bath composition, operating conditions, and mechanical properties obtained are shown in Table IX. Increasing current density at the bath temperature of 100°F (38°C) was observed to significantly decrease tensile strength and increase the elongation in 2 inches.

Foley (19) reported that Avco Corporation had considered use of bright acid copper electrolyte for electroforming heat sinks for titanium missile nose cones. However, it was decided to use the conventional copper sulfate bath with no additives because on atmospheric re-entry conditions, the heating of occluded organic material in the deposit would cause surface rupture and thermodynamic failure.

Lamb, Johnson and Valentine (7) investigated the effects of annealing on acid sulfate deposits containing an addition agent, triisopropanolamine (TIPA). Annealing at 500°C resulted in an 18 percent decrease in density with the formation of interior voids. Deposits exhibited rapid loss of strength with increase in temperature of exposure. It was also reported that the deposit underwent a large permanent expansion as a result of heating. The deposit previously mentioned as plated from a bath containing a proprietary agent ("A") in Table VIII showed a great permanent change in length after exposure to heat and was quite brittle. When tested at various temperatures, the copper deposited from a bath containing TIPA exhibited very poor elongation in a 2 inch segment.

TABLE VII

A SUMMARY OF COMPOSITIONS, OPERATING CONDITIONS, AND MECHANICAL PROPERTIES OF BRIGHT ACID SULFATE DEPOSITS WITH PROPRIETARY ADDITIVES (15) (16)

COMPOSITION:	REFERENCE 15	REFERENCE 16
Copper Sulfate, oz./gal.	30 ± 2	24 - 32
Sulfuric Acid, oz./gal.	6 - 8	6 - 8
Chloride Ion, ppm*	20 - 80	20 - 80
Proprietary Brightener, Volume %	Variable	0.3 - 0.6
OPERATING CONDITIONS:		
Temperature, °F	75 - 95	70 - 80
Cathode Current Density, A/ft.^{2}	30 - 60	30 - 60
Anode Current Density, A/ft.^{2}	15 - 30	15 - 30
Agitation	Vigorous air agitation	Air or rapid solution movement
Filtration	Continuous	Continuous

MECHANICAL PROPERTIES (REFERENCE 15):	BRIGHT LEVELING ACID COPPER	CONVENTIONAL ACID COPPER
Tensile Strength, kpsi (MN/m^2)	55 (379.5)	28 - 38 (193.2 - 262.2)
Elongation in 2 inches, %	15 - 20	22 - 34
Hardness, Knoop		
25 g. load	100 - 150	95 - 115
100 g. load	75 - 120	79 - 90

* Chloride control is critical from a standpoint of proper consumption rates for the proprietary additives (16).

TABLE VIII

SUMMARY OF PROPERTIES OF ACID SULFATE COPPER DEPOSITS FROM ELECTROLYTES WITH ADDITION AGENTS (5)

BATH SYMBOL	ADDITIVE NAME	ADDITIVE g/l	BATH TEMP., °C	CURRENT DENSITY Amp/dm.^{2}	TENSILE STRENGTH kpsi	YIELD STRENGTH kpsi	ELONGATION IN 2 INCHES, PERCENT	HARDNESS KHN 200g. LOAD kg/m.^{2}	INTERNAL STRESS psi *
Cu2-H1	Gelatine	0.003	30	2	41	22	23	88	750
	PSA	1.0	30	2	36	15	31	97	-370
Cu2-H2	Gelatine	0.003	30	2	45	28	8	82	1,000
	PSA	0.7	30	2	33	11	35	73	
	PSA	1.0	30	2	36	15	34	99	250
CU2-H3	Dextrin	0.02	30	2	22		5	60	
	Dextrose	0.05	30	2			0		
	Gelatine	0.01	30	2	53	31	10	131	860
	Gelatine	0.1	30	2	40	34	0.4	148	-4,200
	Glycerol	1.0	30	2	33		11	62	
	Glycine	0.1	30	2	31		4	79	
Cu2-H3	PSA	1.0	20	2	40	18	28	93	1,600
	PSA	1.0	30	2	34	13	32	84	100
	PSA	1.0	30	2	36	14	34	90	
	PSA	1.0	30	8					5,000
	PSA	1.0	40	2	30	9	23	88	380
	PSA	1.0	40	4	33	12	31	87	-260
	SeO2	.0001Se	30	2	47	17	21	123	2,300
	SeO2	.001 Se	30	2	44	16	24	108	2,800
	TIPA	3.5	30	2	39	17	7	129	2,100
	TPA	3.5	30	5	71	43	7	144	7,100
	Proprietary A		22	4	51	40	14	137	
	Proprietary A		28	4	52	40	19	128	2,900
Cu3-H3	PSA	1.0	30	2	34	13	32	82	-420

PSA = Phenolsulfuric Acid   SeO2 = Selenium Oxide   TIPA = Triisopropanolamine
Bath Symbols are the same as shown in Table II
* Positive values are tensile stress, negative values are compressive stress.

TABLE IX

BRIGHT ACID COPPER ELECTRODEPOSITION AT BELL AEROSPACE COMPANY

(M & T AC-94 ELECTROLYTE) - BATH COMPOSITION, OPERATION, & DEPOSIT MECHANICAL PROPERTIES

	ACTUAL BATH OPERATION (17)	SUPPLIER RECOMMENDATIONS (18)
Copper Sulfate, oz./gal.	32	27 - 32
Sulfuric Acid, oz./gal.	10	6.5 - 10 (2.65 - 3.9 vol.%)
Chloride Ion	Approximately 50 ppm	40 to 80 ppm
AC-94 Brightener	0.4 ± 0.1% by vol.	0.4% by vol.
AC-94 Leveler	0.1 ± 0.03% by vol.	0.1% by vol.
Cathode Current Density, A/ft.^{2}	50 - 100	30 - 100 A/ft.^{2}
Anode Current Density, A/ft.^{2}	12 - 15	10 - 40 A/ft.^{2}
Anodes (Phosphorized)	Amphos 40	Cu-Phos or Amphos 40
Temperature	90°F	65 - 85°F
Agitation	Low pressure air and cathode movement	Low pressure air, mechanical, or solution flow
Filtration	Continuous	Continuous
Mechanical Property Data (17)		
Current Density	50 amp/ft.^{2}	100 amp/ft.^{2}
Bath Temperature	90°F	90°F
Ultimate Strength, kpsi (MN/m.^{2})	61 (421)	47 (324)
Yield Strength, kpsi (MN/m.^{2})	49 (338)	38 (262)
Elongation in 2 inches, %	12	27

Safranek (4) notes that copper sulfate deposits from baths containing addition agents have higher impurity levels than those from non-additive sulfate baths:

	Oxygen Content, %	Hydrogen Content, %	Total Impurities, %
Copper Sulfate	0.0005	0.0001	0.0035
Copper Sulfate with 3.5 g/l triisopropanolamine	0.0050	0.0006	0.022
Copper Sulfate with 0.1 g/l gelatin	0.0350	0.0040	0.15

In view of the findings of Rocketdyne (13), the oxygen and other impurity levels in the additive sulfate bath deposits would indicate these products undesirable for exposure to elevated temperature.

D. ACID SULFATE SOLUTIONS WITH PERIODIC REVERSE CURRENT

Brimi and Luck (1) reported that use of periodic reverse current to deposit copper from the acid sulfate bath has been thoroughly investigated. It is claimed that the deposit is usually smoother and more ductile than that produced from baths depending on addition agents to accomplish the same qualities. High current densities may be used such as 20 to 30 amp/dm^2 (186 - 279 amp/ft^2). The time used on each reversal cycle is not as important as keeping the time on the cathodic cycle 7 times the time on the anodic cycle. The best anodes to use with this process are high-purity copper with 0.02 to 0.03 percent phosphorus.

Foley (19) reported the use of periodic reverse electrodeposition of copper for heat sinks for the Titan missile nose cones. The electrolyte was copper sulfate and the periodic reverse (PR) cycle efficiency was 50 to 70 percent. Details of the process, including test data are shown in Table X.

Lamb, Johnson, and Valentine (5) included periodic reverse in their investigation of acid sulfate deposits. Only one sample was tested. The electrolyte contained 36 oz/gal of copper sulfate, 9.8 oz/gal of sulfuric acid, and was operated at a bath temperature of 30°C and a current density of 4 amp/dm^2 (37 amp/ft^2). The periodic reversal cycle consisted of 5 seconds cathodic and 2 seconds anodic with respect to the deposited copper cathode. Mechanical and physical properties were:

Tensile Strength	43,000 psi
Yield Strength	20,000 psi
Elongation in 2 inches	26%

TABLE X

PERIODIC REVERSE PLATING OF COPPER HEAT SINKS FROM THE ACID SULFATE BATH - OPERATING DATA AND DEPOSIT MECHANICAL PROPERTIES (19)

Electrolyte Composition:	
Copper Sulfate (C.P. Grade)	28 - 32 oz./gal.
Sulfuric Acid (C.P. Grade)	10 - 12 oz./gal.
Water (Demineralized)	Balance
Anodes:	
Type	OFHC (conformal)
Anode Bags	Dynal
Ano. - Cathode Ratio	At least 1:1
Electrolyte Temperature	110 ± 2°F
Filtration	Continuous through Darco S-rl carbon and Solka Floc BW-40 (flow rate 12,000 gal./hr.)
Current Density (PR)	Minimum of 40 A/ft.^{2}
Cathode Movement	Rotation at 21 RPM

Strength of Bond to Substrate (316 Stainless Steel):	Test Plate	Heat Sink
Bond Shear Strength, psi	21,570	21,695
Tensile Bond Strength, psi	37,733	35,400
Mechanical Properties of Copper (As Deposited):		
Tensile Strength, psi	31,950	31, 825
Yield Strength, 0.2% offset, psi	14,500	12,475
Elongation in 2 inches, %	No values furnished	
Chemical and Physical Properties:		
Copper, %	99.95 - 99.99	99.95 - 99.99
Hydrogen, %	0.0001 - 0.0003	< 0.0001
Oxygen, %	0.0007 - 0.0018	0.0002 - 0.0008
Density, g/cm^3	8.9398	8.9412

Thermal Test Results:		
Heat Treatment	1 hr. @ 700°F in N_2	3 hrs. @ 1200°F in N_2
Test Temperature	Room	Room
Tensile Strength, psi	31,900	28,900
Yield Strength, psi	12,300	5,900
Elongation in 2 inches,%	38.5	63.0
Reduction in Area, %	35.0	80.0

Hardness, KHN 200 g load	106 Kg/mm^2
Internal Stress	4,100 psi
Density	8.925 g/cm^3

No data were reported (7) on thermal properties of the PR deposits from sulfate baths, The microstructure of the PR deposits exhibited a fine fibrous grain structure much like that described in the Rocketdyne product detailed in Reference (12).

E. COPPER FLUOBORATE BATHS

Copper fluoborate is more soluble in water than copper sulfate and as a result, higher concentrations of copper ion can be maintained in the electrolyte (9). This permits the use of higher current densities for plating or electroforming (1). Several commercial copper fluoborate bath formulations have been given in the literature (3) (20) and data is furnished in Table XI.

According to Diggin (20), the fluoborate bath is relatively insensitive to impurities. Addition agents can be used to cut down nodular growth or treeing with a side effect of increasing hardness and tensile strength. Struyk and Carlson (3) state that the bath is stable and preparation simple, requiring only dilution of the concentrate and adjustment of pH with copper carbonate (to raise pH) or fluoboric acid (to lower pH). Bell Aerospace Company has used this electrolyte and noted a tendency for nodules and "treeing" with no addition agents present.

Lamb, Johnson, and Valentine (5) (7) included deposits from the copper fluoborate bath in their investigation. No addition agents were used. One of the baths used was of high copper concentration similar to that described by Diggins (20). Tensile strength, elongation, hardness, and internal stress were found to decrease with increase of temperature. Data from Struyk and Carlson (3) show similar trends, but elongation increased when temperature increased. Lamb and his coworkers found that increasing current density caused increases in tensile strength, elongation, hardness, and internal stress. Table XII shows the properties obtained (5) (7).

The grain structure of the copper fluoborate bath deposits is fibrous-columnar (7). Annealing results in changes in the grain size in much the same manner as experienced with copper sulfate deposits. The average coefficient of linear thermal expansion and permanent change in specimen length are given (7) as:

Bath Symbol	Average Coefficient x 10^6 = Parts/Unit Length/°C 20° - 200°C	20° - 400°C	Permanent Change in Specimen Lenght after Heating in. in. 6 Inches
F-1 (as deposited)	16.2 - 16.7	17.6	0.0000

TABLE XI

COPPER FLUOBORATE BATH COMPOSITIONS, OPERATING CONDITIONS, AND PROPERTIES OF TYPICAL DEPOSITS (3) (20)

	Regular (3)	High Concentration (3)	Intermediate Concentration (20)
Standard Solution Compositions and Operating Data:			
Copper Fluoborate, g/l	224	448	336
oz./gal.	30	60	45
Copper Metal, g/l	60	120	90
oz./gal.	8	16	12
Gravity at 80°F, °Bé	21 - 22	37.5 - 39	29 - 31
pH (Colorimetric)	1.2 - 1.7	0.6 or less	0.2 - 0.8
Temperature, °C	26.7 - 71.3	26.7 - 71.3	26.7 - 49
°F	80 - 170	80 - 170	80 - 120
Fluoboric Acid, g/l	4 or higher	30	5
oz./gal.	0.5	4	0.6
Boric Acid, g/l	15 - 16	15 - 16	
oz./gal.	2.0 - 2.1	2.0 - 2.1	
Anodes	Electrolytic, rolled annealed, or OFHC cast		Bagged electrolytic or rolled
Anode Efficiency, %	99.5 - 101	100 - 101	99 - 101
Cathode Efficiency, %	98.8 - 100	99.5 - 100	99 - 100
Anode - Cathode Ratio	Not Critical		1:1 (Not critical)
Typical Mechanical Properties:			
Hardness, Rockwell 15T	44 - 45	59 - 63 (68 - 74)*	44 - 74
Tensile Strength, kpsi	17.1	29.5 (32.5)*	17.1 - 32.5
Yield Strength, kpsi	12.9	20.2 (28)*	
Elongation in 2 inches, %	7.3	14.5 (3.2)*	3.2 - 14.5

* Values in parenthesis are for deposits plated at a bath temperature of 95°F. Other values under Reference (3) were from a bath at 120°F.

TABLE XII

PHYSICAL PROPERTIES OF COPPER DEPOSITED FROM THE ACID FLUOBORATE ELECTROLYTE (5) (7)

Bath Symbol and Composition:

	Bath F-1 g/l	Bath F-1 oz./gal.	Bath F-2 g/l	Bath F-2 oz./gal.
Copper Fluoborate	177	24	366	45
Fluoboric Acid	12	1.6	22	3
Boric Acid	12	1.6	22	3
PH	0.8 - 1.0		0.4 - 0.6	

Mechanical and Physical Properties:

Bath Symbol	Bath Temp. °C	Current A/dm.²	Density A/ft.²	Tensile Strength kpsi	Yield Strength kpsi	Elongation in 2 inches Percent	Hardness, KHN 200g load Kg/mm.²	Internal Stress psi	Density 25°C g/cm³
F-1	30	2	18.6	20	9	7	53	0	8.925
	30	8	74.4	37	16	31	81	700	8.926
	60	8	74.4	32	11	16	56	-200	8.925
F-2	30	8	74.4	36	15	31	71	800	8.926
	50	20	186.0	33	12	29	60	1,600	8.925

Mechanical Properties After Annealing (Deposited at Bath Temperature of 30°C and Current Density of 8 A/dm.²):

Bath Symbol	Tensile Strength, kpsi Annealed 150°C 2 hr.	325°C 15 min.	500°C 15 min.	Yield Strength, kpsi Annealed 150°C 2 hr.	325°C 15 min.	500°C 15 min.	Elongation in 2 inches, % Annealed 150°C 2 hr.	325°C 15 min.	500°C 15 min.
F-1	35	33	28	14	13	3	33	29	41

Mechanical Properties at High and Low Temperatures (Deposited as above):

Bath Symbol	Elastic Modulus x 10⁻⁶ psi As Deposited	Annealed 500°C, 15 min.	Tensile Strength, kpsi Pulled at -78°C	Pulled at 150°C	Pulled at 325°C	Elongation in 2 inches, % Pulled at -78°C	Pulled at 150°C	Pulled at 325°C
F-1	13	6	44	28	14	33	22	8

F. COPPER PYROPHOSPHATE ELECTROLYTES

Copper pyrophosphate electrolytes are employed for such applications as stop-off for nitriding, selective carburizing, as a drawing lubricant for stainless steel and steel, as a means of electroforming and printed circuit plating, and for minimizing hydrogen embrittlement (9). The bath most widely used contains potassium copper pyrophosphate as an alkaline complex compound in aqueous solution. The potassium compounds are generally preferred over sodium salts for bathmake-up due to better solubility and a higher transference number (portion of the total current carried by ions of a given species).

Couch and Starek, authors of the section of Reference (9) dealing with pyrophosphate copper, report the bath to contain ammonia and nitrate. The ammonia and an excess of pyrophosphate maintain proper anode corrosion. The ammonia imparts some luster to the deposits. The nitrate increases operating current density by inhibiting the reduction of hydrogen at high current densities. The pyrophosphate bath may be operated over a wide range of concentrations, temperatures, and current densities.

Table XIII shows the compositions and operating conditions most commonly used for pyrophosphate copper deposition. Diggin (20) reported that electroforms deposited to thicknesses of 0.5 inch or greater are smooth and bright. Pitting can be a problem when only cathode movement is used for agitation. This is not a problem with air agitated baths. Wetting agents can be used and the bath has excellent tolerance to impurities.

Dini, Johnson, and Helms (22) investigated the influence of bath constituents and operating conditions on the throwing power of copper pyrophosphate baths. They used the commercial bath described in Reference (21). It is pointed out in this paper that a low ratio of pyrophosphate to copper (6.5:1 or less) causes banded deposits, lowers throwing power, and results in a bluish-white opalescence in the bath and on the anodes. Ratios of 8.5:1 and higher supposedly decrease the bright plating range and promote formation of orthophosphate. Orthophosphate is claimed to be beneficial in promoting anode corrosion. It forms from hydrolysis of pyrophosphate and has no harmful effects until the concentration reaches 75 to 100 grams per liter (13 - 15 oz/gal). Ammonia must be added since it is lost by volatilization. Ammonia is replaced by:

1) Adding 323 ml of ammonium hydroxide (29%) per square meter of bath surface per day.

2) By chemical analysis

3) By additions until the faint odor of ammonia is detected.

Dini (2) also evaluated the throwing power of copper pyrophosphate in comparison with fluoborate and sulfate deposits. He found the throwing power of pyrophosphate to

TABLE XIII

COMPOSITION AND OPERATING CONDITIONS FOR

COMMERICAL COPPER PYROPHOSPHATE ELECTROLYTES (9)

	Reference (9)		Reference (21)		Reference (20)	
Compositions:	g/l	oz./gal.	g/l	oz./gal.	g/l	oz./gal.
Copper Metal	22 - 38	3 - 5	18 - 30	2.5 - 4	33.75	4.5
Pyrophosphate	150 - 250	20 - 33	As required for ratio to copper		335	45
Nitrate	5 - 10	0.67 - 1.33	0.37 - 2.25	0.05 - 0.3	2.5 ml/1 of ammonium hydroxide	
Operating Conditions:						
pH	8.2 - 8.8		8.0 - 8.5		8.1 - 8.6	
Ratio Pyrophosphate to Copper	7.0 - 8.0:1		7.4 - 8.0:1		5.5 - 7.0:1	
Temperature	50 - 60°C (122 - 140°F)		46.1 - 57.2°C (115 - 135°F)		54 - 60°C (130 - 140°F)	
Cathode Current Density	1 - 8 A/dm.^{2} (9.3 - 74 A/ft.^{2})		2.16 - 3.24 A/dm.^{2} (20 - 30 A/ft.^{2})		1.1 - 8.6 A/dm.^{2} (10 - 80 A/ft.^{2})	
Anode Current Density	1 - 8 A/dm.^{2} (9.3 - 74 A/ft.^{2})		2.7 - 5.4 A/dm.^{2} (25 - 50 A/ft.^{2})		1.6 - 4.9 A/dm.^{2} (20 - 45 A/ft.^{2})	
Current Efficiency	Approximately 100%				100%	
Anode-Cathode Ratio	1:1 to 2:1					
Agitation	1 - 1.5 ft.^{3} of air per minute per ft.^{2} of solution surface		1.5 ft.^{3} of air per minute per ft.^{2} of solution surface		Air preferred, cathode movement at lower current densities	
Filtration	Continuous or occasional batch treatment		Continuous at 2 to 4 tank volumes per hour		Continuous	
Anodes	Electrolytic copper sheet, rolled electrolytic copper, or OFHC copper. Bags are not desired.		OFHC cast or rolled phosphorized. Bags are not desired.		OFHC preferred	

be superior to the other baths, but internal stress was high at 9,400 psi (tensile).

Lamb, Johnson and Valentine (5) included deposits from the pyrophosphate bath in their extensive study of the properties of electrodeposited copper. Their bath formulation and mechanical property data are shown in Table XIV.

Diggin (20) reported mechanical properties for copper pyrophosphate deposits as follows:

Hardness	150 to 200 (Diamond Pyramid)
Stress	10,000 psi compressive at 40 A/ft^2 up to 0.001 inch thick deposit
Tensile Strength	60,000 psi
Elongation	10% at break in massive deposit

These values evidently represent deposits from a bath with an addition agent since similar results were reported by Greenwood (23) for a bath containing such agents.

Lamb, Johnson, and Valentine (7) determined the thermal properties of copper pyrophosphate deposits. Their test data is shown in Table XV. The only property significantly affected in the ranges of bath temperature, currently density, and agitation studied was internal stress. This was changed from slightly compressive to slightly tensile by raising current density. The microstructure showed large columnar crystals with very fine substructure. The fatigue strength of pyrophosphate copper deposits was higher than for any other non-additive bath with the exception of cyanide copper using periodic reverse current. The fatigue properties were better than annealed wrought copper and almost equal to half hard copper. The soft-type deposits (sulfate, fluoborate, and pyrophosphate - all without additives) which at low temperature 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 elongation. The ductility of pyrophosphate is significantly higher at 325°C.

Use of copper pyrophosphate in electroforming aerospace hardware has been reported by Missel and Shaheen (24). A procedure is described in which a copper helical antenna was electroformed on a conductive epoxy base at Lockheed Missiles and Space Company, Sunnyvale, California. The bath copper content ranged from 3.5 to 4.9 oz/gal with a pyrophosphate to copper ratio of 7 to 8:1. No additives were used and the bath temperature was controlled to 120 ± 3°F. Mechanical properties were not reported.

TABLE XIV

ELECTROLYTE COMPOSITION AND DEPOSIT MECHANICAL PROPERTIES FOR A COPPER PYROPHOSPHATE ELECTROLYTE (5)

Bath Composition and Operating Conditions:

	g/1	oz./gal.
Copper Pyrophosphate, $Cu_2P_2O_7 \cdot 3H_2O$	90	12
Potassium Pyrophosphate, $K_4P_2O_7$	350	47
Potassium Orthophosphate	80	11
Potassium Nitrate	15	2
Ammonia, Concentrated	2 ml./1	0.25 fl. oz./gal.
Ammonia, Replenishment	1 ml./1/day	
P_2O_7/Cu, wt. ratio	7.2	
pH (electrometric)	8.5	

Mechanical Properties of Deposits:

Bath Temp. °C	Current Density A/dm.^{2}	Current Density A/ft.^{2}	Agitation of Bath	Tensile Strength kpsi	Yield Strength kpsi	Elongation in 2 inches, percent	Harndess, KHN 200g. load, Kg/mm.^{2}	Internal Stress psi*
50	2	18.6	Air Agitation	38	20	39	83	-1,600
50	4	37	Mech. Agitation (0.008" thick)	42	23	23		
50	4	37	Mech. Agitation (0.016" thick)	40	22	31	90	
50	4	37	Air Agitation	40	22	33		1,700
50	4	37	Viotent Air + Mechanical	41	23	35	92	
60	4	37	Air Agitation	39	20	39	80	-1,900

* Positive values indicate tensile stress. Negative values are compressive stress.

TABLE XV

EFFECTS OF ANNEALING ON PROPERTIES OF COPPER PYROPHOSPHATE DEPOSITS AND PROPERTIES AT LOW AND HIGH TEMPERATURES (7)

Bath Composition and Operating Conditions:

The bath composition was as shown in Table XIV. The electrolyte temperature was 50°C and the current density was 2 A/dm.^{2} (18.6 A/ft.^{2}).

Physical Properties Before and After Annealing:

	As Deposited	Annealed 150°C, 2 hrs.	Annealed 325°C, 15 min.	Annealed 500°C, 15 min.
Tensile Strength, kpsi (MN/m.^{2})	38 (262)	38 (262)	36 (248)	31 (214)
Yield Strength, kpsi (MN/m.^{2})	20 (138)	18 (124)	15 (104)	8 (55)
Elongation in 2 inches, %	39	42	46	56
Density at 25°C (g/cm.^{3})	8,926			8,926
Hardness, KHN, 200g, load, Kg/mm.^{2}	83	84	75	60
Elastic Modulus (10^{-6} psi)	17			14

Linear Thermal Expansion (x 10^{-6} = parts/unit length/°C)
Temperature Range 20 - 200°C 16.7
Temperature Range 20 - 400°C 17.5

Mechanical Properties at High and Low Temperatures:

	Pulled at -78°C	Pulled at 150°C	Pulled at 325°C
Tensile Strength, kpsi (MN/m.^{2})	49 (338)	29 (200)	16 (110)
Elongation in 2 inches, %	39	47	25

G. COPPER CYANIDE SOLUTIONS

Mohler provides a useful summary of copper-cyanide solutions in Reference (10). The cyanide baths consist of three types: 1) plain copper cyanide - low efficiency, 2) Rochelle copper cyanide - medium efficiency, and 3) high metal copper cyanide - high efficiency. The first two types of baths have good throwing and covering power. The high metal, high efficiency bath can produce higher plating rates with 100 percent anode and cathode efficiencies. It is also able to produce thicker deposits, but the throwing power is less, and additives are essential to consistent performance. Typical make-up, average compositions and operating data are shown for these electrolytes in Table XVI.

Most cyanide electrolytes are incapable of producing thick electroforms of good surface quality (8). Mohler (10) reports that the plain cyanide baths are used to produce deposits from 0.00001 to 0.0001 inch thick. The Rochelle bath is used to deposit thicknesses up to 0.0005 inch. The high efficiency bath is normally used to build-up thicknesses to 0.002 inch. Thicker deposits are possible using periodic reverse current in the high efficiency bath. The high efficiency bath can be operated with or without Rochelle salt.

Most copper cyanide baths operate at low cathode efficiency and the bath becomes unstable over a period of time (25). Operating these baths within critical ratios of sodium cyanide normality to copper ion normality can improve bath stability. Safranek (26) reports that high strength copper deposited from cyanide solutions has higher ductility than copper of comparable strength from sulfate baths with additives. This data is based on thick copper sulfate deposits and thin cyanide deposits (0.0016 - 0.002 inch thick). He advised that thicker cyanide deposits have decreased strength.

Graham and Lloyd (27) investigated stress in copper cyanide deposits. Their standard bath for this study contained copper ion (4 oz/gal), Rochelle salts (0.8 oz/gal), and sodium carbonate (4 oz/gal). The bath pH was 12.5, the current density was 20 amp/ft^2, and the temperature was 160°F. Cathode rod agitation was used and the cathode efficiency was 87.3 percent. Under these conditions, the internal stress was 8,700 psi tensile. Use of periodic reverse current resulted in a tensile stress of 11,600 psi and the cathode efficiency was lowered. An increase in current density or a decrease in temperature reduced cathode efficiency and raised tensile stress. Omitting Rochelle salt decreased the tensile stress to 6,400 psi. With Rochelle salt present, addition of potassium thiocyanate slightly increased cathode efficiency and made the stress compressive (-4,000 psi). With 2 oz/gal of potassium thiocyanate and no Rochelle salt, the cathode efficiency was 95.3 percent and the stress was compressive at -4,700 psi.

Lamb, Johnson, and Valentine (5) included copper cyanide deposits in their investigation of electrodeposited copper. They stated that it was difficult to get uniform thickness of deposits from top to bottom as related to position of the cathode in

TABLE XVI

TYPICAL MAKE-UP AND OPERATING LIMITS

FOR THE COPPER CYANIDE ELECTROLYTES (10)

	Plain Cyanide	Rochelle Cyanide	High Efficiency
Typical Make-up and Average Composition Data:			
Copper Cyanide, oz./gal.	2	3.5	10
Sodium Cyanide, oz./gal.	3	4.6	12.4
Sodium Carbonate, oz./gal.	2	4	-
Sodium Hydroxide, oz./gal.	-	0.5	4
Rochelle Salt, oz./gal.	-	6	-
Free Sodium Cyanide, oz./gal.	0.8	0.8	1.4
Temperature, °F	130	140	160
Cathode Current Density, Amp/ft.^{2}	20	40	60
Anode Current Density, Amp./ft.^{2}	7	15	25
Cathode Efficiency, %	25	40	100
Anode Efficiency, %	100	60	100
Operating Limits:			
Copper Cyanide, oz./gal.	2.0 - 3.5	3.0 - 4.0	9 - 11
"Free" Sodium Cyanide, oz./gal.	0.7 - 1.4	0.5 - 1.0	0.5 - 1.5
Sodium Carbonate, oz./gal.	2.0 - 8.0	2 - 8	0 - 12
Sodium Hydroxide, oz./gal.	-	-	3 - 5
Rochelle Salt, oz./gal.	-	4 - 8	-
Temperature, °F	70 - 90	140 - 150	160 - 180
Cathode Current Density, Amp/ft.^{2}	5 - 10	30 - 40	30 - 60
pH	11.0 - 12.2	12.2 - 12.8	-

cyanide baths. Thickness varied about ±10 percent. Thick deposits potentially applicable to electroforming applications could only be produced from a few electrolytes as follows:

	Bath Symbol CN-8 g/l	oz/gal	Bath Symbol CN-9 g/l	oz/gal
Copper Cyanide	75	10	75	10
Free Potassium Cyanide	10	1.3	22.5	3
Potassium Hydroxide	40	5.4	22.5	3
Potassium Thiocyanate*	2	0.27		
Proprietary Agent**			Agent B	
pH	13.6			
Temperature °C	80		80	
Current Density A/dm^2	4 - 8		4 - 6	
A/ft^2	37 - 75		37 - 55	

* Thiocyanate only used for selected sample plating
** Proprietary agent was of the selenium type

The mechanical properties obtained are shown in Table XVII. The tensile strengths obtained are excellent when periodic reverse plating is used. Elongation is low in comparison with pyrophosphate,sulfate, and fluoborate deposits produced by these same investigators. Internal stress is high in comparison with deposits from other electrolytes. Additional data (7) indicates that cyanide deposits rapidly lose strength on exposure to temperatures of 150°C or higher. For the specimen plated from Bath CN-8 with potasium thiocyanate and periodic reverse plating, the elongation after annealing (500°C) was good (39 percent in 2 inches), but when tested at temperature (325°C) the elongation in 2 inches was only 7 percent. The electrolyte temperature of 80°C required to produce these properties presents a formidable problem in electroforming regenerative chambers because of the thermal expansion and danger of softening the wax fillers used in the coolant passages during shell fabrication.

H. ELECTROLYTE SELECTION

The choice of electrolyte is based on the mechanical and physical properties obtainable in the deposit when compared with similar data for wrought copper in the annealed condition. This includes performance at elevated temperatures as well as normal room temperature. Such evaluation is critical since the deposits must be capable of being brazed or welded as secondary fabrication operations in thrust

TABLE XVII

MECHANICAL PROPERTIES FOR COPPER DEPOSITS FROM HIGH EFFICIENCY CYANIDE ELECTROLYTES (5)

Bath Symbol	Remarks*	Bath Temp., °C	Current Density A/dm.^{2}	Current Density A/ft.^{2}	Tensile Strength kpsi	Yield Strength kpsi	Elongation in 2 inches percent	Internal Stress psi
CN-8	Mech. Agitation	80	4	37	37			4,500
	Air Agitation	80	4	37	35			
	Nitrogen Agitation	80	4	37	35			
	Mech. Agitation	80	6	55	40			4,500
	Mech. Agitation	80	8	75	39			3,900
	PR, Cycle 15-5 sec	80	6	55	61			4,600
	PR, Cycle 15-5 sec	80	6	55	64	38	12	
	PR, Cycle 15-5 sec	80	8	75	60			
	Tiocyanate with PR, Cycle 1515-sec	80	6	55	86	57	10	5,100
	Thiocyanate with PR, Cucle 30-10 sec.	80	6	55	79	46	10	
CN-9	Mech. Agitation	80	4	37	26			11,000
	Mech. Agitation	80	4	37	28	12	22	
	Mech. Agitation	80	6	55	24			
	PR, Cycle 15-5 sec	80	6	55	66			

* PR indicates periodic reverse current; the cycle lists time for forward and reverse plating respectively.

chamber manufacture. The type and magnitude of residual stress is important in selection of the electrolyte because tensile stresses are known to decrease fatigue strength of the basis metal (4) (7). High residual stresses in the initial deposit become a serious problem in electroforming the outer shell of thrust chambers due to the fact that the bridging of an electrodeposit over the thin conductivizing layer on wax-filled coolant channels can be easily warped, cracked, or peeled to produce structural defects and porosity.

Shortcomings of the bright leveling acid sulfate and copper cyanide electrolytes have been presented. The additives are difficult to control in the bright acid bath and they often lead to undesireable permanent expansion or density changes (indicative or porosity) upon heating. The cyanide bath product shows generally higher internal stress than copper from other electrolytes. Where high strength is achieved with the high efficiency, periodic reverse current bath, ductility is low. For these reasons, only the conventional acid sulfate, acid sulfate with periodic reverse, fluoborate, and pyrophosphate baths are further considered for electroforming copper for thrust chamber applications.

Table XVIII summarizes the significant test results for the various electrolytes suitable for copper electroforming of thrust chamber shells.

Test results at room temperature indicate a similarity between mechanical properties of the Rocketdyne acid sulfate copper (proprietary additive for oxygen control), the acid sulfate with periodic reverse current (Bath C2-H3), and the pyrophosphate copper. These results compare favorably with those for annealed wrought copper.

In Table XIX, the thermal properties of these deposits were compared. At all test temperatures, the best combination of tensile strength and ductility was shown by pyrophosphate deposits. Although data were not available for a wide range of test temperatures or annealing conditions, the Rocketdyne copper sulfate deposits (from a proprietary oxygen control additive bath) and deposits from copper sulfate baths with periodic reverse current appeared nearly equal to pyrophosphate deposit in thermal stability and strength. Conventional copper sulfate and fluoborate deposits showed low values of elongation when tested at 325°C. From the elastic modulus data available on deposits "as-deposited" and after annealing at 500°C, the pyrophosphate copper was superior. The fatigue strength of pyrophosphate deposits was superior to that of conventional copper sulfate, fluoborate, or wrought annealed copper.

Pyrophosphate electrolytes are recommended for electroforming copper outer shells on regeneratively cooled thrust chambers. The Rocketdyne electrolyte deposits and periodically reversed copper sulfate deposits are also considered to be of high quality and suitable for this application. The product of these electrolytes appears similar in microstructure and they are chemically similar in low impurity content level.

TABLE XVIII

COMPARISON OF THE PROPERTIES OF COPPER DEPOSITS FROM THE ACID SULFATE, ACID SULFATE (PR), FLUOBORATE, AND PYROPHOSPHATE BATHS

	Bath Type	Bath Temp. °C	Current Density A/ft.^{2}	Tensile Strength kpsi	Yield Strength kpsi	Elongation in 2 inches percent	Internal Stress psi	Density at 25°C g/cm.^{3}	Data From Table No.
Acid Sulfate:	Cu2-H2	30	18.6	32	11	39	-	8.925	II
	Cu2-H3	20	18.6	37	15	41	2,000	8.926	II
		40	75	37	15	44	2,600	8.926	II
	Cu3-H3	20	37	32	12	42	3,100	8.925	II
	BAC	38	30	32	13	26	-	-	III
	Rocket-dyne	32	20	42-47	26-29	27-30	-	-	V
Acid Sulfate, PR:	Cu2-H3	30	37	43	20	26	4,100	8.925	Ref. (5)
	Avco Corp.	43	40	32	14.5	-	-	8.940	X
Fluoforate:	High Copper	49	300	29.5	20	14.5	-	-	XI
	F-1	30	75	37	16	31	700	8.926	XII
	F-2	30	75	36	15	31	800	8.926	XII
Pyrophosphate:	Lamb, et.al.	50	18.6	38	20	39	-1,600	8.926	XIV
		50	37	40	22	33	1,700	-	XIV
		60	37	39	20	39	-1,900	8.926	XIV
Commercial Copper:	Annealed			31	10	45		8.92 - 8.93	Ref. (7)
	Half Hard			45	38	14			
	Hard			54	48				

TABLE XIX

COMPARISON OF PROPERTIES OF COPPER DEPOSITS AFTER

HEAT TREATMENT OR DURING THERMAL TESTING

Bath Type	Bath Temp. °C	Current Density A/ft.^{2}	Tensile Strength, kpsi Annealed °C 150	325	371	500	Yield Strength, kpsi Annealed °C 150	325	371	500	Elongation in 2 in., % Annealed °C 150	325	371	500
Acid Sulfate														
Cu2-H2	30	18.6	31	31	-	30	9	10	-	5	41	40	-	44
Acid Sulfate, PR														
Avco. Corp.	43	40	-	-	32	-	-	-	12.3	-	-	-	38.5	-
Fluoborate														
F-1	30	75	35	33	-	28	14	13	-	3	33	29	-	41
Pyrophosphate														
Lamb, et.al	50	18.6	38	36	-	31	18	15	-	8	42	46	-	56
Wrought Copper (Annealed)	-	-	-	-	-	31	-	-	-	10	-	-	-	45

Bath Type	Tensile Strength, kpsi Pull at Temp. °C -78	150	325	371	Elongation in 2 in., % Pulled at Temp. °C -78	150	325	371	Elastic Modulus* x 10^{-6} psi As Deposited	Annealed 500°C	Fatigue Strength* σ, kpsi 10-6 Cycles	10-7 Cycles
Acid Sulfate												
Cu2-H2	38	20	11	-	41	13	7	-	14	12	13	11
Rocketdyne	-	-	-	13-14	-	-	-	17-29	-	-	-	-
Fluoborate												
F-1	44	28	14	-	33	22	8	-	13	6	16	13
Pyrophosphate												
Lamb, et.al	49	29	16	-	39	47	25	-	17	14	22	17
Wrought Copper												
Annealed	-	-	17	-	-	-	18	-	-	13-15	15	12

* From Reference (7).

IV. NICKEL ELECTROLYTES

A. ELECTROLYTE TYPES AND RANGE OF PROPERTIES

Nickel can be electroformed to produce a wide range of hardnesses, densities, tensile strengths, and internal stresses by proper selection of the electrolyte and operating conditions. Diggins (20) states that the choice of electrolyte and composition is dictated by the mechanical properties desired in the deposit, and to a lesser degree by such considerations as smoothness of deposit, tendency to form nodules and trees, stress in the deposit, permissible speed of plating, and ease of control of the process.

In electroforming the outer shells on regeneratively cooled thrust chambers, the factors of prime importance are the mechanical properties, thermal stability of the deposits, stress in the deposits, and capability of the electrolyte to be controlled to produce consistently uniform mechanical properties with freedom from porosity and laminations.

Diggins advised that there are six basic types of nickel baths being used for non-decorative nickel deposits. They are: (1) Watts (sulfate) bath with or without addition agents, (2) hard nickel, (3) chloride, (4) cobalt-nickel, (5) fluoborate, and (6) sulfamate. The cobalt-nickel bath is omitted from the following survey for reasons of deposit application (hardness requirements in the electrotyping industry) and the complexity of the bath.

Reference (28) summarizes the various nickel electrolytes by typical composition and approximate mechanical properties of thick nickel deposits. For the electrolytes under consideration for electroforming, this data is summarized in Table XX. For discussion purposes, the chloride-free and chloride-sulfate baths are grouped under Watts electrolytes. Hard sulfamate and hard Watts baths are included in the hard nickel bath group.

B. THE WATTS TYPE ELECTROLYTES

Watts baths have historically been the primary solutions for nickel plating and electroforming. These solutions contain nickel sulfate, nickel chloride, and boric acid. The nickel sulfate to nickel chloride ratio by weight in a true Watts type solution usually varies between 7.5:1 and 3.5:1. The function of each constituent is described by Pinner, Knapp and Diggin (9) as follows:

(1) Nickel Sulfate - Provides the nickel ion necessary for reduction at the cathode. The sulfate salt is highly soluble and readily available commercially.

(2) Nickel Chloride - Supplies chloride ion to improve anode dissolution by reducing polarization. It increases bath conductivity and throwing power.

TABLE XX

A SUMMARY OF NICKEL ELECTROLYTES BY COMPOSITION AND APPROXIMATE MECHANICAL PROPERTIES OF DEPOSITS (28)

Composition (oz./gal.)

Process	Nickel Sulfate	Nickel Sulfamate	Nickel Chloride	Boric Acid	Other	Equiv. Nickel Concentration
All Chloride			40	4		10.0
Chloride-Free	44			4		9.3
Chloride-Sulfate	25		21	5		11.5
Electrotyping		55	1.5	5		10.0
Fluoborate				4	Ni Fluoborate 40	10.0
Hard Sulfamate		33	1	4	Stress Reducer	6.0
Hard Watts	35		6	4	Stress Reducer	8.0
Sulfamate		60	1	5		8.7
Sulfamate (Conc.)		80	0.7	5.4		14.6
Watts	40		8	4		10.4

Mechanical Properties

Process	Plating Conditions			Tensile Strength kpsi	Elongation in 2 inches, percent	Hardness DPN	Internal Stress psi
	Temp. °F	pH	Current Density A/ft.^{2}				
All Chloride	130	2.0	50	100	14	240	50,000
Chloride Free	130	1.5	40	70	28	170	17,000
Chloride-Sulfate	110	4.0	120	70	16	200	8,000
Electrotyping	130	2.7	30.	58	30	150	20,000
Fluoborate	130	5.0	60	130	6	470	-5,000
Hard Sulfamate	122	5.0	50	170	2	350	0
Hard Watts	130	3.0	50	75	20	230	32,000
Sulfamate	140	4.0	50	90	10	200	4,000
Sulfamate (Conc.)	140	4.0	200	70	14	170	4,000
Watts	130	3.0	50	60	28	150	20,000

(3) Boric Acid - Provides a buffering action to control pH in the cathode film to minimize cracking and pitting of the deposits. It also helps maintain pH within the operating range of the bath with best buffering in the pH range of 5 to 6.

A more detailed description of the bath chemistry can be found in Reference (29).

The literature failed to reveal any use of Watts type baths to electroform thrust chambers or nozzles for aerospace or wind tunnel applications. Savage and Bommerscheim (30) reported the use of Watts solution to electroform supersonic pitot-static tubes. Diggins (20) reported mechanical properties typical of a low pH Watts bath. Reference (28) provides data for deposit properties from pH 2.5 - 4.0 Watts baths. This information is summarized in Table XXI.

Reference (31) indicates that best ductility of Watts bath deposit occurs at a bath temperature of 130°F. Mechanical strength from this bath is relatively independent of temperature, current density, and pH, but increases with increasing nickel content or chloride content (which also increases stress).

Bell Aerospace Company (32) has used the Watts bath in connection with the investigation of dispersion strengthened alloys. For a bath with a nickel metal content of 11.5 oz/gal., 6.2 oz/gal. of nickel chloride, 4.7 oz/gal. of boric acid, a pH of 1.5 and a plating temperature of 123°F, the following properties were obtained.

Ultimate Strength, kpsi	60
Yield Strength, kpsi	35
Elongation in 2 inches, %	33

Addition of 25 cc of 30% hydrogen peroxide to this eight gallon bath increased the ductility of the deposit as noted below:

Ultimate Strength, kpsi	58
Yield Strength, kpsi	34
Elongation in 2 inches, %	38

The hydrogen peroxide was added to minimize pitting from hydrogen which is more pronounced at low pH levels in Watts baths (33).

Removal of chloride from the Watts type bath is occasionally practiced when it is necessary to plate interior surfaces of long tubes using insoluble lead anodes (28). The presence of chlorides must be avoided to prevent anode corrosion and lead contamination of the deposit. Such a bath is called the "chloride free" or nickel sulfate bath. The Watts bath can be modified by increasing the ratio of chloride to sulfate to produce the chloride-sulfate bath. This bath has higher conductivity and throwing power than the conventional Watts bath but has the disadvantage of higher internal stress.

TABLE XXI

COMPOSITION, OPERATION, AND DEPOSIT MECHANICAL

PROPERTIES FROM TYPICAL COMMERICAL WATTS BATHS

Composition and Operating Conditions	Reference (30)	Reference (20)	Reference (28)
Nickel Sulfate, oz./gal.	45	44	40
Nickel Chloride, oz./gal.	6	6	8
Boric Acid, oz./gal.	5	5	4
pH	2.0 - 2.3	1.5 - 4.5	3
Temperature, °F	130 - 135	115 - 140	140
Current Density, A/ft.^{2}	30	25 - 100	50
Antipit Agent	Hydrogen Peroxide		
Mechanical Properties at Room Temperature			
Tensile Strength, kpsi	52 - 53	51	55 - 60
Yield Strength, kpsi	No data	No data	No data
Elongation in 2 inches, %	36	30	25 - 30
Hardness	No data	140 - 160 Vickers	150 DPN
Stress, psi	No data	18,000 Tensile	No data
Mechanical Properties at Elevated Temperature			
Test Temperature, °F	1,000	No data	No data
Tensile Strength, kpsi	32 - 34		
Yield Strength, kpsi	No data		
Elongation in 2 inches, %	33 - 36		

Brenner, Jennings, and Zentner (34) investigated the physical properties of the all-sulfate, Watts type, and chloride-sulfate baths. The solution compositions and room temperature properties of deposits are shown in Table XXII.

It is noted that the internal stress in these deposits was tensile and of high value. This is in agreement with stress data reported in other literature (4), (20), (28) for the all-sulfate, Watts, and chloride sulfate baths. It is also noted (34) that chloride content in this series of baths has an effect on tensile strength and elongation. When about 25 percent of the total nickel in the bath is present as the chloride salt, tensile strength is lowest and elongation highest. Tensile strength and elongation properties of all-sulfate bath deposits are roughly equivalent to those in deposits from baths with 50 percent of the nickel present as the chloride salt (chloride-sulfate type). The concentration of nickel in the bath showed significant effects on mechanical properties. Lowest tensile strength and highest elongation occurred from baths containing about 8 oz./gal. of nickel (as metal) within the pH range of 3.0 to 5.0.

Sample and Knapp (35) investigated the thermal properties of Watts bath nickel deposits from a solution composed of:

	g/1	oz./gal.
Nickel Sulfate	300	40
Nickel Chloride	60	8
Boric Acid	37.5	5

Their test results and those of Brenner (34) are shown in Table XXIII.

Safranek (4) has presented data for the coefficient of thermal expansion of Watts bath deposits:

Temperature Range, °C	Expansion Coefficient 10^{-6}/°C
20 to 200	14.6
20 to 400	16.2
20 to 600	16.8
20 to 800	17.2
20 to 1000	17.2

C. BRIGHT AND SEMI-BRIGHT WATTS TYPE BATHS

Bright and semi-bright Watts type baths contain addition agents to produce an as-deposited lustrous surface (9). Most baths employing these additives are proprietary. The brighteners fall into two classes. The first class of brighteners produce bright plate but are unable to build luster. These brighteners are used in relatively high

TABLE XXII

BATH COMPOSITIONS AND PROPERTIES OF NICKEL DEPOSITS FROM THE ALL SULFATE, WATTS TYPE, AND CHLORIDE-SULFATE BATHS (34)

Bath Symbol	Bath Type	Nickel Sulfate g/1	Nickel Sulfate oz./gal.	Nickel Chloride g/1	Nickel Chloride oz./gal.	Boric Acid g/1	Boric Acid oz./gal.
S	All Sulfate	280	38	0	0	30	4
S3-Cl	Watts Type	210	28	60	8	30	4
S3-Cl-1N	Watts Type	105	14	30	4	30	4
S3-Cl-4N	Watts Type	420	47	120	16	30	4
S1-Cl	Chloride-Sulfate	140	19	120	16	30	4
S1-C3	Chloride-Sulfate	70	9.5	180	24	30	4

Bath Symbol	Bath Temp., °C	Current Density A/dm.^{2}	pH	Tensile Strength kpsi	Elongation in 2 inches percent	Stress psi	Density gm/cm^3	Young's Modulus psi x10^6
S	30	5	1.5	81	14	-	-	-
	55	5	1.5	82	20	20,000	8.91	-
	55	5	3.0	66	20	17,000	8.92	23.5
	55	5	5.0	104	6	-	8.92	23.0
	80	5	1.5	60	18	-	-	-
S3-Cl	30	2	5.0	75	18	-	-	-
	30	5	1.5	105	11	-	-	-
	30	5	3.0	75	15	35,000	-	23.8
	30	5	5.0	72	19	-	-	-
	40	5	3.0	75	19	-	-	-
	55	1	3.0	77	27	30,000	-	23.6

TABLE XXII

(continued)

Bath Symbol	Bath Temp., °C	Current Density A/dm.^{2}	pH	Tensile Strength kpsi	Elongation in 2 inches percent	Stress psi	Density gm/cm^3	Young's Modulus psi x10^6
S3-C1 (con't)	55	2	1.5	74	22	-	-	-
	55	2	3.0	56	23	27,000	8.92	-
	55	5	1.5	67	28	24,000	-	-
	55	5	3.0	56	28	17,000	8.91	24.1
	55	5	5.0	59	25	25,000	-	23.7
S3-C1-1N	55	5	3.0	65	18	-	8.90	-
	55	5	5.0	64	19	20,000	8.91	19.7
S3-C1-4N	55	5	3.0	82	8	-	8.91	-
	55	5	5.0	116	2	28,000	8.88	27.2
S1-C1	55	2	3.0	84	18	-	-	-
	55	2	5.0	93	3	-	-	-
	55	5	1.5	73	23	28,000	-	-
	55	5	3.0	74	20	31,000	8.91	25.1
	55	5	5.0	104	8	34,000	8.91	28.2
	80	5	3.0	83	5	-	-	-
S1-C3	55	2	3.0	103	8	-	-	-
	55	5	3.0	92	11	38,000	8.90	20.8
	55	5	5.0	126	7	37,000	-	-
	80	5	3.0	90	4	-	-	-

TABLE XXIII

MECHANICAL PROPERTIES OF ALL-SULFATE, WATTS-TYPE, AND CHLORIDE-SULFATE BATH DEPOSITS AFTER ANNEALING (34) AND WATTS DEPOSITS AT VARIOUS TEST TEMPERATURES (35)

A. Annealed Mechanical Properties (34):

Bath* Symbol	Bath Temp., °C	Current Density A/dm.^{2}	pH	Tensile Strength, kpsi As Deposited	Tensile Strength, kpsi Annealed 400°C	Tensile Strength, kpsi Annealed 1000°C	Elongation in 2 inches, % As Deposited	Elongation in 2 inches, % Annealed 400°C	Elongation in 2 inches, % Annealed 1000°C
S	55	5	1.5	82	77	38	20	22	14
S3-Cl	30	5	3.0	75	62	47	15	39	37
	55	5	1.5	67	58	39	28	35	25
	55	5	3.0	56	53	35	28	39	17
	80	5	3.0	78	71	36	28	27	23
S1-Cl	55	5	3.0	74	64	40	20	30	32
S1-C3	55	5	3.0	92	78	43	11	26	22
Nickel 200, Hot Finished and Annealed (36)						55-80			55-40

* - Refer to Table XXII for bath descriptions

B. Mechanical Properties at Various Test Temperatures (35):

Bath Type	Test Temperature °F	Test Temperature °C	Average Tensile Strength, kpsi	Average Yield Strength, kpsi	Average Elongation in 2 inches, %
Watts	-320	-196	85.1	40.3	48
	-100	-73	69.6	37.4	33
	Room	20	59.5	32.4	30
	400	204	48.5	No Data	25
	800	427	32.3	22.4	29
	120[illegible]	649	18.5	11.9	13
	1400	760	11.5	No Data	6
	1600	871	6.9	No Data	8

concentrations without interfering with ductility and coherence of the deposit. The second class of brighteners tend to produce brittle and stressed deposits. The second class of brighteners are used to produce luster.

The first class of brighteners have a = C-SO_2- molecular group in their structures. The second class of brighteners contains a wide variety of chemicals which include ions of metals with high hydrogen over-voltage in acid solutions, compounds of sulfur, selenium and tellurium, or unsaturated organic molecular groupings.

Leveling agents may also be present to produce smooth, level deposits. Such agents may be coumarin, acetylenic alcohols, and nitrogen containing aromatic compounds.

Reference (4) states that the high sulfur content of bright nickel deposits reduces their ductility and resistance to corrosion. The organo-sulfur compounds that contribute to brightness also refine grain size. Many of these additives result in compressive stresses in the deposit. A sulfur content of 0.01 percent, or higher, will increase strength, but a content of 0.02 percent, or more, causes notch sensitivity. The sulfur content in Watts-type nickel deposits is usually less than 0.005 percent. The bright baths with sulfur containing additives may contain 0.05 to 0.15 percent sulfur in the deposits.

Brenner (34) provides some mechanical property test data on deposits from a bright Watts bath, Table XXIV. These deposits undergo significant density changes upon exposure to temperature. The ductility is poor - especially after heat treatment.

D. ALL CHLORIDE SOLUTIONS

Greenwood (37) points out use of the all-chloride solutions to provide much faster plating speeds than possible with the Watts-type baths. However, the pH range is narrower than the Watts bath - frequent pH checks are required. The deposits are smoother than Watts type but more highly stressed. Diggin (20), Safranek (4), and Brenner (34) report compositions, operating conditions, and mechanical properties of deposits as shown in Table XXV.

Sample and Knapp (35) investigated the mechanical properties of the chloride bath deposits over a range of test temperatures as shown in Table XXVI.

Yang (38) found that the all-chloride bath will produce a deposit of nickel containing the face-centered-cubic and hexagonal-close-packed structures with current densities of over 0.2 A/dm^2. Bath pH had no effect on the structures obtained. At bath temperatures of 40°C, or higher, the hexagonal structure was not obtained. High hydrogen concentration in the deposit was associated with the hexagonal structure. Heating in vacuum at 600°C converted all hexagonal nickel to the normal face-centered-cubic.

TABLE XXIV

BRIGHT WATTS BATH COMPOSITION,

OPERATING CONDITIONS AND PHYSICAL PROPERTIES OF DEPOSITS (34)

Composition:	g/l	oz./gal.
Nickel Sulfate	210	28
Nickel Chloride	60	8
Boric Acid	30	4
Nickel Benzene-disulfonate	7.5	1
Reduced Fuchsin	5-10 mg./liter	

Operating Conditions and Tests Results:

Bath Temp., °C	Current Density A/dm.^{2}	Bath pH	Density (g/cm^3) As Deposited	Density Heat Treated 400°C	Density Heat Treated 1000°C	Tensile Strength, kpsi As Deposited	Tensile Strength Heat Treated 400°C	Tensile Strength Heat Treated 1000°C	Elongation in 2 in., % As Deposited	Elongation Heat Treated 400°C	Elongation Heat Treated 1000°C
55	2	3.5	8.88	8.89	8.85	170	29	25	2	1	5
55	5	3.5	8.86	8.86	8.88	212	35	29	5	0	3
55	10	3.5	8.87	8.89	8.85	233			3		

TABLE XXV

COMPOSITION, OPERATING CONDITIONS, AND MECHANICAL

PROPERTIES OF ALL CHLORIDE NICKEL BATHS (4) (20) (34)

Compositions:

	Reference (20) g/l	Reference (20) oz./gal.	Reference (4) g/l	Reference (4) oz./gal.	Reference (34) g/l	Reference (34) oz./gal.
Nickel Chloride	300	40	180	24	240	32
Boric Acid	30	4	36	4.8	30	4

Reference No.	Bath Temp., °C	Current Density A/ft.^{2}	pH	Tensile Strength kpsi	Yield Strength kpsi	Elongation in 2 inches percent	Internal Stress psi	Density g/cm.^{3}
(4)	60	37	3.0	108-124	92	8	No Data	No Data
(20)	40-70	25-100	5.4-5.8	98.9	No Data	21	40,000-50,000	No Data
(34)	30	46.5	3.0	88	No Data	14	41,000	No Data
	30	46.5	5.0	137	No Data	5	No Data	No Data
	55	9.3	5.0	132	No Data	4	No Data	No Data
	55	46.5	1.5	92	No Data	15	46,000	No Data
	55	46.5	3.0	102	No Data	14	42,000	8.90
	55	46.5	5.0	135	No Data	6	55,000	8.84*

* Density changed with heat treatment as follows:

Temperature, °C	Density, g/cm.^{3}
400	8.88
1000	8.23

TABLE XXVI

NICKEL DEPOSIT MECHANICAL PROPERTIES FROM THE ALL-CHLORIDE BATH AT VARIOUS TEST TEMPERATURES (35)

Bath Composition and Operating Conditions:

Nickel Chloride	300 g/1 (40 oz./gal.)
Boric Acid	37.5 g/1 (5 oz./gal.)
pH	3.0
Temperature	140°F
Current Density	40 A/ft.^{2}

Mechanical Properties:

Test Temperature, °F	-320	-100	Room	400	800	1200	1400
Test Temperature, °C	-196	-73	20	204	427	649	760
Tensile Strength, kpsi	154.1	134.5	116.0	89.3	30.1	8.7	6.6
Yield Strength, kpsi	101.2	92.8	91.5	71.8	17.8	No Data	No Data
Elongation in 2 inches, %	22	15	8	11	20	10	7

Thermal Expansion (Linear):

Temperature Range, °C	Mean Coefficient of Expansion microinches/inch/°C
21 to 187	11.6
187 to 446	15.2
446 to 678.5	15.9
678.5 to 914	36.5
21 to 914	20.3

Bell Aerospace Company has operated an all-chloride bath to investigate codeposition of dispersion strengthening particles. The deposits were internally stressed to such an extent that severe warping and edge cracking were experienced.

E. NICKEL FLUOBORATE ELECTROLYTES

Nickel fluoborate baths are simple to control and highly buffered - pH changes during operation are not rapid (9). Nickel fluoborate is highly soluble, making it possible to operate at greater nickel metal concentrations than in the Watts and chloride-sulfate baths. The fluoborate bath operates with high conductivity and good anode corrosion characteristics. The deposits are smooth, bright in color, and do not tend to form "trees" or nodules in high current density areas. The internal stress is lower than in deposits from the Watts bath.

Struyk and Carlson (39) presented several bath compositions, operating conditions, and mechanical properties for nickel fluoborate baths and deposits, Table XXVII. For baths of the medium nickel content defined in (39), Diggins (20) shows internal tensile stresses ranging from 16,000 to 26,000 psi.

Brenner (34) included nickel fluoborate deposits in his investigation of mechanical and other physical properties of electrodeposited nickel. Test data is shown in Table XXVIII. Information was lacking on elevated temperature properties of fluoborate nickel deposits.

F. HARD NICKEL BATHS

Greenwood (37) recognizes the hard nickel bath as applicable for electroforming hardware requiring arduous service conditions in which hardness of the deposit is important. The bath is operated in much the same manner as the Watts-type or all-chloride, except that the pH control is more critical. Deposits from this bath in the range of greatest hardness cannot be easily machined - grinding is required. Bath compositions are suggested by Greenwood (37) and Diggins (20); only the later reference gives corresponding property data, Table XXIX. Diggins points out that the tensile strength increases and ductility decreases with increase in pH and a decrease in temperature. The bath has disadvantages in that there is a high tendency to form nodules and trees and the internal stress is very high.

G. NICKEL SULFAMATE BATHS - NO CHLORIDE

The sulfamate electrolyte has several advantages over other nickel plating and electroforming solutions in that 1) low stress deposits are obtained, 2) the bath can operate at high current density at lower temperatures, 3) bath composition, control and maintenance is simple, 4) deposits of high purity are obtained, 5) a wide range of easily reproducible properties of the deposit are possible, 6) excellent grain structure and ductility are produced, 7) fatigue strength of the base metal is improved, and 8) the bath operates over a wide range of conditions (40).

TABLE XXVII

TYPICAL NICKEL FLUOBORATE BATH COMPOSITIONS, OPERATING CONDITIONS, AND DEPOSIT MECHANICAL PROPERTIES (39)

Bath Composition and Operating Variables:

	Low Nickel		Medium Nickel		High Nickel	
	g/l	oz./gal	g/l	oz./gal.	g/l	oz./gal.
Nickel Fluoborate	220	29.5	300	40	440	59
Nickel Metal	55	7.4	75	10	110	14.8
Free Fluoboric Acid	4-38	0.5-5	4-38	0.5-5	4-38	0.5-5
Free Boric Acid	30	4	30	5	30	4
pH (Colorimetric)	2.0 - 3.5		2.0 - 3.5		2.0 - 3.5	
Temperature, °F	100 - 170		100 - 170		100 - 170	

Mechanical Property Data:

Nickel Metal g/l	pH	Temp. °F	Current Density A/ft.^{2}	Tensile Strength kpsi	Yield Strength kpsi	Elongation in 2 inches percent	Vickers Hardness
110	2.0	130	75	54.8	40.3	20.4	164
75	2.5	130	75	74.5	52.7	16.6	183
75	3.5	130	75	69.8	44.6	13.0	159
55	2.5	130	75	81.4	58.3	14.4	204
55	2.5	90	50	99.6	83.0	10.4	270
55	3.5	90	50	100.5	84.0	13.5	243
55	4.0	90	50	106.6	79.3	7.6	280
55	3.5	90	25	120.8	66.2	5.5	305

TABLE XXVIII

NICKEL FLUOBORATE DEPOSIT PROPERTIES AND ELECTROLYTE COMPOSITION-OPERATING CONDITIONS (34)

Electrolyte Composition:

	g/1	oz./gal.
Nickel Fluoborate	232	31
Boric Acid	30	4

Properties of Deposits:

Bath Temp. °C	Current Density A/dm.^{2}	Bath pH	Density, g/cm^3 As Deposited	Density, g/cm^3 Heat Treated 400°C	Density, g/cm^3 Heat Treated 1000°C	Tensile Strength kpsi	Elongation in 2 inches percent	Stress psi	Young's Modulus kpsi$\times 10^6$
55	5	3.0	8.91	8.91	8.90	62	30	No Data	20.4
55	5	4.5	8.92	No Data	No Data	69	22	No Data	No Data
55	5	2.0	No Data			No Data		30,000	No Data

TABLE XXIX

COMPOSITION, OPERATING CONDITIONS, AND DEPOSIT MECHANICAL PROPERTIES OF THE HARD NICKEL ELECTROLYTE (20) (37)

Bath Composition and Operating Conditions:

	Reference (20)		Reference (37)	
	g/l	oz./gal.	g/l	oz./gal.
Nickel Sulfate	255	34	180	30
Ammonium Chloride	25	3.3	25	3.3
Boric Acid	30	4.0	30	4.0
pH	5.4 to 5.8		5.0 - 5.9	
Temperature	49 - 60°C (120 - 140°F)		45 - 60°C (110 - 140°F)	
Current Density	2 - 11 A/dm.^{2} (20 - 100 A/ft.^{2})		2.7 - 5.4 A/dm^2 (25 - 50 A/ft.^{2})	

Mechanical Properties:

	Reference (20)	Reference (37)
Hardness (Vickers)	350 - 500	No data
Tensile Strength, kpsi	152	
Elongation in 2 inches, %	5 - 8	
Stress (Tensile), psi	44,000	

The low stress and resulting improved fatigue performance has led to adoption of sulfamate baths for nickel electroforming of hardware in the aerospace industry - Barrett's (40) recommended electrolyte composition, operating conditions, and deposit mechanical properties are shown in Table XXX. Boric acid control is said to be not critical and can be analyzed infrequently. The pH is preferably checked daily. It will tend to rise slowly with use and may be quickly adjusted with additions of sulfamic acid.

Filtration should be continuous. Activated carbon treatment to remove organic impurities is not recommended on a continuous basis as it will remove any wetting agents present. Barrett states that anode corrosion is 100 percent efficient without the use of chloride ion to promote dissolution. He states that anodes must be 99 percent plus in purity and rolled depolarized or electrolytic sheet. (This is questionable since such electrolytes were found to be unstable without chloride unless sulfur depolarized anodes were used.)

Excessive internal stresses can cause peeling, cracking, crazing, warping, blistering, distortion, and even complete destructive failure of deposits. Stresses of a tensile nature can produce premature fatigue failure of the underlying metal. The effects of bath variables upon stress are summarized as:

pH - Stress has slight minimum at pH 4.0. It rises slowly at lower pH values and sharply at values above 6.0.

Metal Content - No appreciable effect on stress.

Temperature - Stress decreases with increase in bath temperature and increases with temperature drop - usually not more than a total of ±5,000 psi for the extremes.

Chlorides - Stress rises sharply and linearly with increasing chloride content - approximately 3,000 psi for each 10 percent increase of chloride as nickel chloride.

Current Density - Stress increases gradually with increase of current density.

Agitation - Agitation reduces the rate of increase of stress with increase of current density.

Boric Acid - No appreciable effect between 2.0 to 5.0 oz./gal.

Wetting Agent - Acts slightly as a stress reducer.

Asher and Harding (41) determined the mechanical properties of nickel sulfamate bath deposits. Their test samples were 0.010 to 0.015 inch thick. The bath composition, operating conditions, and deposit test results are shown in Table XXXI. (The elongation results in this work appear low for deposits from this type of electrolyte. It is possible that the use of depolarized nickel anodes at these current densities in the absence of chloride contributed to the problem). These investigators concluded that:

1) The strength decreases with increasing current density.

2) The elongation increases with increasing current density but at a gradual rate.

TABLE XXX

COMPOSITION, OPERATING RANGES, AND AVERAGE DEPOSIT MECHANICAL PROPERTIES FROM THE CHLORIDE-FREE SULFAMATE ELECTROLYTE (40)

Composition and Operating Conditions:	
Nickel Sulfamate, oz./gal.	60
Nickel Metal Content, oz./gal.	10.2
Boric Acid, oz./gal.	4
Anti-pit Agent, oz./gal.	0.05
Temperature Range, °F	100 - 140
pH Range	3.0 - 5.0
Density, °Baume'	29 - 31
Anodes	99% plus, rolled depolarized
Maximum Cathode Current Density	300 A/ft.^{2} at 140°F 150 A/ft.^{2} at 100°F
Agitation	Cathode bar movement or Solution circulation
Tank Voltage	6 - 9 volts
Anode Efficiency	100 percent
Cathode Efficiency	98 - 100 percent
Average Mechanical Properties:	
Hardness, Vickers	250 - 350
Tensile Strength, kpsi	90
Elongation in 2 inches, %	20 - 30
Internal Stress (Tensile), psi	500

TABLE XXXI

RESULTS OF ASHER AND HARDING (41) INVESTIGATION OF NICKEL SULFAMATE DEPOSIT MECHANICAL PROPERTIES

Bath Composition and Operating Conditions:

Nickel Sulfamate, oz./gal.	60
Boric Acid, oz./gal.	Saturated
Anti-pit	0.05 oz./gal.
Anodes	Depolarized nickel bagged in Dynel
Filtration	Continuous at 0.2 to 0.3 gallons per minute
Bath Volume	4.5 gallons
Agitation	Mechanical (Propellor)

Mechanical Properties of Test Samples:

Bath pH	Bath Temp. °F	Current Density A/ft.^{2}	Tensile Strength kpsi	Yield Strength kpsi	Elongation, % (gauge length not given)
3.5	100	18	67	44	22
		19	75	50	11
		30	63	44	18
		48	65	40	15
		65	70	45	16
3.5	120	14	98	70	4
		16	114	93	4
		19	108	83	4
		31	77	57	5
		66	100	76	8
		67	58	39	24
		86	91	64	10
3.5	140	24	104	76	3
		30	92	68	2
		33	100	80	2
		60	73	50	3
4.0	100	19	95	67	10
		27	98	62	5
		54	75	41	13
		70	113	65	6
4.0	120	12	110	No Data	3
		24	96	95	3
		62	85	65	4
4.0	140	21	103	87	2

3) The strength increases as the temperature increases to around 120°F and then decreases.

4) The ductility decreases rapidly with increasing bath temperature.

5) Raising the pH from 3.5 to 4.0 increases the strength at 100°F bath temperature but has little effect at 120 and 140°F.

Klingenmaier (42) and Knaap (43) investigated the effects of anode behaviour on the internal stress and mechanical properties of chloride-free sulfamate baths. Each investigator found that poor anode efficiency in the absence of chlorides in the bath promoted solution instability wherein a product identified as azodisulfonate formed. This product acts as a stress reducing agent leading to compressive stresses and higher sulfur content in the deposit. This would account for the low ductility noted in Asher and Hardings' data in Table XXXI. The ultimate solution to this problem was the use of sulfur depolarized anodes in place of depolarized nickel, cast nickel, or rolled nickel for sulfamate baths without chloride ion. Klingenmaier noted that sulfur depolarized anodes resulted in greater tensile stress in deposits than was found with depolarized nickel but the reduction of sulfur content was more desireable.

Reference (44) describes the experiences of Lockheed Missile and Space Company in electroforming nickel on ceramic parts required for missile and space applications. Nickel sulfamate was selected based on previous experience which indicated the deposits would afford excellent thermal shock protection and low internal stress as deposited. This bath was operated as follows:

Specific Gravity	28 - 33° Baume'
Boric Acid	45 g/1 (5.3 oz./gal.)
pH	3.0 - 3.6
Wetting Agent	Controlled with 3 inch and 5 inch rings for film holding
Temperature	53 - 56°C (127 - 133°F)
Current Density	30 - 50 A/ft^2
Filtration	Continuous
Agitation	Cathode Movement

No mechanical property data was given.

Rocketdyne Division of North American Rockwell (45) uses the nickel sulfamate electrolyte with no chloride to electroform the outer shells of regeneratively cooled thrust chambers. This deposit may be applied directly over the coolant passages or after a preliminary close-out of the channels with electroformed copper. Procurement requirements are placed on the nickel sulfamate concentrate used to make-up the electrolyte. No additives or brighteners are permitted. The chemical purity requirements are as follows:

pH	4.3 - 4.7
Nickel as metal	150 g/liter minimum
Sulfate ion	0.5 percnet by weight maximum
Ammonium ion	300 ppm maximum
Iron	6 ppm maximum
Copper	6 ppm maximum
Lead	1 ppm maximum
Zinc	6 ppm maximum
Chromium	1 ppm maximum
Chloride	100 ppm maximum

For newly formulated nickel sulfamate baths, Rocketdyne requires that the bath and deposits meet the requirements shown in Table XXXII (45). For electrodeposition of structural nickel closures, for thrust chamber coolant passages, Rocketdyne requires that the bath and deposits meet the requirements shown in Table XXXIII (46). The reference to SNAP (sulfamate nickel anti-pit) and SNAC (sulfamate nickel acid controller) in these tables and the impurity limits imposed on the sulfamate concentrate indicate that the Barrett sulfamate bath (Allied Kelite Division, The Richardson Company) is being used.

Rocketdyne (47) has determined the minimum expected properties of deposits from their sulfamate nickel bath, Table XXXIV. Some of their test data from Space Shuttle Main Combustion Chamber samples of electrodeposited nickel are shown in Table XXXV (48).

It is appropriate to mention that the sulfamate bath can be operated with stress reducing additives which impart a compressive stress in the deposits (10) (20). Such additives normally increase the sulfur content of the deposits (4) (8) (49) which contributes to reduced ductility, poorer notch sensitivity, and unsatisfactory performance at elevated temperatures. Such deposits would be inappropriate for use where welding or brazing would be required after electroforming.

H. NICKEL SULFAMATE BATHS WITH CHLORIDE

The literature revealed that most sulfamate electrolytes used to produce electrodeposits for engineering applications are operated with some nickel present as the chloride salt. The requirement that chloride be present is based on the types of anodes available for use. Without chloride ions or some other ion (e.g. - bromide) capable of dissolving the nickel anode at a suitably controlled rate, there is a tendency for the bath to

TABLE XXXII

ROCKETDYNE NICKEL SULFAMATE "NEW ELECTROLYTE"

MAKE-UP, OPERATING, AND DEPOSIT REQUIREMENTS (45)

Composition and Operating Conditions:		Requirements
Nickel Content		72 - 85 g/l
Boric Acid		37 - 45 g/l
Sulfamate Nickel Anti-Pit (SNAP)		.65 - .75 g/l as measured by 15 sec. minimum bubble on 3 inch diameter ring
Specific Gravity		1.26 - 1.30
Anodes		Nickel chips in titanium basket with Polypropylene cover bags
Make-up Water		Minimum specific resistance of 1 Megohm/cm
Temperature		120 ± 5°F
pH		3.8 - 4.2*
Filtration		10 Micron Polypropylene Cores
Filtration Rate		1.5 Tank volumes/hour minimum
Current Density		20 ± 2 A/ft.^{2}
Agitation		Cathode
Required Properties (New Electrolytes):		
Ultimate Strength	As Deposited	85 kpsi maximum
Yield Strength	As Deposited	55 kpsi maximum
Elongation in 0.5 inches	As Deposited	20 percent minimum
	Stress Relieved**	40 percent minimum
Microstructure	As Deposited	Uniform and clean
	Annealed***	Free from grain boundary inclusions

* - pH will initially be 3.4 and will increase upon electrolysis of the bath.

** - Stress relieved by holding at 650 ± 15°F for one hour in argon.

*** - Annealed by holding at 1800 ± 25°F for one hour in hydrogen.

TABLE XXXIII

ROCKETDYNE REQUIREMENTS FOR ELECTROFORMING STRUCTURAL NICKEL FROM THE SULFAMATE BATH - BATH COMPOSITION, OPERATING CONDITIONS, AND REQUIRED MECHANICAL PROPERTIES (46)

Composition and Operating Conditions:	Requirement
Nickel Metal Content	72 - 80 g/l
Boric Acid	27 g/l minimum
Iron	6 ppm maximum
Copper	6 ppm maximum
Zinc	6 ppm maximum
Lead	6 ppm maximum
Chromium	2 ppm maximum
Chloride	500 ppm maximum
Sulfamate Nickel Anti-Pit (SNAP)	As required to obtain 15 seconds minimum bubble on 3 inch diameter ring
Anodes	S.D. nickel chips in titanium basket with Polypropylene covers
Water	Minimum specific resistance 1 Megohm/cm
Temperature	115 - 125°F
Specific Gravity	1.25 - 1.30
pH (Adjust with Sulfamate Nickel Acid Controller - SNAC)	3.8 - 4.2
Filtration	10 micron polypropylene core and element
Filtration Rate	2 tank volumes/hr. minimum
Current Density	20 ± 2 A/ft.^{2}
Agitation	Cathode and electrolyte flow
Minimum Mechanical Properties of Deposits:	
Ultimate Strength, kpsi	90
Yield Strength, kpsi	60
Elongation in 0.5 inch., %	16
Hardness, R_b	90
As Deposited	Columnar, no lamination striations, banding or voids. Uniform and clean.
Annealed	Free from grain boundary inclusions.

TABLE XXXIV

EXPECTED MINIMUM PROPERTIES OF ROCKETDYNE

ELECTRODEPOSITED NICKEL FROM THE "NO CHLORIDE" SULFAMATE BATH (47)

		As Deposited	Stress Relieved (1)
Tensile Ultimate Strength (KSI) Expected Minimum		77	65
Tensile Yield Strength (KSI) Expected Minimum		54	39
Tensile Elongation (pct.) Expected Minimum		10	36
Reduction in Area (pct.) Predicted Minimum			50
Thermal Conductivity (Btu-Ft/Hr-Ft^2-F)	(Typical)	34	-
Elastic Modulus (10^6 psi)	(Typical)	26.2	-
Poisson's Ratio	(Typical)	.34	-
Density (lb/in^3)	(Typical)	.32	-

(1) - Stress Relief - 650°F

TABLE XXXV

TENSILE STRENGTH - ELECTRODEPOSITED NICKEL FROM

SPACE SHUTTLE MAIN COMBUSTION CHAMBER SAMPLES -

ROCKETDYNE (48)

(EDNi STRESS RELIEVED @ 650 F 1 HR.)

Type Bar	Ultimate Strength (kpsi)	Yield Strength (kpsi)	Reduction of Area	Panel Number
-	65	39	50	(Minimum Requirements)
TR 125	84	62	90	MTD-4
TR 125	83	62	92	MTD-4
TRC 210	77	55	98	MTD-4
TRC 210	78	59	97	MTD-4
TR 125	79	58	90	9001-4
TRC 210	85	61	96	9001-4
TRC 210	85	57	96	9001-4
TR 125	84	61	87	0001-4
TR 125	83	60	89	0001-4
TRC 210	79	64	97	0001-4
TRC 210	78	56	97	0001-4

TR 125 - Tensile round with electrodeposited nickel structure perpendicular to direction of loading (Hoop direction). No bonds in samples.

TRC 210 - Tensile round - conical head - Electrodeposited nickel parallel to direction of loading. All bond interfaces included. No bond interface failure in tests.

NOTE: TR 125 samples are from a specific electrodeposited nickel layer while TRC 210 samples test all electrodeposited nickel layers, thus lower value for TRC 210 samples reflect the strength of the weakest electrodeposited nickel layer.

become unstable and produce deposits with higher sulfur contents (42) (43). The use of sulfur depolarized anode chips has made chloride additions no longer necessary, but many sulfamate bath users continue to maintain a low chloride content so that other types of anodes may be employed.

Klingenmeier (42) found that air agitation of a sulfamate bath using depolarized anodes contributed to anode passivity. When mechanical agitation was used, good bath stability with depolarized nickel anodes required 2.4 to 4.8 g/1 of nickel chloride. His findings also disclosed a tensile stress in deposits of 2 to 3 kpsi with nickel chloride concentration at 2.4 g/1 and about 10 kpsi with nickel chloride levels of 4.8 g/1. Using sulfur depolarized anodes, chloride was not necessary, but tensile stress was present. Addition of 0.8 g/1 of nickel chloride increased stress about 20 percent.

In similar work Knapp (43) reported that sulfur depolarized nickel and rolled depolarized nickel anodes remained active with as little as 0.2 g/1 of chloride. He also found that all commercially available anodes corroded properly at chloride concentrations of 1.5 g/1.

Diggin (20) presented data from the work of Fanner and Hammond which shows the effect of chloride concentration on internal stress of nickel sulfamate deposits based on bath temperature and current density, Table XXXVI. From this data it appears that tensile stress is not excessive in the bath temperature range of 113 to 123°F (45 to 50°C) and at current densities ranging from 20 to 60 A/ft^2.

Typical compositions, operating conditions, and deposit mechanical properties for sulfamate nickel baths with varied amounts of chloride content are found in the literature. Suggested formulations by ASTM Committee B-8 (31), Diggin (20), and International Nickel (50) are shown in Table XXXVII.

ARDE, Inc. (51) selected the sulfamate nickel bath with low chloride content to electroform multicycling metallic bladders for storage and positive expulsion of liquid hydrogen. Deposits were only 0.004 inches (0.0001m) thick. Commercial sulfamate baths were evaluated but not individually identified. Data furnished was:

	Bath A	Bath B	Bath C	Bath D
Nickel Metal, oz/gal.	10.5	10.5	11.1	6.7
Nickel Chloride, oz/gal.	0.9	0.9	0.3	0.7
Boric Acid, oz/gal.	5.5	5.5	4.25	3.7
pH	4.75	4.75	3.95	3.5
Temperature, °F	115.0	115.0	104.0	115.0
Current Density, A/ft^2	20.0	10.0	10.0	35.0
Hardness, DPH	150.0	150.0	150.0	132.0
Stress (Tensile) psi	500.0	500.0	800.0	2,000.0

TABLE XXXVI

DATA FOR INTERNAL STRESS OF NICKEL SULFAMATE DEPOSITS FROM ELECTROLYTES CONTAINING NICKEL CHLORIDE (20)

Electrolyte Composition:

Nickel Sulfamate	Not given in Reference (20)
Nickel Chloride	5 g/l (0.44 oz./gal.)
Boric Acid	Not given in Reference (20)
pH	4.0 ± 0.1

Effect of Bath Temperature on Internal Stress, Hardness, and Cathode Efficiency at a Current Density of 0.43 A/dm.^{2} (40 A/ft.^{2}):

Temperature °C	Temperature °F	Tensile Stress psi	Hardness, Vickers Diamond	Cathode Efficiency percent
30	87	10,800	204	99.3
35	96	7,400	170	99.4
40	105	7,400	168	99.4
45	113	4,400	No Data	No Data
50	123	3,000	174	99.4
55	132	4,600	No Data	No Data
60	141	5,800	173	99.3

Effect of Current Density in Sulfamate Bath on Stress, Hardness, and Cathode Efficiency (pH 4.0, Temperature 123°F):

Cathode Current Density, A/ft.^{2}	Tensile Stress psi	Hardness, Vickers Diamond	Cathode Efficiency percent
20	2,200	168	99.1
30	3,200	166	99.2
40	3,000	166	99.2
50	3,600	166	99.4
60	4,000	168	99.4

TABLE XXXVII

TYPICAL SULFAMATE NICKEL BATH (WITH CHLORIDE) COMPOSITIONS,

OPERATING CONDITIONS AND DEPOSIT MECHANICAL PROPERTY RANGES (20) (31) (50)

	Reference (20) Range	Reference (20) Optimum	Reference (31) Range	Reference (50) Range
Composition Range:				
Nickel Sulfamate, g/l	225-405	338	315 - 450	300 - 450
(oz./gal.)	(30-54)	(45)	(42 - 60)	(40 - 60)
Nickel Metal Content, g/l	52-94	77		
(oz./gal.)	(7-12.5)	(10.25)		
Nickel Chloride, g/l	6-30	6-15	0 - 22.5	0 - 15
(oz./gal.)	(0.8-4.0)	(0.8-2.0)	(0 - 3)	(0 - 2)
Boric Acid, g/l	30-45	30	30 - 45	30 - 45
(oz./gal.)	(4-6)	(4)	(4 - 6)	(4 - 6)
Operating Conditions:				
Temperature, °C	28-60	49	32 - 60	38 - 60
(°F)	(82-140)	120	(90 - 140)	(100 - 140)
pH (Electrometric)	3.5-4.2		3.5 - 4.5	3.5 - 4.5
Cathode Current Density $A/dm.^2$	2.2-6.5	4.3	0.5 - 32	2.7 - 10.8
$(A/ft.^2)$	20-140	40	(5 - 300)	(25 - 100)
Agitation	Air preferred; cathode movement or electrolyte flow		Air or mechanical	Air, solution pumping, cathode movement
Mechanical Properties (Typical):				
Tensile Strength, kpsi	108		60 - 190	60 - 110
Elongation in 2 in., %	15 - 20		10 - 25	5 - 30
Stress (Tensile), psi	1,500 - 10,000		0 - 8,000	1,000 - 6,000
Hardness, Vickers	140 - 190		170 - 230	140 - 250

It was noted that the stress data represented approximate values.

Reference (52) reports the use of sulfamate electrolyte containing chloride to electroform injectors for rocket engines. Camin Laboratories performed this work and data concerning the bath composition, operating conditions, and deposit mechanical properties at room and elevated temperature is shown in Table XXXVIII. Machined round test bars were used as deposit test specimens.

Electro-Optical Systems, Inc. developed procedures for electroforming cryogenic pressure vessels and large mass solar panel structures for aerospace applications (53). For the pressure vessels, the nickel sulfamate bath, with chloride for anode corrosion, was used. Reference (53) states that this formulation was selected as typical for a bath which must produce a heavy wall electroform requiring high elongation. Temperature and current density were monitored hourly and other conditions daily. For the solar panel structures, a sulfamate bath with lower chloride content was used. Operating data and some mechanical property data were reported, Table XXXIX. (It was unexpected to note that compressive stresses were reported for the low chloride bath, since no stress reducing additives were reported.) The selection of a sulfamate bath containing chloride to produce high elongation is in conflict with the statement by Such (54) that use of chloride in the sulfamate bath reduces ductility.

Dini, Johnson and Helms (55) report use of a sulfamate nickel bath containing chloride to electroform a bonding joint between aluminum and stainless steel. No mechanical property data on the nickel deposits were given but the electrolyte composition and operating conditions were:

Nickel Sulfamate, oz/gal.	60
Nickel Metal Content, oz/gal.	10 to 11
Nickel Chloride, oz/gal.	1.0
Boric Acid, oz/gal.	4 to 5.5
Surface Tension, Dynes/cm	34 to 38
pH	3.8 to 4.0
Temperature, °F	127 to 133
Anodes	Sulfur Depolarized
Filtration	Continuous
Current Density, A/ft^2	25

McCandless and Davies (56) investigated techniques for electroforming stronger nickel to allow a fuller utilization of electroforming as a reliable and low cost fabrication technique for regeneratively cooled thrust chambers. The target mechanical properties sought were 100,000 psi tensile strength with 10 percent elongation in a two-inch

TABLE XXXVIII

NICKEL SULFAMATE ELECTROLYTE COMPOSITION, OPERATING RANGE, AND DEPOSIT MECHANICAL PROPERTIES CAMIN LABORATORIES (52)

Bath-Composition and Operating Range:

Nickel Sulfamate, oz./gal.	45
Nickel Metal Content, oz./gal.	10.2
Nickel Chloride, oz./gal.	0.8 to 2.0
Boric Acid, oz./gal.	4
Temperature, °F	100 - 140
pH (Electrometric)	3.5 - 5.0
Density, °Baume'	29 - 31
Tank Voltage, volts	6 - 9

Mechanical Property Data:

	Test Temperature		
	Room	500°F	1000°F
Ultimate Strength, kpsi	106.5	71.5	27.6
Elongation in 2 inches, %	20	25	42

TABLE XXXIX

SULFAMATE NICKEL BATH COMPOSITION, OPERATING CONDITIONS, AND DEPOSIT MECHANICAL PROPERTIES - ELECTRO-OPTICAL SYSTEMS, PASADENA, CALIF. (53)

Structural Application:	Cryogenic Tanks		Solar Panels	
	g/1	oz./gal.	g/1	oz./gal.
Electrolyte Composition:				
Nickel Metal Content	62	8.3	70	9.3
Nickel Chloride	28	4.0	3.1	0.4
Boric Acid	37	4.9	40	5.3
Operating Conditions:				
pH (Electrometric)	3.0 to 3.7		4.2 to 4.8	
Temperature	38°C	(100°F)	54-57°C	(130-135°F)
Current Density $A/dm.^2$	2.1		2.1	
$A/ft.^2$	20		20	
Mechanical Property Results:				
Stress, Tensile, psi	5,000 to 10,000		-	
Stress, Compressive, psi	-		0 to 5000	
Before Electroforming				
Ultimate Strength, kpsi	80.16		No Data	
Yield Strength, kpsi	56.4		Reported	
Elongation in 2 inches, %	13.5		-	
Modulus of Elasticity, psi	21.7×10^6		-	
After Electroforming				
Ultimate Strength, kpsi	81.54		-	
Yield Strength, kpsi	55.22		-	
Elongation in 2 inches, %	12.0		-	
Modulus of Elasticity, psi	21.8×10^6		-	

gauge length. It was reported that the electrolyte was a Barrett (Allied-Kelite division, The Richardson Company) sulfamate nickel plating solution. Although the Barrett bath normally is chloride-free, the formulation used in this work contained 0.5 oz/gal. (3.7 g/l) of chloride. The chloride presence enabled the investigators to use rolled depolarized nickel anodes without danger or electrolyte instability.

During the first 4800 amp-hours of bath operation, the deposits had a tensile strength of 100,000 psi, or greater, but an elongation below 10 percent. During the next 15,000 amp-hours of operation, the mechanical properties changed to an elongation greater than 10 percent, but the tensile strength decreased to less than 100,000 psi. To increase tensile strength, small additions of chloride ion were made to bring the total chloride content of the bath to 1.1 oz/gal. (8.25 g/l). The bath composition, operating data, and deposit mechanical properties are summarized in Table XL.

Sample and Knapp (35) included the nickel sulfamate bath with low chloride content in their study of the mechanical properties of nickel at various test temperatures. The chloride content was 1.3 g/l and the tensile stress in the deposits was reported as 8,400 psi for a current density of 40 A/ft^2 and a bath temperature of 135°F. The bath composition, operating conditions and deposit mechanical properties are summarized in Table XLI. This data indicates that tensile strength and ductility increase with the thickness of the deposit.

Bell Aerospace Company (17) normally uses the nickel sulfamate bath with chloride additions for electroforming structural hardware, including regeneratively cooled thrust chamber outer shells. In a recent program to investigate response of such structures to nondestructive evaluation techniques, this electrolyte was used to produce coolant passage closures of differing mechanical strengths. The electrolyte used for this work has been in operation for approximately six years with a minimal, but routine, maintenance to provide closely controlled properties. This electrolyte is operated with no wetting agents or other additives. The bath is continuously filtered and carbon treated to provide electrodeposits which can be welded or heat treated with no detrimental effects.

Bell normally operates the sulfamate bath in a temperature range of 105 to 115°F to minimize expansion of wax filler materials used in recesses or coolant passages of chamber liners. Agitation is provided by three separate circulation systems. These are:

1) The primary polypropylene filter system.
2) The carbon treatment system.
3) The primary electrolyte circulation system in which electrolyte is sprayed against the cathode or workpiece.

TABLE XL

NICKEL SULFAMATE-CHLORIDE ELECTROLYTE

COMPOSITION, OPERATING CONDITIONS AND DEPOSIT MECHANICAL PROPERTIES - GENERAL TECHNOLOGIES CORPORATION (56)

Electrolyte Composition:	oz./gal.	g/l
Nickel Sulfamate	60	450
Nickel Metal	10.2	76.5
Boric Acid	5.75	39.4
Nickel Chloride	1.1	8.25
Anti-pit Agent	0.05	0.38

Bath Operating Conditions:	
pH (electrometric)	4.0 ±0.2
Temperature	50 ±2°C (122 ±3.6°F)
Current Density	$40 A/ft^2$ ($4.3 A/dm^2$)

Mechanical Property Test Data:

Results of General Technologies Corp. tests:

Test No.	Tensile Strength Kpsi	Yield Strength Kpsi	Elongation in 1 inch, %	Elongation in 2 inches, %
1	99.7	Not tested	Not tested	10.6
2	97.9	-	-	11.3
3	96.8	-	-	11.1
4	101	-	-	10.4
Results of NASA-Lewis Research Center tests:				
1	101	69.5	17	Not tested
2	100	69.6	16	-
3	101.2	66.9	16	-
Results from Specimen annealed at 1500°F:				
4	51.2	6.45	47	Not tested

TABLE XLI

DATA FROM SAMPLE AND KNAPP (35) ON ELECTRODEPOSITED NICKEL FROM THE SULFAMATE ELECTROLYTE CONTAINING LOW CHLORIDE CONTENT

Electrolyte Composition and Operating Conditions:

	g/l	oz./gal.
Nickel sulfamate	450	60
Nickel chloride	1.3	0.17
Boric acid	4	30
pH (electrometric)	[illegible] 5	
Temperature	57°C	135°F
Current Density	4.3 A/dm^2	40A/ft^2
Anodes	Rolled Depolarized Nickel	

Mechanical Properties at Various Test Temperatures:

Property	Deposit Thickness (inches)	Temperature of Test °F (°C): -320 (-196)	-100 (-73)	Room (20)	400 (204)	800 (427)	1200 (649)	1400 (760)	1600 (871)
Tensile Strength, Kpsi	.027	144.5	123.9	111.0	87.2	45.2	14.7	No Data	
	.052	145.6	127.5	113.0	84.1	45.4	12.3	6.5	5.1
	.094	149.0	129.0	119.2	86.0	40.1	15.1	No Data	
Yield Strength, Kpsi	.027	89.9	79.6	78.5	59.2	26.4	10.8	No Data	
	.052	89.6	83.6	73.5	N.D.	28.1	8.6	No Data	
	.094	95.3	84.3	No Data					
Elongation in 2 inches, %	.027	13	6	7	11	15	3	No Data	
	.052	21	14	12	14	24	10	9	2
	.094	22	17	14	18	36	15	No Data	

With this electrolyte, it is possible to use sulfur depolarized, or rolled depolarized anodes, or combinations thereof. The mechanical properties at two different current densities were as reported in Table XLII.

Table XLIII presents additional mechanical property data for nickel deposits from Bell's sulfamate bath over widely different deposition conditions. In general, decreasing current density results in higher tensile strength and yield strength, but elongation is decreased. Similar effects were noted when the bath temperature was increased while maintaining the current density constant. Minimum deposit thickness was 0.014 inch (0.36 mm).

Messerschmitt-Bolkow-Blohm of Munich, Germany has provided extensive data on their thrust chamber electroforming capability. They use the sulfamate nickel electrolyte. This solution is employed to electroform aerospace products such as satellite components, heat exchangers, and rocket engines. At present, they are electroforming the HM7 thrust chamber for the Ariane Third Stage Propulsion System.

Messerschmitt-Bolkow-Blohm electroforms flat tensile test bars which are approximately 2.5 mm (0.10 inch) thick. The mechanical properties at two different current densities are shown in Table XLIV for a range of test temperatures (58).

I. ELECTROLYTE SELECTION

The nickel sulfamate solution without chloride, or with low chloride content, is recommended for electroforming structural nickel subject to elevated temperature exposure.

Nickel can be deposited from a large variety of electrolytes. The Watts type solution provides the best ductility of all the baths surveyed. However, the deposits are highly tensile stressed. The lowest tensile stresses reported were 17,000 psi (34). At this stress level, the elongation was excellent (28 percent in 2 inches), but the tensile strength was low for electrodeposited nickel (58 kpsi). Under bath compositions and operating conditions which afford higher strength nickel, the tensile stress appears to increase to values of 30 kpsi or higher.

Stress relieving by heat treatment can be applied to remove most stress (45) (59). However, a fundamental problem in the electroforming of thrust chambers with coolant passages exists which stress relieving will not solve. When the passages are filled with an inert material and made conductive, the first layer of nickel deposited must contain low stress - otherwise, distortion, cracking, and peeling will occur at the channel filler - channel rib interface, resulting in an unsatisfactory structure.

The all-sulfate (chloride-free), sulfate-chloride, and all-chloride electrolytes produce deposits with high levels of tensile stress. The sulfate-chloride deposit tensile stress is generally in the range of 28 to 38 kpsi. Stress in all-chloride deposits is the highest with values of 40 to 55 kpsi being common.

TABLE XLII

ELECTROFORMED NICKEL MECHANICAL PROPERTIES AND ELECTROLYTE DATA FOR THE SULFAMATE NICKEL BATH WITH CHLORIDE (17)

Bath Composition:	g/l	oz./gal.
Nickel Metal	74.2	9.9
Nickel Chloride	3.07	0.41
Boric Acid	33.0	4.4
Wetting Agent	None	None

Bath Operation:	High Strength	Low Strength
pH (electrometric)	4.2	4.2
Temperature, °F	105	110
Current Density, A/ft.^{2}	30	70
Nickel Anodes	Sulfur Depolarized	Sulfur Depolarized
Agitation	10 micron polypropylene filters with an integral pumping system; a 300 gal./hr. circulation pumping system; a carbon treatment system with integral pump.	

Deposit Mechanical Properties:	High Strength	Low Strength
Ultimate Strength, Kpsi	101	76
(MN/m.^{2})	(697)	(524)
Yield Strength, Kpsi	67	49
(MN/m.^{2})	(462)	(331)
Elongation in 2 inches, %	9	12

TABLE XLIII
MECHANICAL PROPERTIES FROM BELL AEROSPACE NICKEL SULFAMATE ELECTRODEPOSITS (57)

Nickel Metal (Oz./Gal.)	Nickel Chloride (Oz./Gal.)	Boric Acid (Oz./Gal.)	Acidity (pH)	Temp. (°F)	Current Density (ASF)	Ultimate Strength (psi)	Yield Strength (psi)	Elong. in 2 in. (%)	Deposition Rates .001 in./hr.
10.8	1.4	5.5	3.7	105	75	59,000	38,000	23	2.5
Electrolyte agitation was mild using low pressure air.			3.9	120	75	63,000	42,000	23	2.5
			3.9	135	75	72,000	47,000	13	2.5
10.3	1.6	4.6	3.9	110	30	105,000	70,000	11	1.0
Electrolyte agitation was with compressed air and pumped electrolyte.			4.0	110	50	73,000	46,000	13	1.7
9.2	1.5	4.6	3.9	120	18	115,000	74,000	6	0.6
Electrolyte agitation was with compressed air and pumped electrolyte.			3.9	120	28	112,000	70,000	10	1.0
			3.9	120	55	87,000	55,000	9	2.0
9.7	1.0	4.5	3.9	120	105	70,000	45,000	13	3.5
High velocity electrolyte pumping for agitation.			3.9	120	145	68,000	43,000	14	5.0

TABLE XLIV

NICKEL SULFAMATE BATH DATA AND DEPOSIT MECHANICAL PROPERTIES - MESSERSCHMITT-BOLKOW-BLOHM (58)

Bath Composition:	g/l	oz./gal.
Nickel Sulfamate	450	60
Nickel Chloride	No Data	
Boric Acid	No Data	
Wetting Agent	No Data	

Operating Conditions:

Temperature 50°C (122°F)

Current Density, A/dm.^{2} 3 to 5

Current Density, A/ft.^{2} 28 to 45.5

Mechanical Properties (Average):

Current Density A/dm.^{2}	Current Density A/ft.^{2}	Test Temperature °C	Test Temperature °F	Ultimate Strength kg/mm.^{2}	Ultimate Strength kpsi	Yield Strength 0.2% Offset kg/mm.^{2}	Yield Strength 0.2% Offset kpsi	Elongation in 10 mm. (0.381 in.), %
5	45.5	-196	-320	75	106.5	43	61.1	28
		20	68	56	79.5	36	51.1	18.5
		200	392	42	59.6	29	41.2	15
		400	752	24	34.1	18	25.6	43
		600	1112	11	15.6	7	9.9	16
3	28	-196	-320	67	95.1	37	52.5	33
		20	68	48	68.2	33	46.9	18
		200	392	39	55.4	27	38.3	11
		400	752	26	36.9	20	28.4	27
		600	1112	10	14.2	6	8.5	7

The bright and semi-bright Watts type baths can be controlled to produce deposits of acceptable stress levels by use of organic additives. Many of these additives contribute to an increase in sulfur content in the deposit which results in a severe loss of ductility at elevated temperature, poor notch sensitivity, and inferior thermal stability. Such electrolytes are undesireable for producing electroforms which must be welded or subjected to service environments in excess of 500°F.

Nickel fluoborate baths are capable of producing deposits with excellent mechanical properties at relatively low electrolyte temperatures, Table XXVII. High deposition rates are possible and the solution is easy to control. The major disadvantage of this bath is that deposits have higher tensile stress than desired in electroforming regeneratively cooled thrust chambers. The bath has potential use in thrust chamber manufacture as a rapid electroforming process once the initial shell deposit has been applied from a bath producing lower stress nickel. Stress relieving could then be used to remove residual tensile stress.

Hard nickel baths are unsuitable for many aerospace applications because of high internal stresses in the deposits. Bath control, particularly acidity is critical, and there is a high tendency to form nodules and dendrites.

The sulfamate baths offer the best combination of controlled mechanical properties, low tensile stress in the deposits, and ease of operation. Nearly all nickel electrolytes currently used to produce aerospace hardware (thrust chambers in particular) are the sulfamate type. Lowest stress is produced in deposits from the sulfamate bath containing no chloride ion (40). Reference (60) advised that chloride-free sulfamate deposits can be expected to have a tensile stress of 0 to 4,000 psi when the bath is operated at a pH of 4.0, a temperature of 120°F, and a current density of 25 A/ft^2. Rocketdyne uses such an electrolyte for electroforming outer shells on the Space Shuttle Main Engine. Stress relieving is subsequently performed to improve fatigue life and decrease susceptibility to hydrogen embrittlement. Sulfur depolarized anodes must be used with the chloride-free sulfamate bath.

Addition of small amounts of chloride to the sulfamate electrolyte enables the electroformer to use either sulfur depolarized or rolled depolarized anodes without adverse effects on bath stability. The range of controlled mechanical properties obtainable is broad as shown in Tables XXXVII through XLIV. From the data of Diggins(20), acceptable low tensile stress can be obtained in deposits from sulfamate electrolytes containing chloride by observing the following precautions:

1. Maintain the concentration of nickel chloride at about 6 grams per liter (or less if sulfur depolarized anode chips are used).
2. Operate the electrolyte at a temperature of 43 to 49°C (110 to 120°F) and a pH of 3.5 to 4.0.
3. Use current densities within the range of 2.2 to 4.3 A/dm^2 (20 to 40 A/ft^2).

The mechanical properties at various temperatures for some nickel electrodeposits are compared with hot rolled, annealed Nickel 200 in Table XLV. As pointed out by Sample and Knapp (35), the better ductility in wrought nickel may be due to the fact that malleabilizing additives such as manganese and magnesium are present to counteract the harmful effects of sulfur. No similar compensation exists in the electroformed counterpart. The Watts and sulfamate deposits in Table XLV were reported to contain less than 0.001 percent by weight sulfur. Lead impurities were also reported to effect hot ductility. These same deposits contained varying amounts of lead - from less than 0.001 to 0.008 percent by weight.

TABLE XLV

TYPICAL MECHANICAL PROPERTIES OF ELECTRODEPOSITED NICKEL AND NICKEL 200 AT VARIOUS TEST TEMPERATURES (35) (61)

	TEST TEMPERATURE °F						
	-320	-100	Room	400	800	1200	1400
Watts Bath Nickel (35)							
Ultimate Strength, kpsi	85.1	69.6	69.5	48.5	32.3	18.5	11.5
Yield Strength, kpsi	40.3	37.4	32.4	No Data	22.4	11.9	No Data
Elongation in 2 inches, %	48	33	30	25	29	13	5
All-Chloride Bath Nickel (35)							
Ultimate Strength, kpsi	154.1	134.5	116.0	89.3	30.1	8.7	6.6
Yield Strength, kpsi	101.2	92.8	91.5	71.8	17.8	No Data	No Data
Elongation in 2 inches, %	22	15	8	11	20	10	7
Sulfamate Bath Nickel (35)							
Ultimate Strength, kpsi	146.4	126.8	114.4	85.8	43.6	14.0	6.5
Yield Strength, kpsi	91.6	82.5	76.0	59.2	17.3	9.7	No Data
Elongation in 2 inches, %	19	12	11	14	25	9	9
Nickel 200, Hot Rolled, Annealed (61)							
Ultimate Strength, kpsi	102.7	81.4	67.0	66.5	44	21.5	14.0
Yield Strength, kpsi	33.1	25.3	21.5	20.2	16.5	10.0	7.0
Elongation in 2 inches, %	54	58	47	44	65	76	89

V. PREPARATION OF THE BASIS METAL FOR ELECTROFORMING

A. PRELIMINARY CLEANING TREATMENTS

The preliminary cleaning treatment refers to that process or procedure necessary to clean the basis metal after fixturing and prior to application of masking, wax, or other stop-off material to be used to control regions in which electrodeposition is to be directed. The preliminary cleaning cycle to be used is based on the type and degree of contamination expected on the surface of the mandrel (or form) to be prepared for electroforming.

The inner liner, or hot gas wall, of the regeneratively cooled thrust chamber is the mandrel upon which deposition of the outer shell is accomplished. Fulton (62) reported the fabrication process by Rocketdyne for liners of Nickel 200, Amzirc (zirconium-copper), and NARloy-Z (a copper base alloy containing zirconium and silver). Dietrich and Leach (63) described fabrication of a TD nickel liner for a chamber built by Bell Aerospace Company. All of these liners were hot-spun to the chamber size and shape, stress relieved (annealed), and machined to the required design thicknesses. Hammer and Czacka (64) reported fabrication of experimental chambers at Camin Laboratories whereby the thrust chamber liner was electroformed upon a removable mandrel and the deposit was machined to the desired thickness. In all of the above references, the liner surfaces subject to bonding had been machined.

Machining provides a surface which is essentially free of any heavy oxides or other surface imperfections arising from the primary and secondary fabrication operations, as well as the final liner forming and shaping processes.

Coolant passages are often machined into the liner wall prior to any electroforming of the outer shell structure (63). Rocketdyne (65) sometimes applies a strike (thin layer) deposit of electrodeposited metal on the liner surface prior to machining the channels. The main advantages of such a strike deposit are:

(1) The liner alloy can now be treated and processed as if it were the pure electrodeposited metal.

(2) Adherance of the initial electrodeposit and the base metal activation process can be checked for adequacy by the channel machining operation. Poorly adherent deposits will peel or separate from the base metal in machining.

A disadvantage in the strike treatment is the fact that two bonding treatments become necessary before closing out the channel passages with the electroformed shell. This increases the risk of introducing a poor bond at an early stage of the shell fabrication.

Prior to masking and filling the coolant channels with an inert stop-off material (to control regions of deposition), the machined liner should be degreased, cleaned and inspected. Blum and Hogaboom (66) classify three main groups of foreign materials likely to be present as:

(1) Grease or soil - includes grease, soils, and machining coolants accumulated during machining and handling of the liner prior to transfer to the electroforming operation.

(2) Foreign particles - includes all solid particles that are not derived from the basic metal such as polishing, buffing, or grinding compounds and dust from the environment.

(3) Metal compounds - includes oxides or sulfides which may be present from reaction of the machined basic metal surface with the atmosphere.

In Reference (8), Baker and Hetrick provide a thorough discussion of solvent cleaning. Vapor degreasing is recommended by these authors because it is effective in removing greases, fats, oils, wakes, tars, and like materials. Trichloroethylene and perchloroethylene are normally used for vapor degreasing of thrust chamber liners or other parts to receive heavy electrodeposits (8) (37) (63). According to Greenwood (37), the solvent cleaning will remove heavy grease and oil but will not leave the surface adequately clean for subsequent operations (37). It is necessary to alkaline clean the liner to remove certain soils and compounded oils. Alkaline cleaning may be performed by hot solution dipping or by electrolytic means. The later is preferred since the alkaline cleaner action is supplemented by the mechanical action of gases liberated at the work piece. Ultrasonic agitation may also be used to supplement the alkaline cleaning action (8).

Where non-ferrous materials such as copper and copper alloys are to be alkaline cleaned electrochemically, Reference (8) suggests use of direct current-reverse current at about 10 to 25 amperes per square foot. The reverse current part of the cycle should be brief.

Most alkaline cleaning solutions are prepared from proprietary commercial formulations. The supplier's instructions should be followed for the solution operating conditions. Greenwood (37) suggests a formulation and operating conditions as follows:

Sodium hydroxide	50 - 100 g/l
Anhydrous sodium carbonate	50 - 100 g/l
Temperature	140 - 180°F (60 - 80°C)
Tank	mild steel
Current density*	10 - 100 A/ft^2 (1 - 10 A/dm^2)

* General purpose current density range.

Greenwood suggests further cleaning by manually scrubbing the work piece with a pumice powder and a bristle brush. Most electroformers employ this cleaning as noted in several references in the literature. The last cleaning step is followed by a liberal rinse, preferrably in running water or an overflow type rinse tank.

ASTM Committee B-8 (67) has developed a specification for cleaning of metals prior to electroplating. Special care must be exercised in use of this document since many of the processes requiring hot cleaning solutions cannot be used after tape masking or wax stop-offs have been applied to the workpiece (chamber liner). The choices of precleaning methods for the basis metal are as follows:

(1) Cold Solvent - Several chlorinated solvents are suggested, but cold solvent cleaning is not very effective unless supplemented with brush scrubbing and subsequent alkaline cleaning.

(2) Vapor Degreasing - This method is effective on solvent-soluble soils and chemically active lubricants. Insoluble soils such as buffing compounds, metal chips, and dust are flushed away as the grease and oils dissolve. Metallic salts, scale, carbon deposits and some fingerprints are not effectively removed.

(3) Emulsion Cleaners - This method uses oils and high boiling hydrocarbons such as Kerosene to dissolve most greases. Emulsifier, soaps, and wetting agents improve the cleaning ability.

Reference (67) classifies the alkaline cleaning as an intermediate cleaning prior to electroplating. The choice of methods is as follows:

(1) Soak Alkaline Cleaning - The cleaner is operated at 82°C (178°F) to boiling. Alkaline salt concentration is usually 30 to 120 g/l (4 to 16 oz./gal.). The soak period ranges from 3 to 15 minutes. Temperatures of 70°C (158°F) to boiling are employed if ultrasonics are used to supplement the soak cleaning action.

(2) Spray Alkaline Cleaning - The alkaline salt concentration varies from 4 to 15 g/l (0.5 to 2 oz./gal.) at temperatures of 50 to 82°C (122 to 180°F). Spray pressures are 10 to 50 psi.

Final rinses - hot, followed by cold, are recommended.

B. APPLICATION OF STOP-OFFS AND INERT FILLERS

Thrust chamber liners are usually thin in wall section and subject to damage if not handled with the utmost caution. They are generally secured on an internal mandrel, or holding device, which minimizes shape distortion and provides a means of fixturing the workpiece in the electroforming solution. Illustrations of mandrels used in electroforming regeneratively cooled thrust chamber shells can be found in References (62) and (64). McCandless and Davies (56) reported use of an undersize stainless steel mandrel coated with a layer of low temperature melting alloy to allow separation of the hardware being electroformed.

Bell Aerospace Company uses both aluminum and stainless steel mandrels for the machining and electroforming of thrust chambers. Figure 2 shows a stainless steel mandrel supporting a chamber liner during machining of the coolant passages. The large openings in the mandrel end-plates allow internal surface coverage during the wax masking process.

Wax or wax-like materials are generally used for filling recesses and edges where electrodeposition is not desired. The machined channels are filled with such materials to preserve the passage integrity during electroforming of the outer shell. References (62), (63), (64), and (68) cite the use of wax for channel filling by Rocketdyne, Bell Aerospace Company and Camin Laboratories.

Greenwood (37) notes that use of waxes for insulation to prevent electrodeposition from occurring in selected areas is common in Great Britain. Wax is reported to have the advantage of being easily removed after electroforming by immersing in boiling water. For nickel plating, a wax with a melting range of 82°C (180 to 190°F) is commonly employed. Bell Aerospace Company uses a wax with a similar melting range (63).

Waxes suitable for stop-off and coolant passage fillers are discussed below. This is not a complete list, but these waxes described have been used or could be used in the thrust chamber shell electroforming procedure.

(1) Unichrome Compound 314 (69) - This wax melts at about 82°C (180°F). Parts can be coated by dipping as shown in Figure 3. Bell Aerospace Company uses this material extensively (63). The wax has a tendency to soften when exposed to electrolytes at temperatures of 52°C (125°F) or higher. This wax can be readily removed in boiling water followed by vapor degreasing.

(2) Unichrome Compound 321 (70) - This compound melts at a higher temperature than Compound 314. It provides good protection and stability at most electrolyte temperatures and can be applied by dipping the workpiece in a conventional melt tank. It is best removed by immersion in the molten compound, draining, and vapor degreasing.

(3) Rigidax Type W I, Light Blue (71) - This is a tooling compound with a pouring temperature of 121°C (250°F). It is manufactured by M. Argueso and Company, Mamaroneck, New York. Rocketdyne presently uses this material as

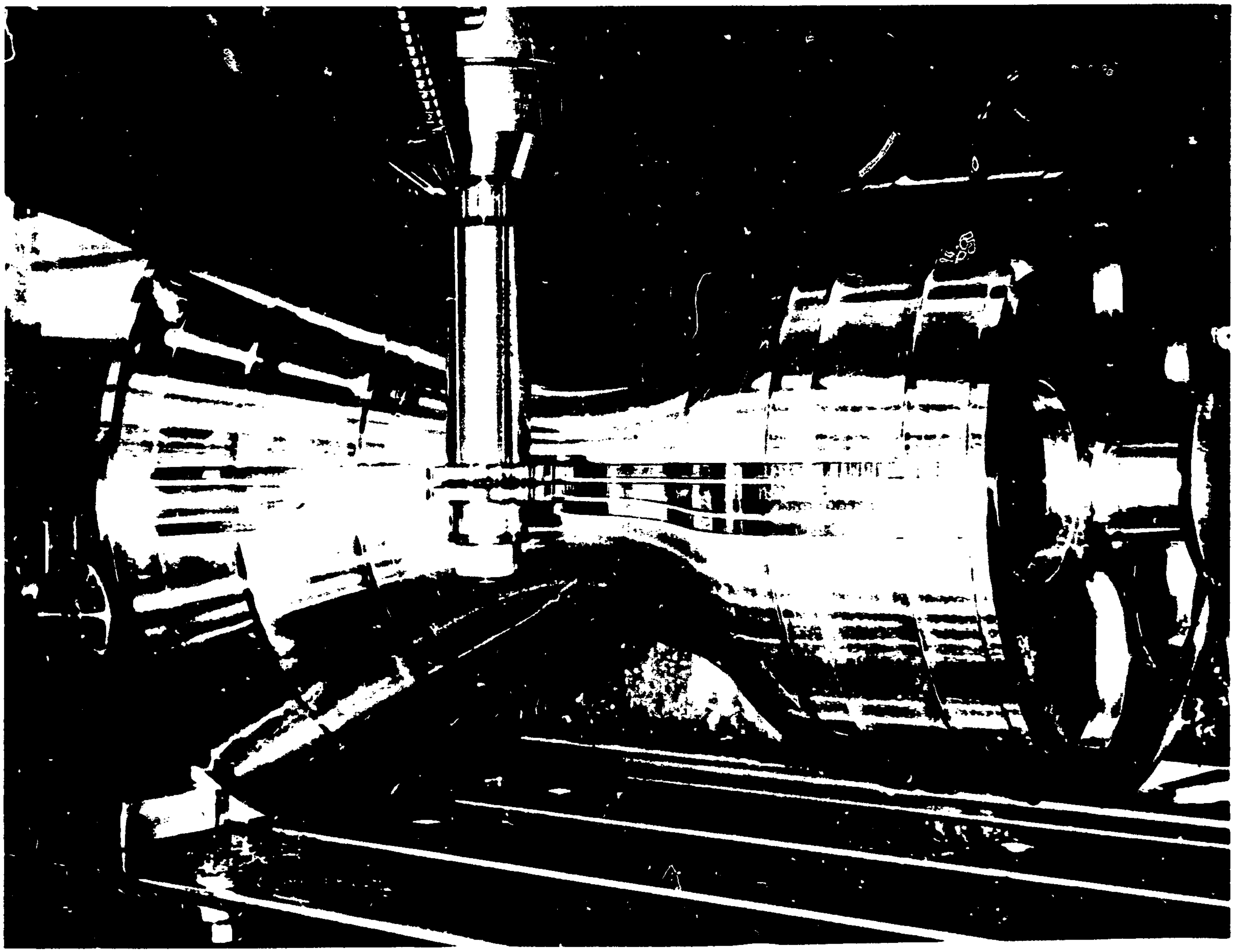

Figure 2. Chamber Liner Mounted on a Stainless Steel Mandrel for Channel Machining

Figure 3. Wax Dipping of Thrust Chamber Liners to Fill Coolant Channel Passages

inert filler for coolant passages in regeneratively cooled thrust chamber liners during electroforming. This material can be machined or hand sanded.

After waxing, it is essential that the excess compound be machined, sanded, or otherwise removed to produce a smooth contour with the coolant passage ribs which will receive the electroform bond when the outer shell is fabricated. In the case of softer waxes, it is advisable to lightly solvent wipe wax smears from surfaces to be bonded. This should be followed by hand scrubbing with a detergent cleaner and bristle brush. Pumice compounds should be avoided, since they will imbed in the wax and interfere with subsequent conductivizing.

Greenwood (37) describes the waxing process in detail. When the dipping process is used, it is critical that the workpiece (chamber liner) be held in the molten wax until it reaches the wax temperature. This will promote good adhesion during subsequent trimming operations. Several dip coats can be applied until the desired thickness is achieved.

After the coolant passages are protected by wax, it is advisable to chemically etch the channel ribs and all other areas where bonding of the shell is required. Since the chamber liner has been machined and cold work or metal smearing introduced, the surface crystal structure is disturbed. The preliminary cleaning cycle will not correct this condition. The detrimental effect of this layer (Beilby layer) on the adhesion and structure of subsequent electrodeposits is discussed in References (66) and (73). The purposes of an acid etch treatment at this point in processing are:

(1) Removal of deformed surface metal to expose sound basis metal so that the crystals of the deposited metal can form a perfect linkage with the crystal structure of the substrate (37).

(2) Neutralization of any alkaline residues remaining from the pretreatment cleaning (1).

(3) Removal of any light oxides which may have formed since the workpiece was machined and handled prior to preparation for plating (1) and (8).

(4) Inspection of the surface after etching will usually disclose contaminated areas if present since these will not etch uniformly. The reliability of the water break test is enhanced by a brief acid dip followed by an immediate rinse in clean water (74).

The water break test is one of the most commonly used tests to evaluate the cleanliness of a surface prior to electroplating (8).

The acid dips for etching used by Bell Aerospace Company (17) are operated at room temperature. Etching rates are determined for the basis metal to prevent excess metal removal. For OFHC copper, the acid dip contains 25 percent by volume sulfuric acid in water. Immersion time is three minutes followed by a thorough rinse in distilled water. Stains, if present, are removed by a quick immersion in 30 percent by volume nitric acid in water. A similar procedure for beryllium copper is recommended by Morana (75) but the sulfuric acid solution temperature is 160 to 180°F. Snavely and Faust (8) suggest addition of dichromate to the sulfuric acid solution to increase the etch rate where desired.

C. CONDUCTIVIZING NON-METALLIC SURFACES

Once the coolant passages are filled with an inert removeable material, it is necessary to make the inert substance conductive to close-out the channels during the outer shell electroforming.

Reference (63) cites the experience of Bell Aerospace Company with several types of material for making non-metallic materials conductive. Blending conductive powders such as graphite and copper with the wax was evaluated but proved unsatisfactory due to excessive encapsulation by the wax - even after various cleaning treatments were tried. Rubbing graphite powder over the surface of the wax produced suitable conductivity, but residual graphite on the bonding ribs (channel lands) contributed to poor bond strength. The smeared graphite could not be effectively removed by anodic or cathodic treatment. Conductive paints produced good conductivity over the wax, but the application of such films was a tedious manual operation which often resulted in paint overlap onto the bond surface. Successful results were achieved by using a silver reduction spray technique described by Narcus (72).

Bell Aerospace Company abandoned the silver reduction spray technique when it was found that channel porosity could not be adequately controlled (17). Further development work disclosed that rubbing a fine silver powder into the wax surface provided a more stable conductive film upon which a nonporous electrodeposit could be produced. Currently Bell Aerospace Company uses a silver brazing powder (Englehard, Type G-3) for conductivizing.

Fulton (62) describes the conductivizing of wax-filled channels at Rocketdyne using a copper powder. Rocketdyne also uses silver powder which is hand-burnished onto the wax-filled coolant passage surfaces. Special care must be exercised to prevent silver contamination of the bonding ribs during subsequent bond activation procedures (76).

Several other references cite use of conductivizing films but no specific details are given.

It should be noted that manual application of conductive powders to wax-filled channels requires use of clean covering for the hands since fingerprints are difficult to remove once the conductivizing is complete. Use of disposable plastic gloves is suggested.

D. PROCEDURES FOR BONDING ELECTRODEPOSITED COPPER TO COPPER AND COPPER ALLOYS

ASTM Practice B281-58 (77) outlines recommended procedures for electrodepositing copper on copper and copper alloys, Table XLVI. These procedures include the preliminary cleaning treatments such as vapor degreasing and hot alkaline cleaning. This process will produce adherent deposits of copper on copper and copper alloys, but it is not satisfactory for use on regeneratively cooled thrust chamber liners due to the presence of waxes and the conductivizing film. Solutions for cleaning and activating must be low in temperature to minimize wax softening and expansion. The use of acid dips or bright dips containing nitric acid are undesireable due to chemical attack on the conductivizer. This ASTM practice would be suitable for preparation of partially electroformed outer shells for continued electroforming provided all coolant passages were closed-out by an electrodeposit layer.

Pope (78) provides a detailed account of experience at Stanford University in electroforming linear accelerator structures with copper. Bonding of a large number of OFHC copper discs to the electroformed outer wall was of importance to produce a piece of hardware with good overall mechanical strength and low radio frequency power losses. The OFHC copper components were assembled on a stainless steel mandrel and processed as shown in Table XLVII. Aluminum spacers were preplated with copper from a cyanide bath prior to insertion between the OFHC copper components and subsequent electroforming to produce a structural wall.

All components to be electroformed were vapor degreased in trichloroethylene and soaked in Enthone No. 160 copper cleaner at 180°F. This solution (79) is a commercial general purpose electrolytic and soak type cleaner operated as follows (for copper):

1. Soak Cleaning

Enbond 160 salts	6 to 10 oz/gal.
Temperature	160 to 200°F
Time	1 to 5 minutes

2. Electrolytic Cleaning

Enbond 160 salts	8 to 10 oz/gal.
Temperature	160 to 180°F
Time	10 seconds to 2 minutes
Current Density	50 - 75 amps/ft^2 anodic

TABLE XLVI

ASTM RECOMMENDED PRACTICE FOR PREPARATION OF COPPER AND COPPER-BASE ALLOYS FOR ELECTROPLATING (77)

1. Oil and grease removal - vapor degrease or immerse in soak tanks containing emulsion cleaners.
2. Rinse
3. Alkaline electroclean - the basis metal is made anodic, or cathodic followed by anodic.

   A typical cleaner is:

	Weight Percent
Sodium Carbonate	40 to 50
Trisodium Phosphate	25 to 40
Sodium Hydroxide	10 to 25
Surface Active Agent	1 (approximately)

   This mixture is used in a solution concentration of 4 to 6 oz./gal. (30 to 45 g/1).

Temperature	140 to 160°F (60 to 71°C)
Current Density	10 to 30 amp./ft.^{2}
Time	1 to 3 minutes cathodic and 5 to 10 seconds anodic

4. Rinse
5. Acid dipping - used to neutralize residual alkalies before entering an acid copper or nickel plating bath. The most common dips used are 5 to 10 volume percent of 66° Baume' sulfuric acid, or 10 to 20 volume percent of 20° Baume' hydrochloric acid. Five to ten volume percent of 42 to 45 percent strength fluoboric acid can be used prior to copper fluoborate plating. These dips are at room temperature.
6. Cyanide dipping - two to six oz./gal. of sodium cyanide at room temperature is used as a dip prior to alkaline copper plating to remove tarnish from copper basis metals.
7. Rinse
8. Bright dipping - this dip is normally used to activate the basis metal surface for bonding. It may be used in place of the acid dip in Step 5. Immersion is brief (5 to 10 seconds).

   A typical solution is:

Sulfuric Acid (66° Baume')	60 to 75 vol. %
Nitric Acid (42° Baume')	20 to 35 vol. %
Water	5 to 10 vol. %
Hydrochloric Acid (20° Baume')	1/8 oz./gal.

   A mild alkaline solution dip should be used prior to alkaline plating.
9. Double rinse.
10. Electroplate

TABLE XLVII

STANFORD UNIVERSITY PROCEDURE FOR BONDING

ELECTRODEPOSITED COPPER TO OFHC COPPER BASIS METALS(78)

1. Precleaning Treatment of Copper Components
   a. Vapor degrease in trichloroethylene
   b. Alkaline clean copper parts in Enthone No. 160 at 180°F (soak clean)
   c. Water rinse
2. Electropolishing Treatment
   a. Composition of bath and operating conditions

Phosphoric acid	65 percent by volume
Water	35 percent by volume
Temperature	Room
Cathodes	Copper
Current Density	150 amps/ft.^{2}
Time	40 seconds

   b. Water rinse
3. Cathodic Activation in Sulfuric Acid
   a. Composition of bath and operating conditions

Sulfuric acid, C.P. grade	20 percent by volume
Water	80 percent by volume
Temperature	Room
Anodes	Chemical lead
Current Density	100 amps/ft.^{2}
Time	15 seconds

   b. Water rinse and inspect quickly for water break
   c. Water rinse
4. Electroforming
   a. Immerse in copper sulfate electrolyte composed of:

Copper sulfate, tech. grade	32 oz./gal.
Sulfuric acid, C.P. grade	10 oz./gal.

   b. Operating conditions

Temperature	90°F
Current Density	40 amps/ft.^{2}
Agitation	Cathode movement
Anodes	Rolled annealed oval copper
Filtration	Continuous with carbon treatment

Pope points out the importance of cautious handling of components to be electroformed once the preliminary cleaning is completed. All handling of parts is accomplished while wearing surgical gloves. The component assembly is immersed in an electropolishing tank and electropolished (anodically) for forty seconds at 150 amperes per square foot of surface. The next step is water rinsing. Table XLVII gives details of the electropolishing solution composition and operation.

The electropolishing renders the copper surfaces passive by an oxide-phosphate film. This surface which must be activated to assure a sound bond is obtained during electroforming in a subsequent acid copper bath. Activation is accomplished by cathodic treatment in sulfuric acid. This is followed by a double water rinse. A water break inspection for surface cleanliness is made between rinses. The activated assembly is placed in an acid copper sulfate bath and electroformed at 40 amperes per square foot current density.

In this same paper, Pope points out successful electroforming of these structures using a copper pyrophosphate bath operated at 130°F to produce the initial deposit layer. The bath pH was 8.0 and the current density was 20 amp/ft^2. Adhesion of the deposit was excellent and certain improvements in the structure resulted from the stress-free properties of the pyrophosphate deposit. Pope emphasized the importance of the cathodic activation treatment in sulfuric acid to produce the most satisfactory bonds in electroforming.

Blum and Hogaboom (66) describe procedures used for pickling, dipping, and electropolishing of copper alloys for subsequent electroplating. Heavy scale, if present, is removed by a mixture of sulfuric acid and dichromate. Light scale removal is accomplished by immersion in dilute sulfuric acid (8 oz/gal.) in water. This is followed by a bright dip in a solution containing sulfuric and nitric acid with a small amount of hydrochloric acid. Solution temperature is maintained below 104°F (40°C). These solutions can be used on copper alloy liners for thrust chambers if used prior to conductivizing the wax filled channels.

Blum and Hogaboom suggest electropolishing to provide a bright clean surface for electroplating. A process for copper alloys such as brass is:

	g/l	oz/gal.
Phosphoric acid	200	27
Chromic acid	180	24
Sodium dichromate	420	56
Sulfuric acid	90	12
Hydrochloric acid	5	0.7
Propionic acid	120	16

C-2

	g/l	oz/gal.
Water, to make	1 liter	1 gal.
Temperature	24°C	(75°F)
Current density	140 to 350 amp/ft^2	

Brimi and Luck (1) mention several solutions and processes for preparing various basis metals for electrodeposit bonding. The precleaning is performed with the same choice of solvents for oil and grease removal outlined in ASTM Practice B281-58. Chemical (alkaline) cleaning can be accomplished in one of many available commercial solutions having high alkalinity, good dispersing power for solids, good rinsability, low surface tension, and wetting ability. A general purpose cleaner is suggested which contains 6 oz/gal. solium metasilicate, 6 oz/gal. trisodium phosphate, and 2 oz/gal. wetting agent.

These investigators suggest that alkaline cleaning be followed by an acid dip to remove traces of alkalinity and oxides on the metal surface. For heavy scale removal, immersion in 10 percent sulfuric acid or 50 percent hydrochloric acid will suffice. This should be followed by a dip in 4 oz/gal. sodium or potassium dichromate and 0.5 pints per gallon sulfuric acid to brighten copper alloy. For light oxide removal, a bright dip is recommended such as:

Sulfuric acid	2 gallons
Nitric acid	1 gallon
Hydrochloric acid	5 ounces
Water	1 quart

This dip must be brief (10 to 20 seconds) since it attacks the base metal. (The above treatments must be performed prior to conductivizing the waxes applied to thrust chamber liners for reasons previously mentioned.)

Electropolishing (usually applied prior to metal activation for bonding) is also discussed by Brimi and Luck (1). Copper may be electropolished in cyanide, caustic soda, or phosphoric acid electrolytes. In the phosphoric acid electrolytes, the acid concentration is about 40% and addition of agents such as ethylenediamine tetra-acetic acid (EDTA), ammonium phosphate, citric acid, tartaric acid, or glycerol to minimize pitting.

Greenwood (37) notes that good adhesion of copper deposits on brass or bronze basis metals is obtained by scrubbing and rinsing followed by an anodic etch in a sodium hydroxide solution as follows:

Sodium hydroxide	200 g/l (32 oz/gal.)
Sodium cyanide	6 g/l (1 oz/gal.)
Temperature	Room
Current density	50 to 100 amp/ft^2 (5.5 to 11 amp/dm^2)
Time	1 to 2 minutes

After etching, the parts should be rinsed thoroughly and dipped in a clean 10% solution of hydrochloric acid. This should be followed by rinsing to assure removal of all chlorides and then the parts are transfrred to the copper electrolyte for electroplating or electroforming..

Rocketdyne (80) deposits 0.005 to 0.010 inch of copper over the Space Shuttle Main Engine liner as a coolant passage close-out to prevent hydrogen embrittlement of the electroformed nickel outer shell. The procedure for electrodeposited copper bonding to the NARloy-Z alloy liner consists of anodic cleaning (electropolishing or electroetching) in phosphoric acid followed by rinsing and cathodic activation in sulfuric acid.

Bell Aerospace Company (17) reported a procedure for bonding electrodeposited copper on OFHC copper baseplates containing machined coolant passages to simulate regeneratively cooled thrust chamber walls. Before wax filling the channels, the copper baseplates were chemically etched in a nitric acid-water solution containing small amounts of ferric chloride. The plates were thoroughly rinsed and alkaline scrub cleaned. After waxing and scrub cleaning to obtain a non-contaminated surface of exposed copper, the baseplates were dipped in a 25% by volume solution of sulfuric acid at room temperature for three minutes. A thorough rinse in distilled water was performed prior to entering the acid copper sulfate bath in order to obtain a good bond. Voltage was applied before immersion in the electrolyte. Unreliable bonds were found to result if the distilled water rinse was not used or if the rinse was subjected to continued reuse. Good bonds were found to equal the ultimate strength of the OFHC copper baseplate material when subjected to hydrostatic testing. The ultimate strength of the OFHC copper was 35.4 kpsi (244.3 MN/m^2) and the planned "full bond" failure was calculated to be 37.0 kpsi (255 MN/m^2). These values are within the expected experimental agreement.

Messerschmitt-Bolkow-Blohm (58) reported the bond strength of electrodeposited copper from the acid sulfate bath on various substrates, including copper and two copper alloys. The details of the procedure used to clean and activate the basis metals was not furnished, but the results of the adhesion tests are shown in Table XLVIII. The test used was similar to the Ollard test described in Reference (81). Results of hydrostatic testing of similar bonds at room temperature are shown for comparison. These results were invariably lower in strength than the Ollard type test results.

TABLE XLVIII

MESSERSCHMITT-BOLKOW-BLOHM TEST DATA FOR BOND STRENGTH OF ELECTRODEPOSITED COPPER ON WROUGHT COPPER, ELECTRODEPOSITED COPPER, ZIRCONIUM COPPER ALLOY, AND SILVER-ZIRCONIUM COPPER ALLOY (58)

Ollard Type Test (Mechanical):

Test Temperature °C	Test Temperature °F	Wrought Copper kgf./mm.^{2}	Wrought Copper kpsi	Electrodeposited Cu kgf./mm.^{2}	Electrodeposited Cu kpsi	Zr Copper kgf./mm.^{2}	Zr Copper kpsi	Ag-Zr Copper kgf./mm.^{2}	Ag-Zr Copper kpsi
		Bond Strength on Indicated Base Metal (Average)							
-196	-320	54	76.7	74	105.1	50	71.0	No Data	
20	68	37	52.5	45	63.9	39	55.4	33	46.9
200	392	22	31.2	12	17.0	14	21.3	23	32.7
400	752	4	5.7	4	5.7	7.5	10.7	5	7.1
500	932	3	4.3	3	4.3	3	4.3	3	4.3
Hydrostatic Test with Water:									
20	68	30	42.6	33	46.9	30	42.6	24	34.1

E. PROCEDURES FOR BONDING ELECTRODEPOSITED NICKEL TO COPPER AND COPPER ALLOYS

ASTM Committee B-8 (77) recommends essentially the same procedure for bonding electrodeposited nickel or electrodeposited copper to copper and copper alloy basis metals. This procedure is shown in Table XLVI. Use of this process of thrust chamber liners would not be practical once a silver conductivizing film was applied over the wax filled channels. Any nitric acid in the bright dip would excessively attack the thin silver conductivizing layer. This process would be practical for preparation of copper alloys for bonding if all hot solution immersions for cleaning were conducted before the wax was applied to the coolant passages. After waxing the bright dip could be used if it were desired to apply a nickel strike to cover all exposed copper prior to conductivizing the wax-filled channels.

Greenwood (37) describes typical processes used in the United Kingdom for bonding heavy nickel deposits to copper, brass, and bronze. The usual precleaning treatment of the basis metal is performed by vapor degreasing in trichloroethylene or an alkaline degreasing facility. Stopping-off of areas not to be plated is performed by wax dipping. Wax in areas to be bonded is removed. Pickling of the basis metal, if necessary, is conducted in dilute inhibited hydrochloric acid, followed by a rinse. Manual scrubbing the exposed surfaces with a bristle brush and a pumice powder is often conducted prior to the pickling. Etching to prepare the surfaces for bonding is performed in a caustic soda solution. The etch process requires anodic treatment of the copper basis metal at 100 amp/ft^2 (11 amp/dm^2) for 10 to 30 minutes. This is followed by a rinse and a dip in 10% hydrochloric acid. A final rinse is conducted and the part is immersed immediately in the nickel electroforming bath and current applied as soon as possible. On brasses and bronzes, an acid copper strike is often applied just prior to nickel to improve adhesion.

Greenwood advises that the critical step in nickel plating involves the transfer time from the final rinse to the start of plating in the nickel electrolyte. He suggests that the starting current be about 75% of the required total current for plating due to the fact that the workpiece will be cold when it enters the electrolyte. The temperature of the cathode film electrolyte will be reduced and burning or deposit peeling may result in high current density areas. The current is slowly adjusted to the required value over a period of 5 minutes to 1 hour, depending on the size of the workpiece.

Dini, Johnson, and Helms (55) reported the bonding of electrodeposited nickel to an electrodeposited copper strike during their investigation of methods to join aluminum and stainless steel by electroplating. The stainless steel member was given a Wood's nickel strike, a copper cyanide strike, and an electrodeposited bond using nickel sulfamate to produce a deposit about 0.050 inch thick. In a shear test of stainless steel rods prepared in this manner, all failures occurred in the copper deposit. Data is shown in Table XLIX.

TABLE XLIX

DINI, JOHNSON, AND HELMS SHEAR TEST DATA FOR ELECTRODEPOSITED NICKEL BONDED TO ELECTRODEPOSITED COPPER (55)

Cleaning and Plating Cycle	Shear Strength[b] (psi)	Location of Failure in Shear Test
Copper Strike Process		
Caustic clean; 18% HCl; Wood's nickel strike, 150 A/ft^2; copper strike 10 min.; overnight set; pumice; 18% HCl; nickel sulfamate	35,700	Shear in copper deposit
Caustic clean; 18% HCl; Wood's nickel strike, 150 A/ft^2; copper strike 10 min.; overnight set; Metex; HCl; ammonium persulfate; HCl; nickel sulfamate	37,700	Shear in copper deposit
Caustic clean; 30% HCl; Wood's nickel strike, 25 A/ft^2; copper strike 60 min.; overnight set; pumice; 22 g/l sulfamic acid; nickel sulfamate	27,100	Shear in copper deposit
Caustic clean; 30% HCl; Wood's nickel strike, 25 A/ft^2 5 min.; copper strike, 30 min.; dry and set, 4 hours; pumice; 22 g/l sulfamic acid; nickel sulfamate, 5-min. immersion before current turned on.	33,400	Shear in copper deposit
Caustic clean; 30% HCl; Wood's nickel strike, 25 A/ft^2 5 min.; copper strike, 30 min.; dry and set, 4 hours; pumice; 22 g/l sulfamic acid; nickel sulfamate, 10-min. immersion before current turned on	34,500	Shear in copper deposit

NOTES:

[a] Rod diameter was 0.500 inch; die diameter varied from 0.506 to 0.514 inch.

[b] Average of 10 tests. Thickness of the nickel sulfamate deposit was about 50 mils.

Solution Compositions

Nickel Chloride Strike (Wood's)

Nickel Chloride	32 oz/gal
Hydrochloric Acid	16 oz/gal

Copper Strike Solution

Copper Cyanide	5.5 oz/gal
Total Sodium Cyanide	6.5 oz/gal
Sodium Carbonate	4.0 oz/gal
Rochelle Salt	8.0 oz/gal
Free Sodium Cyanide	0.5 oz/gal (maximum)
Temperature	100 to 110°F
pH	10.2 to 10.5

Current density was 15 A/ft^2; plating rate was slightly greater than 0.1 mil per 10 minutes.

Sulfamic Acid Solution 25 g/l

Nickel Sulfamate Solution

Nickel Sulfamate	60 oz/gal
Nickel Chloride	1.0 oz/gal
Metallic Nickel	10 to 11 oz/gal
Boric Acid	4 to 5.5 oz/gal
Surface Tension	34 to 38 dyne/cm
pH	3.8 to 4.0
Temperature	127 to 133°F
Anodes	sulfur depolarized nickel
Filtration	continuous
Current Density	25 A/ft^2

Bell Aerospace Company (17) reported good bonds for electrodeposited nickel from the sulfamate bath on OFHC copper substrates. The test samples consisted of OFHC copper baseplates with machined coolant passages which were closed-out by electrodeposited nickel coverplates. The baseplates were pickled in a nitric acid-water solution containing a small amount of ferric chloride. This dip was brief to prevent excess loss of channel dimensions. After rinsing and drying, the channels were wax-filled and the panels were lightly solvent wiped to remove excess wax from the surfaces to be bonded.

The exposed copper surfaces were then alkaline scrub cleaned and rinsed. This was followed by a dip of the panels in a 25% by volume solution of sulfuric acid to brighten and activate the copper for plating. The panels were transferred, with cathodic voltage applied to the nickel sulfamate bath and plated for sufficient time to cover all surfaces with a thin nickel layer (approximately 0.00025 inch thickness). A low initial current was used to minimize burning and peeling in high current density regions such as channel edges. The panels were then rinsed and the wax-filled channels conductivized for further plating. Hydrostatic pressure test results indicated a bond strength of 40,000 psi (276 MN/m^2), or higher, could be obtained by this method. This result was unexpectedly high since the measured tensile strength of the OFHC copper baseplate stock was only 35,400 psi (244.3 MN/m^2).

Rocketdyne (80) cleans and activates the thin electrodeposited copper channel close-out layer on the Space Shuttle Main Engine Chamber for buildup of the outer nickel shell by anodic treatment in a phosphoric acid solution, followed by cathodic treatment in a sulfuric acid solution.

Messerschmitt-Bolkow-Bolm (58) reported Ollard type adhesion test results for electrodeposited nickel on wrought nickel, electrodeposited nickel, and two copper alloy substrates. Details of the bonding processes were not disclosed. The test results are shown in Table I

F. PROCEDURES FOR BONDING ELECTRODEPOSITED COPPER TO ELECTRODEPOSITED COPPER (ELECTROFORMING RESTARTS)

Little data concerning electroplating or electroforming restart procedures were noted in the literature for copper deposition on electrodeposited copper. Pope (78) described transfer of pyrophosphate copper electroforms into the acid copper bath with only a rinse to remove the slightly alkaline pyrophosphate solution. He also noted that the aluminum spacers coated with cyanide copper deposits were given the previously described anodic phosphoric acid - cathodic sulfuric treatment and rinse for producing soundly bonded linear accelerator structures.

Bell Aerospace Company (17) frequently employed copper electroforming restarts in producing panels simulated thrust chamber walls. An activation dip in 25% by volume sulfuric acid prior to re-entering the acid copper electrolyte afforded satisfactory bonds. No delaminations were evident in metallurgical sections prepared from panels with electrodeposited copper coverplates after pressurizing to failure.

TABLE L

MESSERSCHMITT-BOLKOW-BLOHM TEST DATA FOR BOND STRENGTH OF ELECTRODEPOSITED NICKEL ON WROUGHT NICKEL, ELECTRODEPOSITED NICKEL, ZIRCONIUM COPPER ALLOY, AND SILVER-ZIRCONIUM COPPER ALLOY (58)

Ollard Type Test (Mechanical):

Test Temp °C	°F	Electrodeposited Ni kgf/m.^{2}	Electrodeposited Ni kpsi	Wrought Nickel * kgf/m.^{2}	Wrought Nickel * kpsi	Zirconium Copper kgf/m.^{2}	Zirconium Copper kpsi	Az-Zr Copper kgf/m.^{2}	Az-Zr Copper kpsi
		Bond Strength on Indicated Base Metal (Average)							
-196	-320	75	106.5	69	98.0	39	55.4	45	63.9
20	68	56	79.5	51	72.4	27.5	39.1	34	48.3
200	392	40	56.8	42	59.6	22	31.2	27	38.3
400	752	32	45.4	31	44.0	17.5	24.9	26	36.9
600	1112	5	7.1	13	18.5	8	11.4	10	14.2

Hydrostatic Test with Water:

Test Temp °C	°F	Electrodeposited Ni kgf/m.^{2}	Electrodeposited Ni kpsi	Wrought Nickel * kgf/m.^{2}	Wrought Nickel * kpsi	Zirconium Copper kgf/m.^{2}	Zirconium Copper kpsi	Az-Zr Copper kgf/m.^{2}	Az-Zr Copper kpsi
20	68	39	55.4	38	54.0	20.5	29.1	26	36.9

* - Nickel in forged or cold worked condition.

G. PROCEDURES FOR BONDING ELECTRODEPOSITED NICKEL TO ELECTRODEPOSITED NICKEL (ELECTROFORMING RESTARTS)

ASTM Practice B343-67 (82) describes recommended procedures for preparation of wrought nickel and electrodeposited nickel for plating adherent nickel deposits. If the surface of the basis metal has been machined, ground, or subjected to any operations wherein oil or fingerprints are present, it is recommended that the normal pretreatment of vapor degreasing and electrolytic alkaline cleaning be used. If anodic alkaline cleaning is used, an oxide film forms on the nickel surface. This film must be removed in subsequent treatments. An acid dip or a mild anodic etch in sulfuric acid is usually not adequate for complete removal of the oxide film. A heavy anodic etch in sulfuric acid, an electropolishing treatment, a low pH nickel bath, or the acid-nickel chloride (Wood's bath) treatment is usually required to obtain good adhesion.

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