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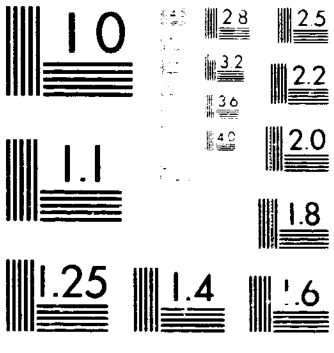

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FINAL REPORT
INVESTIGATION OF ELECTROFORMING TECHNIQUES

by

G.A. Malone

BELL AEROSPACE COMPANY
DIVISION OF TEXTRON, INC.

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16. Abstract

The objective of this program was 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 structures of regeneratively cooled thrust chambers. This report describes the selection of electrolytes for copper and nickel deposition, the development studies performed to refine and complete the processes necessary for successful chamber shell fabrication, and the testing employed to verify the applicability of the processes and procedures to small scale hardware. Specifications were developed to afford a guideline for the electroforming of high quality outer shells on regeneratively cooled thrust chamber liners.

Test results indicated repeatable mechanical properties could be produced in copper deposits from the copper sulfate electrolyte with periodic current reversal and in nickel deposits from the sulfamate solution. Use of inert, removable channel fillers and the conductivizing of such is described. Techniques (verified by test) which produce high integrity bonds to copper and copper alloy liners are discussed.

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I. SUMMARY

The objective of the program conducted under Contract NAS 3-17823 was 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 structures of regeneratively cooled thrust chambers. This report describes the selection of electrolytes for electroforming, the development studies conducted to refine and complete the processes necessary for producing high quality thrust chamber outer shells, and the testing employed to demonstrate the applicability of these processes and procedures when applied to small-scale hardware.

Specifications were developed and modified from observations and test results in the development effort. Procedures, processes, and controls were detailed for electroforming copper and nickel, for preparation of copper and copper alloys for electroform bonding, and for the specialized technology unique to thrust chamber electroforming - treatment of coolant passages by temporary fillings, conductivizing, and bond activation.

Copper alloy (Amzirc) test cylinders, containing passages simulating those of actual regeneratively cooled thrust chamber liners, were electroformed with copper and nickel for destructive evaluation to verify that high bond integrity and good mechanical properties were obtained using the specifications developed. Results disclosed that the electroformed bonds always exhibited strengths at least equal to the tensile strength of the weaker component metal. Mechanical properties of the electroformed copper and nickel were at least equal to those of the annealed wrought counterpart or were superior from a standpoint of structural application and had excellent thermal stability.

II. INTRODUCTION

One of the primary methods of fabricating the outer shells of regeneratively cooled thrust chambers for advanced design rocket engines is by electroforming. A typical rocket engine is shown schematically in Figure 1. The cooled thrust chamber section is composed of a combustion chamber where burning of high energy fuel and oxidizer occurs, a throat restriction to convert the high pressure gases into high velocity vector flow, and a nozzle to increase gas velocity and amplify thrust.

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 one of the propellants) to maintain the hot gas wall at a safely low operating temperature. The outer shell closes out the coolant passages and provides structural support for the liner coolant system. Electroformed nickel or copper is generally utilized for the outer shell due to available experience with the deposition of these metals and the useful properties obtainable with them.

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 in producing hardware meeting the rigid service requirements demanded is limited. Processes and procedures are, for the most part, proprietary. As a result, the product of one electroformer will frequently 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 describes the development of processes and procedures for the preparation of specifications for electroforming nickel and copper outer shells on regeneratively cooled thrust chamber liners. These specifications represent a merging of technical contributions from many sources into a guide for those considering the electrodeposition of aerospace structures.

Since most procedures and practices for electroforming complex structures subject to arduous service environments are highly proprietary, it is anticipated that the specifications contained herein will be continually improved as various electroforming investigators add their own personal knowledge and experience to the available literature. For the present, this work provides a basic document on which the electroformer may compare his product with that of another.

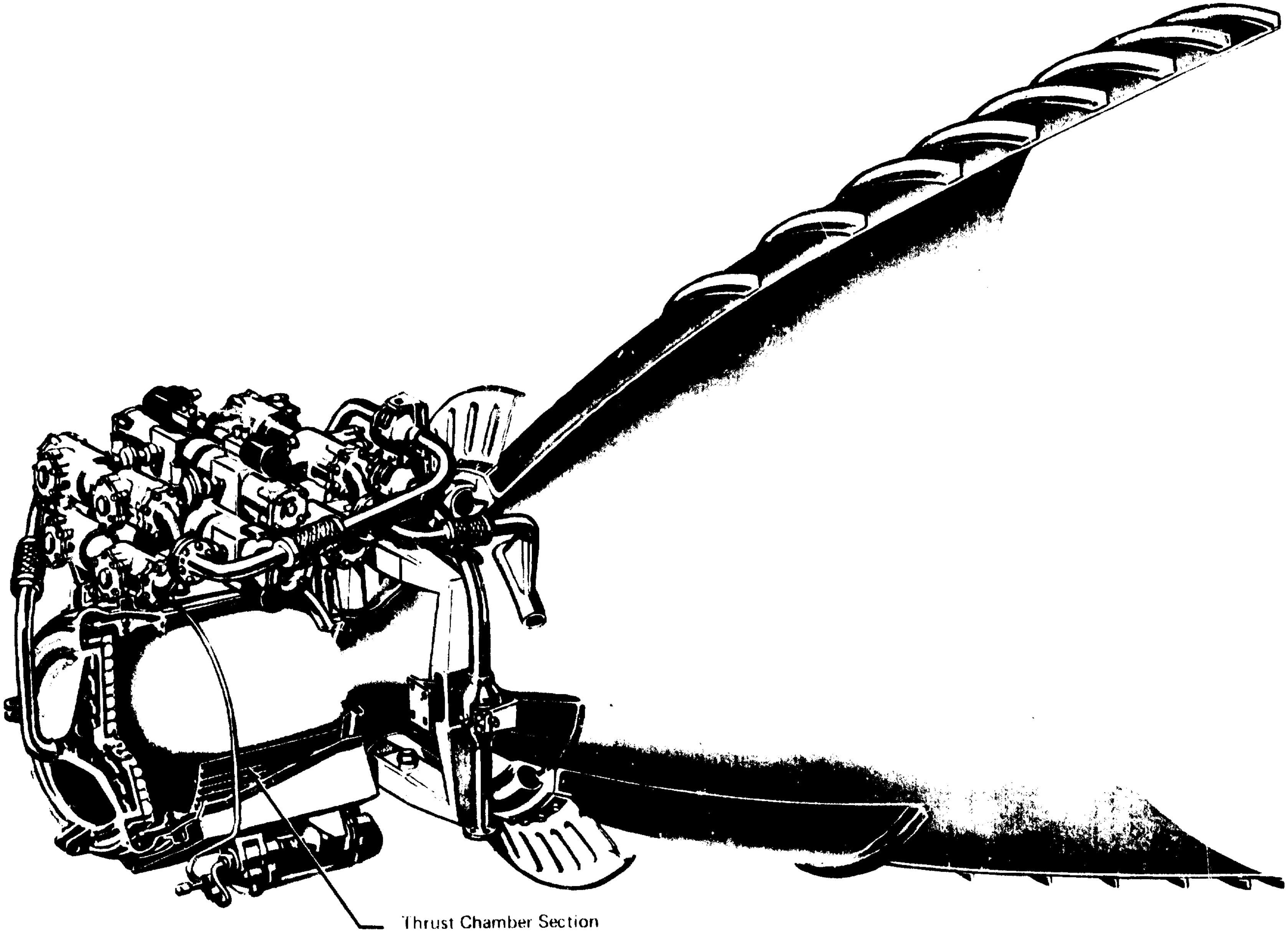


Figure 1. Schematic Section of a Typical Regeneratively Cooled Thrust Chamber

III. LITERATURE ANALYSIS

Electroforming the outer shells of regeneratively cooled thrust chambers is a unique electrochemical process for it is a hybrid operation between true electroforming where the mandrel is removed to leave a free standing structure and heavy electroplating where a highly reliable bond to the substrate metal is required. Possibly the most difficult task in electroforming regeneratively cooled thrust chambers is the requirement that a delicately conductivized film over the material used to fill the coolant passages must be bridged with a non-porous layer of electrodeposited metal while simultaneously obtaining a highly reliable bond to the metal surfaces adjacent to the passages.

In effectively meeting the above requirements it was necessary to consider all processes by which the desired electrodeposits could be made and the benefits or disadvantages in mechanical properties available from each. A literature search was conducted to screen all candidate processes for the deposition of copper and nickel as the electrodeposited outer shell material. These metals are the most commonly used by virtue of available deposition experience, controlled mechanical properties, and favorable thermal properties. Included in this survey were all procedures and processes related to bonding on metal substrates - with particular requirements for bonding to copper and copper alloys.

The complete literature analysis has been published in Report No. NASA CR-134776, "Investigation of Electroforming Techniques" [1]. From this survey acid copper sulfate with periodic reverse current and copper pyrophosphate were selected as the most promising commercially available electrolytes for copper electroforming. This choice of electrolytes was based on the mechanical and physical properties obtainable in the deposit when compared to similar data for wrought annealed copper. This included performance at elevated temperatures as well as room temperature. Such evaluation was critical since the deposits are subject to being brazed or welded as secondary fabrication operations in thrust chamber manufacture. Reasonably low residual stresses in the deposits from these electrolytes was also considered a favorable factor since high tensile stresses in deposits can decrease fatigue strength in the substrate metal.

It was noted that "as deposited" mechanical properties from the product of bright leveling acid sulfate electrolytes are often superior to those of the copper solutions selected in this program. However, this is a result of grain refinement from organic additives. Such additives can contribute to deposit impurities which result in porosity or embrittlement upon exposure to elevated temperature. Such electrolytes represented a high risk selection pending a detailed investigation of their thermal behavior and this was beyond the scope of the present program.

For nickel deposition, the nickel sulfamate electrolyte with low chloride content (or no chloride content) was selected for electroforming structural nickel subjected to elevated temperature exposure. The sulfamate baths offer the best combination of controlled mechanical properties, low tensile stress in the deposits, and ease of operation.

The literature review disclosed two primary techniques for preparing copper and copper alloy surfaces for bonding. The most promising approach appeared to be a Stanford University [2] recommended procedure in which all activation solutions and conditions were considered compatible with the conductivized film required on the wax-filled channel surfaces. Most other techniques were high-risk, based on potential chemical attack on the conductivizing media.

The literature also disclosed the use of various waxes for filling recesses for subsequent conductivizing. Experience has shown certain wax short-comings as contributing to poor dimensional control of channels and in some instances to porosity in deposits immediately over the coolant passages. From recommendations in the literature, a specific filling compound, Rigidax WI Light Blue was selected for investigation.

IV. ELECTROFORMING DEVELOPMENT

A. GENERAL

A development program was established to investigate the most promising electrolytes selected from the literature analysis to electroform outer shells on regeneratively cooled thrust chambers. The two copper electrolytes selected were the pyrophosphate solution and the acid copper sulfate bath with periodic current reversal. Neither of the two systems is commonly used to produce heavy electrodeposits in the aerospace industry, so it was considered necessary to develop or verify the mechanical properties obtainable from each bath. The nickel sulfamate electrolyte selected was investigated primarily for information as to necessary controls to maintain the useful structural properties known to be possible with this solution.

Frequent references in the literature to waxes used to fill coolant passages in chamber liners has been made, but little description of the problems associated with their application and consequent effects on conductivizing films or the structure of electrodeposits has been made. The investigation of several commercially available waxes was included in this study.

B. COPPER PYROPHOSPHATE ELECTROLYTE INVESTIGATION

A 56.8 liter (15 gallon) bath of pyrophosphate copper solution was prepared from commercial plating grade salts. The bath was hydrogen peroxide treated, carbon treated, and filtered prior to use. A series of flat test panels were produced on a stainless steel mandrel and removed for mechanical property testing. As work continued with this bath, a series of modifications were made to determine the effects of improved filtration and solution agitation on the mechanical properties.

The normal operating range and solution chemistry for pyrophosphate copper electrolytes is shown in Table I.

TABLE I
NORMAL RANGE OF CHEMISTRY AND OPERATING CONDITIONS
FOR COPPER PYROPHOSPHATE BATHS [5]

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

*High densities possible with good aitation of electrolyte.

The primary objective of this study was the determination of means to improve ductility in the deposits. Lamb, Johnson, and Valentine [3] reported excellent ductility of 39 percent elongation in a 50.8 mm (2 in.) gauge length in the "as deposited" condition. Other investigators have shown 10 percent elongation or less [1].

The appendix presents a tabulation of the pyrophosphate copper electrolyte analyses, operating conditions, and deposit test results during this study. Only data for those flat panels physically tested is reported. The remaining panels were considered unsuitable for test due to brittleness, abnormal roughness, or "burning."

Test Panels 1 and 6 were produced from an electrolyte high in ammonia content which would account for the high luster of the deposits. A spiral contractometer was used to obtain the residual stress value reported in Panel 1. This compressive stress of 24.66 MN/m² (3.58 Kpsi) for a current density of 2.15 A/dm² (20 amps/ft²) was about twice that reported in the literature [3]. The tensile strength results for Panels 1 and 6 were abnormally high for an electrolyte with no additives. The low ductility on these same panels indicated that codeposition of particulate matter might be occurring, or the air agitation might be insufficient to maintain good electrolyte movement at the cathode surface.

Panels 7 and 8 were produced from the same electrolyte after the ammonia content was adjusted to the normal operating range. The functions of this ingredient are: (1) to aid in proper anode corrosion, and (2) to maintain deposit brightness. A recirculating pump system was added with a filter chamber to provide 10 micron nominal filtration to the electrolyte. Mechanical property test results for Panel 7 indicated that reducing the ammonia concentration and use of 10 micron filtration did not improve the ductility of the deposits. Reducing the anode-cathode area ratio (Panel 8) appeared to result in a decrease in the deposit mechanical strength but did not improve ductility.

Air agitation had been supplied by a single low pressure, oil-less air compressor and dividing the air supply equally between the anodes and cathode. For the remainder of the study, the entire air supply was used to agitate the electrolyte in the area of the cathode. The filtration system was improved by installation of 2 micron nominal rated filters and continuous carbon treatment.

Panel 9 was electroformed under the improved conditions and tested for mechanical properties. An improvement in material ductility was noted in that the elongation in 50.8 mm (2 in.) gauge length ranged from 17 to 21 percent. Heating a sample of this panel at 176.7°C (350°F) for one hour improved the elongation to 23 percent.

Mechanical property results from Panel 10 specimens indicated an increase in brittleness as expected when the copper metal content is high or the pyrophosphate copper ratio is low. In this case, both conditions existed. Heat treating this material at 176.7°C (350°F) for one hour improved the ductility. These results indicated that the pyrophosphate copper ratio must be maintained higher than 7:1 for good mechanical properties - particularly elongation.

Panel 12 was produced under what was considered the best electrolyte conditions based on previous findings. The excellent mechanical properties obtained compared favorably with the data of Lamb, Johnson, and Valentine [3]. The tensile bars exhibited nearly ideal neck-down and fracture

The microstructure is shown in Figure 2. The material contains a generally coarse appearing equiaxed grain structure containing fine sub-grains. This agrees completely with the findings of Lamb, Johnson, and Valentine. It is possible that the high yield strength exhibited by pyrophosphate copper may be related to this unique structure. The mechanical properties for specimens from this panel are compared with those reported in the literature [4] for wrought annealed OFHC copper, Table II.

TABLE II
COMPARISON OF MECHANICAL PROPERTIES OF ANNEALED
OFHC COPPER AND "AS DEPOSITED" PYROPHOSPHATE COPPER

	Tensile Strength		Yield Strength		Elongation%	
	Kpsi	MN/m²	Kpsi	MN/m²	8 in.	2 in.
OFHC Copper Annealed Rod	31 to 32	213.7 to 220.6	12 to 13	82.7 to 89.6	42 to 43.5	
Pyrophosphate Copper, Panel 12	43.3 to 45.9	298.6 to 316.5	24.5 to 25.7	168.9 to 177.2		27 to 37

On Panel 15 the air agitation system was inadvertently misaligned while all other electrolyte operating conditions and solution chemistry were in proper control. The mechanical properties obtained were similar to those on Panel 12, except for the ductility being greatly decreased. The same was true for Panel 16. Panel 20 was produced when the pyrophosphate copper ratio was at the low side of the permissible operating range. The ammonia content was low, but within the operating range. Mechanical property results indicated a general increase in ultimate strength and yield strength. The ductility was lower than desired.

Panel 25 was produced under optimum electrolyte composition and operating conditions during the first portion of the electroforming period. Midway in the deposition run the panel was raised from the electrolyte for a brief inspection. It was replaced in the electrolyte, but in a slightly different position with respect to the air agitation system. Some of the air furnishing electrolyte agitation was directed behind the mandrel rather than over the face being electroformed. This reduced electrolyte movement resulted in a duplexed microstructure as shown in Figures 3 and 4. The mechanical properties were good; however, the ductility was not as good as that of Panel 12.

The test panels in this study could be categorized by mechanical properties and then associated with electrolyte controls (or discrepancies) which contributed to these results, Table III.

From this investigation it was indicated that all of the mechanical properties are affected by electrolyte copper content, pyrophosphate copper ratio, and the degree of filtration (fineness of particulate removed). Air agitation, or uniformity, does not appear to significantly affect the deposit mechanical strength or yield strength, but it does significantly determine the ductility obtainable as shown in Table III.

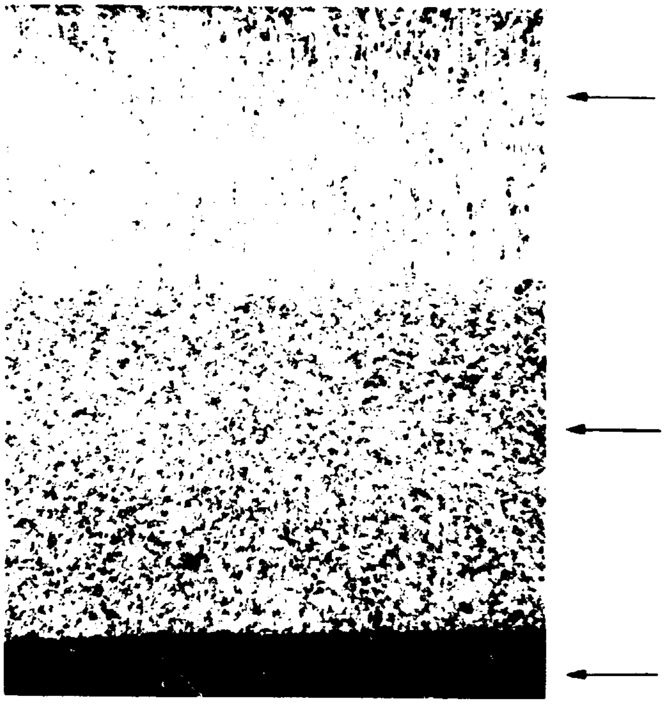
Panel 12 Magnification 100X

The above photomicrograph was taken from a non-strained region of a tensile test specimen which indicated mechanical properties of:

	Kpsi	MN/m.^{2}
Ultimate Strength	43.3	298.6
Yield Strength	25.5	175.8
Elongation, % in 2 Inches	37	

The microstructure appears to be medium coarse equiaxed with the fine subgrain structure described by Lamb, Johnson, and Valentine (6).

Figure 2. Microstructure of Copper Pyrophosphate Deposits



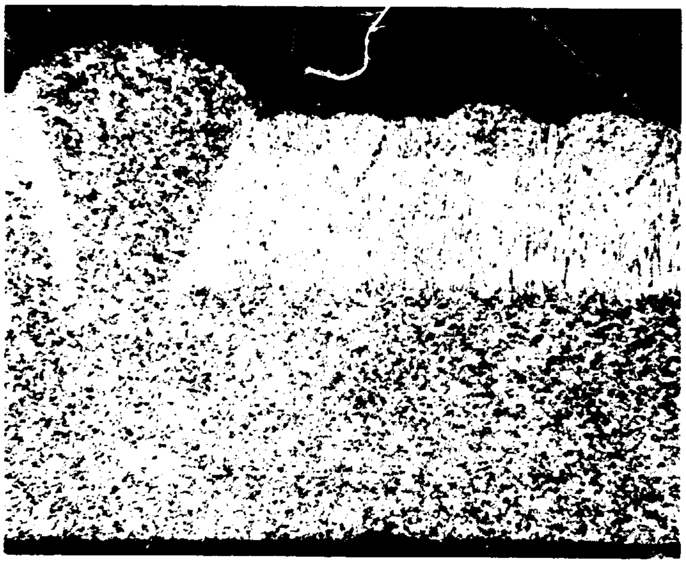
Region of columnar grain structure indicated to have originated from a change in electrolyte agitation conditions.

Region of equiaxed grain structure typical of that expected in copper pyrophosphate deposits from highly agitated electrolytes.

Surface from which deposition was initiated.

Panel 25 Magnification 50X

Figure 3. Duplex Grain Structure in Copper Pyrophosphate Electroformed Panel



Region of nodular or rough deposit surface in the same specimen as illustrated in Figure 3. The areas of duplex grain structure appear to vary as a result of localized changes in electrolyte agitation conditions at the cathode surface.

Panel 25 Magnification 32X

Figure 4. Region of Nodular Surface in Copper Pyrophosphate Electroformed Panel

TABLE III
CATEGORIZATION OF PYROPHOSPHATE COPPER DEPOSITS BY MECHANICAL PROPERTIES AND RELATED ELECTROLYTE CONTROLS

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

Specimens from Panel 25 were supplied to the NASA Lewis Research Center for independent evaluation. The material was found to weld satisfactorily.

It is concluded that electrodeposits from the pyrophosphate copper electrolyte are satisfactory for application to regeneratively cooled thrust chamber outer shells. However, the application of this process will require additional studies by the user to develop a satisfactory electrolyte agitation system which will assure good solution circulation in recessed areas (chamber throat region) in actual hardware.

C. INVESTIGATION OF ACID COPPER SULFATE ELECTROLYTE DEPOSITS WITH PERIODIC CURRENT REVERSAL

A 120 gallon (454.2 liter) tank used for plating bright leveling acid copper was converted to conventional acid sulfate with periodic current reversal capability for this study. A new electrolyte was prepared which analyzed 48g/l. (6.4 oz/gal) copper as metal, 187.5 g/l. (25 oz/gal) copper sulfate, and 75 g/l. (10 oz/gal) sulfuric acid. The phosphorized OFHC copper anodes were replaced with OFHC copper anodes. The solution was hydrogen peroxide treated, heated to 60°C (140°F) to drive off residual peroxide, and subjected to continuous filtration.

The first panels electroformed were to determine the effects of bath agitation on the physical appearance of the deposits. No periodic current reversal was used. Air agitation of the bath without cathode movement resulted in a rough, nodular deposit of unsuitable quality for testing. Cathode movement on a reciprocating rod improved the second panel, but the surface quality was not as desired. An excessive number of anodes were present which resulted in abnormally low anode current density. This was corrected and a recirculating pump and spray system installed to improve electrolyte flow. The electroforming tank, including an electroform rotation system and periodic current reversal unit is illustrated in Figure 5.

The next panel was electroformed at a current density of 4.84 A/dm^2 (45A/ft^2) and a bath temperature of 32.2°C (90°F). The mechanical properties obtained were.

	Ult. Strength		Yield Strength		Elongation
Test Strip	Kpsi	MN/m^2	Kpsi	MN/m^2	% in 2 inches
1	49.6	342.0	31.0	213.7	9
2	39.1	338.5	30.4	209.6	19
3	51.4	354.4	30.5	210.3	18

The high tensile strength and lower than expected ductility indicated some of the old bright leveling bath may have been left in the recirculation, filtering, and carbon treatment systems. Correction was made by peroxide treatment and replacement of the filters and carbon.

A new series of test panels were electroformed with and without the use of periodic current reversal. The electrolyte temperature was maintained between 32.2 and 35.6°C. The electrolyte was continuously filtered and carbon treated. The mechanical property test results for the control panels (with no periodic current reversal) are shown in Table IV. Corresponding data under similar electrolyte controls for deposits electroformed with periodic current reversal are shown in Table V.

The most significant finding in that portion of the study concerning mechanical properties of conventionally electroformed copper from the acid sulfate bath was the beneficial effect of vigorous agitation of electrolyte at the cathode. At 4.84 A/dm^2 (45 Amp/ft^2) the mechanical property test results showed an excellent combination of strength and ductility (Panel 2, Table IV). As expected, these results could not be duplicated at greater deposit thicknesses. Panel 3, Table IV, was electroformed to almost 2.5 mm (0.10 inch) in thickness using the same current density as was used to deposit Panel 2. The resulting mechanical properties at this thickness were unsuitable for most structural applications. Grain coarsening during thick electroforming led to greater impurity codeposition and microstructural faults with attendant poor mechanical strength and low ductility as illustrated in Figure 6.

Table V shows the benefits of periodic current reversal on the mechanical properties of acid copper deposits. The mechanical properties of all deposits produced at current densities of 4.84 A/dm^2 (45A/ft^2) or 6.46 A/dm^2 (60 A/ft^2) are good with the former being excellent - particularly in regards to ultimate and yield strengths. The most striking advantage to periodic current reversal appears to be the ability to maintain these properties at any deposit thickness as evident for Panels PR-3 and PR-4. The deposits were very smooth and of excellent visual quality. A photomicrograph, Figure 7, shows the uniform columnar grain structure typical for periodic reversal.

The only disadvantage to periodic current reversal appears to be the longer deposition times necessary to obtain a given electroform thickness. Ninety-three hours were required to deposit the 2.184 mm (0.086 inch) of buildup in Panel PR-4. The adjustment of the periodic current reversal cycle to a longer forward plating time will increase the deposition rate - in fact, cycles up to 7:1 for forward to reverse plating ratio have been suggested in the literature.

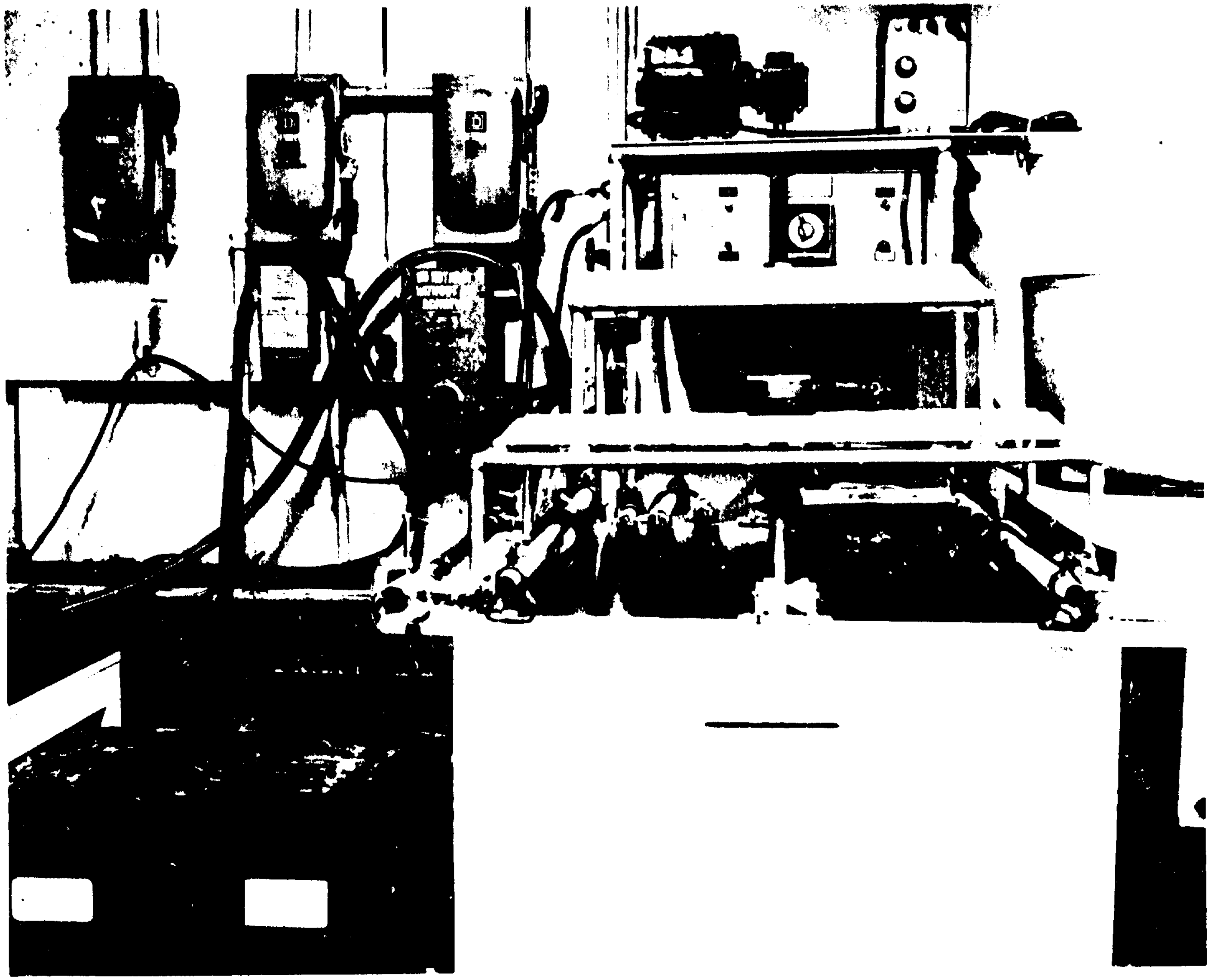


Figure 5. Acid Copper Electroforming Facility with Electroforming Drive System and Periodic Current Reversal Capability

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

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

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

TABLE V
MECHANICAL PROPERTIES OF ACID COPPER SULFATE DEPOSITS ELECTROFORMED WITH PERIODIC CURRENT REVERSAL

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

Panel No.	Periodic Current Cycle	Bath Temp. °C	Current Density		Specimen Thickness		Mechanical Properties				
							Ult. Str.		Yield Str.		Elongation % in 2 in.
			A/ft²	A/dm	in.	mm	Kpsi	MN/m	Kpsi	MN/m	
PR-1	8 sec. forward 4 sec. reverse	32.2	30	3.23	0.031	0.787	35.1	242.0	12.4	85.5	36
					0.027	0.686	30.0	206.9	8.1	55.8	30
					0.025	0.635	26.1	180.0	14.0	96.5	17
PR-2	8 sec. forward 4 sec. reverse	32.2	45	4.84	0.019	0.483	44.7	308.2	20.5	141.3	31
					0.019	0.483	55.1	379.9	25.6	176.5	31
					0.017	0.432	44.2	304.8	19.2	132.4	30
PR-3	8 sec. forward 4 sec. reverse	32.2	60	6.46	0.036	0.914	40.6	279.9	16.7	115.1	36
					0.035	0.889	36.1	248.9	14.9	102.7	39
					0.030	0.762	35.6	245.5	12.6	86.9	38
PR-4	8 sec. forward 4 sec. reverse	32.2	60	6.46	0.086	2.184	37.5	258.6	17.3	119.3	35

For subsequent work in this program, the periodic reverse cycle was changed from a ratio of 2:1 to 3:1 and 4:1 to reduce deposition time. The effects of this change were more severe on mechanical properties than expected. The grain structure was coarsened and lower mechanical strength was obtained. Typical mechanical properties for the longer cathodic periodic reverse cycles are shown in Table XIII.

Microstructure of a thick copper electrodeposit from the acid sulfate electrolyte using no periodic current reversal. Note the fine columnar grain in the initial deposit layer. The grain structure quickly coarsens and voids or inclusion areas may form to weaken the structural properties. The deposit average thickness was about 2,515 mm (0.099 inch).

Panel 3
Current Density: 4.84 A/dm^2 (45 A/ft^2)

Magnification 32X

Figure 6. Microstructure of a Thick Electroformed Deposit from the Acid Sulfate Electrolyte Using No Periodic Current Reversal

Microstructure of a thick copper electrodeposit from the acid sulfate electrolyte using periodic current reversal at a cycle of 8 seconds forward plate and 4 seconds reverse plate. The deposit has a thickness of (2.184 mm) 0.086 inch and contains a fine columnar grain structure, indicative of the good mechanical properties obtained.

Panel PR-4
Current Density: 6.46 A/dm^2 (60 A/ft^2)

Magnification 32X

Figure 7. Microstructure of a Thick Electroformed Deposit from the Acid Sulfate Electrolyte Using Periodic Current Reversal

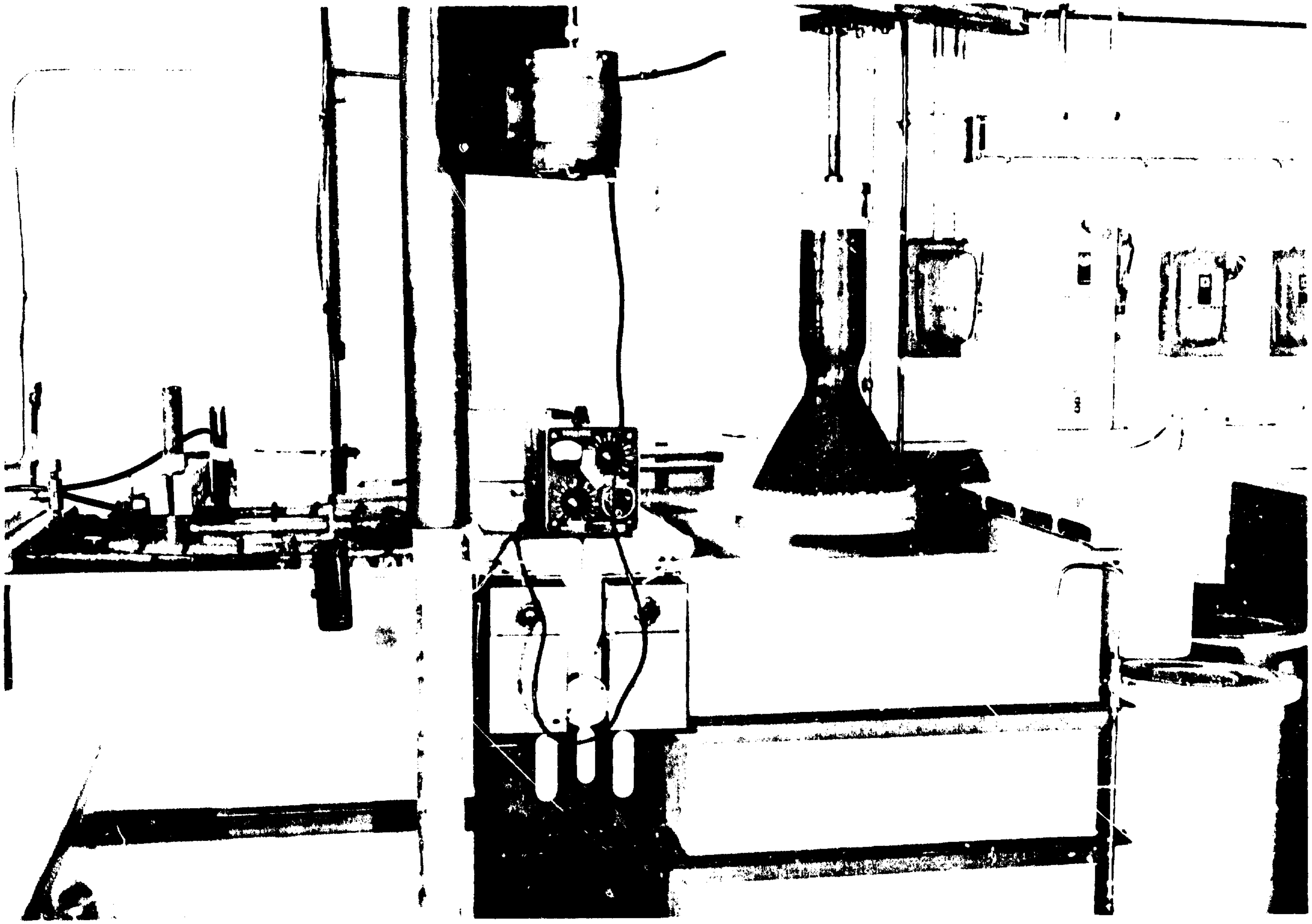


Figure 8. 180 Gallon Nickel Sulfamate Electroforming Facility - Electroforming Tank (Left) and Solution Make-up Tank (Right)

D. INVESTIGATION OF ELECTRODEPOSITED NICKEL FROM THE SULFAMATE NICKEL ELECTROLYTE

A conventional nickel sulfamate electrolyte containing no additives other than a small amount of nickel chloride was used in this study. The facility is shown in Figure 8. The bath volume was 681.3 liters (180 gallons). This particular solution had been in continuous service for a period of at least six years. No wetting agents are ever employed in the electrolyte, and the solution is continuously carbon treated with sulfur-free granular carbon and filtered through 10 microm nominal polypropylene filters. An open pumping system capable of flowing 56.8 liters (15 gallons) per minute against a rotating cathode (workpiece) surface is independent of the filtration system. Electrolyte level is maintained by automatic distilled water additions triggered by a pressure sensitive transducer system mounted in the tank wall.

Operating at temperatures of 43.3 to 54.4°C (110 to 130°F) and current densities of 2.15 to 4.30 A/dm^2 (20 to 40 A/ft^2), this bath is analyzed only once per month for chemical composition. No additions to correct nickel metal content have been necessary in the past five years. Occasionally, boric acid requires adjustment due to operation shut-downs when precipitation in the filter chambers may occur. Aging (hydrolysis of sulfamate to form nickel sulfate) is corrected by electrolyte treatment with barium sulfamate to precipitate barium sulfate which is removed by 0.5 micron filters in a separate operation. This need only be performed once every two years. The barium sulfamate treatment is also used to remove excessive sulfate drag-in from base metal activation treatments where cathodic treatment in sulfuric acid may be the final step.

Where possible, only sulfur depolarized nickel anodes are used. Frequent acidity (pH) measurements are made (every three days of electroforming) to determine if electrolyte performance is normal. A slowly rising pH is indicative of good bath operation. No rise in pH or a pH drop indicates that a complete analysis - particularly for nickel metal - should be performed.

Once a bath has been "broken-in", there should be no problem in maintenance. Titanium baskets housing anode slugs or chips must be kept full. The nickel sulfamate bath is probably the simplest bath to maintain and control for nickel electroforming. Maintaining the chloride content at a low level, as opposed to using no chloride, does not appear to afford any disadvantage other than promoting some residual stress in the deposit. Even this is questionable, providing the chloride is maintained sufficiently low (below 4.5 g/l. or 0.6 oz/gallon).

Test panels were electroformed over the range of current densities and electrolyte temperatures considered normal for fabricating outer shells for regeneratively cooled thrust chambers. The electrolyte analysis and operating conditions for the various panels are reported in Table VI. For the electroforming conditions used, Panel 4 represents material which should have the higher residual stress by virtue of the higher current density. The residual stress was 4,850 psi. tensile.

The mechanical property test results indicate good structural properties are obtained over a wide range of electrolyte temperature and current densities. A comparison of test results from Panels 2 and 3 indicated improved mechanical strength with satisfactory ductility could be obtained at lower electrolyte temperatures. Panels produced at comparable electrolyte temperatures, but differing current densities disclosed improved mechanical properties at the lower current density. Figure 9 shows the typical fine columnar grain structure found in high strength nickel from the sulfamate electrolyte.

TABLE VI
NICKEL SULFAMATE ELECTRODEPOSIT MECHANICAL PROPERTIES AND ELECTROLYTE OPERATING CONDITIONS

Electrolyte Chemistry:

Nickel Metal	9.28 oz/gal.	(69.6 g/1.)
Nickel Chloride	0.48 oz/gal.	(3.6 g/1.)
Boric Acid	4.50 oz/gal.	(33.75 g/1.)
pH	4.0 to 4.4	

Panel No.	Current Density		Electrolyte Temp.		Specimen Thickness		Mechanical Properties				
							Ult. Strength		Yield Strength		Elongation % in 1 in.
	A/ft²	A/dm²	°C	°F	in.	mm	Kpsi	MN/m²	Kpsi	MN/m²	
1	20	2.15	51.7	125	0.024	0.610	105.1	724.7	73.6	507.5	15
					0.024	0.610	112.3	774.3	77.9	537.1	14
2	30	3.23	50.6	123	0.030	0.762	92.5	637.8	61.5	424.0	16
					0.030	0.762	96.7	666.7	59.3	408.9	17
3	30	3.23	43.3	110	0.025	0.635	103.8	715.7	70.5	486.1	12
					0.025	0.635	112.6	776.4	75.2	520.7	14
4*	40	4.30	44.4	112	0.033	0.838	97.7	673.6	61.4	423.4	10
					0.033	0.838	94.6	652.3	64.8	446.8	11

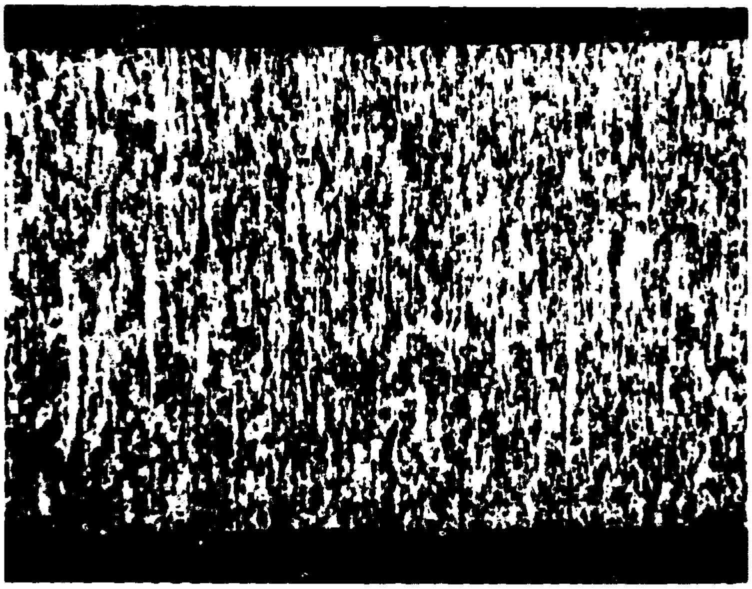
*Residual Stress: 4,850 psi (tensile) as determined by spiral contractometer

All elongation values for tested nickel specimens are reported in percent elongation in a one inch gauge length. This is due to the size of the cylindrical specimens electroformed for these tests. Each flat test bar was approximately 177.8 mm (7 inches) long. No shielding was used to minimize edge buildup. Use of the standard two inch gauge length resulted in a length of sufficient thickness variation to provide results misleading as to the true ductility of the metal. An example of a tested flat bar showing the neck-down and angular shear line at failure is found in Figure 10.

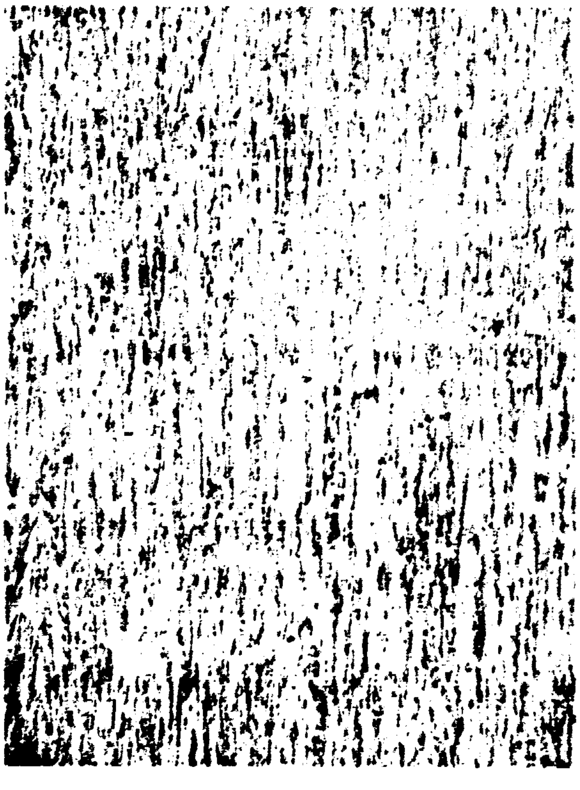
E. EVALUATION OF CHANNEL FILLING COMPOUNDS

This investigation was conducted simultaneously with the bonding study discussed later. Flat plates 6.35 mm (0.25 inch) thick OFHC copper and Amzirc (a copper alloy containing up to 0.2 percent by weight zirconium) were machined to produce coolant passages and connecting manifolds similar to those existing on actual regeneratively cooled thrust chamber liners.

Several commercially available waxes used as electroplating stop-offs or as recess filling compounds were evaluated in the channels on the various test panels. It was found that Unichrome Compound 314 was easily applied by melting at 85°C (185°F) and pouring it into the channels. The test plate had been preheated to the same temperature prior to pouring the wax. On cooling, the wax was found to separate slightly from the side walls of the channels. Prior experience with this wax indicated such separation on shrinkage of the compound would result in pin-holes in the overlying

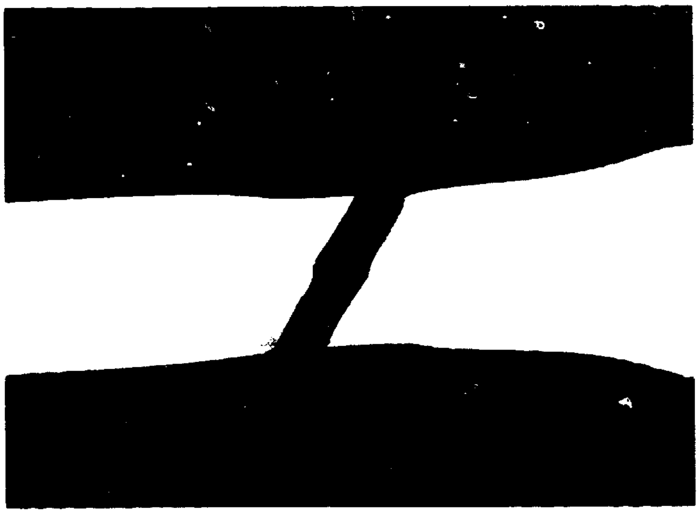


Panel 4 Magnification 50X



Panel 4 Magnification 100X

Figure 9. Typical Fine Columnar Grained Microstructure of High Strength Nickel Sulfamate Electrodeposits



Magnification 2X

A typical electroformed nickel tensile test bar showing localized neck-down and ductile failure after testing.

Magnification 6X

The above photograph illustrates the fracture surface of a typical electroformed nickel tensile test bar after failure in test. Although the elongation occurred over a localized region, the fracture indicated excellent ductility.

Figure 10. Typical Electroformed Nickel Test Bars After Failure in Mechanical Property Tests

electrodeposit along the channel side wall - wax interface. This compound also softens substantially at temperatures of about 51.7°C (125°F), making it a high risk material for use in copper pyrophosphate electrolytes or nickel sulfamate solutions operated at higher temperatures.

Rigidax Compound WI Light Blue was next evaluated. This material has received publicity as a channel filling compound by information releases through the electroforming trade literature.

The test plates were preheated to a temperature of about 65.6°C (150°F) on a hot plate. The Rigidax WI Light Blue was melted at 121.1°C (250°F) and poured into the channels. After cooling to room temperature, the panels were placed under running water and scraped to remove excess wax. The final wax finish was brought dimensionally in line with the tops of the bonding ribs of the plates by scrubbing with a pad of "Scotch-brite" or by wet sanding with 160 to 220 grit papers.

Application of silver conductivizing powder to the waxed surface at room temperature proved difficult because it was necessary to burnish the material into the wax compound to obtain adherence, Figure 11. Warming the wax to temperatures of 48.9°C (120°F) or higher made the conductivizing and burnishing much easier due to wax softening. After cleaning and activating the panel surfaces, electroforming of a copper or nickel close-out layer was accomplished.

These panels were machined to provide a uniform electroform thickness, the wax was removed by melting and degreasing, and the panels were hydrostatically tested to failure. Of the first three copper electroformed panels, two leaked through the electrodeposit. A similar experience was encountered with the nickel electroformed plates.

A new series of OFHC copper and Amzirc plates containing coolant channels were prepared. After heating the plates, filling channels with Rigidax WI Light Blue, and removing excess wax, the entire plate was reheated with a hot air blower (similar to a hair drying gun). Air bubbles were observed to evolve from the wax subsurface. After the bubbles were dissipated, the wax surface was reflowed to produce a sound material on which conductivizing and electroforming could be conducted.

It was discovered that the hand labor required to burnish silver powder into the wax surface could be reduced by simply heating the waxed part to exactly the melt point of 65.6°C (150°F) in an oven, followed by painting the silver onto the wax with a camel hair brush, Figure 12. At this temperature the wax does not flow and is very receptive to the conductivizing powder.

This wax and conductivizing procedure worked very well in all electrolytes used on this program with the exception of the copper pyrophosphate solution operated at 54.4°C (130°F) or higher. At this temperature, the Rigidax WI Light Blue softened and the severe agitation washed the silver away in localized areas.

A new compound, Rigidax WI HT 11-27 Red, was evaluated. This material was applied to several panels in the same manner as the Rigidax WI Light Blue, except the part preheat temperature was 79 to 93°C (175 to 200°F), the melt point was 101.1°C (214°F) and the pour temperature was 135 to 149°C (275 to 300°F). This material was found to retain the conductivized layer under the severe environment imposed by the copper pyrophosphate electrolyte.

Figure 11. Manual Burnishing of Silver Conductivizing Powder on the Rigidax Filled Test Panel Channels

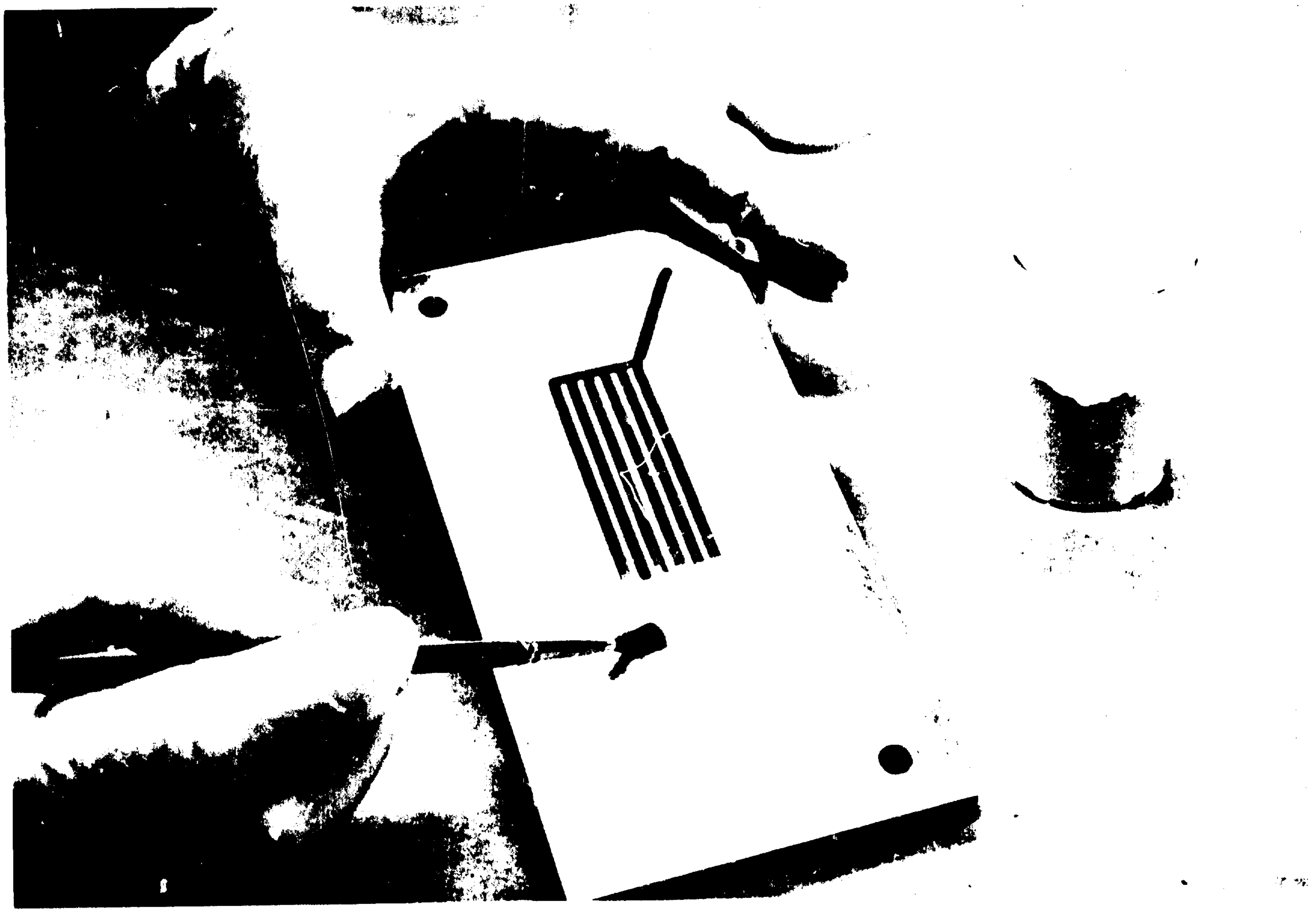


Figure 12. Painting Silver Conductivizing Powder on the Heated Rigidax Channel Filling Compound

F. SELECTION OF CONDUCTIVIZING MEDIUM

One conductivizing material was investigated in this program. The material selected was a fine silver powder, Engelhard G-3. The material is easy to apply, provides good electrical conductivity, and is readily removed in dilute nitric acid. Other materials of similar composition, bronzing powders, or fine copper powders should work equally well. Removal of other powders after melting channel fillers should be investigated before use.

G. INVESTIGATION OF BONDING OF ELECTROFORMED COPPER TO OFHC COPPER AND AMZIRC LINERS

The plan to evaluate processes and procedures for cleaning and activating copper and copper alloys for bonding with electrodeposited copper and nickel required the use of a specially designed test plate containing machined channels and connecting manifolds similar to those in actual regeneratively cooled thrust chamber liners. The electrodeposited bonds were to be evaluated by hydrostatically pressurizing until the bonded joint failed and the electroformed coverplate bulged. These test plates (baseplates) were OFHC copper and Amzirc. Figure 13 illustrates the panel design.

Prediction of the pressure required to fail a high integrity bond would require a knowledge of the mechanical properties of the metals composing the bonded joint. The mechanical properties of the electroformed metals comprising the coverplates have previously been determined. It was necessary to determine the mechanical properties of the OFHC copper and Amzirc baseplate stock. Because of a crack flaw found in the first Amzirc forging used to fabricate baseplates, a second forging was used to complete this study. Any Amzirc panels identified as A-1 through A-10 are from the first forging, while those identified as A-11 or higher, are from the second forging. Mechanical property test results for each of the baseplate materials are shown in Table VII. The lower than expected mechanical strength of the Amzirc in the first forging was believed due to improper solution annealing and age hardening.

All baseplates were degreased and alkaline scrub cleaned with a mixture of a fine pumice scrubbing compound and a commercial detergent cleaner, Alconox. All baseplate thickness dimensions were recorded as references for machining after electroforming to assure a known coverplate (electrodeposit) thickness. The channels were filled with Rigidax Type WI Light Blue Compound as previously described. The plates were preheated on a hot plate to 63.3 to 65.6°C (140 to 150°F) prior to wax pouring. After the wax was dressed to provide the desired surface uniformity, the panels were bright dipped for ten seconds in a room temperature solution of:

ASTM B281 Formulation	Concentration
Sulfuric Acid, 66° Be′	60 to 70 volume %
Nitric Acid, 42° Be′	20 to 35 volume %
Water	5 to 10 volume %
Hydrochloric Acid, 20° Be′	0.94 g/l.

The panels were rinsed in distilled water after bright dipping. After drying, the panels were coated with silver conductivizing powder over the waxed channels. This material was manually burnished into the wax.

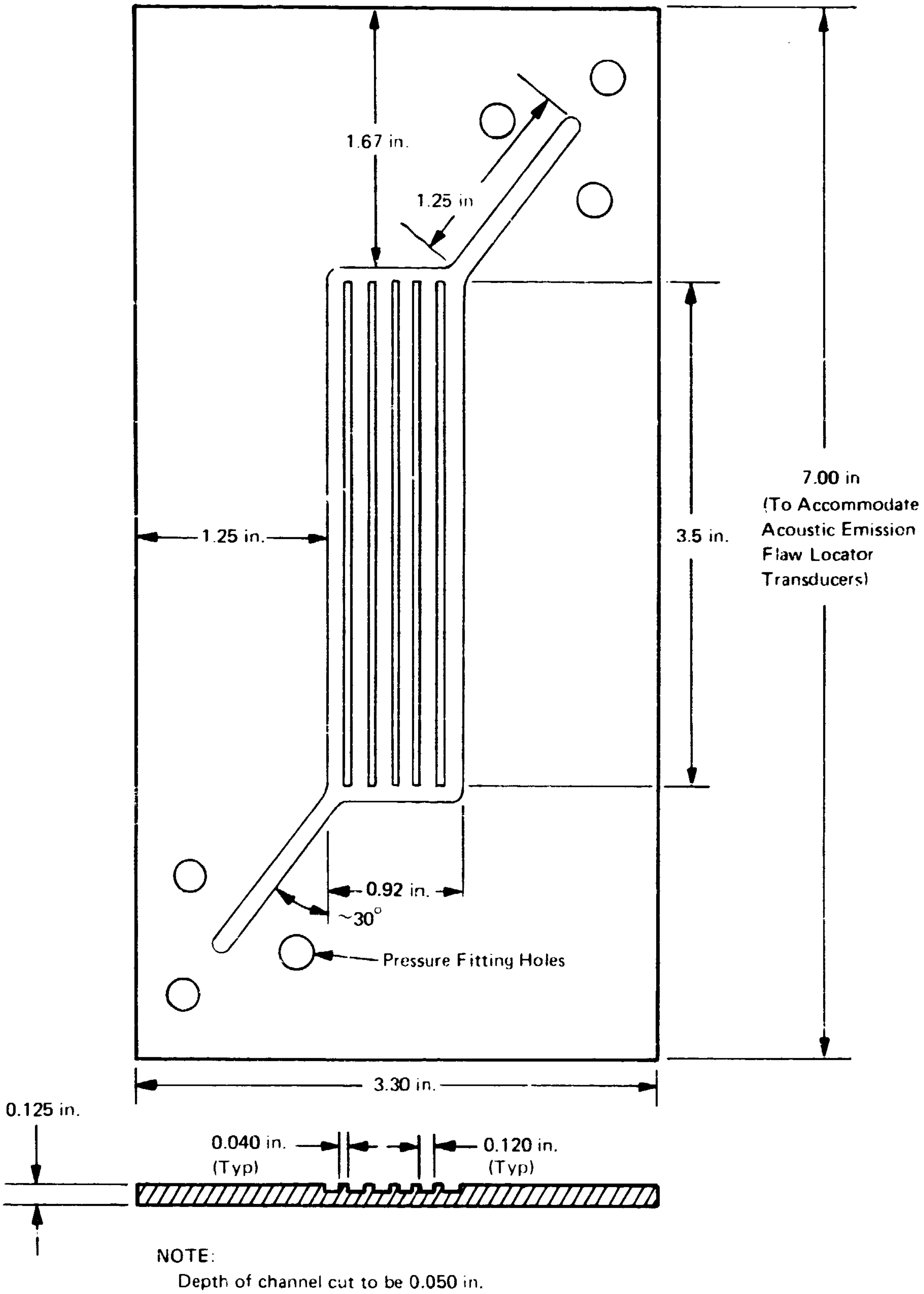


Figure 13. Flat Panel Baseplate Design

TABLE VII
MECHANICAL PROPERTIES OF OFHC COPPER AND AMZIRC BASEPLATE STOCK FOR FLAT TEST PANELS

OFHC Copper - Cold rolled, light anneal per ASTM B-152, 0.635 mm (0.25 in.) thick

			Mechanical Properties				
			Ult. Strength		Yield Strength		Elongation % in 2 in.
Chemistry	Copper	Oxygen	Kpsi	MN/m²	Kpsi	MN/m²	
Required Actual	99.95 min 99.99	0.000 0.000	35.4	244.3	28.0	193.2	47

Amzirc - Forged and solution annealed to commercial specification

Chemistry			Test Bar Thickness		Mechanical Properties				Elongation % in 2 in.
					Ult. Strength		Yield Strength		
			in.	mm	Kpsi	MN/m²	Kpsi	MN/m²	
Lot A	Copper	99.75	0.255	6.477	31.4	216.5	25.3	174.4	41
	Zirconium	.25	0.254	6.451	32.1	221.3	26.0	179.3	39
			0.254	6.452	32.0	220.6	25.0	172.4	41
Lot B	Copper		0.254	6.426	37.1	255.8	34.9	240.6	14
	Zirconium	99.79	0.253	6.426	40.9	282.0	38.5	265.5	14
		.21	0.254	6.452	38.0	262.0	34.2	235.8	13
			0.255	6.477	38.9	268.2	35.2	242.7	17

The first bonding procedure evaluated was the process used at Stanford University and described by Pope [2], Table VIII. OFHC copper baseplates C-1 and C-2 were anodically treated in phosphoric acid solution and cathodically cleaned in sulfuric acid in accordance with Pope's recommendations. The panels were double rinsed in distilled water and placed in the acid copper sulfate electrolyte with cathodic voltage applied. After a brief period of electroforming with direct current at 6.46 A/dm² (60 A/ft²), periodic current reversal at the same current density was applied. When the high current density activation treatment was applied in phosphoric acid, there appeared to be some disturbance of the silver conductivizing layer and the adjacent copper surfaces were somewhat smutty in appearance.

OFHC copper panels C-3 and C-4 were prepared in a like manner, except that the anodic treatment in phosphoric acid was performed at a current density of 2.69 A/dm² (25 A/ft²) and the time lengthened to 90 seconds in an effort to minimize disturbance of the silver conductivizing film. The cathodic treatment in sulfuric acid was at the recommended current density, but the time was increased to 120 seconds. These panels were double rinsed and electroforming started at a current density of 4.84 A/dm² (45 A/ft²) before application of periodic current reversal at 6.46 A/dm² (60 A/ft²). The copper sulfate electrolyte was maintained at 32.2°C (90°F) for all electroforming. The electrodeposited copper was expected to have mechanical properties similar to those of Specimen PR-4 in Table V.

Two Amzirc baseplates, A-1 and A-2, were activated for bonding and electroformed exactly in the manner as Panels C-3 and C-4.

TABLE VIII
STANFORD UNIVERSITY PROCEDURE FOR BONDING ELECTRODEPOSITED COPPER TO OFHC COPPER BASIS METALS(2)

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

To provide a bond evaluation comparison, a second method of bonding was investigated. ASTM recommended practice B 281-58 [7] was modified to exclude any solutions containing nitric acid which would attack the silver conductivizing layer. OFHC Panel C-5 and Amzirc Panel A-3 were solvent degreased, rinsed, and alkaline electrocleaned cathodically for 2 minutes at a current density of 3.23 A/dm^2 (30 A/ft^2) and anodically for 10 seconds at the same current density. The electrocleaning solution contained 37.5 g/l. (5 oz/gal) of an alkaline compound made up of 45 percent by weight sodium carbonate, 35 percent by weight trisodium phosphate, and 20 percent by weight dium hydroxide. The solution temperature was maintained at 60 to 71.1°C (140 to 160°F). The baseplates were rinsed, dried, and waxed. The panels were heated prior to conductivizing to provide improved silver adherence to the blue wax. Base metal activation was provided by immersing the panels in a ten percent by volume solution of sulfuric acid at room temperature for three minutes. After double rinsing in distilled water, the panels were electroformed with copper in a like manner as Panels C-3 and C-4.

All of the above panels were machined to provide a uniform coverplate (electroformed) thickness. The wax channel filling compound was removed by melting and solvent degreasing. Pressure fitting mounting holes were drilled in the panels and hydrostatic pressurizing to failure was conducted. Figure 14 illustrates the panel channel pattern prior to electroforming, the panel fixtured for pressure testing, and a bulged coverplate after test.

The hydrostatic pressure at which joint failure and bulging occurred for each panel was recorded. The tests were monitored by means of acoustic emission equipment to verify when failure actually started and to analyze the emission characteristics of the various material combinations. Procedures used were as described in Ref. 8. The bond strength of the electroformed coverplate and baseplate combinations was determined from the following formula:

$$S = P \times \frac{A_c}{A_r}$$

Where: S represents the bond or joint strength, Kpsi

P is the hydrostatic pressure required to fail the bond or joint, Kpsi

A_c is the area of the electrodeposited coverplate over the pressurized channels, $in.^2$

A_r is the area of the baseplate ribs to which the electroformed bond is made, $in.^2$

It should be noted that when low angle buckling or bulging of the coverplate occurs prior to joint failure, the value for the term A_c will increase. For most electroformed copper coverplates in this study, the increase in A_c from permanent deformation over the entire channel and manifold areas varied from 10 to 20 percent. A value of 10 percent has been selected as a correction factor in order to conservatively calculate bond strengths for copper electroformed panels.

Table IX presents the destructive test data used to determine bond strengths for the initial groups of panels fabricated in the bonding process development effort. All of the bond strengths realized were below those expected in a high integrity bond. Figure 15 presents photomacrographs of two typical bond failures from the above panels. Each panel appears to have failed at the bond interface. No correlation of acoustic emission count and the material combinations used in this group of panels could be made. Since all bonds were weak, a high level of emissions were recorded.

To improve the electroformed copper bonds on Amzirc substrates, two new innovations were applied. Prior to silvering the wax filled channels, the high current density anodic treatment in phosphoric acid was applied to improve the Amzirc or OFHC copper substrate surface. This treatment could be lengthened in time to several minutes or repeated as necessary until a suitably bright smooth surface was obtained. After this treatment, the panels were rinsed, dried, and brought to the wax melt point temperature in an oven. Applying the silver powder to the warm wax surface promoted better film adhesion which was found to withstand further anodic treatment in phosphoric acid at high current density.

Amzirc Panels A-10, A-11, and A-16 were processed in this manner using the anodic treatment in phosphoric acid before and after conductivizing. Anodic treatment at 16.1 A/dm^2 (150 A ft^2) did not degrade the conductivized layer on the wax. These panels were cathodically treated in sulfuric acid, double rinsed in distilled water, and electroformed under the same conditions as the pre-

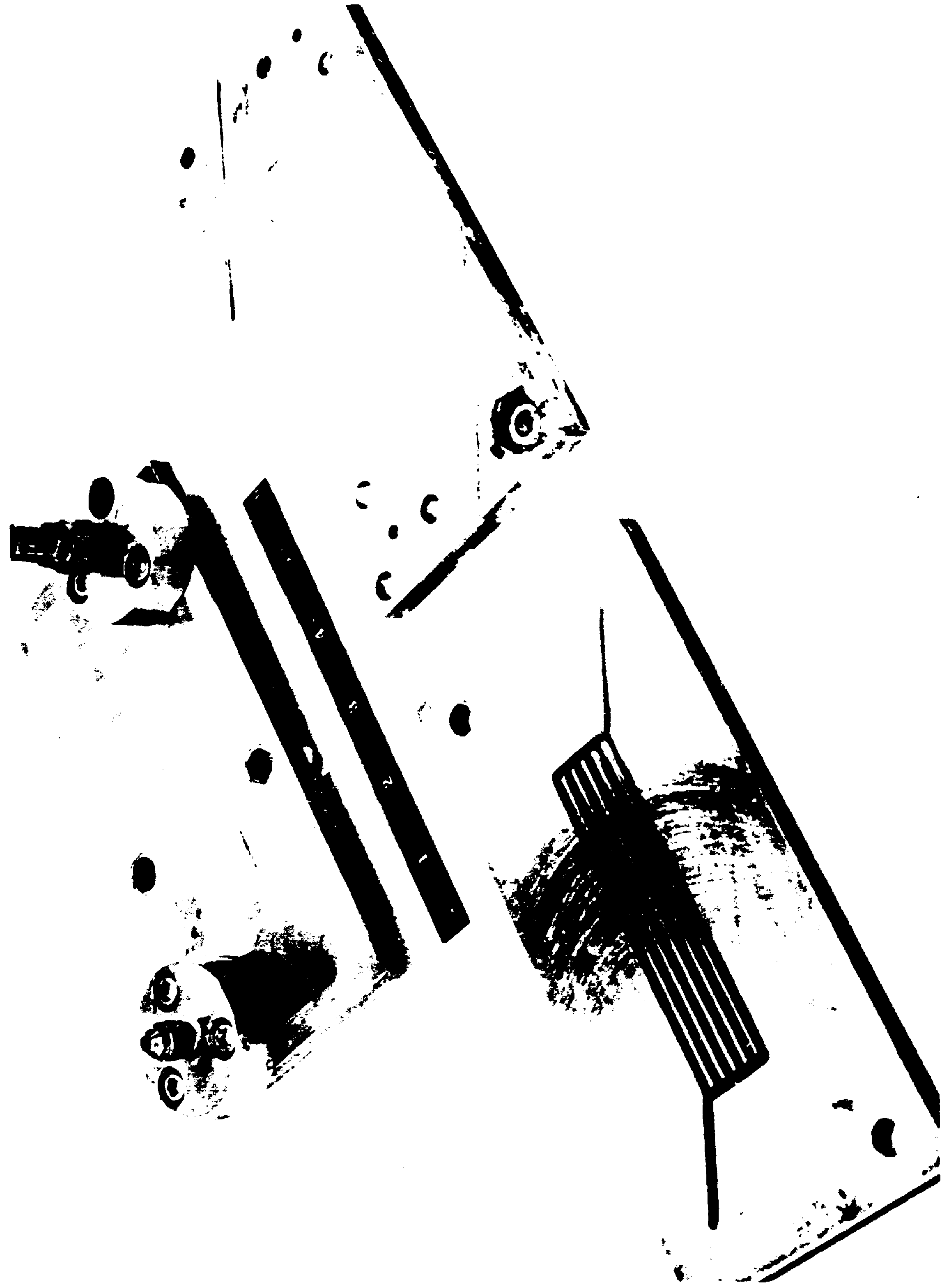
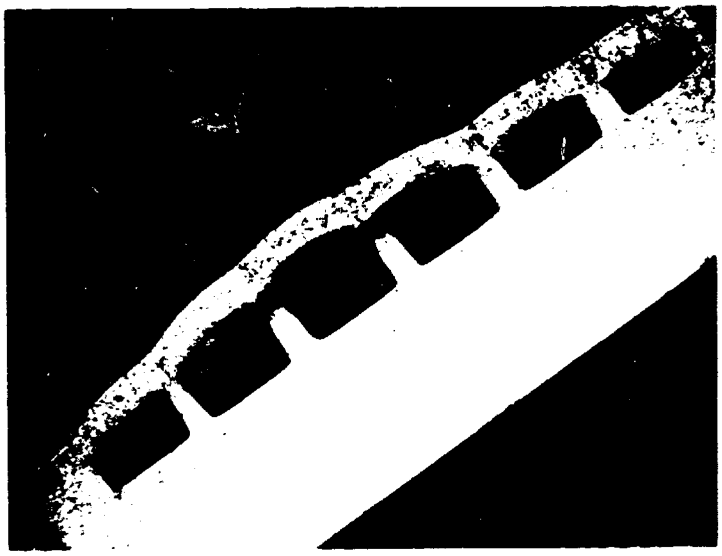


Figure 14. Typical Flat Panels Used for Bonding Process Development and Testing

TABLE IX
BOND STRENGTH CALCULATIONS FOR COPPER ELECTROFORMED PANEL C-1 THROUGH C-5 (OFHC BASEPLATES) AND A-1 THROUGH A-3 (AMZIRC BASEPLATES)

Test Panel No.	Baseplate Thickness		Electroformed Copper Cover Thickness		Pressure to Fail Panel		Approx. Bulge Area	Bonding Rib Area Area	Pressurized Channel Area	Calculated Bond Strength	
	in.	mm	in.	mm	Kpsi	MN/m²	in²	in.²	in.²	Kpsi	MN/m²
Bonding Process: Stanford Method (unmodified)											
C-1	0.262	6.655	0.048	1.219	Leaked through coverplate - not tested						
C-2	0.263	6.680	0.041	1.041	6.0	41.4	0.138	0.70	2.43*	20.8	143.4
Bonding Process: *Stanford Method (low anodic current density)*											
C-3	0.263	6.680	0.045	1.143	7.5	51.7	0.150	0.70	2.43*	26.0	179.3
C-4	0.263	6.680	0.045	1.143	6.1	42.1	0.138	0.70	2.43*	21.2	146.2
A-1	0.265	6.731	0.041	1.041	5.1	35.2	0.230	0.70	2.43*	17.7	122.0
A-2	0.263	6.680	0.042	1.067	Leaked at 2,800 psi		not tested				
Bonding Process: ASTM B281-58 (modified to protect silver conductivizing)											
C-5	0.267	6.782	0.050	1.270	4.5	31.0	1.840	0.70	2.21	14.2	97.9
A-3	0.251	6.375	0.048	1.219	4.4	30.3	1.250	0.70	2.21	13.9	95.8

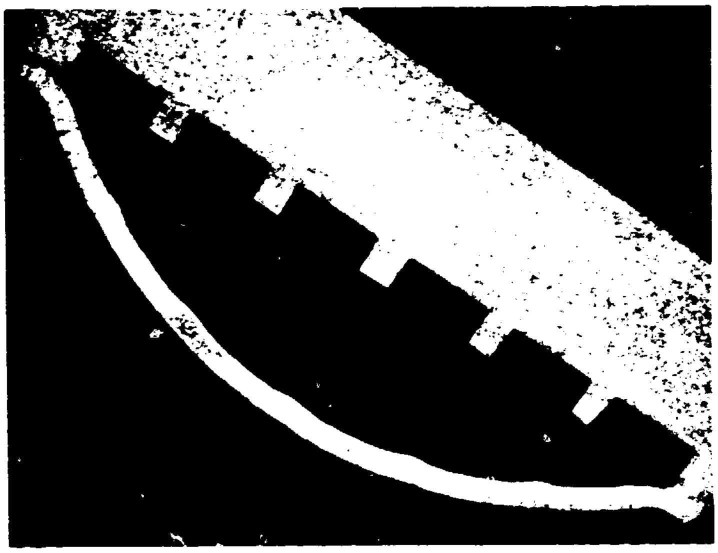
*Channel area corrected to account for change in pressure loaded surface of coverplate due to buckling (low angle bulging). Correction factor is 10 percent only when buckling occurred over total channel area.



This section of the failed area of Panel C-3 shows some plastic deformation of the OFHC copper bonding ribs. Some tearing of parent metal in the failed joints is evident, but the failure appears to be in the same plane as the electroformed bondline. This panel had the best bond strength of all panels listed in Table IX.

Magnification 4X

Panel C-3 Calculated Bond Strength: 179.3 NM/m^2 (20.8 Kpsi)



Panel C-5 exhibited very poor bond strength as evident by the lack of any visible deformation of the bonding ribs or any signs of tearing of the electroformed copper coverplate.

Magnification 4X

Panel C-5 Calculated Bond Strength: 97.9 MN/m^2 (14.2 Kpsi)

Figure 15. Photomacrographs Illustrating Bonds of Inferior Integrity

vious panels. Destructive test results for these panels are shown in Table X. The bond strengths were excellent. All failures occurred in the electroformed copper coverplates as is evident in Figure 16.

Although it was possible to produce high integrity bonds of electroformed copper on OFHC copper and Amzirc, it was expected that the test panels with these combinations would fail at higher destructive test pressures. It was concluded that since all copper-to-copper bond failures occurred at the ends of bonding ribs, stress concentrations existed due to the cross-manifold and failure in the electroformed copper coverplate occurred. This may have influenced the location of panel failures, but it will be shown in Section VI, Electroforming and Tests, that the periodic current reversal cycle employed actually reduced the mechanical strength of the electroformed copper.

H. INVESTIGATION OF BONDING OF ELECTROFORMED NICKEL TO OFHC COPPER AND AMZIRC LINERS

Similar studies were performed on OFHC and Amzirc baseplates using sulfamate nickel deposits as the coverplate material. Baseplate panels C-6 and A-4 were waxed and anodically treated in phosphoric acid at a current density of 16.14 A/dm^2 (150 A/ft^2) for sufficient time to obtain bright and clean metal surfaces. Silver conductivizing was performed with the Rigidax wax warm to achieve good film bonding. Activation for bonding was performed by dipping the panels in 30 percent by volume sulfuric acid at room temperature for 3 minutes. This was followed by a double rinse in distilled water, applying cathodic voltage to the panels, and immersing them in the nickel electrolyte. Electroforming was performed at a current density of 3.23 A/dm^2 (30 A/ft^2) at a bath temperature of 47.8°C (118°F). A plating stop and restart was intentionally introduced on these panels.

Panels A-17, A-18, and A-19 (Amzirc baseplates) were submitted to the double anodic treatment in 65 percent by volume phosphoric acid. One of these treatments was before waxing. The silver was applied while the wax was warm. After the second anodic phosphoric acid treatment, the panels were made cathodic in sulfuric acid, double rinsed, and electroformed at a nickel sulfamate bath temperature of 44.4°C (112°F) and a current density of 2.14 A/dm^2 (20 A/ft^2).

After machining the nickel electroformed coverplates to a uniform thickness, the panels were pressurized to failure. Results of testing for all nickel electroformed panels are shown in Table XI. The bond strengths were excellent for both bonding processes used for preparing copper alloy for nickel electroform bonds. The modified Stanford procedure with two anodic treatment cycles in phosphoric acid is preferred since the activated substrate can be maintained cathodic in going from the subsequent sulfuric acid treatment to the electroforming bath. Figures 17 and 18 illustrate the mode of failure of the high integrity nickel electroform bonds obtained in this study.

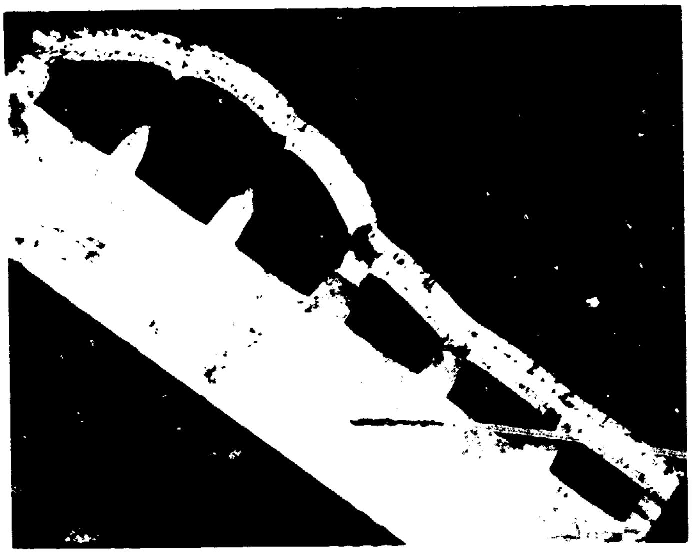
I. SPECIAL TESTING FOR CRYOGENIC MECHANICAL PROPERTY DATA

Samples of several electroformed flat panels representing acid copper sulfate (without periodic current reversal) acid copper sulfate (with periodic current reversal) and copper pyrophosphate deposits were submitted to NASA's Lewis Research Center for independent evaluation. Portions of these panels underwent successful welding trials. Remaining portions were cryogenically tested at liquid nitrogen and room temperatures to determine what changes would occur in mechanical properties. The test results are shown in Table XII.

TABLE X
BOND STRENGTH CALCULATIONS FOR COPPER ELECTROFORMED PANELS A-10, A-11, AND A-16 USING DOUBLE ANODIC TREATMENT IN PHOSPHORIC ACID

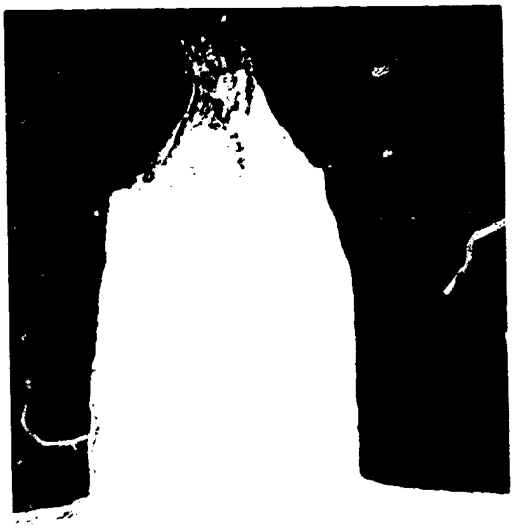
Test Panel No.	Baseplate Thickness		Electroformed Copper Cover Thickness		Pressure to Fail Panel		Approx. Bulge Area	Bonding Rib Area	Pressurized Channel Area	Calculated Bond Strength	
	in.	mm	in.	mm	Kpsi	MN/m^2	in.^{2}	in.^{2}	in.^{2}	Kpsi	MN/m^2
A-10	0.241	6.121	0.048	1.219	8.9	61.4	0.276	0.70	2.43*	30.9	213.1
A 11	0.248	6.299	0.051	1.295	8.9	61.4	0.270	0.70	2.43*	30.9	213.1
A-16	0.254	6.452	0.051	1.295	8.95	61.7	0.300	0.70	2.43*	31.1	214.4

*Channel area corrected to account for change in pressure loaded surface of coverplate due to buckling (low angle bulging). Correction factor is 10 percent only when buckling occurred over total channel area.



Section from failed area of Panel A-11 showing neck-down of Amzirc bonding rib and failure of the electroformed copper coverplate over a second bonding rib. This is indicative of a high integrity bond.

Panel A-11 Magnification 4X



Panel A-11 Magnification 32X

View of joint failure showing electroformed bondline and tensile failure in electroformed copper shell (coverplate)

Panel A-11 Magnification 32X

Failed joint showing the electroformed bondline unbroken. Electroformed copper coverplate failed in shear.

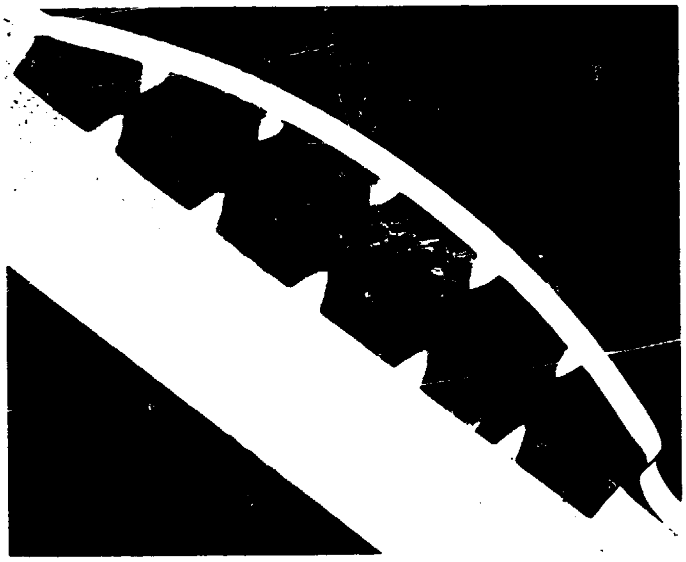
Figure 16. Illustrations of the Failure Mode in High Integrity Electroformed Bonds

TABLE XI
BOND STRENGTH CALCULATIONS FOR NICKEL SULFAMATE ELECTROFORMED PANELS C-6 (OFHC COPPER BASEPLATE) AND A-4, A-17, A-18, A-19 (AMZIRC BASEPLATES)

Test Panel No.	Baseplate Thickness		Electroformed Nickel Cover Thickness		Pressure to Fail Panel		Approx. Bulge Area in.^{2}	Bonding Rib Area in.^{2}	Pressurized Channel Area* in.^{2}	Calculated Bond Strength	
	in.	mm	in.	mm	Kpsi	MN/m^2				Kpsi	MN/m^2
Bonding Activation: Anodic treatment in phosphoric acid and 3 minute dip in 30% sulfuric acid.											
C-6	0.266	6.756	0.038	0.965	11.6	80.0	1.29	0.70	2.21	36.6	252.4
A-4	0.249	6.325	0.044	1.118	11.2	77.2	1.93	0.70	2.21	35.4	244.1
Bonding Activation: Standford procedure modified to anodic treat in phosphoric acid before and after conductivizing.											
A-17	0.250	6.350	0.039	0.991	15.3	105.5	0.74	0.70	2.21	48.3	333.0**
A-18	0.248	6.289	0.039	0.991	11.6	80.0	1.29	0.70	2.21	36.6	252.4
A-19	0.251	6.375	0.038	0.965	11.3	77.9	0.92	0.70	2.21	35.7	246.2

*Channel area does not show buckling or bulging except at region of failure.

**Panel was high pressure cycled twice. Amzirc work hardening may have occurred in the bonding ribs.



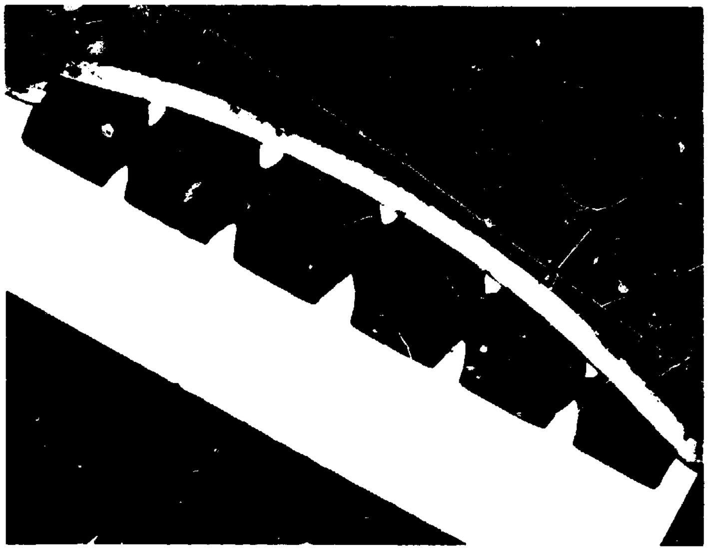
Panel C-6 failed at a pressure of 80.0 MN/m² (11,600 psi. The baseplate material is) OFHC copper and the coverplate is electroformed nickel. The use of a high current density anodic treatment of the copper baseplate in phosphoric acid prior to conductivizing the waxed channels leads to a surface very amenable to making high integrity bonds. Note the uniformity of tensile neck-down of the bonding ribs before they failed.

Panel C-6 Magnification 4X

The adjacent photomicrograph shows one of the bonding ribs which failed in Panel C-6 on destructive testing. The bond shows no evidence of disturbance. This particular specimen was preferentially etched to display grain structure in the copper bonding ribs.

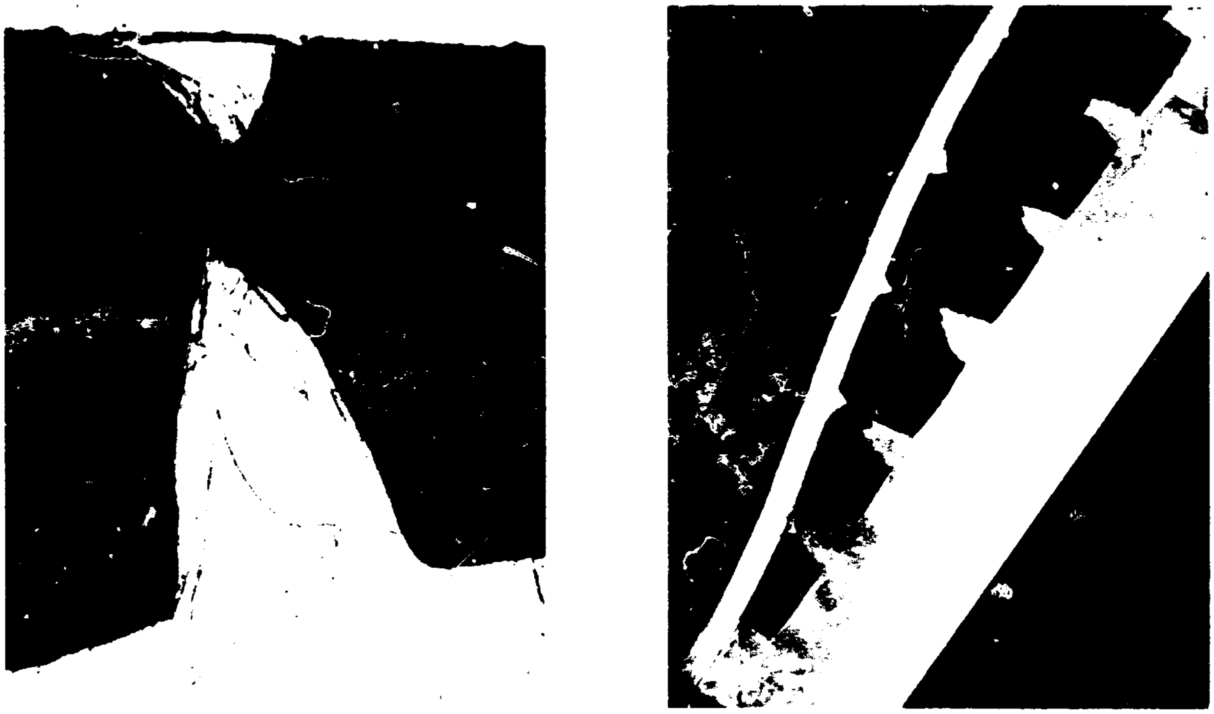
Panel C-6 Magnification 37X

Figure 17. Typical Failures in Copper - Copper Alloy Baseplates Bonded with Electroformed Nickel Coverplates Using a Modification of the Stanford and ASTM Recommended Processes



Panel A 18 failed at 80.0 $\mathrm{MN/m^2}$ (11,600 psi) in destructive test. Note the variation in Amzirc bonding rib width caused by inaccuracies in the milling head travel with respect to the template used to fabricate these experimental base plates. This discrepancy did not appear to affect the test results. All failures occurred in the Amzirc ribs and not in the electroformed bondline.

Panel A 18 Magnification 4X



Panel A 18 Magnification 32X

Panel A 17 Magnification 4X

Magnified view of an Amzirc bonding rib failure showing the etch delineated bondline unfailed.

Panel A-17 failed at a pressure of 105.5 $\mathrm{MN/m^2}$ (15,300 psi). Failure occurred in the Amzirc bonding ribs.

Figure 18 Typical Failures in Nickel Coverplate - Amzirc Baseplate Flat Panels Electroform Bonded by the Modified Stanford University Recommended Process

TABLE XII
RESULTS OF ROOM TEMPERATURE AND LIQUID NITROGEN TEMPERATURE MECHANICAL PROPERTY TESTING OF ELECTROFORMED COPPER SPECIMENS - LEWIS RESEARCH CENTER

Deposited Material	Electrolyte Temperature °C	Current Density		Test Temp.	Specimen Thickness		Mechanical Properties				Elong. % in 1 in.
							Ult. Strength		Yield Strength		
		A/ft^2	A/dm^2		in.	mm	Kpsi	MN/m^2	Kpsi	MN/m^2	
Copper Sulfate, no periodic reversal	32.2	45	4.84	Room	0.099	2.515	17.7	122.0	13.4	92.4	Not Reported
				LN$_2$	0.099	2.515	41.1	283.4	13.8	95.2	33
				LN$_2$	0.099	2.515	43.8	302.0	14.1	97.2	46
Copper Sulfate, periodic rev. cycle: 8 sec. cathodic and 4 sec. anodic	32.2	60	6.46	Room	0.086	2.184	38.0	262.0	21.9	151.0	21
				LN$_2$	0.086	2.184	58.2	401.3	22.2	153.1	35
				LN$_2$	0.086	2.184	56.7	390.9	21.7	149.6	33
Pyrophosphate Copper	51.1	36	3.87	Room	0.061	1.549	40.9	282.0	26.4	182.0	20
				LN$_2$	0.061	1.549	61.6	424.7	32.2	222.0	26
				LN$_2$	0.061	1.549	63.1	435.1	30.6	211.0	40

V. ELECTROFORMING SPECIFICATIONS

A. GENERAL

The following specifications represent detailed procedures and practices to be followed in electroforming nickel and copper outer shells on regeneratively cooled thrust chamber liners. Adherence to the recommended processes and techniques will aid in the electroforming of products of high structural integrity, reproducible mechanical properties, good thermal stability, and with high bond reliability.

The first specification controls the manner in which the copper or copper alloy chamber liner (substrate) is prepared for close-out of the coolant passages and activation of the surfaces for electroform bonding. The next three specifications govern the control and operation of the various electroforming solutions recommended for fabrication of the thrust chamber outer shell. These specifications include the mechanical property ranges which should be obtained from a properly controlled nickel or copper electrolyte containing no grain refining additives. The final specification controls post-electroforming operations to remove residual materials such as channel fillers and conductivizing media after machining the electroformed chamber shell to final dimensions.

These specifications can be modified or amended as new knowledge or improved techniques are acquired. They are primarily intended to provide a guide for products meeting an acceptable standard.

B. SPECIFICATION FOR PREPARING COPPER AND COPPER ALLOY REGENERATIVELY COOLED THRUST CHAMBER LINERS (INNER SHELLS) FOR ELECTROFORMING

1. Scope

This specification establishes the procedures to be followed in preparing copper and copper alloy thrust chamber liners (inner shells) for electroforming outer shells of copper or nickel. The procedures include precleaning, fixturing, masking, deoxidizing, wax filling of coolant passages, conductivizing of wax surfaces, and activation of exposed metal surfaces for electroform bonding. Alternate techniques are provided to accommodate various acceptable methods of cleaning and applying wax filling material. This is to provide the electroform supplier some degree of latitude in fabrication based on the facilities available and the production factors of part complexity, size, and quantity to be produced.

2. APPLICABLE DOCUMENTS AND MATERIALS

SPECIFICATIONS

ASTM B281	Recommended Practice for Preparation of Copper and Copper Base Alloys for Electroplating

MATERIALS

Trichlorethylene, Stabilized, Degreasing Grade	Specification MIL-T-7003
Nitric Acid, ACS Reagent Grade	Commercial
Sulfuric Acid, ACS Reagent Grade	Commercial
Hydrochloric Acid, ACS Reagent Grade	Commercial
Phosphoric Acid, ACS Reagent Grade	Commercial
Sodium Carbonate, Technical Grade	Commercial
Sodium Phosphate, Technical Grade	Commercial
Sodium Hydroxide, Technical Grade	Commercial
Detergent Cleaning Compound, Alconox Brand (or Equivalent)	Alconox, Inc. New York, NY 10003
Scrub Cleaning Compound, Shipley No. 11 (or Equivalent)	The Shipley Company Newton, Mass. 02162
Vinyl Plastisol Masking Compound, Unichrome 218X (or Equivalent)	M&T Chemicals Rahway, N.Y. 07065

2. APPLICABLE DOCUMENTS AND MATERIALS

MATERIALS (Continued)

Platers' Tape, Scotch Brand No. 470 (or Equivalent)	3M Company St. Paul, Minn. 55110
Wax Stop-off Compound, Unichrome Compound 314 (or Equivalent)	M&T Chemicals Rahway, N.J. 07065
Channel Filling Compound, Rigidax Tooling Compound WI Light Blue	M. Argueso Company Mamaroneck, NY 10544
Channel Filling Compound, Rigidax Tooling Compound WI HT11-27 Red	M. Argueso Company Mamaroneck, NY 10544
Silver Conductivizing Powder, Engelhard No. G-3	Engelhard Industries Newark, N.J. 07105
PVC Pipe Cement, "Weld-on" Brand (or Equivalent)	Industrial Polychemical Service, Gardena, Calif. 90247

3. PREPARATION FOR ELECTROFORMING PROCESS

3.1 DEGREASING CHAMBER LINER

Degreasing shall be accomplished to remove any oils or greases present from prior machining and handling operations A separate handling fixture - especially for large liners - shall be designed and used which will allow free circulation of the degreasing media over all surfaces of the liner. This fixture shall be clean and free from any coatings susceptible to attack by the solvent. The fixture shall be affixed in such manner that the liner is protected from scratching or other damage during degreasing and transport. Any one of the degreasing methods below may be used. A device such as that shown in Figure 19 is recommended for large liners. Small liners may be placed vertically in a metal degreasing basket.

3.1.1 VAPOR DEGREASING

Vapor degrease the liner in hot trichloroethane (trichloroethylene or perchloroethylene are acceptable substitutes). The liner shall be suspended in the hot solvent vapors until it reaches the solvent temperature as noted by solvent ceasing to condense over the entire surface of the part.

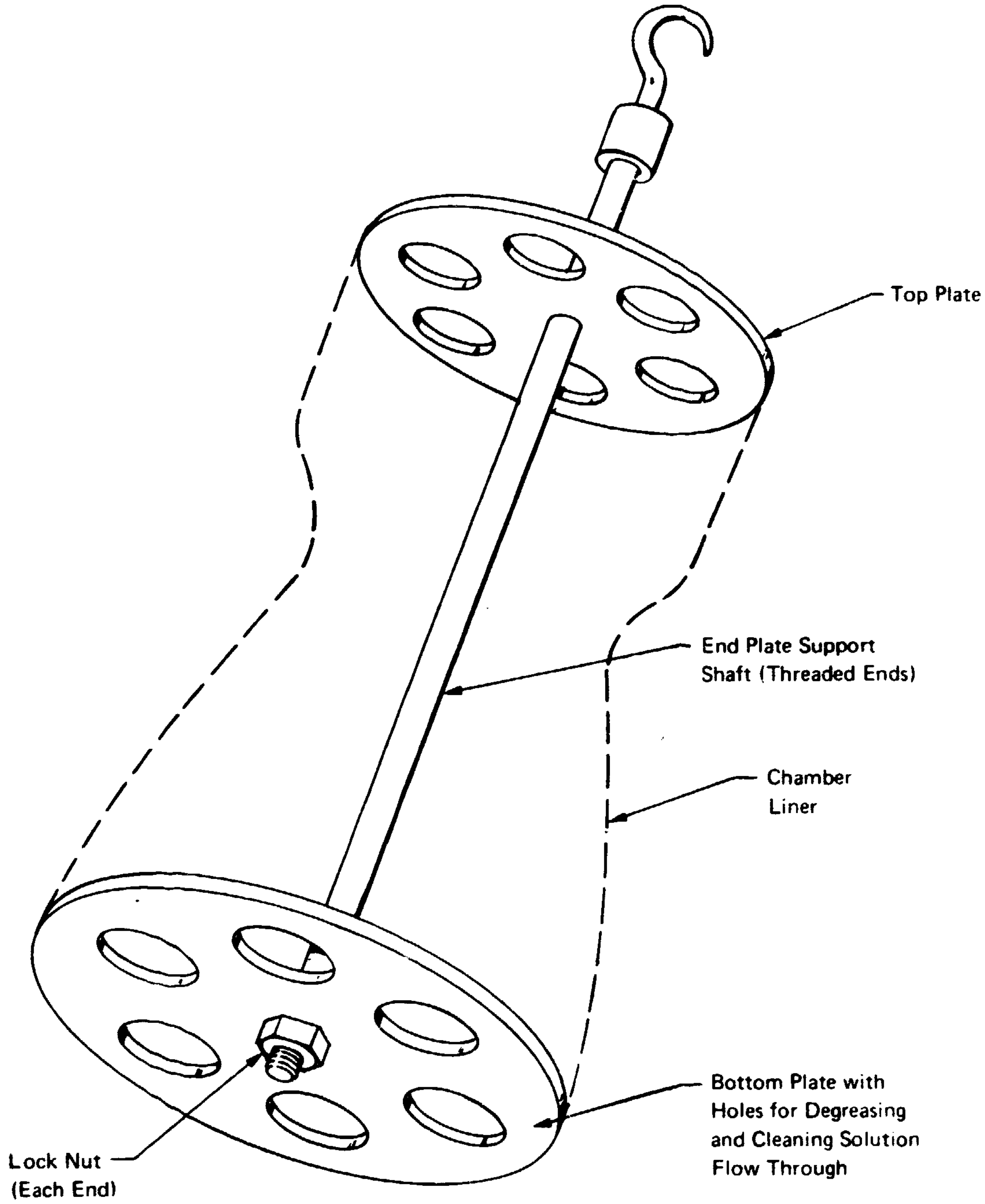


Figure 19. Typical Liner Fixture for Degreasing, Cleaning and Handling Operations

3.1.2 COLD OR WARM SOLVENT DEGREASING

Immerse the liner in a tank of cold or warm trichloroethane (or trichloroethylene or perchloroethylene) for that time necessary to remove all visible traces of oil or grease. Replace the cold or warm solvent as soon as an off color begins to occur to prevent re-contamination of subsequently degreased parts.

3.1.3 EMULSION CLEANING

Place the liner in a tank filled with an emulsion cleaning formulation for the time and temperature recommended by the supplier of the cleaner. This shall be followed by a thorough rinse with water to remove any cleaner drag-out residues.

3.2 ALKALINE OR DETERGENT PRECLEAN

Either electrolytic alkaline or detergent scrub cleaning shall be used to remove dirt or other foreign matter from the surface of the chamber liner. This shall be accomplished prior to affixing the liner to the electroforming fixture since it is later necessary to mask the inside surfaces of the liner.

3.2.1 ELECTROLYTIC ALKALINE CLEANING

The handling fixture used for degreasing is satisfactory for the alkaline cleaning operation if it provides good electrical contact to the chamber liner. Small parts can be electrolytically cleaned in shallow baskets. Carbon steel, titanium, or stainless steel may be used as the fixture or basket construction material.

A recommended electrocleaner per ASTM B281 is made from salts mixed in the following proportions:

	Weight Percent*
Sodium Carbonate (Na_2CO_3)	40 to 50
Trisodium Phosphate ($Na_3PO_4 \cdot 12H_2O$)	25 to 40
Sodium Hydroxide (NaOH)	10 to 25
Surface Active Agent (e.g., Sodium Lauryl Sulfate)	1 approx.

*Ingredients adjusted to give 100 percent. This mixture is used in a solution concentration of 30 to 45/l (4 to 6 oz./gal.). Operating temperature shall be 60 to 71°C (140 to 160°F). The workpiece (chamber liner) is made the cathode and electrocleaned at 2.15 to 3.23 Amp/dm^2 (20 to 30 Amp/ft^2) of surface area for 2 to 3 minutes. The part is then made anodic and cleaned for 5 to 10 seconds at the same current density.

Proprietary commercial electrocleaners may be used for this operation provided the manufacturer's directions for copper cleaning are carefully followed.

3.2.2 SCRUB CLEANING METHOD

The advantage of this technique is that no special fixturing is required to perform the operation. The chamber liner shall be positioned on a wash table, taking care not to damage or scratch the part. A detergent powder such as Alconox shall be mixed with an equal part of a fine pumice scrubbing compound such as Shipley Scrub Cleaner No. 11. This mixture is wetted to form a soft paste. Using a firm bristle brush (wire brushes not permitted), apply the paste to the part and thoroughly scrub all surfaces. Rinse the cleaned surfaces with running water or pour clean water over the surfaces until all signs of detergent and scrubbing compound are removed. Water should break evenly from all surfaces after rinsing if proper cleaning has been performed.

The liner shall be oven dried at 100 to 121°C (212 to 250°F). An alternate method of drying with pressurized clean dry nitrogen or oil free, filtered air is permitted.

3.3 THE ELECTROFORMING FIXTURE

This device serves to support the chamber liner, provides an electrical pathway from the liner to the DC power supply, and imparts rotation to the workpiece to assure uniform exposure of all electroformed surfaces to the anodes. A representative device is shown schematically in Figure 20.

The fixture shall be coated to protect all surfaces in contact with the electroforming solution. This coating shall extend onto the rotating shaft to a distance of at least 15 cm. (approximately 6 inches) above the electrolyte level.

Vinyl plastisol masking compounds provide the most satisfactory semi-permanent coatings for the electroforming fixture due to the excellent chemical resistance of these materials to alkaline or acid electrolytes over a wide temperature range. Unichrome Compound 218X is a representative example of such material. The surface to be coated shall be primed and the coating applied in accordance with the manufacturer's directions. The coating shall be trimmed away on surfaces making electrical contact with the chamber liner. These exposed surfaces shall be completely clean of any electrically resistive film.

3.4 OXIDE REMOVAL FROM LINER SURFACES

This operation shall only be performed when visible oxides or tarnish are present on the exterior surfaces of the copper or copper alloy liner. It is normally used to restore a chemically clean condition to the liner when atmospheric oxidation or tarnish has occurred due to a delay between precleaning and wax filling of the channels.

Affix the liner to the masked electroforming fixture and immerse into a copper bright dipping solution. The immersion time and solution temperature for this operation shall not be exceeded. Either of the following two solutions (operated as described) may be used:

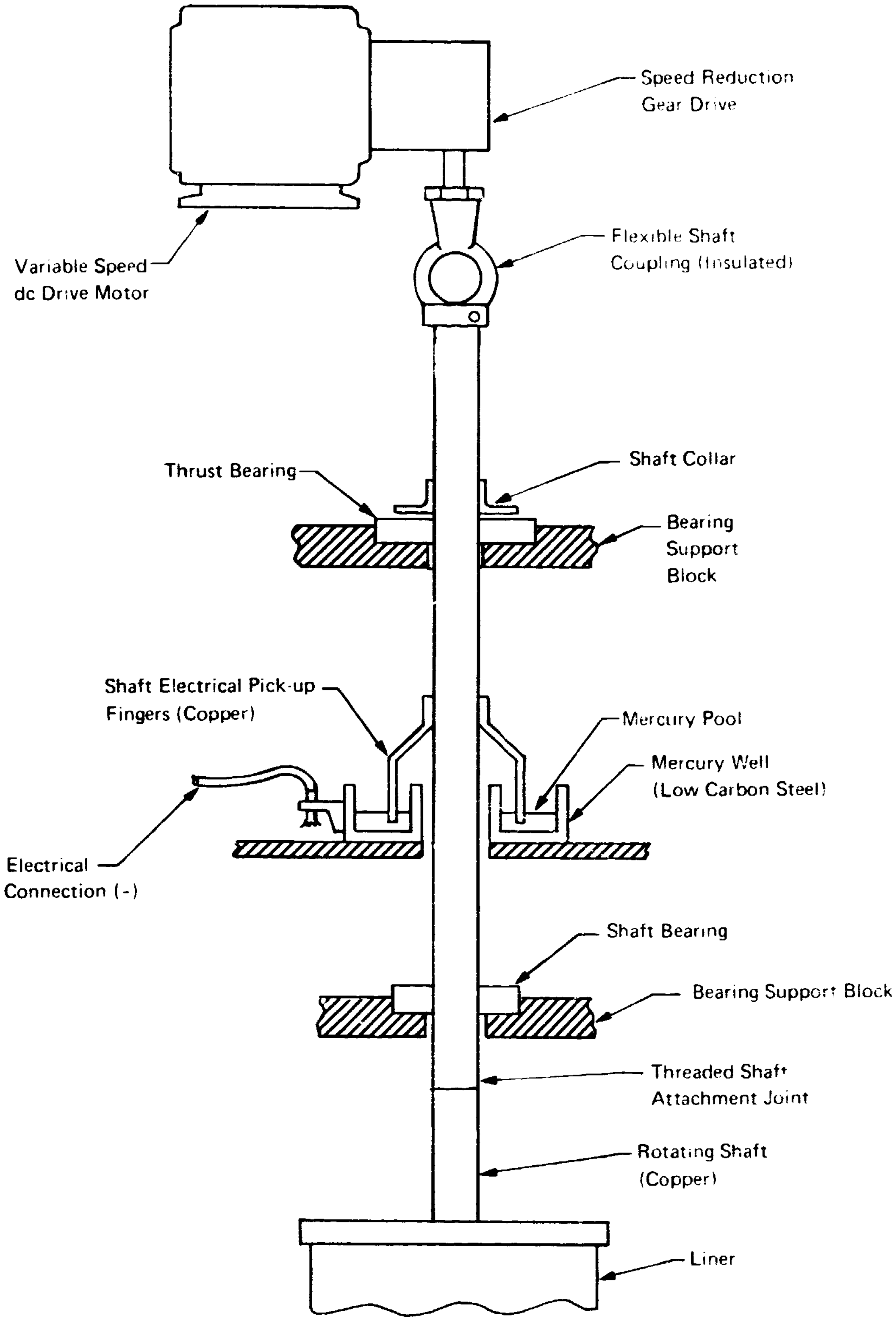


Figure 20. A Representative Electroforming Fixture and Rotating System

	Concentration
ASTM B281 Formulation	
Sulfuric Acid, 66° Be'	60 to 75 volume %
Nitric Acid, 42° Be'	20 to 35 volume %
Water	5 to 10 volume %
Hydrochloric Acid, 20° Be'	9.94 g/l (1/8 oz/gal)
Temperature	Room
Time	5 to 10 seconds
Metal Finishing Guidebook Formulation	
Sulfuric Acid	44 volume %
Nitric Acid	22 volume %
Water	33 volume %
Hydrochloric Acid	1 volume %
Temperature	Room
Time	20 seconds maximum

Immediately dip the fixture with liner into an acid neutralizing tank containing mildly alkaline water at room temperature. This shall be followed by a soak in a clean, room temperature water rinse tank.

3.5 CHANNEL FILLING AND LINER MASKING

The liner coolant passages shall be filled with a wax suitable for conductivizing to close out the channels during electroforming. The wax may be applied by dipping the liner in a tank of molten wax, by pouring the wax onto the liner exterior, or by pour casting using a split mold placed around the liner. The wax employed shall have excellent bonding capability to the side walls of the coolant passages to prevent shrinkage separation which leads to improper channel cross-sectional structure and porosity.

Rigidax Tooling Compound WI Light Blue (M. Argueso Company) shall be used to fill the coolant passages. This material is suitable for exposure to electrolyte temperatures of 49°C (120°F) or lower for that period of time required to complete closure of the coolant passages during electroforming. It maintains excellent adhesion at temperatures required for nickel sulfamate, and copper sulfate electroforming. It shall not be used as an interior or exterior liner surface maskant (stop-off) due to potential leaching of the adhesive material from the wax.

For pyrophosphate copper electroforming, the recommended channel filling compound is Rigidax Type WI HT 11-27 Red. The conductivizing media will adhere better to this compound than to the Type WI Light Blue under the severe conditions of agitation and temperature required in the pyrophosphate electrolyte. Use of this material as a surface maskant (stop-off) has not been evaluated.

3.5.1 CHANNEL FILLING PROCEDURES

The fixtured liner shall be dry before applying any wax to the coolant channels. Drying shall be accomplished as described under para. 3.2.2. Any of the following techniques may be used to apply the Rigidax Tooling Compound WI Light Blue or HT 11-27 Red

3.5.1.1 DIP METHOD

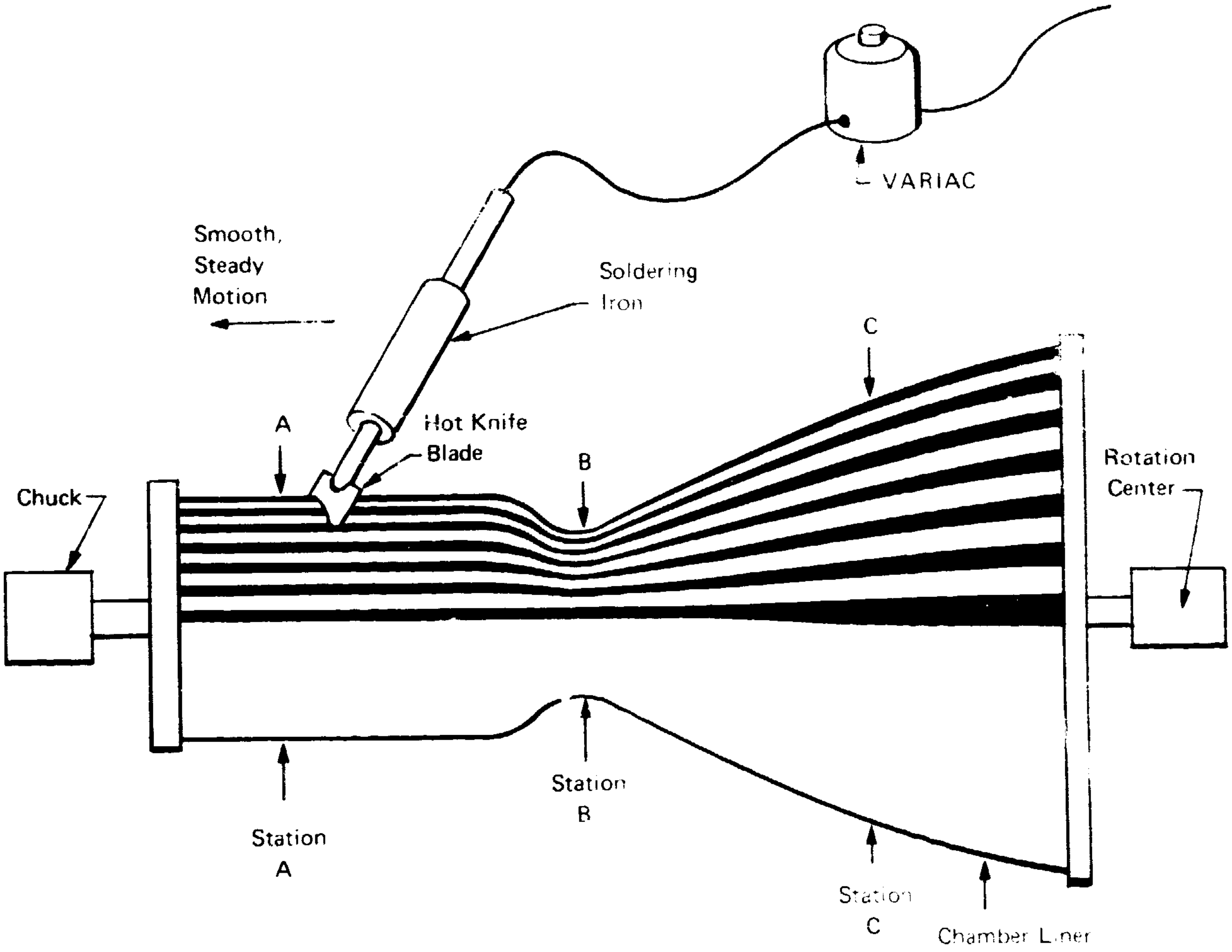
This is the least preferred method of wax application due to the fact that wax will coat the fixture and surfaces of the liner where electroforming is not required. If not removed, the material may lose some of the adhesive qualities through leaching by the electrolyte during long electroforming periods. This is especially true for electroforming in the copper pyrophosphate solution.

If dipping must be used, the wax not essential to coolant passage closure (i.e., all wax subject to prolonged contact with the electrolyte) shall be removed. This is best accomplished by use of a hot knife and solvent wiping with trichloroethylene. The wax is applied by immersing the liner in a tank of the molten wax at approximately 121°C (250°F) and allowing the part to reach the temperature of the wax. The part is withdrawn and allowed to air cool until no further wax run-off is observed. While still warm, the part is again immersed for a shorter period of time to add wax to the first layer. This process is repeated until the desired thickness is achieved. The coating shall be allowed to cool to room temperature before trimming to final dimensions as described in para. 3.5.1.2. Inspection and localized repair of the waxed channels shall be made as noted in para. 3.5.1.2.

3.5.1.2 POUR METHOD

The liner, mounted on the electroforming fixture, shall be placed in a horizontal position on a cradle or mounted in a conventional lathe to allow rotation during the pouring process. The liner exterior shall be heated to a temperature of 60 to 72.5°C (140 to 160°F) using heating lamps or a hot air dryer. The Rigidax wax, previously heated until melted, shall be poured over the external surface of the liner while rotating at a very slow speed. Slow rotation shall be maintained while the wax is cooling. Once the wax is cool, the rotation is stopped, and the wax inspected for adequate filling of the channels (and adjoining manifolds, where applicable). The process is repeated as necessary to build-up the wax coating. It is suggested that a plater's masking tape (such as Scotch Brand No. 470, or equivalent) be applied to areas outside of the channel (or channel-manifold area) to facilitate removal of excess Rigidax which may run out into these regions.

The liner and wax is allowed to cool to room temperature before removing the excess channel filling material. A hot knife such as shown in Figure 21 shall be used to remove the excess wax. The blade of this knife shall not have a sharp edge. It shall have a wax trimming edge which is contoured to the outside radius of the chamber liner. The corners of the blade shall be rounded to prevent damage to the coolant lands (ribs). Several



Typical Hot Knife
Blade Configurations:

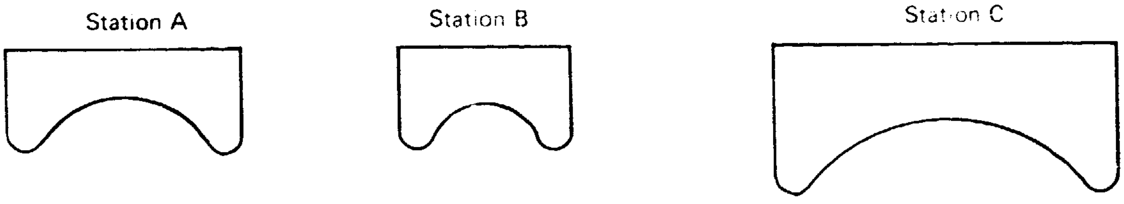


Figure 21. Removal of Excess Channel Filling Compound with a Hot-Knife

blades of differing radii shall be used as necessary due to varying shape of the chamber liner. The blade is best constructed of brass or a soft material which will not scratch the liner surfaces.

The hot knife shall be stroked with moderate pressure in a direction parallel to the coolant lands of the liner. The knife shall not dwell at any spot on the liner since it is only desired to melt and remove excess wax by controlled, localized heat.

After excess wax is removed, the surface of the liner shall be finished to provide a smooth, continuous surface of wax and exposed liner metal to meet design dimensional requirements. If possible a radius shall be maintained in the wax surface corresponding with that of the liner exterior.

Wax finishing shall be accomplished by wet sanding with fine grit papers. During this operation the wax shall be maintained in a hard state by running cold water over the liner surface This will help remove abrasive particles and wax during the sanding. Wet sand papers shall have a grit range of 160 to 220, the later being used for finish sanding. The part may be rotated at low speed during sanding, provided a cold water flow is maintained on the surface. Care shall be taken to prevent unnecessary removal of metal from the channel ribs as wax is sanded away. Localized spots of the wax remaining on channel ribs shall be removed by careful scraping with the edge of a smooth piece of acrylic sheet such as Plexiglas (a piece of hard rubber or Teflon will work equally well).

The liner surface shall be maintained cool with cold tap water and cleaned by scrubbing with a firm bristle brush and a detergent cleaner such as Alconox. Do not use pumice cleaning compounds which may imbed in the wax. Inspect the liner surface under at least 7X magnification for removal of wax from all surfaces requiring an electroform bond. Do not solvent wipe with trichloroethylene or other chlorinated solvents to remove traces of wax from the channel or manifold areas since these solvents will attack the wax and adhesive ingredients.

The finished exterior surfaces of the liner shall be inspected for subsurface air bubbles in the wax which might open and cause pits or porosity during electroforming. Heat the liner surface to a temperature of the melt point of 65.5°C (150°F) in the case of Rigidax Type WI Light Blue or 101°C (214°F) for Rigidax Type WI HT 11-27 Red. This can be done by heating with a hot air dryer or placing the liner in a controlled temperature oven. After the liner reaches this temperature, inspect the wax surfaces for bubble evolution. Repair any wax defects by melting wax on a spatula or hot knife blade and flowing it over the defect. Repeat the scraping, sanding, and cleaning steps as necessary to assure a sound, dimensionally accurate waxed surface.

3.5.1.3 CASTING METHOD

The coolant channels may be filled by casting Rigidax WI Light Blue Compound or Rigidax WI Red Compound in a split mold placed around the liner. The liner and mold should be pre-heated to at least 65.5°C (150°F) for the light blue compound or 93.3°C

(200°F) for the red compound prior to wax pouring. The mold should be coated with a mold release compound or made from a material which will not adhere to the wax upon cooling. Such materials shall be evaluated independently prior to use.

After casting and cooling, the wax filled channels should be finished to the required surface dimensions of the liner as described under the pour method (para. 3.5.1.2). Inspection of sub-surface porosity in the wax should be made as previously described.

3.5.1.4 LINER MASKING PROCEDURE

The interior and exterior surfaces of the liner not subject to electrodeposit coverage shall be masked prior to anodic treatment and conductivizing. This step may be performed prior to filling the channels with wax only when the masking media will not degrade when heated to the temperatures required to fill the coolant passages. The liner shall be removed from the electroforming (rotation) fixture prior to internal masking.

Any of a number of commercially available masking compounds are acceptable if they are demonstrated to resist attack from the electrolyte at the electroforming temperature and can be removed without difficulty. Special caution shall be exercised in selection of such maskants for use in hot copper pyrophosphate solutions due to the high electrolyte agitation requirements and the possibility of maskant peeling. Plater's tape, such as Scotch Brand No. 470 (or equivalent), may be applied over surfaces to be masked followed by painting with a melted stop-off wax such as Unichrome 314 (or equivalent). This system is limited to use with low electrolyte temperatures of 48.9°C (120°F) or less.

A most satisfactory masking system which will withstand acid copper sulfate, nickel sulfamate, and pyrophosphate copper at temperatures to 57°C (135°F) is the use of polyvinyl chloride pipe cement. The compound can be painted on clean metal surfaces and allowed to cure at room temperature over a 24 hour period. It can be removed by peeling or heating to 82°C (180°F) or higher which shrinks the masking and breaks the film adhesion. For localized removal, the polyvinyl chloride film can be attacked by methylene chloride and scraped off with a plastic tool. Care shall be taken to protect the areas filled with the channel filling compound during masking operations.

The liner shall be detergent scrub cleaned to remove any maskant particles or other contamination and then remounted on the electroforming fixture (rotation shaft).

3.6 ANODIC TREATMENTS (ELECTROPOLISH)

The liner shall be anodically treated in a phosphoric acid solution to chemically remove the thin cold worked layer on the surfaces to receive a bond during electroforming. This step shall be performed prior to conductivizing the wax filled passages in order to minimize conductivizing media removal at the high current density required.

The solution to be employed and operating conditions are as follows:

Phosphoric Acid, C.P. Grade		60 to 70 volume %
Water, Distilled		30 to 40 volume %
Temperature		Room
Current Density	Amp/dm^2	15.1 to 17.2
	Amp/ft^2	(140 to 160)
Time, Minutes		2 to 5
Anode		Chamber Liner
Cathodes		Copper

The liner shall be rotated and the anodic treatment bath shall be large enough to prevent temperature changes in excess of 5.5°C (10°F) during the anodic treatment.

The liner shall be thoroughly rinsed with clean cool or cold tap water and final rinsed in distilled water. All exposed liner metallic surfaces shall be bright and clean when visually inspected. Any areas not bright shall be examined for contamination at 7X magnification. Recleaning shall be performed by detergent scrub cleaning and thorough double rinsing, if inspection indicates contamination. A uniform water break (water break tests) after rinsing may be used as an aid in detecting contamination.

3.7 CONDUCTIVIZING

The clean, dry liner mounted on the electroforming shaft shall be placed in a fixture suitable for rotation in the horizontal position. This area shall be protected as well as possible from airborne contamination. The liner surface shall be heated to 65.5°C (150°F) when Rigidax WI Light Blue Compound is used to fill the channels or 101°C (214°F) when the Rigidax WI HT 11-27 Red Compound is employed in order to allow the filler surface to accept the conductivizing powder. This is best accomplished by heating in an oven carefully controlled by means of a thermocouple touching the liner surface. When the required temperature (controlled to ± 1.1°C or (± 2°F)) is attained, the temperature shall be held for at least 45 minutes to assure that the entire chamber liner is thermally stable.

Remove the chamber liner from the oven and immediately start the application of the conductivizing powder to the waxed channels. Using a soft camel hair brush (or a similar soft bristle bursh) the conductivizing powder shall be applied to the wax filled recesses where electroforming of the chamber shell will be made.

The conductivizing media shall be a fine silver powder such as Engelhard G-3, or equivalent. Fine copper powder can be used providing it can be demonstrated that loose powder removal is achieved in the final channel cleaning process after electroforming. Graphite powder is not recommended due to the difficulty of removal by chemical means without jeopardizing channel dimensions.

After the conductivizing media is applied, the liner with waxed channels is allowed to cool to room temperature. Using monofilament nylon gloves or polyethylene disposable gloves, the silver shall be lightly hand rubbed to remove excess silver powder and produce a bright smooth conductive layer having good adherence to the wax. Additional conductivizing powder shall be applied by brush and rubbed by gloved hand into the wax as needed (after reheating the part and wax).

Excess conductivizing powder shall be brushed off the wax. The liner surface shall be detergent cleaned at room temperature using a soft brush to remove the bulk of the remaining excess conductivizing media. A properly applied conductivizing layer will withstand this treatment. Rinse the conductivized liner in clean distilled water at room temperature.

3.8 ACTIVATION OF LINER SURFACES FOR ELECTROFORMING

The conductivized liner, attached to the electroforming fixture, shall be anodically treated in a phosphoric acid solution and cathodically treated in a sulfuric acid solution to assure no conductivizing media contaminates the liner surfaces to receive the bond of the electroform shell.

The anodic treatment is performed in the same phosphoric acid solution used in para. 3.6. All operating conditions are identical except that the time shall be 90 to 120 seconds.

The anodic treatment shall be followed by a room temperature clean water rinse to remove all phosphoric acid drag-out.

The cathodic treatment shall be made in the following solution at the conditions specified:

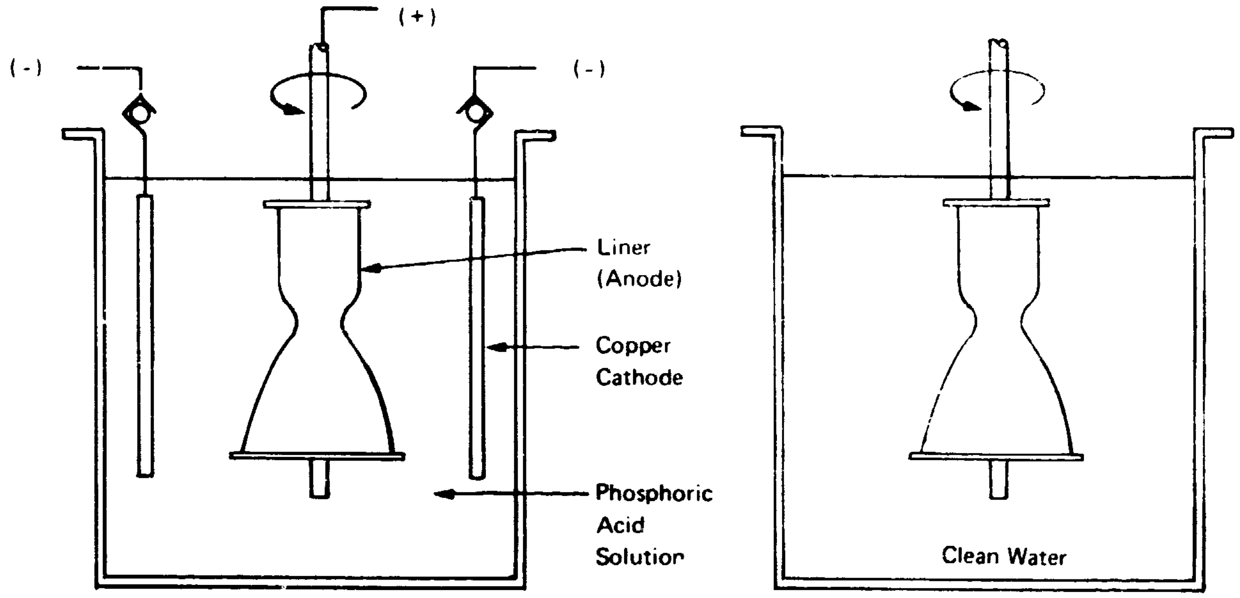
Sulfuric Acid, C.P. Grade	20 to 30 vol. %
Water	70 to 80 vol. %
Temperature	Room
Anodes	Chemical Lead
Cathode	Chamber Liner
Time	15 to 60 seconds
Cathode Rotation	6 to 12 rpm
Current Density, Amp/dm^2	10.8 to 12.9
Amp/ft^2	(100 to 120)

For complex shaped liners, the chemical lead anodes shall be conformal to insure uniform cathode current density.

A schematic diagram of the activation process is shown in Figure 22.

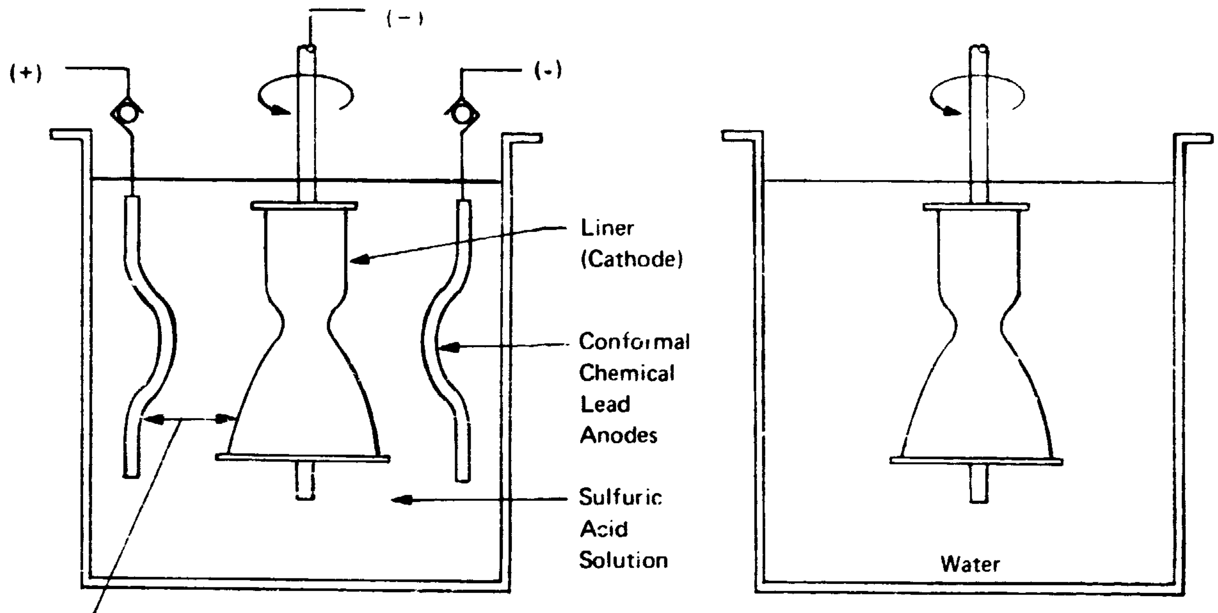
A liner shall be immediately transferred to the first of two room temperature water rinses for a period of 15 to 30 seconds. Rotate the part to assure thorough rinsing of interior surfaces around the fixture. All sulfuric acid shall be removed.

Transfer the liner to the second water rinse which shall be room temperature distilled or at least 500,000 ohm resistance demineralized water. During the transfer, inspect the



1. Anodic Treatment Step

2. Rinse Step



Anode-Cathode Distance shall be 4 to 6 Inches when Conformal Anodes are Used

3. Cathodic Activation Step

4. Water Rinse
5. Distilled Water Rinse

Figure 22. Anodic Cleaning and Cathodic Activation for Electroform Bonding

first rinse for a satisfactory water break (uniform water run-off). Also, inspect for complete coverage of the conductivizing media as noted by visibility of the blue or red channel wax. If not satisfactory, reclean and conductivize until a satisfactory run-off is noted. Rinse for 10 to 20 seconds in the distilled water.

Apply a low cathodic voltage to the liner (only the negative lead to the rectifier is used: the other lead being connected to the plating tank anodes). Transfer quickly to the electrolyte keeping the current low (roughly fifty percent of that required in the electroforming operation). Start the rotation of the chamber liner. After 2 to 3 minutes, adjust the current to the required operating level. This is to minimize high current density "burning" of copper or copper alloys near masked edges upon entry into the electrolyte.

If periodic reverse electroforming of copper is being employed, do not start the reversal cycles until at least 20 minutes of forward electrodeposition has occurred. Otherwise, removal of conductivizing media (particularly, silver at high current densities) may occur.

C. SPECIFICATION FOR NICKEL ELECTROFORMING OF OUTER SHELLS OF REGENERATIVELY COOLED THRUST CHAMBERS FROM THE NICKEL SULFAMATE ELECTROLYTE

1. SCOPE

This specification establishes the procedures to be used in electroforming the outer shells of regeneratively cooled thrust chambers from nickel as deposited from the nickel sulfamate electrolyte. The nickel sulfamate electrolyte is particularly suited to electroforming outer nickel shells on thrust chamber liners by virtue of the excellent combinations of mechanical strength and ductility possible with this electrolyte and the low deposit stress levels that can be maintained. A fine fibrous columnar grain microstructure can be maintained which is indicative of high mechanical strength in deposits from this solution.

2. APPLICABLE DOCUMENTS AND MATERIALS

SPECIFICATIONS

ASTM B-503	Recommended Practice for Use of Copper and Nickel Electroplating Solutions for Electroforming.

COMMERCIAL LITERATURE

Barrett Sulfamate Nickel Plating Process. Type SN	Allied-Kelite Division The Richardson Company Des Plaines, Illinois 60018
Sheet No. P-Ni-Sn. M&T Sulfamate Nickel Plating Process	M&T Chemicals, Inc. Rahway, New Jersey 07065

MATERIALS

Nickel Sulfamate Concentrate, Plating Grade	Commercial
Nickel Chloride ACS Reagent Grade *	Commercial
Boric Acid ACS Reagent Grade *	Commercial
Sulfamic Acid ACS Reagent Grade *	Commercial
Nickel Carbonate ACS Reagent Grade *	Commercial

Carbon, Granular, Plating Grade, Sulfur Free	Commercial
Sulfur Depolarized Nickel Anode Slugs or Chips	Commercial

*Electrolyte purification required if lower grade chemicals are used.

3. ELECTROFORMING EQUIPMENT REQUIREMENTS

3.1 TANKS

Nickel sulfamate electroforming tanks shall be made from a non-reactive material such as sulfur-free rubber, plastisol or plastic lined steel, fiberglass, glass, or polypropylene. The tank shall be of sufficient size to allow at least an eight inch clearance between the anodes and cathode (workpiece). Suitable clearance for heaters and recirculation pipes to the pumping and filtering systems shall be available.

New tanks shall be leached with a two to four percent by weight solution of sulfamic acid for at least twelve hours to remove organic materials which are harmful to the electrolyte. A small amount of a wetting agent compatible with nickel sulfamate solution may be added to the tank leaching solution. After removal of the leaching solution, the tank shall be rinsed and drained.

A liquid level controlling device is recommended on the tank. This device may be made to sound an alarm or automatically add distilled make-up water to maintain electrolyte level.

3.2 TEMPERATURE CONTROLS AND HEATING EQUIPMENT

Heating equipment shall be capable of maintaining an electrolyte temperature in the range of 43.5 to 51.5°C (110 to 125°F). Temperature control capability shall be within ±1.7°C (±3°F). Heaters shall be composed of Karbate steam coils, quartz immersion heaters, or nickel, Karbate, Pyrex, or Duriron external heat exchangers. Sufficient electrolyte agitation shall be used to prevent localized heating of the solution to 71°C (160°F) or higher which leads to hydrolysis of the sulfamate ion into ammonium and sulfate ions.

Heater guards exposed to the electrolyte shall be plastisol coated or of a material which is compatible with the electrolyte.

3.3 AGITATION

Air agitation to circulate the electrolyte and dislodge hydrogen bubbles from the cathode (workpiece) surface is not recommended. Air agitation suffers several disadvantages in nickel sulfamate electroforming in that:

a. Particulate matter at the bottom of the tank becomes agitated and may codeposit with nickel at the cathode.

b. Anode sludge in the anode bags may be dislodged and lead to deposit roughness.

c. Air agitation is ineffective in providing electrolyte circulation in recesses at the cathode (i.e., the nozzle area on regeneratively cooled thrust chambers)

Rotation of the cathode shall be used to ensure uniform exposure of all surfaces to the anodes. Cathode rotation is not an effective means of electrolyte agitation since complex cathode shapes will result in regions of differing peripheral velocities.

Forced pumping of the electrolyte through spray nozzles shall be used as the primary method of electrolyte agitation. These sprays shall be oriented to impinge electrolyte directly onto the cathode surface as shown in Figure 23. To assure effective removal of hydrogen bubbles at the cathode surface, the speed of cathode rotation shall be slow - preferably in the range of five to ten revolutions per minute.

The area and shape of the chamber liner on which deposition is being performed shall dictate the number and placement of electrolyte sprays. More than one pump and spray system may be required on large cathodes. Open pumping (no in-line filter) may be employed if the electroforming facility is equipped with an independent filtering system of adequate capacity.

If shielding is employed to locally control the deposition rate on the cathode, care shall be exercised to prevent any obstruction to the spray impingement, Figure 23.

The spray system materials of construction shall be inert to the nickel sulfamate electrolyte. Metal spray heads are not recommended since they may react as bi-polar anodes and lead to impurities in the deposit. Polyvinyl chloride piping and pipe caps are suitable. The pipe caps shall be drilled or slotted to produce the desired electrolyte spray pattern.

Conventional air agitation piping may be used to provide general solution circulation in the region of the heaters. The air used must be filtered and oil-free. It shall not directly impinge on the anodes.

3.4 FILTRATION

The nickel sulfamate electrolyte shall be continuously filtered. The filtration rate shall at least be equivalent to one tank volume per hour - two volumes per hour is preferred. The filter housing and filter material shall be compatible with nickel sulfamate solution. Cartridge filters shall be rated at 10 microns nominal or finer. Recommended filter cartridge materials are Dynel and polypropylene. Since new filters and filter cartridges may contain extractable substances, they shall be leached with a sulfamic acid solution for at least 24 hours before using.

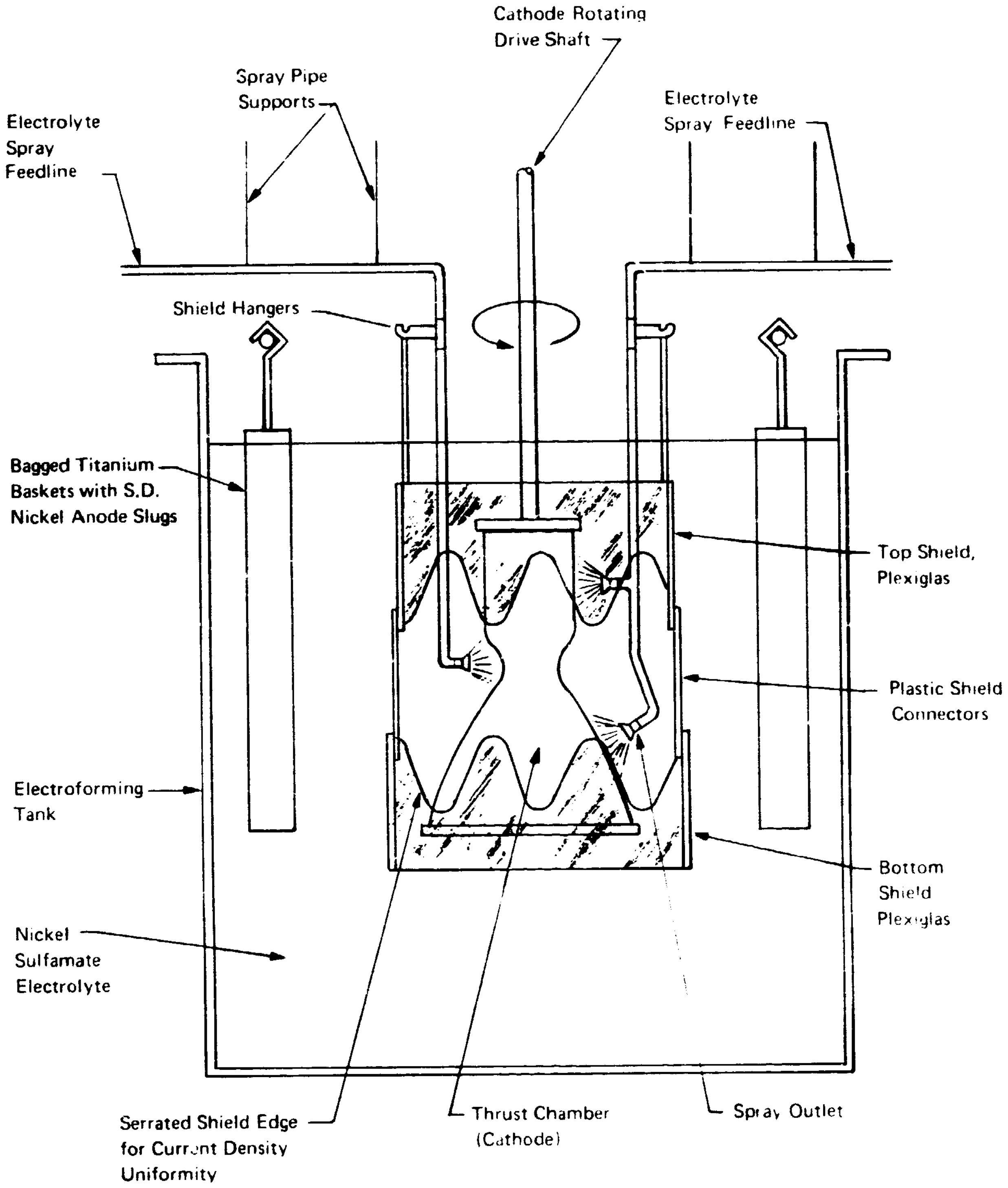


Figure 23. Schematic Diagram of Pumped Electrolyte Agitation System with Stationary Shield to Control Cathode Current Distribution

The nickel sulfamate electrolyte shall be continuously filtered for at least 24 hours before the start of electroforming operations. The inlet and outlet lines of the filter system shall be on opposite sides of the electroforming tank to assure optimum circulation and filtration of the entire electrolyte.

3.5 CURRENT SOURCE AND CONTROL

A standard D.C. plating supply of 12 volts maximum rating is generally satisfactory. Ripple should be held to 5 percent or under. It is also advisable to have a manual restart switch installed which will not allow the rectifier to automatically resume electroforming after a power failure. The 12 volt limit is necessary to prevent anodic attack on titanium anode baskets. If higher voltages are necessary the titanium anode baskets should be protected by coating and making electrical contact to anode chips by means of nickel rods inserted into the chips.

The current output for the voltage capacity of the power source should be greater than that required to achieve a current density of 3.24 Amp/dm^2 (30 Amp/ft^2) for the largest parts to be electroformed.

In event of a power failure, the part being electroformed shall be removed from the nickel sulfamate solution, rinsed, and reactivated for nickel to nickel bonding. This is performed in separate anodic and cathodic treatments with an intermediate rinse:

a. **Anodic Treatment**

Sulfuric Acid, C.P. Grade	20 to 30 Vol. %
Water	70 to 80 Vol. %
Temperature	Room
Anode	Thrust Chamber
Cathode	Chemical Lead
Time	2 to 5 Minutes
Cathode Rotation	2 to 12 rpm
Current Density (Anode), Amp/dm^2 (Amp/ft^2)	5.4 to 10.8 (50 to 100)

NOTE: A 60 to 70 volume percent phosphoric acid solution may be used in place of sulfuric acid. The anodic current density is 15.1 to 17.2 Amp/dm^2 (140 to 160 Amp/ft^2) and the bath is at room temperature. Do not anodically treat copper and nickel in the same acid bath - use separate baths.

b. **Rinse**

Room temperature water (to remove anodic bath drag-out).

c. **Cathodic Treatment**

Use a separate sulfuric acid bath identical in composition to that for the anodic treatment. The chamber liner shall be made cathodic at 10.8 to 12.9 Amp/dm^2 (100 to

120 Amp/ft²). The part shall be rotated at 6 to 12 rpm. After cathodic activation, the part shall be removed with cathodic voltage (2 volts minimum) applied, allowed to drain (no longer than 30 seconds), and transferred into the nickel electroforming solution.

NOTE: The power source for electroforming shall have the manual restart switch depressed before hand so that no delay will occur in applying plating current to the thrust chamber.

4. ANODES

Sulfur depolarized (SD) nickel chips shall be the only anode material normally permitted. Such anode material will dissolve satisfactorily at low levels of chloride in the electrolyte or when no chloride is present. Under special circumstances rolled depolarized nickel anodes may be used where conformal anodes are essential. When such are used, it is necessary to have sufficient chloride present in the electrolyte to permit proper anodic dissolution of the anode material. Since it is necessary to keep the nickel chloride concentration below 4.5g/l (0.6 oz/gal) to minimize residual stress in the deposits, the selection of any anode material other than sulfur depolarized should be cautiously considered.

All nickel anodes shall be bagged to prevent sludge from entering the electrolyte. Anode bags shall be Dynel, polypropylene or cotton duck. All bags shall be leached for at least 24 hours in a four to five percent by weight solution of sulfamic acid prior to exposure to the nickel sulfamate electrolyte.

A periodic check of the level of SD nickel chips in the titanium anode baskets should be made. An examination of the chip level should be made at least every four days of deposition operations. New chips should be added to bring anode material above the electrolyte level.

5. ELECTROLYTE MAKE-UP

The new electrolyte should be prepared in a storage tank which has been carefully leached and cleaned to assure removal of dirt, grease, and any other contaminants. A four to five percent by weight solution of sulfamic acid or sulfuric acid may be used for leaching if followed by a thorough water rinse.

The concentrate of nickel sulfamate is usually supplied with a nickel metal content of 150 g/l (20 oz/gal). It also contains boric acid and may contain nickel chloride - depending upon the supplier. On this basis it is recommended that the following procedure be followed for each 378.5 liters (100 gallons) of electrolyte to be prepared:

a. Add 189.2 liters (50 gallons) of distilled water to the clean storage tank. Add 189.2 liters (50 gallons) of nickel sulfamate (20 ounces per gallon of nickel metal) concentrate. If the concentrate contains 24 ounces per gallon of nickel metal, add only 157.4 liters (41.6 gallons) of concentrate.

b. Thoroughly mix the solution in the storage tank. Perform a chemical analysis for nickel metal, nickel chloride, and boric acid. The procedure for analysis can be found in the commercial literature listed under para. 2 of this specification.

c. Adjust the boric acid concentration after heating the electrolyte to the operating temperature range to be employed for electroforming. The concentration of boric acid shall be increased to 33.8 to 37.5 g/l (4.5 to 5.0 oz/gal) for an electrolyte temperature range of 43 to 49°C (110 to 120°F).

d. Addition of nickel chloride is not necessary when SD nickel anodes are used. A small amount may be added if desired or if use of rolled depolarized is required. In no case shall the concentration exceed 4.5 g/l (0.6 oz/gal).

e. The pH of the electrolyte shall be determined electrometrically and adjusted to the range of 3.6 to 4.2. Lowering the pH is accomplished with sulfamic acid. Raising the pH requires addition of nickel carbonate. Nickel carbonate is difficult to dissolve in the electrolyte. It is best added to the filter cartridge and slowly dissolved by circulation through a filter pump system. It can be added to the electrolyte in the make-up tank by bagging and hanging the bag in the tank.

f. Some nickel sulfamate concentrates are sold as completely purified and ready for use. It is advisable to still conduct a purification process to remove metallic and organic contaminants prior to use. The standard procedure of "dummy" electrolysis using corrugated cathodes should be used to remove metallic contaminants such as copper, lead, and zinc. The recommended current density is 0.2 to 0.5 Amp/dm^2 (2 to 5 Amp/ft^2). Solution agitation aids this operation. The amount of electrolysis is usually based on five ampere hours per 378.5 liters (100 gallons) of electrolyte. Organic contamination removal shall be accomplished by carbon treatment in the make-up tank. Raise the temperature of the electrolyte to 54 to 60°C (130 to 140°F). Add 1.4 to 2.3 kg (3 to 5 lb) of fresh sulfur-free activated carbon per 378.5 liters (100 gallons) of electrolyte and agitate for 3 to 4 hours. Adding 473 ml (1 pint) of 30 percent hydrogen peroxide per 378.5 liters (100 gal.) of electrolyte often aids in removal of stubborn organics. Allow the solution to settle at least 4 hours or preferably overnight. Filter the electrolyte from the make-up tank into the electroforming tank.

g. Re-check and adjust the pH to the range of 3.6 to 4.2. "Dummy" electrolysis will usually increase the pH and adjustment is necessary with sulfamic acid.

h. Heat the electrolyte to the required operating range with circulation provided by the filter pumps and the main circulation pump (or pumps). Allow the solution to cirulate through the continuous carbon treating and filtration system for at least 24 hours before electroforming.

i. The use of anti-pit agents (wetting agents) should be avoided if possible. Continuous carbon treatment benefits are lost if wetting agents are used. If wetting agents are found necessary they shall be controlled to the recommended concentrations by monitoring with a stalagomometer or with the technique of film holding capability of wire rings. Such procedures are described in the literature.

6. ELECTROLYTE OPERATING RANGE

The electrolyte shall be operated in the following range of concentrations:

	grams/liter	oz/gal
Nickel (as metal)	67.5 to 82.5	9 to 11
Boric Acid	33.7 to 39.8	4.5 to 5.3
Nickel Chloride	0 to 4.5	0 to 0.6
pH (electrometric)	3.6 to 4.4	
Temperature	43° to 54°C	110° to 130°F
Cathode Current Density	2.16 to 3.24 Amp/dm^2	20 to 30 Amp/ft^2

7. MECHANICAL PROPERTIES

Mechanical properties of nickel sulfamate deposits shall be in the following ranges:

	MN/m^2	Kpsi
Ultimate Strength	655.1 to 793.0	95 to 115
Yield Strength	482.7 to 620.6	70 to 90
Elongation, % in 1 inch		10 minimum
Residual Stress (Tensile)	41.4 MN/m^2 max	6 Kpsi max

Adjustment of mechanical properties may be made using the guidelines of Table 6, ASTM B-503. If difficulty is encountered in obtaining the above mechanical properties the elctrolyte may not be sufficiently broken in or may contain metallic contaminants requiring more elaborate purification treatment. Rapid break-in of an electrolyte is enhanced by electrolyzing the bath at a high current density such as 4.32 Amp/dm^2 (40 Amp/ft^2).

Special purification treatments involve the removal of iron and chromium by high pH treatment at 60°C (140°F), addition of hydrogen peroxide to oxidize the iron and reduce the chrome, cooling the electrolyte and filtering to remove precipitates. Details may be found in the literature.

Residual stress shall be measured by means of a spiral contractometer. Operation of this instrument is described in the Journal of Research, National Bureau of Standards, February 1949. High stresses shall be avoided due to distortion of initial electroformed layers over conductivized wax surfaces and the adverse effect of tensile stress on the fatigue life of the substrates on which deposits are bonded.

8. QUALITY ASSURANCE PROVISIONS

8.1 VISUAL INSPECTION

All hardware electroformed to the requirements of this specification shall be visually inspected to assure that:

a. Dimensional requirements are met.

b. The electroform contains no pits or voids which will remain after final machining.

c. The surface is free of burrs cracks, blisters, or other obvious defects.

8.2 ELECTROLYTE ANALYSIS

The nickel sulfamate electrolyte shall be frequently analyzed and records maintained to demonstrate control of the process. As a minimum the following analytical schedule will be followed:

a. **New Solutions** - Nickel metal in solution, nickel chloride, boric acid, and pH shall be determined at start-up of bath. pH shall be checked daily. Nickel metal content shall be checked weekly during the first month of operation.

b. **Routine Analysis** - Nickel metal in solution, nickel chloride, boric acid, and pH shall be determined monthly. pH shall be checked every third day and adjusted as required. Failure of the pH to rise is indication of abnormal electrolyte behavior and requies an analysis for nickel metal, chloride, and boric acid.

8.3 METALLURGICAL TESTING

A specimen shall be electroformed from any new electrolyte to confirm mechanical properties. This specimen shall be at least 0.635 mm (0.025 inch) thick. The specimen shall be electroformed under the conditions of electrolyte temperature, composition, and current density conditions specified under Section 6 of this specification. During electroforming, the residual stress of the deposit shall be determined by means of the spiral contractometer.

A separate specimen shall be electroformed concurrently with the deliverable electroformed hardware. This specimen shall be subject to metallographic examination of at least 100X for grain structure, deposit cleanliness, and freedom from voids or other imperfections which might affect the service life of the delivered item. This specimen shall also be subject to heat treatments or thermal cycling to assure that welds or other secondary fabrication operations will not develop laminations, voids, cracking, or blisters.

Basis metal surface activation for electroform bonding shall be performed in exactly the same manner as that used for the chamber liner.

Tensile property verification specimens shall be provided if requested. These shall be produced immediately prior to the electroforming of the deliverable hardware and from the same electrolyte under identical electroforming controls. Specific specimen length and thickness shall be as specified by the procuring agency.

D. SPECIFICATION FOR COPPER ELECTROFORMING OF OUTER SHELLS OF REGENERATIVELY COOLED THRUST CHAMBERS FROM THE COPPER PYROPHOSPHATE ELECTROLYTE

1. SCOPE

This specification establishes the procedures to be used in electroforming the outer shells of regeneratively cooled thrust chambers from copper as deposited from the copper pyrophosphate electrolyte. The copper pyrophosphate solution is particularly suited to electroforming aerospace structural hardware by virtue of the excellent combination of ductility and mechanical strength possible in the deposits. The electrolyte has good throwing power and leveling ability. The microstructure is typically coarse grained in general appearance but composed of fine equiaxed subgrains, a factor contributing to the excellent mechanical properties. Good ductility is retained at test temperatures to 325°C (617°F) and higher.

2. APPLICABLE DOCUMENTS AND MATERIALS

SPECIFICATIONS

ASTM B-170	Oxygen-Free Electrolytic Copper Wire, Bars, Billets and Cakes

COMMERCIAL LITERATURE

Sheet No. P-An-C-10-Xb	Methods of Analysis for the "Unichrome" Copper Plating Solution M&T Chemicals, Inc., Rahway, New Jersey 07065

MATERIALS

Ammonium Hydroxide 29 to 30% ACS Reagent Grade	Commercial
Potassium Pyrophosphate Plating Grade	Commercial
Copper Pyrophosphate Plating Grade	Commercial
Potassium Hydroxide ACS Reagent Grade	Commercial
Pyrophosphoric Acid Plating Grade	Commercial

3. ELECTROFORMING EQUIPMENT REQUIREMENTS

3.1 TANKS

The main electroforming tank shall be steel lined with rubber or polyvinyl chloride. A polypropylene tank is acceptable. The tank shall be wide enough to allow a clearance of 6 to 8 inches between the anodes and the cathode or workpiece being electroformed. It shall be deep enough to allow at least 12 inches clearance between cathode and the tank bottom. A 12 inch freeboard shall be provided between the electrolyte level and the top of the tank to prevent excessive splash loss of electrolyte due to the vigorous agitation required.

New tanks, or tanks converted from service with other electrolytes, shall be thoroughly leached by filling with a solution of 0.5 to 1.0 ounces per gallon potassium hydroxide for 24 hours. This shall be followed by a complete rinsing with clean water.

A spare tank for electrolyte preparation and purification is required. This tank must be leached before use.

3.2 TEMPERATURE CONTROLS AND HEATING EQUIPMENT

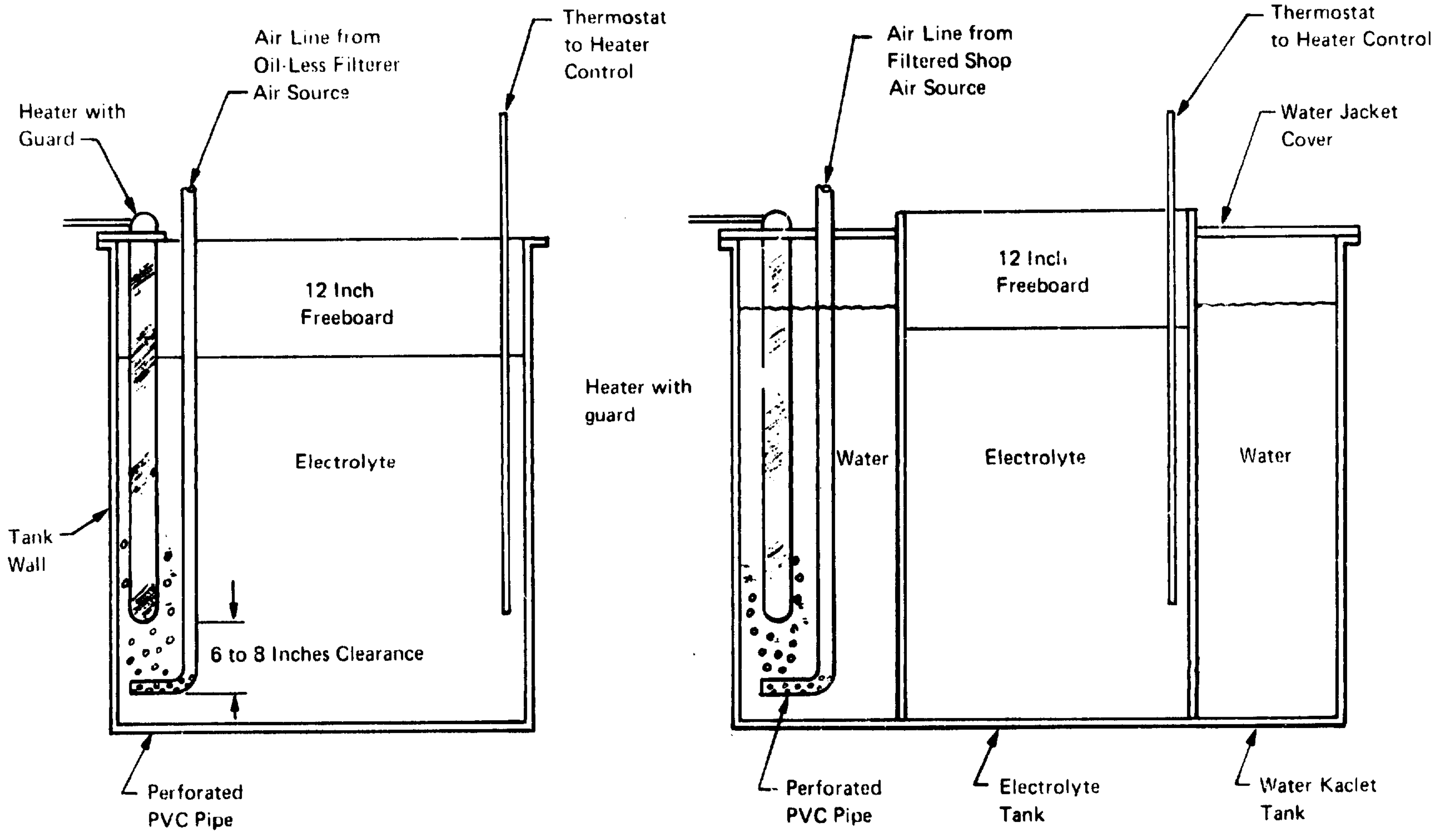
A low thermal density heat exchanger or immersion heater is required. The heater shall be stainless steel, nickel, Karbate, or quartz. If an immersion heater is used, the electrolyte circulation in the heater area must be sufficient to prevent localized overheating of the solution to 60°C (140°F) or higher. This will lead to decomposition of the pyrophosphate into orthophosphate. Figure 24 illustrates the system employed to immersion heat a copper pyrophosphate bath. The air line outlet holes shall be sufficiently below the heater to allow air expansion to provide adequate agitation at the bottom of the heater. A water filled heating jacket around the electroforming tank is recommended for smaller installations. Figure 24 shows an example of the water jacket heating system. A pump or mechanical stirring may be used to circulate the water in the jacket to provide uniform temperature. A cover over the water jacket will minimize evaporation losses and insulating foam or fiberglass around the outside will help retain heat.

The heating equipment shall have the capacity to maintain the electrolyte temperature in the range of 48.9°C to 60°C (120 to 140°F). Temperature control shall be regulated to 1.7°C (±3°F).

If immersion heaters are used, periodic maintenance must be exercised to remove baked-on electrolyte salts resulting from splash and evaporation. Flaking of this residue contributes to roughness in the deposit.

3.3 AGITATION

Vigorous electrolyte agitation shall be used in electroforming from the pyrophosphate electrolyte. Oil-free air shall be used for this purpose. An oil-less low pressure blower-type compressor may be used.



Direct Immersion Heating System

Water Jacket Heating System

Figure 24. Typical Systems for Heating Copper Pyrophosphate Electrolyte

Air capacity shall be at least 1.5 cubic feet per minute per square foot of electrolyte surface (0.762 cc/sec/cm^2). Air pressure shall be at least 1.45 mm of Hg (0.75 psi).

The air outlet into the electrolyte shall be through a pipe manifolding arrangement whereby the maximum electrolyte agitation occurs along the cathode (workpiece) surface. Piping for the air agitation system shall be polypropylene, rubber, or polyvinyl chloride.

A separate air agitation system may be used to provide general electrolyte circulation in the tank and to agitate the electrolyte in the vicinity of immersion heaters, if present.

Supplementing the air agitation system with open pumping of the electrolyte directly towards the cathode (workpiece) will improve the electrodeposit quality. Since most thrust chamber liners will have a shape which converges at the nozzle, air agitation alone is not sufficient to prevent deposit roughness and severe brittleness. The forced flow of electrolyte against any recessed surface is mandatory. Figure 25 shows a recommended agitation arrangement for a chamber liner. Note that the liner is positioned with the combustion chamber (small diameter) down in order to make most effective use of the air to provide agitation at the cathode surface.

3.4 FILTRATION

Pyrophosphate electrolyte shall be continuously filtered to minimize roughness and brittleness in the electrodeposits. Pyrophosphate electrolyte shall be filtered through filter media with at least a rating of 3 microns nominal.

Filter construction materials shall be stainless steel, rubber, plastisol lined steel, or polypropylene. Alpha cellulose, "Solka-floc" or "Fiberbestos" may be used as filter aids, but will reduce the electrolyte flow.

Continuous carbon treatment is recommended. Intermittent carbon treatment shall be used as a minimal requirement. Only sulfur-free carbon is permitted for this treatment. The carbon shall be washed (if granular carbon is used) to remove fines before being bagged and placed in the carbon treating unit. Extra precautions shall be exercised to insure that proper filters (3 micron nominal or less) are installed downstream from the carbon treating unit to prevent carbon fines from entering the electrolyte.

The filter area shall be sufficient to provide a no-load flow capacity of three tank volumes per hour. New filter cartridges shall be leached in pyrophosphate solution for at least 24 hours before use. Figure 26 shows a recommended filtering and carbon treating system.

3.5 CURRENT SOURCE AND CONTROL

A standard DC plating supply of 6 volts maximum rating at required maximum current rating is necessary. It is optional to use periodic reverse current for pyrophosphate electroforming. Both the DC power supply and the periodic reversing unit shall have current capacities capable of furnishing up to 5.4 Amp/dm^2 (50 Amp/ft^2) as a cathode (workpiece) current density. It is also an option to use periodic current interruption as an alternate to periodic reversal to minimize roughness in thick deposits.

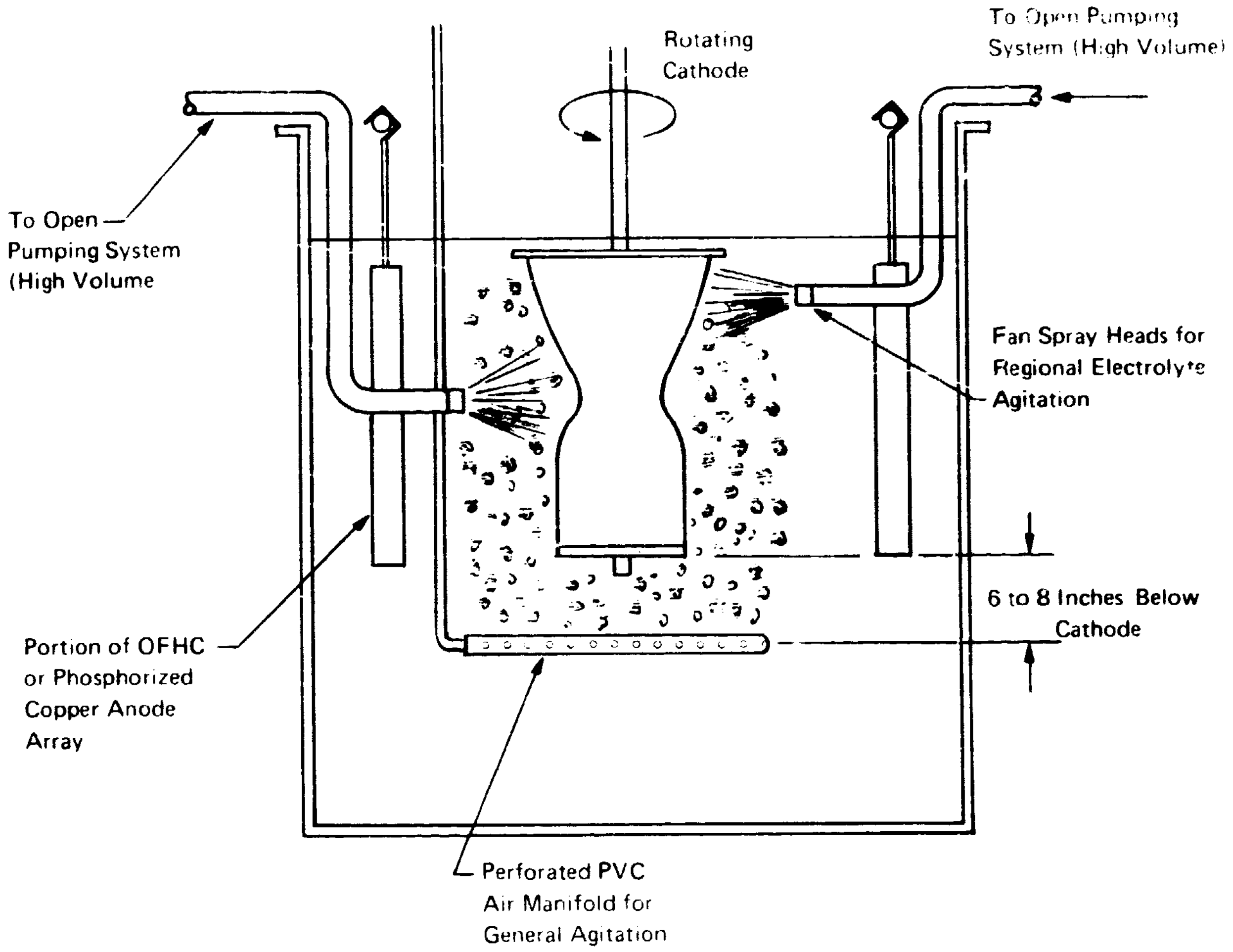
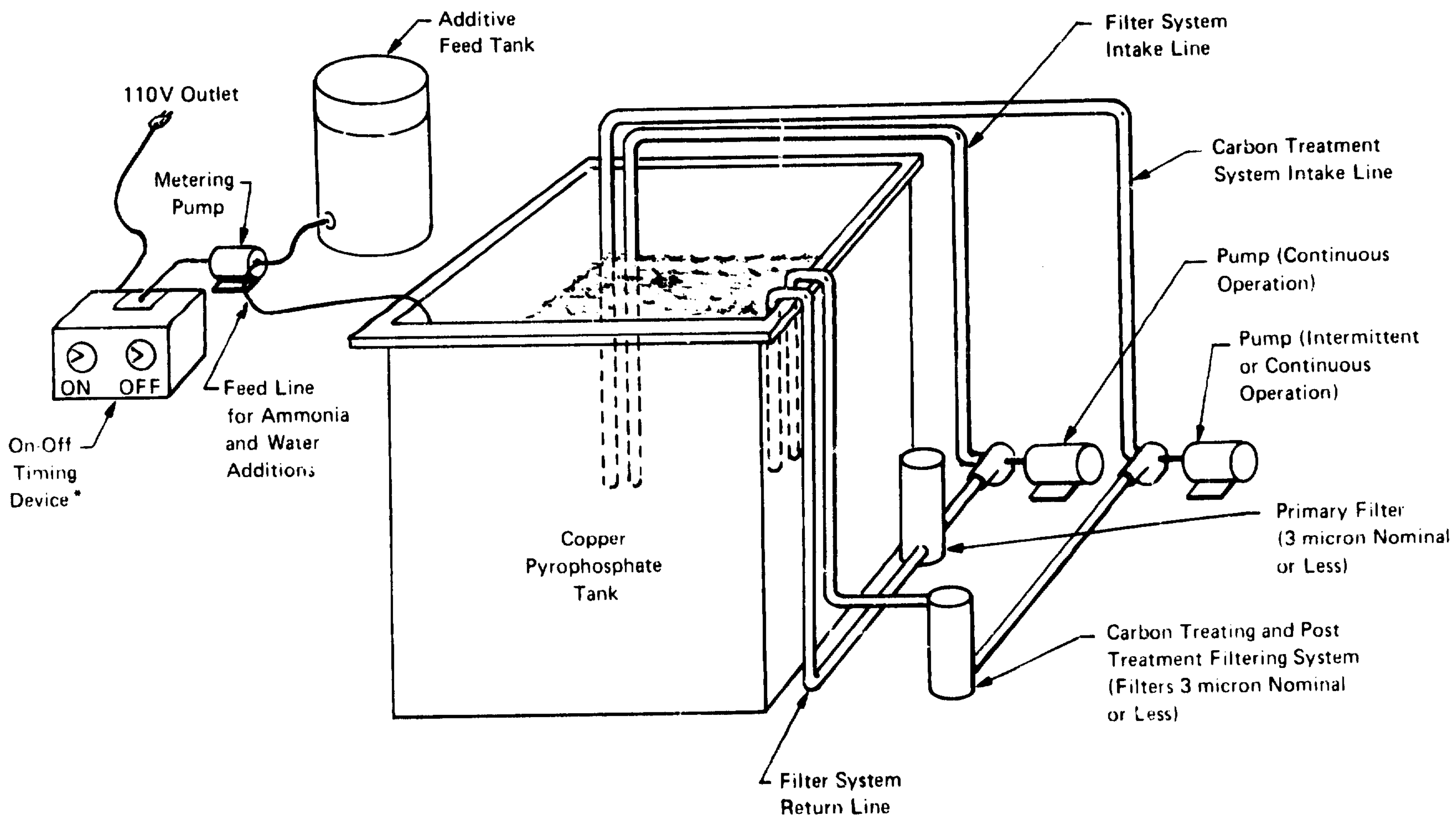


Figure 25. Combination Air and Open Pumping System for Agitating the Pyrophosphate Electrolyte when Electroforming Recessed Shapes



*Duplicate Unit may be Used to Periodically Interrupt dc Power Supply if this Electroforming Option is Used. Use of the Automatic Addition System is Optional but Recommended.

Figure 26. Copper Pyrophosphate Tank Maintenance and Support Equipment (Excluding Power Supply)

The following anodic-cathodic timing ranges are suggested for periodic reversal and periodic interruption:

	Anodic Cycle	Cathodic Cycle
Periodic Reversal (Polarity of Cathode)	3 to 5 sec.	20 to 50 sec.
	Current Off	Current On
Periodic Interruption (Polarity of Cathode)	60 to 90 sec.	120 to 180 min.

4. ANODES

Either oxygen-free high conductivity (OFHC) or rolled phosphorized copper anodes are required in the pyrophosphate electrolyte. Anode material shall meet the chemical requirements of ASTM Specification B-170.

Use of anode bags is not permitted since they interfere with solution circulation around the anodes and contribute to passive oxide layers and particulate generation.

Careful attention to anode area and proper anode corrosion shall be given. The anode current density for electroforming shall be between 2.7 to 5.4 Amp/dm^2 (25 and 50 Amp/ft^2). If the current density is too low, a brown cuprous oxide film will form which leads to anode passivity and deposit roughness. Excessive anode current density results in a black anode film and excessive tank voltage. Proper anode corrosion shall be verified by an examination of an arbitrarily selected anode at least every three days of continuous electroforming operation. The anode shall show a light tan or colorless film. A voltage increase of 1.0 volt for any current density being employed shall be cause to check for proper anode area and correction if needed.

Each anode used in the pyrophosphate electrolyte shall be totally submerged in the electrolyte. Exposed anodes will collect salts from evaporated splashing and oxides from atmospheric exposure. This contributes to roughness and poor ductility in the deposits. Titanium anode hooks shall be used to submerge the anodes.

5. ELECTROLYTE MAKE-UP

The pyrophosphate electrolyte shall be made from dry salts or pre-purified solutions. Using dry salts, a new solution shall be prepared as follows:

a. Fill a spare tank to about two-thirds of the required volume with water (distilled). Heat to 54.4°C (130°F).

b. Add in order for each 100 gallons (378.5 liters) of electrolyte (stirring after each addition):

1) 4.536 kg (10 lb) of potassium pyrophosphate.

2) 127.1 kg (280 lb) of copper pyrophosphate.

c. Add to the above dissolved solution one pint of 30 to 35 percent hydrogen peroxide for each 100 gallons of electrolyte. This is to break down organic impurities. Stir 30 minutes.

d. For each 378.5 liters (100 gallons) of solution, add 0.857 kg (2 to 3 pounds) of sulfur-free activated carbon. Stir for 2 to 3 hours and allow the solution to settle for one hour. Filter the electrolyte into the electroforming tank after checking the filtered product for solids (pass through standard filter paper and check the paper for solids). If solids are observed, improved filtration is required.

e. Add 1.89 liters (0.5 gallon) of 29 to 30 percent ammonium hydroxide for each 100 gallons of electrolyte and stir.

f. Hang the unbagged anodes in the tank and add distilled water to the required final volume. Turn on the air agitation system.

g. Check the solution pH (acidity). If the pH is above 8.6, lower to 8.4 with pyrophosphoric acid. If it is below 8.2, raise with potassium hydroxide to 8.4.

h. Perform a chemical analysis for copper metal content, pyrophosphate, orthophosphate and ammonia in accordance with the document referenced under Section 2 of this specification, or an equivalent analytical procedure. From the analysis, adjust the electrolyte composition as required to meet the operating range.

6. ELECTROLYTE OPERATING RANGE

The electrolyte shall be operated in the following range of concentrations:

	grams/liter	oz/gal
Copper (as metal)	24.75 to 28.50	3.3 to 3.8
Pyrophosphate-Copper Ratio	7.4 to 8.0:1	
Ammonia as NH_3	1.12 to 1.87	0.15 to 0.25
pH (electrometric)	8.2 to 8.6	
Temperature	48.9 to 57.2°C	120 to 135°F
Cathode Current Density	2.16 to 4.32 A/dm^2	20 to 40 A/ft^2
Anode Current Density	2.7 to 5.4 A/dm^2	25 to 50 A/ft^2

7. MECHANICAL PROPERTIES

Mechanical properties of pyrophosphate deposits shall be in the following ranges:

	MN/m^2	Kpsi
Ultimate Strength	262.0 to 310.3	38 to 45
Yield Strength	172.4 to 206.8	25 to 30
Elongation, % in 2 inches		20 minimum*

* NOTE: Higher plating temperatures favor increased ductility at some sacrifice of electrolyte throwing power and efficiency. The elongation is otherwise a function of the degree of filtration used to remove very fine particulate matter from the electrolyte (and good agitation).

8. QUALITY ASSURANCE PROVISIONS

8.1 VISUAL INSPECTION

All hardware electroformed to the requirements of this specification shall be visually inspected to assure that:

a. Dimensional requirements are met.

b. The electroform contains no pits or voids which will remain after final external machining.

c. The surface is free of burns, cracks, blisters, or other obvious defects.

8.2 ELECTROLYTE ANALYSIS

The pyrophosphate electrolyte shall be frequently analyzed and records maintained to demonstrate control of the process. As a minimum, the following analytical schedule will be followed:

a. New Solutions - Ammonia, copper, and pyrophosphate shall be determined every other day during the first week of operation. pH shall be checked twice daily.

b. Routine Analysis - Ammonia, copper, and pyrophosphate shall be determined every four days. Additional ammonia checks shall be made every second day of continuous operation. pH shall be checked daily. Orthophosphate shall be determined weekly.

8.3 METALLURGICAL TESTING

A separate specimen shall be electroformed concurrently with the deliverable electroformed hardware. This specimen shall be subject to metallographic examination at at least 100X for grain structure, deposit cleanliness, and freedom from voids or other imperfections which might affect the service life of the delivered item. This specimen is also subject to heat treatments or thermal cycling to assure that welds or other secondary fabrication operations will not develop laminations, voids, cracking, or blisters.

Basic metal surface activation for electroform bonding shall be performed in exactly the same manner as that used for the chamber liner.

Tensile property verification specimens shall be provided if required. These shall be produced immediately prior to the electroforming of the deliverable hardware and from the same electrolyte under identical electroforming controls. Specific specimen lengths and thickness shall be as specified by the procuring agency.

E. SPECIFICATION FOR COPPER ELECTROFORMING OF OUTER SHELLS OF REGENERATIVELY COOLED THRUST CHAMBERS FROM THE ACID COPPER SULFATE ELECTROLYTE WITH PERIODIC CURRENT REVERSAL

1.0 SCOPE

This specification establishes the procedures to be used in electroforming the outer shells of regeneratively cooled thrust chambers from copper as deposited from the acid copper sulfate electrolyte using periodically reversed current (PR). The acid copper sulfate electrolyte with periodic current reversal produces better and more uniform mechanical properties than the conventional acid sulfate electrolyte due to the controlled fine grain structure which can be maintained constant throughout extremely thick electroforming operations.

2.0 APPLICABLE DOCUMENTS AND MATERIALS

SPECIFICATIONS

ASTM B-170	Oxygen-Free Electrolytic Copper Wire, Bars, Billets and Cakes

MATERIALS

Copper Sulfate Plating Grade or ACS Reagent Grade	Commercial
Sulfuric Acid ACS Reagent Grade	Commercial

3.0 ELECTROFORMING EQUIPMENT REQUIREMENTS

3.1 TANKS

The electroforming tank shall be polyvinyl chloride lined steel, rubber lined steel, or polypropylene. The tank shall be of sufficient size to allow a 6 to 12 inch clearance between anodes and the cathode (workpiece). The bottom of the tank shall clear the cathode by at least 12 inches to allow full electrolyte circulation and sufficient area for sludge or other impurities to settle for withdrawal by the filter pump.

New tanks shall be leached for at least 24 hours using a solution of 5 percent by volume sulfuric acid in water. This shall be followed by a thorough rinse. A representative tank with support equipment is illustrated in Figure 27.

3.2 TEMPERATURE CONTROL AND HEATING EQUIPMENT

The plating tank shall be heated by coils, heat exchangers or immersion heaters made of titanium, tantalum, Karbate, or quartz. Where immersion heaters are used, provision

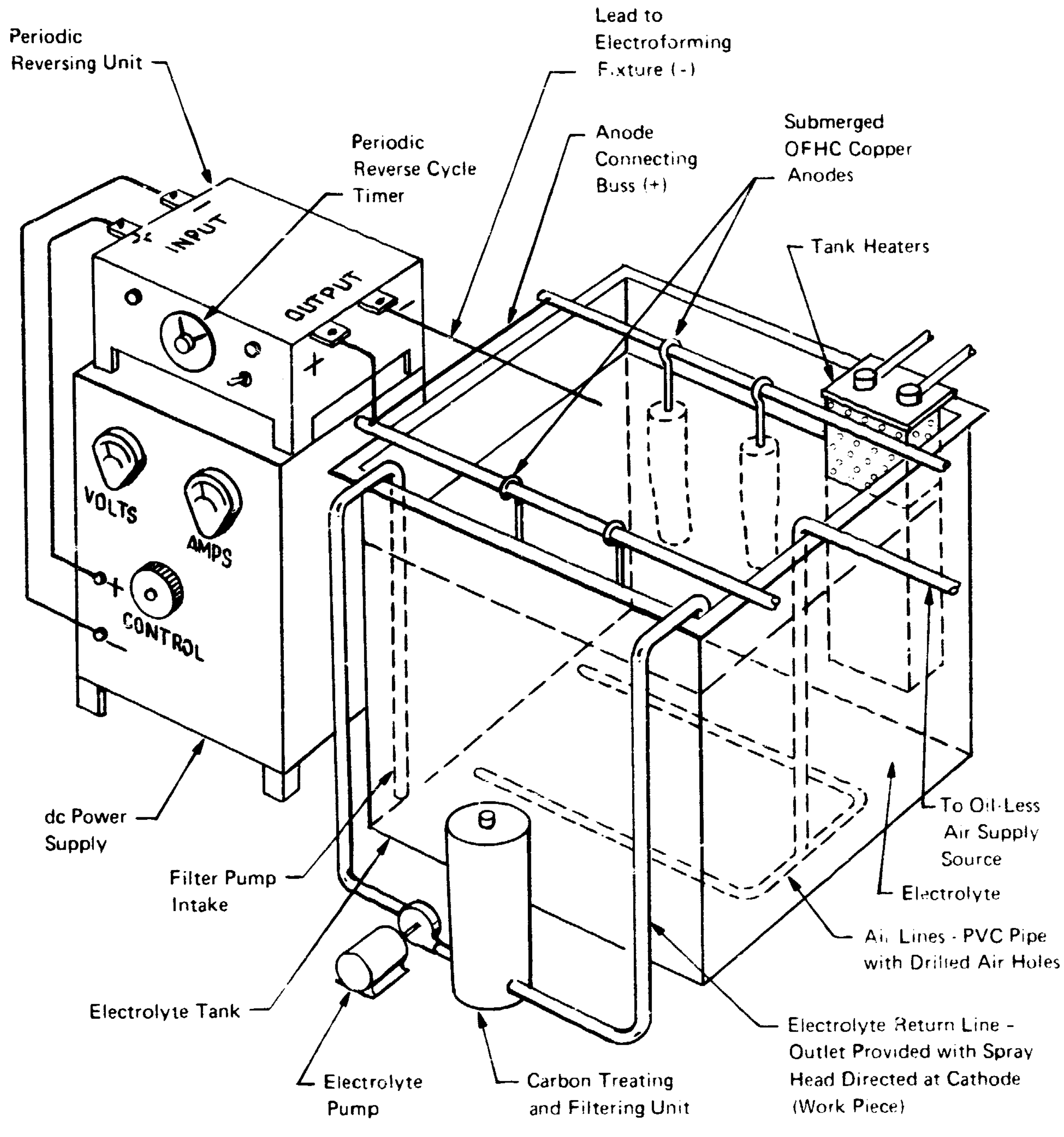


Figure 27. Representative Acid Copper Sulfate Electroforming Tank with Periodic Current Reversal Capability

shall be made to adequately circulate the electrolyte to prevent overheating which could lead to decomposition of the tank lining or heater guard coating.

The heating equipment shall be capable of maintaining a temperature of 26.7 to 37.7°C (80 to 100°F) and shall be capable of regulating the temperature to 1.1°C (±2°F).

3.3 ELECTROLYTE AGITATION

Primary circulation shall be provided by filter pumps. Air agitation, as provided by low pressure air blower systems which are oil-free and filtered, is allowed. If air agitation is used, the air shall not impinge directly on the anodes or cathode. Clean, filtered nitrogen may be used in place of air where available.

The air agitation shall be introduced through polyvinyl chloride or polypropylene piping containing drilled outlet holes. Such piping shall be at least two inches off the bottom of the tank so as not to force settled particulate up against the workpiece being electroformed.

3.4 FILTRATION

The electrolyte shall be continuously filtered through a filter of 10 micron nominal rating or finer. Filter aids are permitted providing they contain no cellulose type material. The filter area and pump capacity shall be such that under a no loading condition the system can circulate double the electrolyte volume every hour. All filter pumps and housings shall be made of materials suitable for use in acid plating baths. All cartridge type filters shall be leached in a 10 percent solution of sulfuric acid in water or a container of the acid sulfate plating solution for at least 24 hours before use to remove sizing compounds. Cartridge filters shall be polypropylene or Dynel material.

3.5 CARBON TREATMENT

All new electrolytes shall be carbon treated as later described in this document. This treatment shall be repeated at least once for every 10 days of accumulated operation of the electrolyte. Peroxide treatment is permitted when stubborn organic contamination exists. This periodic treatment is not required if continuous carbon treatment is employed. Only sulfur-free carbon shall be used for carbon treatment.

3.6 CURRENT SOURCE AND CONTROL

A standard D.C. plating supply of 6 volts minimum rating at required maximum current rating is necessary. The D.C. power supply shall have current capacity capable of furnishing up to 5.4 A/dm^2 (50 amp/ft^2) as a cathode (workpiece) current density. Since the sulfate electrolyte is acidic and will slowly etch the surface of copper when no current is flowing, the power supply shall be equipped with a manual reset switch to protect the cathode from laminations in event of power failure.

The periodic reversing unit shall be capable of providing the same direct current output as the power supply. The unit shall be capable of providing the cathode (workpiece) with anodic cycles from 3 to 6 seconds and with cathodic cycles from 9 to 30 seconds and have full timing capability within these ranges.

4.0 ANODES

Only oxygen free high conductivity copper anodes conforming to specification ASTM B-170 are permitted for copper electroforming. These anodes may be in the form of ovals, slabs, or chips. All anodes shall be cleaned before using. Such cleaning shall include a bright dip to remove any copper oxide on the surface. This shall be followed by a thorough rinse in tap water and a final rinse with distilled water.

Only titanium anode hooks (or titanium anode baskets for chips) shall be used. Anode hooks shall be long enough to operate the anode completely submerged. This is to minimize anode waste. Anodes shall be bagged with polypropylene or Dynel anode bags. The bags shall be leached to remove sizing materials before use (soaking in a 5 to 10% solution of sulfuric acid in water or acid sulfate plating solution for 24 hours is required.

5.0 ELECTROLYTE MAKE-UP

a. Fill a spare tank, of suitable material for exposure to acid electrolytes, with distilled water to a level representing two-thirds of the final required electrolyte volume. This tank shall have been leached with a sulfuric acid solution prior to use.

b. Heat the distilled water to 60°C (140°F) and agitate with oil-free, filtered low pressure air or nitrogen.

c. To the hot water, add the required amount of copper sulfate crystals. This will require approximately 0.907 Kg (2 lb) of the pentahydrate copper sulfate per gallon of final electrolyte volume.

d. If technical or plating grade copper sulfate is used, a standard hydrogen peroxide treatment shall be made to oxidize any iron present and to decompose stubborn organic matter. The tank shall be kept at temperature 60°C (140°F) for at least one hour with agitation to drive off residual hydrogen peroxide. One pint of 30 to 35% hydrogen peroxide per 100 gallons of electrolyte is sufficient for this operation. If ACS grade copper sulfate is used, the peroxide treatment may be omitted.

e. Add 1.36 to 2.27 Kg (3 to 5 lb) of sulfur-free activated carbon per 100 gallons of electrolyte. Mix for at least one hour, shut off the agitation, and allow the solution to settle for at least four hours.

f. Carefully filter the treated solution into the electroforming tank, using a filter that has been pre-coated with a non-cellulose type filter aid. Check the effluent for carbon or other particulate by filtering through a standard filter paper. Remove and replace the filters in the filter pump after this operation. Flush the system with clean water followed by distilled water.

g. Turn on the tank agitation and filter pump systems. Slowly add the required amount of concentrated reagent grade sulfuric acid 60 to 75 grams/liter (8 to 10 oz/gal) to the electrolyte. CAUTION: Heat is generated and protective clothing shall be worn to prevent injury from splashing.

h. Position the bagged OFHC copper anodes in the electroforming tank. Adjust the electrolyte temperature to 32.2°C (90°F).

i. Sample the electrolyte and perform a chemical analysis to the operating range specified in this document. Adjust the concentrations as required with properly purified solutions.

6.0 ELECTROLYTE OPERATING RANGE

The acid copper sulfate electrolyte shall contain no brighteners, leveling agents, or other organic additives when used with periodic current reversal The following range of concentrations shall be maintained.

	Grams/Liter	Oz/Gal
Copper Sulfate Pentahydrate	195 to 240	26 to 32
Sulfuric Acid (66°Bé, C.P.)	60 to 75	8 to 10

The following operating ranges shall be used:

Temperature	31.1 to 33.3°C	88 to 92°F
Anode Current Density	2.16 to 4.32 A/dm^2	20 to 40 A/ft^2
Cathode Current Density	4.32 to 5.4 A/dm^2	40 to 50 A/ft^2

Periodic Reversal Cycle*

Cathode-Anodic	3 to 4 sec
Cathode-Cathodic	6 to 12 sec
Ratio of Cathodic:Anodic	2:1 to 4:1

*Periodic reversal shall not be used in the first twenty minutes of electroforming where bonding on a waxed and conductivized surface is involved. Decreasing the ratio of cathodic to anodic improves tensile strength in the deposit.

7.0 MECHANICAL

Mechanical properties of acid copper sulfate deposits with periodic current reversal shall be in the following ranges:

	MN/m^2	Kpsi
Ultimate Strength	220.7 to 310.3	32 to 45
Yield Strength	110.3 to 151.7	16 to 22

Elongation, % in 2 inches 25 minimum*

*Raising the current density from 40 A/ft^2 to 50 A/ft^2 lowers the ultimate strength and increases the elongation value.

8.0 QUALITY ASSURANCE PROVISIONS

8.1 VISUAL INSPECTION

All hardware electroformed to the requirements of this specification shall be visually inspected to assure that:

a. Dimensional requirements are met.

b. The electroform contains no pits or voids which will remain after final external machining.

c. The surface is free of burns, cracks, blisters, or other obvious defects.

8.2 ELECTROLYTE ANALYSIS

The acid sulfate electrolyte shall be analyzed and records maintained to demonstrate control of the process. As a minimum, the following analytical schedule will be followed:

a.	New Electrolyte	Analyze for copper sulfate and sulfuric acid before using to electroform any deliverable hardware or tensile specimens.
b.	In-Service Electrolyte	— Analyze for copper sulfate and sulfuric acid every two weeks of continuous operation or when significant voltage increases occur for a specific electroforming current output from the power source. Maintain records of all analyses and an anode area log (loss of anode area will cause a voltage increase for a fixed current).

8.3 METALLURGICAL TESTING

A separate specimen shall be electroformed concurrently with the deliverable electroformed hardware. This specimen shall be subject to metallographic examination at least 100X for grain structure, deposit cleanliness, and freedom from voids or other imperfections which might affect the service life of the delivered item. It shall also be subject to hardness tests. This specimen is also subject to heat treatments or thermal cycling to assure that welds or other secondary fabrication operations will not develop laminations, voids, cracking, or blisters.

Basic metal surface activation for electroform bonding shall be performed in exactly the same manner as that used for the chamber liner.

Tensile property verification specimens shall be provided if required. These shall be produced immediately prior to the electroforming of the deliverable hardware and from the same electrolyte under identical electroforming controls. Specific specimen lengths and thickness shall be as specified by the procuring agency.

F. SPECIFICATION FOR REMOVAL OF CHANNEL FILLING AND CONDUCTIVIZING MATERIAL FROM ELECTROFORMED REGENERATIVELY COOLED THRUST CHAMBERS

1.0 SCOPE

This specification establishes procedures to be used to remove channel filling waxes and conductivizing media prior to coolant manifold assembly operations on the regeneratively cooled thrust chamber.

2.0 APPLICABLE DOCUMENTS AND MATERIALS

SPECIFICATIONS	None.

MATERIALS

Trichlorethylene, Stabilized, Degreasing Grade	Specification MIL-T-7003
Methylene Chloride	Commercial
Nitric Acid, ACS Reagent Grade	Commercial
Sodium Carbonate, Technical Grade	Commercial
Detergent Cleaning Compound, Alconox Brand (or Equivalent)	Alconox, Inc. New York, NY 10003

3.0 PROCEDURES

3.1 OUTER SHELL MACHINING

The electroforming fixture shall be removed from the thrust chamber and replaced by a suitable fixture for final machining of the outer shell. It may be necessary to remove liner interior masking by solvent wiping with trichlorethylene or methylene chloride to remove wax, lacquer, or painted polyvinyl chloride coating in order to accurately fit the machining fixture to the chamber liner. Channel and manifold filling compound should not be removed until the machining operation is complete. This will prevent metal chips from entering the channels. Any machining burrs present at channel openings shall be removed.

3.2 CHANNEL FILLER REMOVAL

Platers tape and other coatings which might bake onto the chamber interior surface at 121°C (250°F) exposure should be removed before channel wax removal.

After the machining operation, the channel filler (wax) should be visible at both manifold ends of the chamber. Any machining coolants shall be removed by solvent wiping before wax removal. The chamber shall be placed in a vertical position on a shallow tray and carefully placed in an oven controlled to a temperature not to exceed 126.5°C (260°F). The chamber will remain in the oven until the channel wax has been observed to flow into the shallow tray. The time for this process will depend on the oven heating time and the complexity of the chamber design.

Remove the chamber from the oven and allow it to cool. If polyvinyl chloride masking has been applied to the chamber interior surface as a maskant, the oven heat will have caused it to shrink and peel from the liner. It may now be removed.

The chamber shall be placed on a degreasing fixture, or in a degreasing basket, and exposed to a vapor degreasing operation with trichlorethylene (or perchlorethylene). The Rigidax W.I. Light Blue Compound used for channel filling is readily soluble in trichlorethylene vapors at approximately 87°C (189°F). Soaking the chamber in cold solvent will remove the filler wax but at a slower rate. Vapor degreasing should be continued for at least 30 minutes after the chamber reaches the solvent vapor temperature. Trichloroethane may be used in place of other solvents.

It shall be verified that the channel passages are open and clear by injecting clean room temperature degreasing solvent into the channel openings and observing the flow out of the outer openings. Any blue coloration of the solvent indicates a need for further vapor degreasing.

3.3 REMOVAL OF CONDUCTIVIZING MEDIA

If silver powder is used to conductivize the channel filling wax, the removal is greatly simplified. The chamber is first detergent scrub cleaned with a mild compound such as Alconox in water. After a thorough rinse in clean water, the chamber is quickly dipped into a nitric acid solution with strict observance of the following conditions:

Nitric Acid, ACS Reagent Grade	25% by vol.
Distilled water	75% by vol.
Temperature	Room
Time	15 to 30 seconds

Immediately withdraw the chamber and transfer into a room temperature clean water rinse for 10 to 15 seconds. Transfer the chamber to an acid neutralizing solution of mild alkalinity. Such a solution may be made by adding sodium carbonate to water at a concentration of 3.7 to 7.5 g/l. (0.5 to 1.0 oz/gal).

The chamber is then allowed to soak in clean tap water to remove the alkaline solution followed by a final rinse in distilled or demineralized water.

If conductivizing media other than silver is used it will be necessary to develop and demonstrate effective removal techniques which will assure that loose conductivizing media will not later dislodge and contaminate or plug the orifices of the rocket engine injector.

3.4 FINAL CLEANING FOR COSMETIC PURPOSE

Any strains or discoloration on the copper or copper alloy surfaces may be minimized by scrub cleaning with a stiff bristle brush (no wire bristles). A detergent solution may be made up by adding Alconox and fine scrubbing grade pumice powder to form a soft paste with water. After scrubbing a thorough rinse and flushing of the channels shall be made with distilled or demineralized water.

VI. ELECTROFORMING AND TESTS

A. GENERAL

The objective of this portion of the program was to demonstrate that the specifications previously developed were suitable for electroforming copper and nickel outer shells on regeneratively cooled thrust chamber liners to produce consistently reliable bonds of the shell to the copper alloy inner shell. The objective was also to verify that repeatable mechanical properties could be obtained in the nickel or copper electrodeposit which were equivalent to those expected in the corresponding annealed wrought metal.

The approach to this task included the fabrication of ten Amzirc cylinders with machined coolant passages and connecting manifolds similar to those in actual thrust chamber liners, Figure 28. Five of these cylinders were electroformed with nickel outer shells and tested to destruction to verify bond strength. Provision for obtaining tensile test strips from the outer shells was made. The remaining five cylinders were electroformed with copper outer shells and similarly tested.

B. AMZIRC CYLINDER FABRICATION AND PREPARATION

Each Amzirc cylinder forging was machined to produce two test cylinder liners. Centering diameters were machined into the ends of each cylinder to provide accurate locations for machining the final diameter of the Amzirc surface and for machining the final electroformed outer shell to uniform thickness. The channels and manifolds were milled to closely controlled tolerances to assure that each cylinder duplicated the others and conformed to the dimensions of Figure 28. Each cylinder was stamped with a code at one end to designate the numerical sequence of electroforming and the type of outer shell (i.e., nickel or copper).

The liner cleaning and channel waxing procedures described in Section V, Electroforming Specifications, were carefully followed. The wax filling operation is shown in Figure 29. The cylinder being prepared in this photograph was for a "spool" chamber fabricated for the low cycle thermal fatigue study program in progress at NASA's Lewis Research Center, Cleveland, Ohio. Each cylinder was fixtured between two Teflon end plates with a threaded metal shaft through the center. The shaft extension was mounted in a lathe chuck and rotated at a slow speed while Rigidax Type WI Light Blue Compound was melted onto the cylinder surface. The wax was allowed to cool while the cylinder rotated.

The excess wax was removed using a hot-knife as illustrated in Figure 30. The hot-knife blade temperature was controlled by a Variac and a thermocouple with direct temperature reading instrumentation. In this work the hot-knife was held stationary and the chamber liner moved by hand. Large liners would be secured on rotation centers and the hot-knife moved.

The wax finishing was accomplished by wet sanding with fine grit papers under running water to produce the liner surface shown in Figure 31.

Prior to conductivizing the wax-filled channels, it was necessary to chemically passivate sections of the cylinder adjacent to the channel test areas. The object of this operation was to produce cylinder length strips of the outer shell with no bond to the Amzirc cylinder. These areas were to be

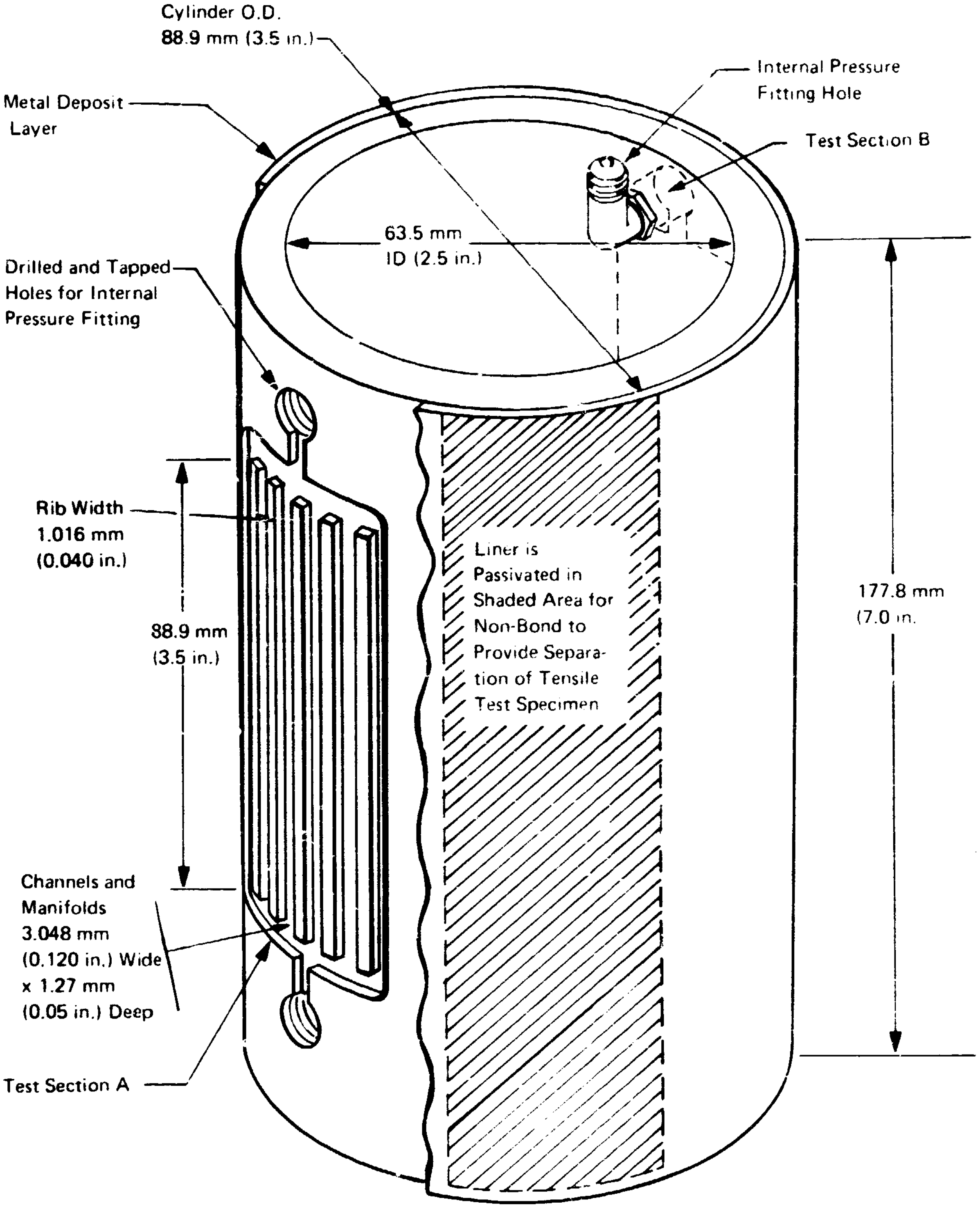


Figure 28. Final Test Cylinder Design

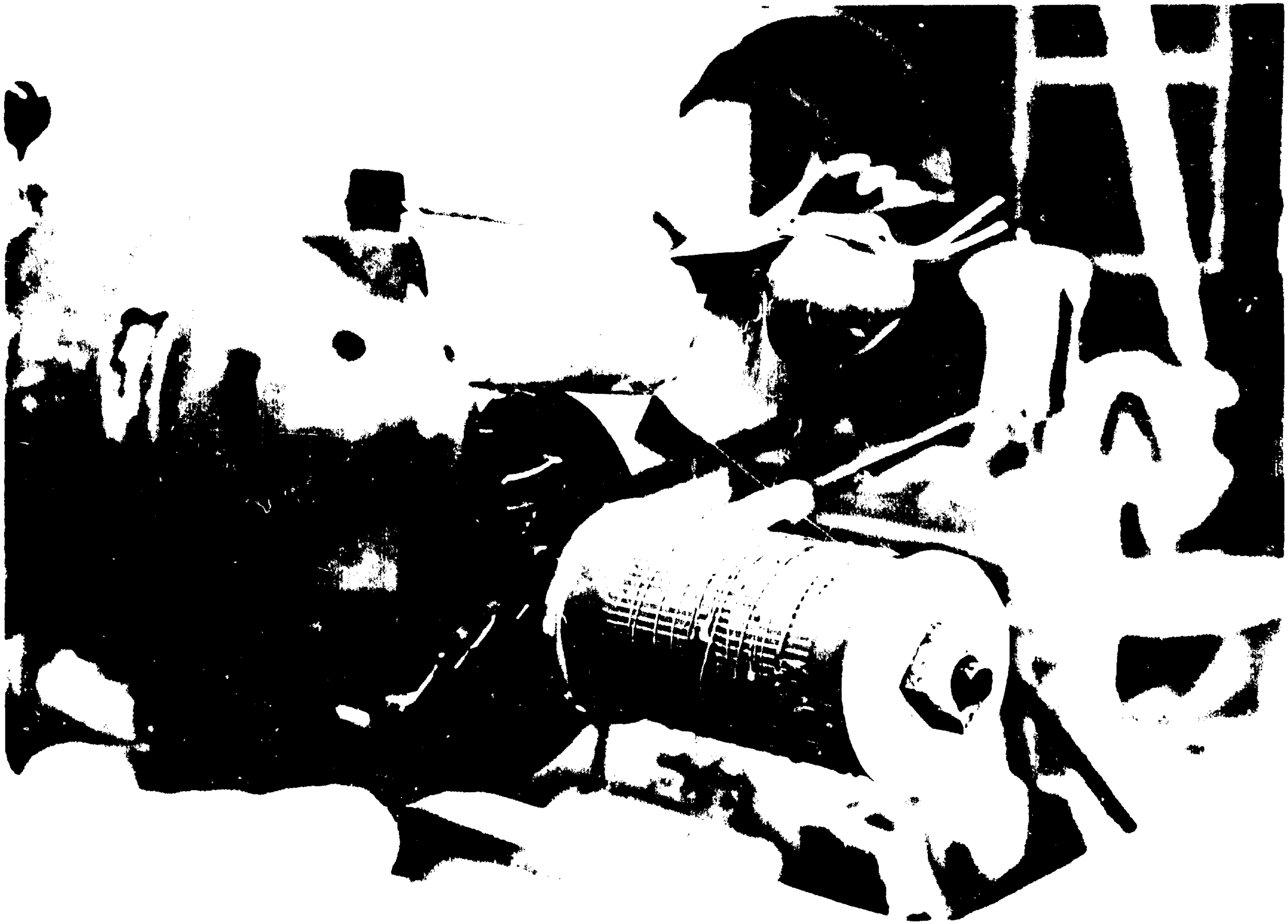


Figure 29. Filling Channel Passages with Rigidax Type WI Light Blue Compound

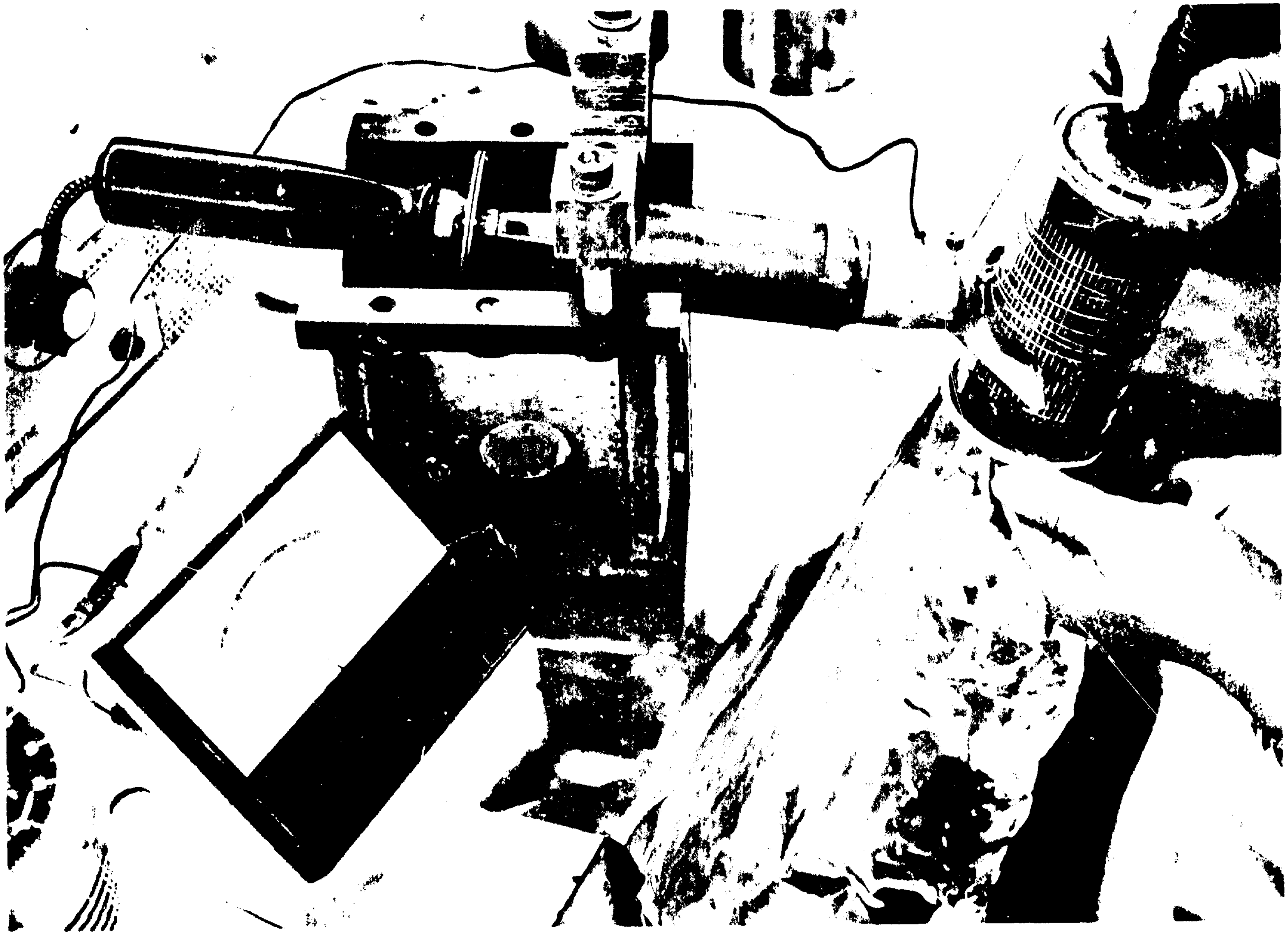


Figure 30. Removing Excess Channel-filling Compound with a Hot-knife

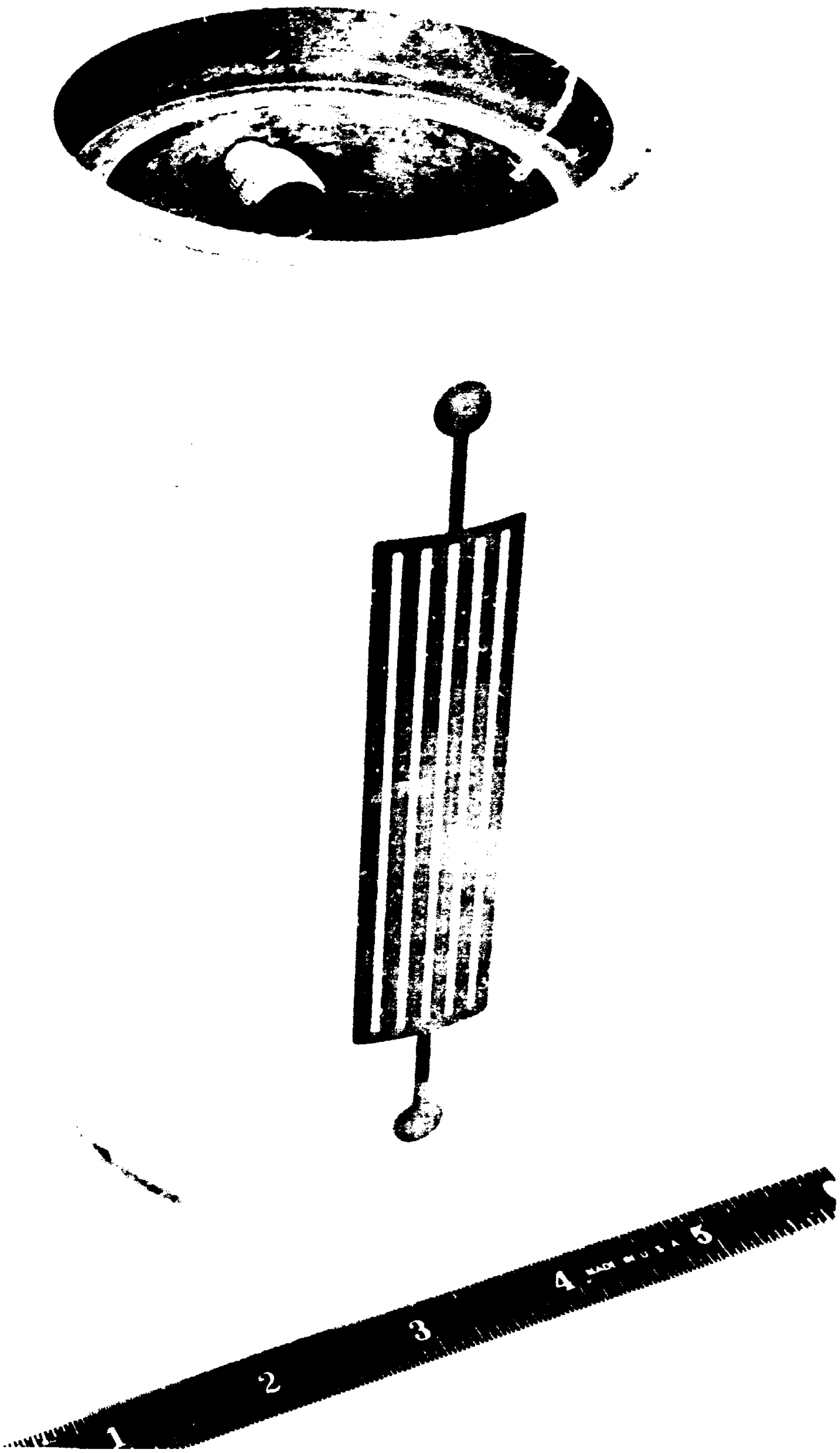


Figure 31. Amzirc Test Cylinder with Rigidax Type WI Light Blue Compound Filling Channels of Test Pattern

saw-cut to afford strips for making tensile test specimens. The cylinders were masked as shown in Figure 32. Each cylinder was cathodically treated in a passivating solution as follows:

Sodium Dichromate	26 to 30 g/l.
Water	Balance of Solution
Temperature	48.9°C (120°F)
Current Density	1.08 A/dm^2 (10 A/ft^2)
Time	60 to 90 seconds
Anodes	Stainless Steel

After a double rinse to remove all chromate ion, the masked cylinders were electroplated in an acid copper sulfate electrolyte to obtain a non-bond deposit of copper approximately 0.0178 mm (0.0007 in.) thick. Each cylinder was rinsed, the masking over the waxed channels removed, and all surfaces scrubbed clean with a mild detergent and water. Prior to conductivizing the wax-filled channels, the exposed Amzirc was anodically etched in 65 percent by volume phosphoric acid using a current density of 16.14 A/dm^2 (150 A/ft^2) for 90 to 120 seconds, or until the Amzirc surface appeared uniformly bright. This pre-treatment appears to substantially remove the Beilby layer (zone of disturbed or contaminated metal crystal structure).

Each cylinder was rinsed, allowed to drain, and placed in a circulating air oven to bring the channel-filling compound to the melt point. After a thermal stabilization period, the cylinders were removed from the oven and conductivized with silver powder. The powder was brushed onto the warm wax surface and allowed to cool. The silver was lightly hand rubbed (using disposable plastic gloves) as shown in Figure 33. In this photograph, the NASA spool chamber was used as the example. The bright, short cylindrical portion with no channels is a separate test specimen of Amzirc.

C. ELECTROFORMING OF OUTER SHELLS

All conductivized cylinders were activated for bonding by the modified Stanford University recommended process using anodic treatment in phosphoric acid followed by cathodic reduction in sulfuric acid. Cylinders required to have a copper outer shell were double rinsed and transferred with applied cathodic voltage to the acid copper sulfate tank. After twenty minutes of conventional plating, periodic current reversal was applied until a shell thickness of about 1.52 mm (0.060 in.) or greater was achieved. The electroforming was performed at a current density of 4.84 A/dm^2 (45 A/ft^2) and a bath temperature of 32.2°C (90°F). The periodic current reversal cycle ratio was maintained between 4:1 and 3:1 (cathodic to anodic ratio).

The five nickel electroformed cylinders were produced in a low chloride nickel sulfamate bath operated at 44.4°C (112°F) and a current density of 2.15 A/dm^2 (20 A/ft^2). The shells were electroformed to a thickness of 1.27 mm (0.050 in.) or greater. All cylinders, except those to be welded, (see Section D below), were machined to a uniform shell thickness. The two welded cylinders were machined after welding to remove surface irregularities from the girth weld and provide a uniform shell thickness for pressure testing. After final machining, the channel filling compound was removed and the passages flushed with a solvent. The wax was removed prior to welding on the special two cylinders. Figure 34 illustrates typical cylinders after machining and prior to destructive testing.

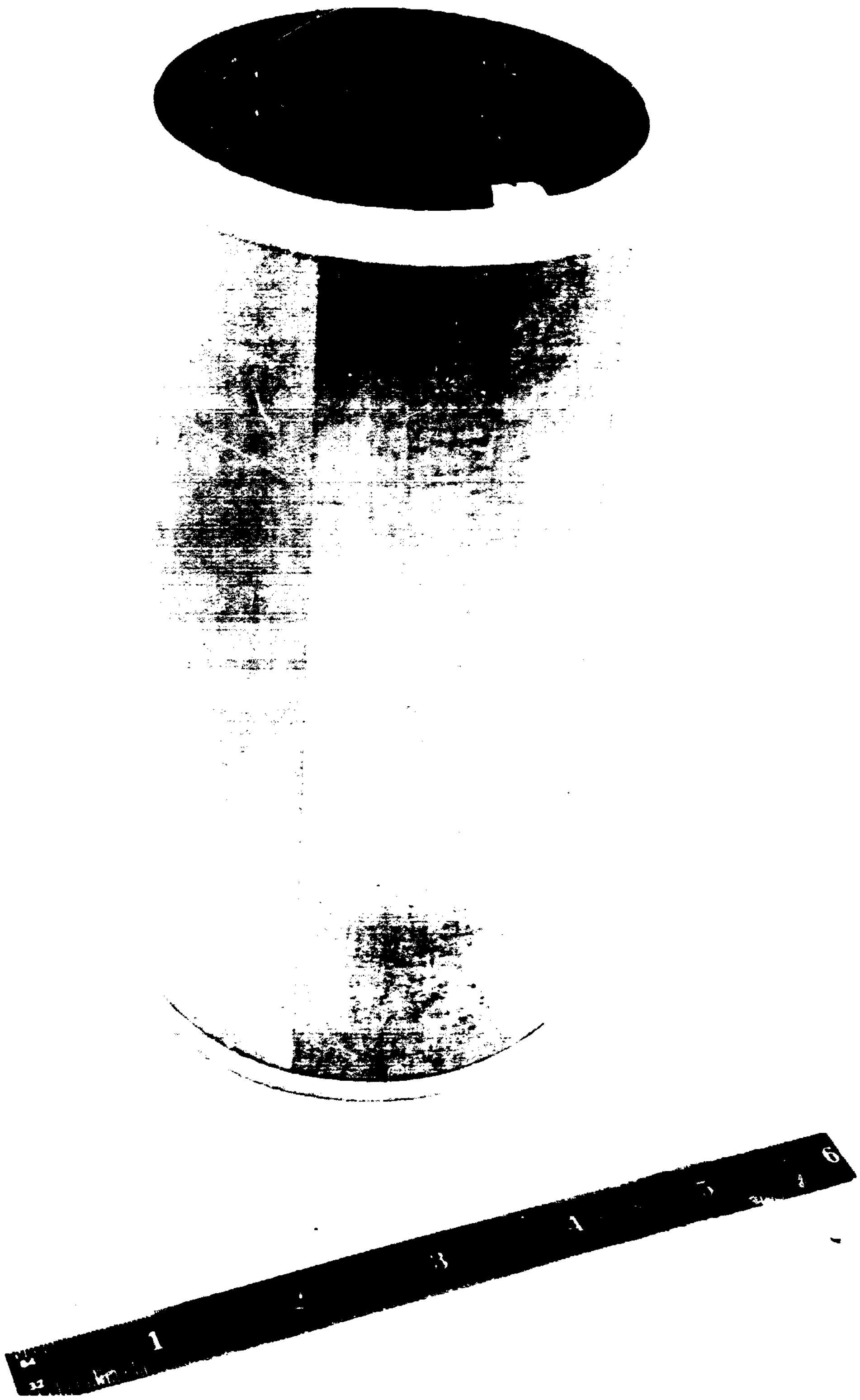


Figure 32. Amzirc Cylinder Masked for Passivating to Prevent Electroform Bonding Where Tensile Test Strips are to be Obtained

Figure 33. Manual Burnishing (Rubbing) of the Silver Conductivizing Layer for Uniformity

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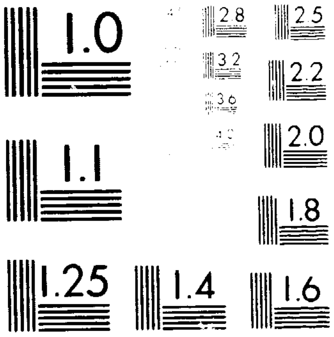

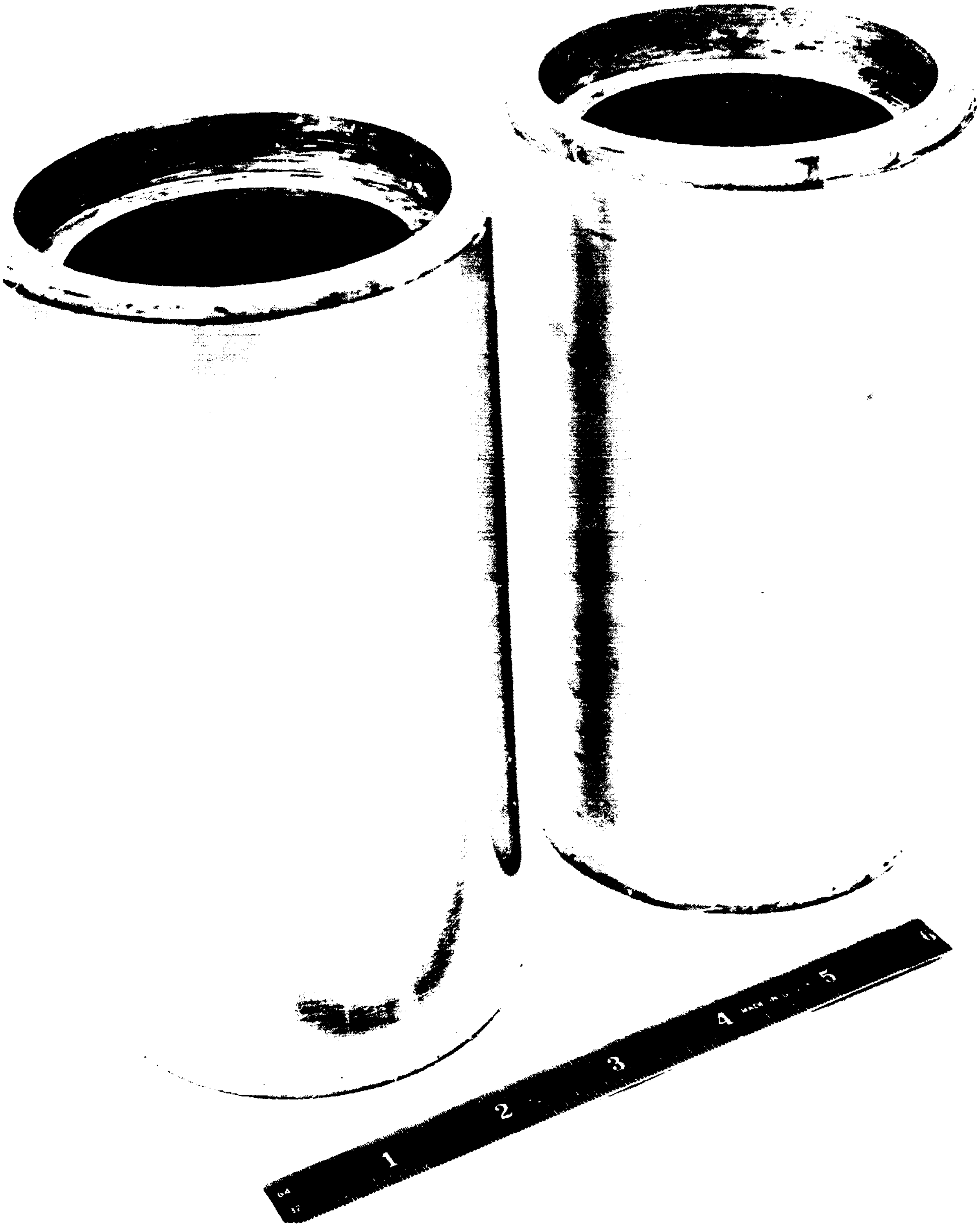

Figure 34. Typical Amzirc Cylinders with Electroformed Outer Shells after Machining and Prior to Destructive Testing

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D. TIG WELDING

One cylinder with a nickel shell, Cylinder N-3, and one with a copper shell, Cylinder C-5, were TIG welded to determine the effect of severe thermal exposure on the shell-liner bond integrity. Both cylinders performed well in the welding operation with respect to minimal outgassing and good metal melting. However, in attempting to achieve metal flow temperatures on the copper shell cylinder, an excessive melt area was produced which damaged one of the two test patterns. All welds were around the middle of each cylinder.

E. HOLOGRAPHIC TEST RESULTS

Unwelded Cylinders N-1 and C-1 were holographically inspected to determine the general bond integrity prior to high pressure testing to failure. Again, procedures as described in Ref. 8 were used. Gaseous nitrogen was used as the pressurizing media for all holographic work. The holograms for Cylinders N-1 and C-1 indicated high integrity bonds by virtue of the straight and firm bands visible over the channel areas. The holograms are shown in Figure 35.

The holograms were produced by photographically exposing the test area with no pressurization and superimposing a second photographic image on the original after pressurization. Finite movement of the electroformed shell causes light interference patterns. The shape and intensity of these patterns is related to the pressure applied, the configuration of the test area, and the integrity of the bonded joint.

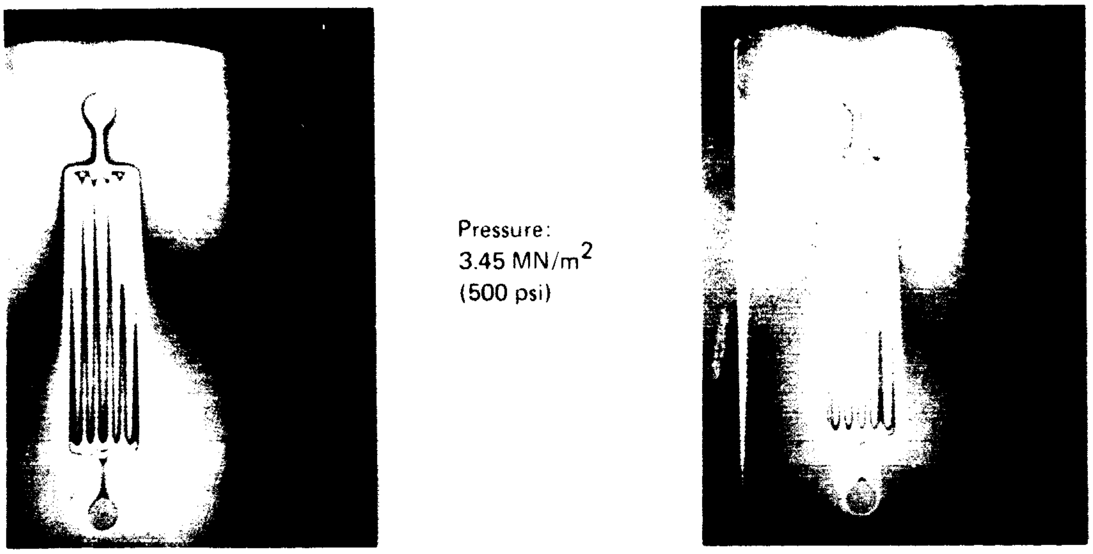
When Cylinder N-1 was pressure tested to determine the nickel shell bond strength, leakage was detected in the two test patterns. This was initiated at pressures of 41.4 MN/m^2 (6.0 Kpsi) in Test Area A and 34.5 MN/m^2 (5.0 Kpsi) in Test Area B. Pressurization was continued to 86.2 MN/m^2 (12.5 Kpsi) in Area A and 93.1 MN/m^2 (13.5 Kpsi) in Area B. At these pressures leakage was severe and it was suspected that joint failures may have occurred.

Cylinder N-1 was repaired by vibratory peening, to close the leakage pin-holes, and plating 0.127 mm (0.005 in.) of nickel over the electroformed outer shell. Holographic inspection of the repaired cylinder, Figure 36, disclosed all bonds were unfailed. The bands formed by the reflected light in the holograms tend to be pointed at the ends of some bonding ribs (Area A) or show shadows in the channels (Area B). Both conditions are indicative of severe joint strain. A failed joint would show light bands running across the bonding rib. From this information it was correctly concluded that the test cylinder should be retested to a higher pressure where joint failure would occur.

The two welded cylinders were holographically inspected to determine if any bond degradation had occurred as a result of the severe thermal exposure. The holograms shown in Figure 37 reveal no abnormalities in the bonded joints after welding.

F. DESTRUCTIVE TESTING

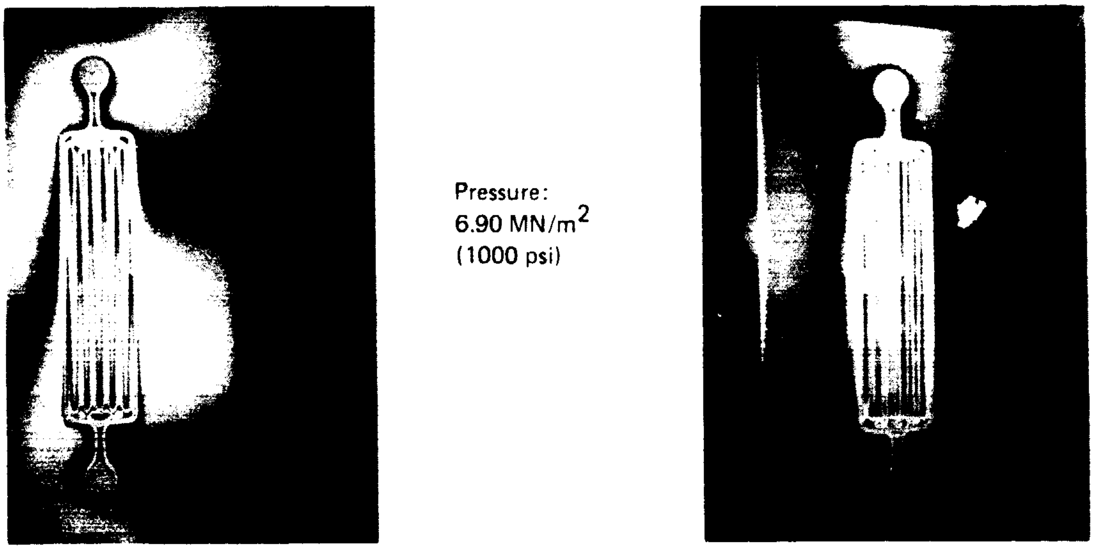
All of the Amzirc test cylinders were fabricated to accommodate pressure fitting attachment to the inside surface. This permitted the use of external restraining blocks to prevent buckling of the electroformed outer shells over the 9.52 mm (0.375 in.) diameter tapped holes into which were screwed the pressure fittings. Figure 38 illustrates the fixturing used for high pressure testing. All destructive testing was performed under the surveillance of Quality Engineering personnel.



Pressure:
3.45 MN/m^2
(500 psi)

Cylinder C-1 Area A

Cylinder C-1 Area B



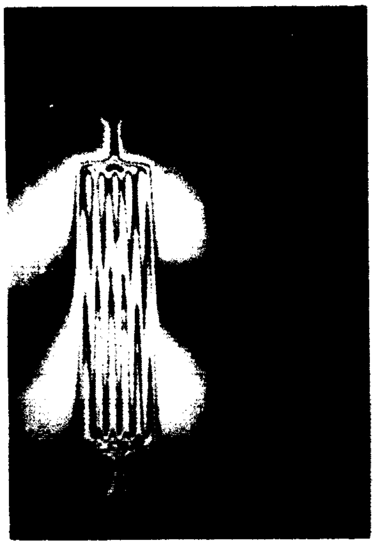
Pressure:
6.90 MN/m^2
(1000 psi)

Cylinder N-1 Area A

Cylinder N-1 Area B

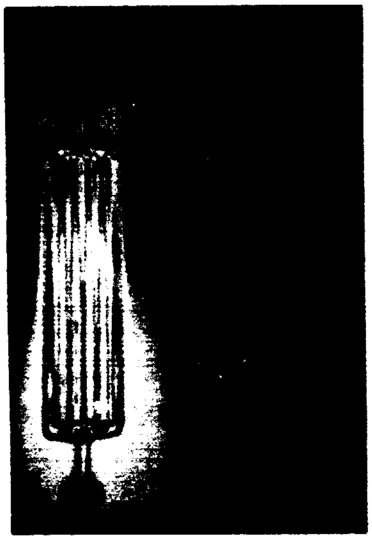
Holograms indicate high integrity bonds exist as denoted by the straight and firm bands of light reflected over the channel patterns.

Figure 35. Holograms for Test Cylinders N-1 and C-1 Prior to Destructive Testing



Cylinder N-1
Test Area A

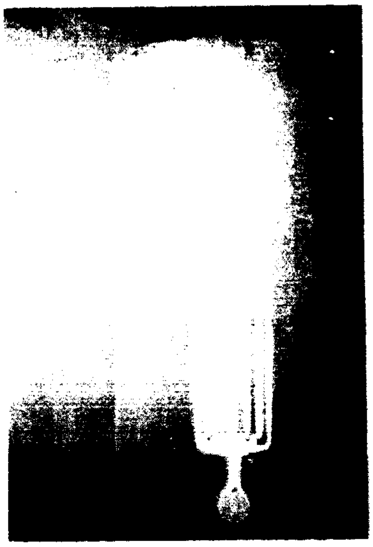
Hologram of Test Area A after exposure of the channels to a hydrostatic pressure of 86.2 MN/m^2 (12.5 Kpsi). A constraining fixture was applied over each end of the cylinder to prevent buckling over the large diameter threaded holes housing the pressure fittings. These fixtures were placed so as to afford no restraint of the cross-manifolds connecting the test area channels. The pressure applied to obtain the hologram was 6.9 MN/m^2 (1 Kpsi). The "pointed" light bands in the test pattern indicate severe deformation of at least one member of the bonded joint. No joint failure is evident.



Cylinder N-1
Test Area B

Hologram of Test Area B after exposure of the channels to a hydrostatic pressure of 93.1 MN/m^2 (13.5 Kpsi). The fixtures used to constrain buckling of the outer shell over the pressure fitting holes were located to also constrain deformation of the cross-manifolds connecting the individual test channels. The use of these fixtures was restricted to the high pressure testing. They were not used in the holography investigation. The pressure applied to obtain the hologram was 6.9 MN/m^2 (1 Kpsi). The hologram bands are not as pointed as was noted in Test Area A (probably due to the manifold constraining fixtures). However, the shadows in some channels indicate a severe strain has occurred in some joints, particularly at the second and third bonding ribs (from the left of the test pattern).

Figure 36. Holograms from Cylinder N-1 Used to Determine Bonded Joint Degradation after High Pressure Exposure

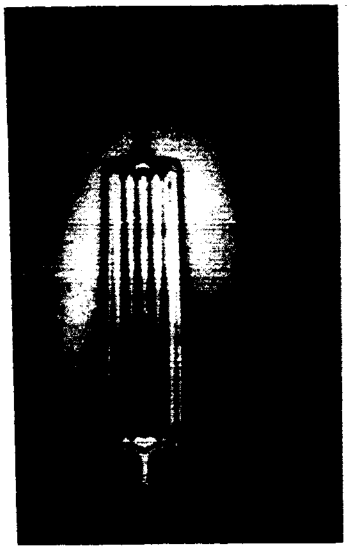


Pressure:
5.17 MN/m2
(0.75 Kpsi)

Cylinder N-3
Test Area A

Cylinder N-3
Test Area B

The above holograms were from Cylinder N-3 containing an electroformed nickel outer shell. A TIG weld was made around the middle of the cylinder. No evidence of electroform bond degradation was noted. This investigation was made prior to high pressure testing of the cylinder.



The adjacent hologram shows the TIG weld on Cylinder C-5 which contained an electroformed copper outer shell. The weld is identified as a black line at the middle left of the hologram. The weld is visible only due to the circumstance that a recess was left at this area of the weld from metal flow when the copper melt occurred. The pressure applied to make the hologram was 5.17 MN/m^2 (0.75 Kpsi). No bond degradation is evident from the welding operation.

Cylinder C 5
Test Area B

Figure 37. Holograms from TIG Welded Test Cylinders

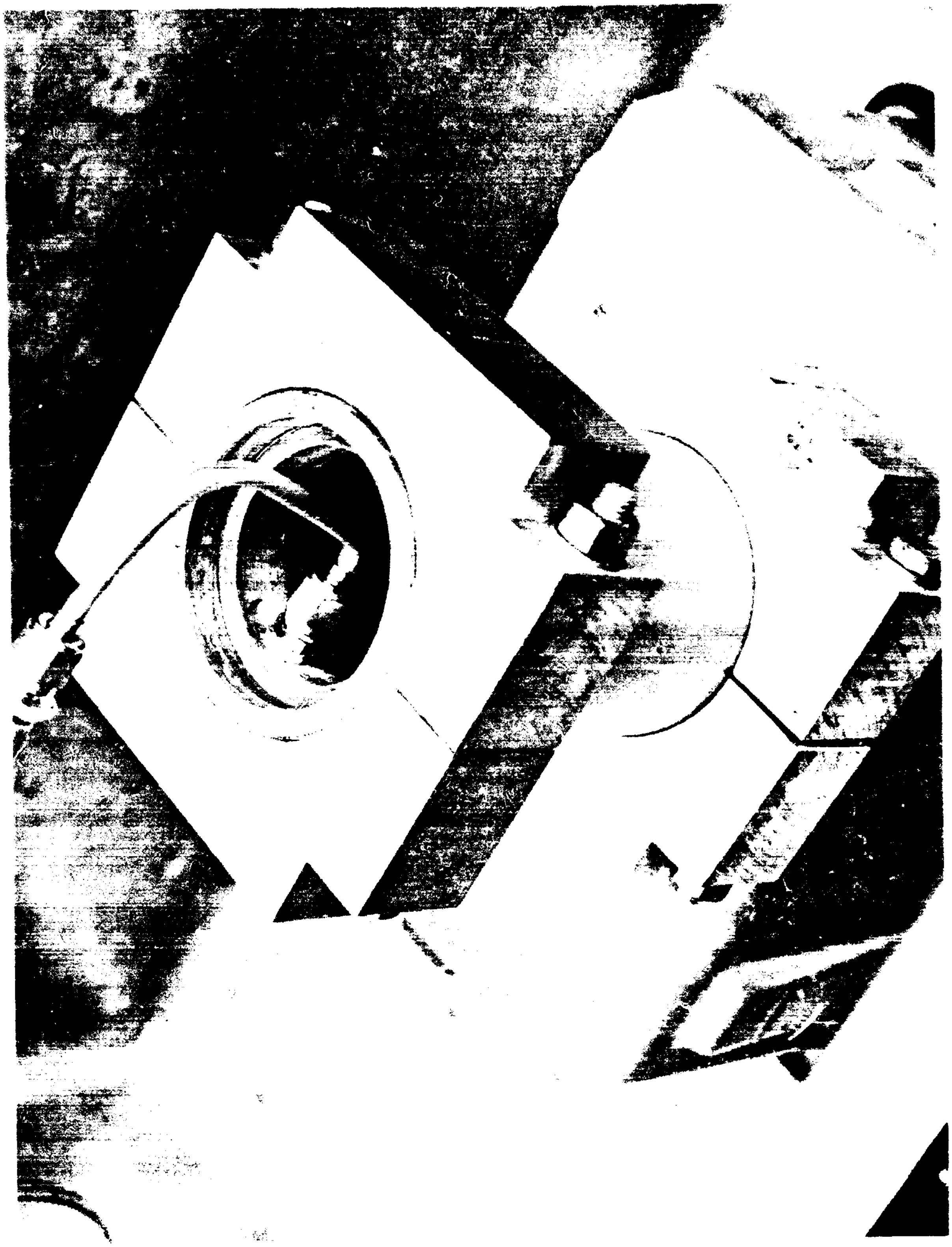


Figure 38. Fixturing of Electroformed Cylinders for Destructive Testing

The pressurization system contained a positive displacement pump and regulators to achieve the high hydrostatic pressures required and to maintain reliable pressure control. An attempt was made to obtain acoustic emission on each cylinder test section during destructive testing. Pressure was increased in 3.45 MN/m^2 (0.5 Kpsi) increments and acoustic emission counts recorded for each increment. It was found that accurate emission count could not be obtained due to external noise and vibrations generated by the positive displacement pump. Acoustic monitoring was continued using the audio output system, since this afforded a reliable indication of when cylinder failure occurred.

Figure 39 shows a typical failure in nickel electroformed outer shells. The bulge is shallow due to the high buckling strength of the electroformed nickel. Invariably, failure of the nickel shell and Amzirc liner joints occurred away from the ends of the bonding ribs. Figure 40 depicts a typical failure of the cylinders electroformed with copper to produce the outer shell. All failures occurred at, or near, the ends of the bonding ribs, except in one case when the restraining blocks were located to inhibit failure at this location and in another instance when the cylinder had been TIG welded. The presence of minor bulging (buckling) can be seen over the entire channel and cross-manifold area of the cylinder shown in Figure 40. This was also observed on all destructively tested cylinders with copper outer shells.

The preference of the copper electroformed cylinders to fail at bonding rib ends is possibly related to simultaneous buckling (bulging) in both the channels and the cross-manifolds. This contributes to high stress concentrations at the rib ends where failures appear to start. This was not observed in the nickel electroformed cylinders where buckling strength of the electrodeposits over the channels was in excess of the hydrostatic loading required to fail the bonding ribs. Since buckling of the nickel shells could not occur, except on the TIG welded cylinder, the hydrostatic pressure loading was more uniformly distributed over all bonding ribs. This probably contributed to the random location of failures along the bonding ribs of these cylinders.

G. MECHANICAL PROPERTY DETERMINATIONS

It was expected that high integrity bonds would be obtained in all of the electroformed cylinders, and destructive testing would result in failures occurring in the weaker of the two metals comprising the bonded joints. On this basis the calculated bond strengths to be determined from the hydrostatic pressures required to fail the cylinders would be expected to be in close agreement with the tensile strength of the weaker metal involved in the bond.

Mechanical property test strips representing the electrodeposited outer shell were cut from the regions of the cylinders which had been passivated to prevent bonding. Figure 41 shows a typical nickel electroformed cylinder with the two mechanical property test strips removed. Difficulty was experienced in the removal of these test strips from one nickel shell cylinder, and three of the copper shell cylinders. This was due to localized bonding and indicated that the passivation treatment may have been for too short a period. Where localized bonding occurred, the strips were generally deformed, scratched, or contained small areas where metal was torn away during removal from the Amzirc liners.

Full length specimens were cut from three randomly selected Amzirc cylinder forgings after the outer shell mechanical property test strips had been removed. These were surface ground, using a grinding coolant, to produce flat tensile test bars.

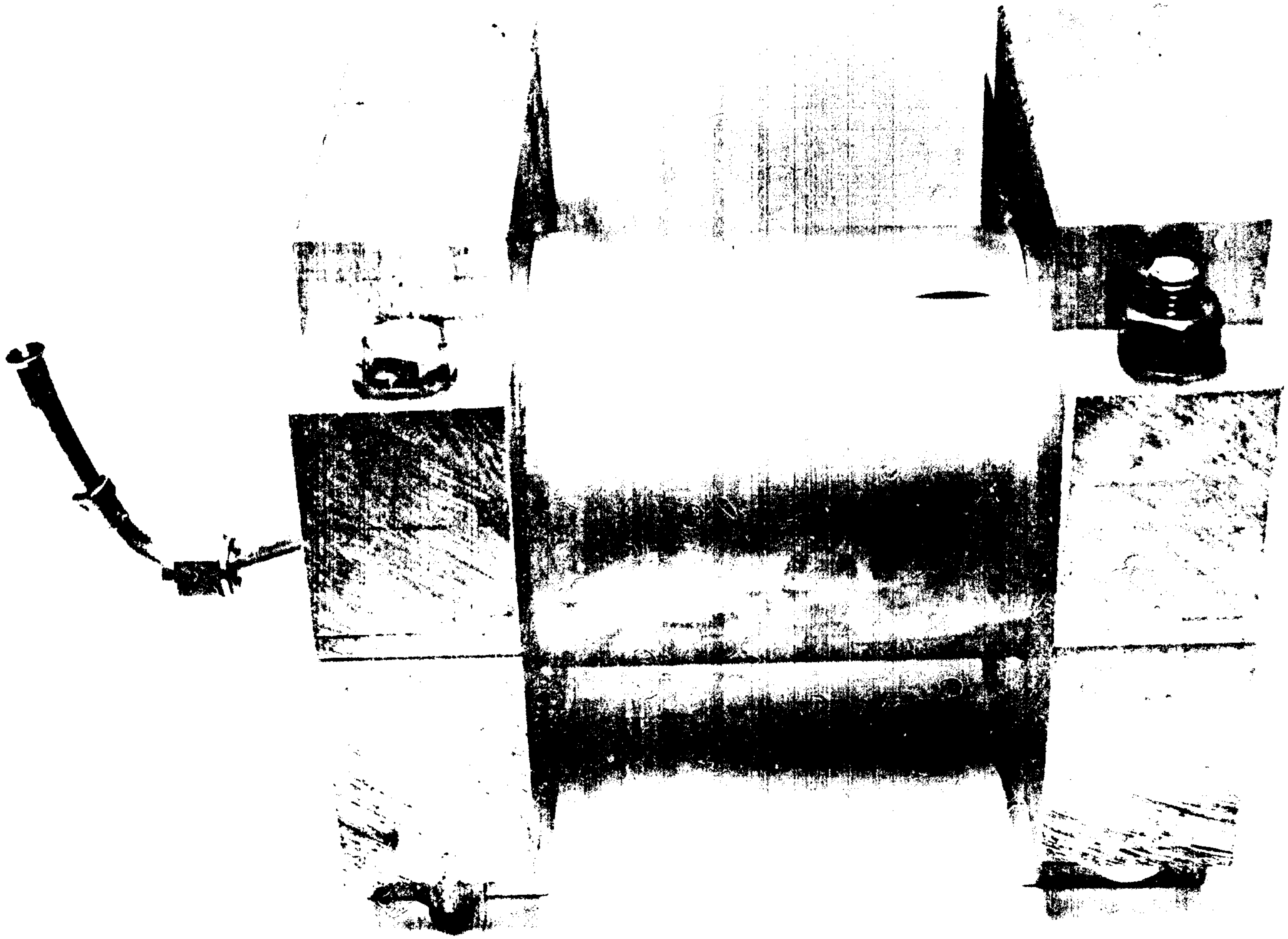


Figure 39. Typical Failure Pattern in Cylinders with Nickel Electroformed Outer Shells

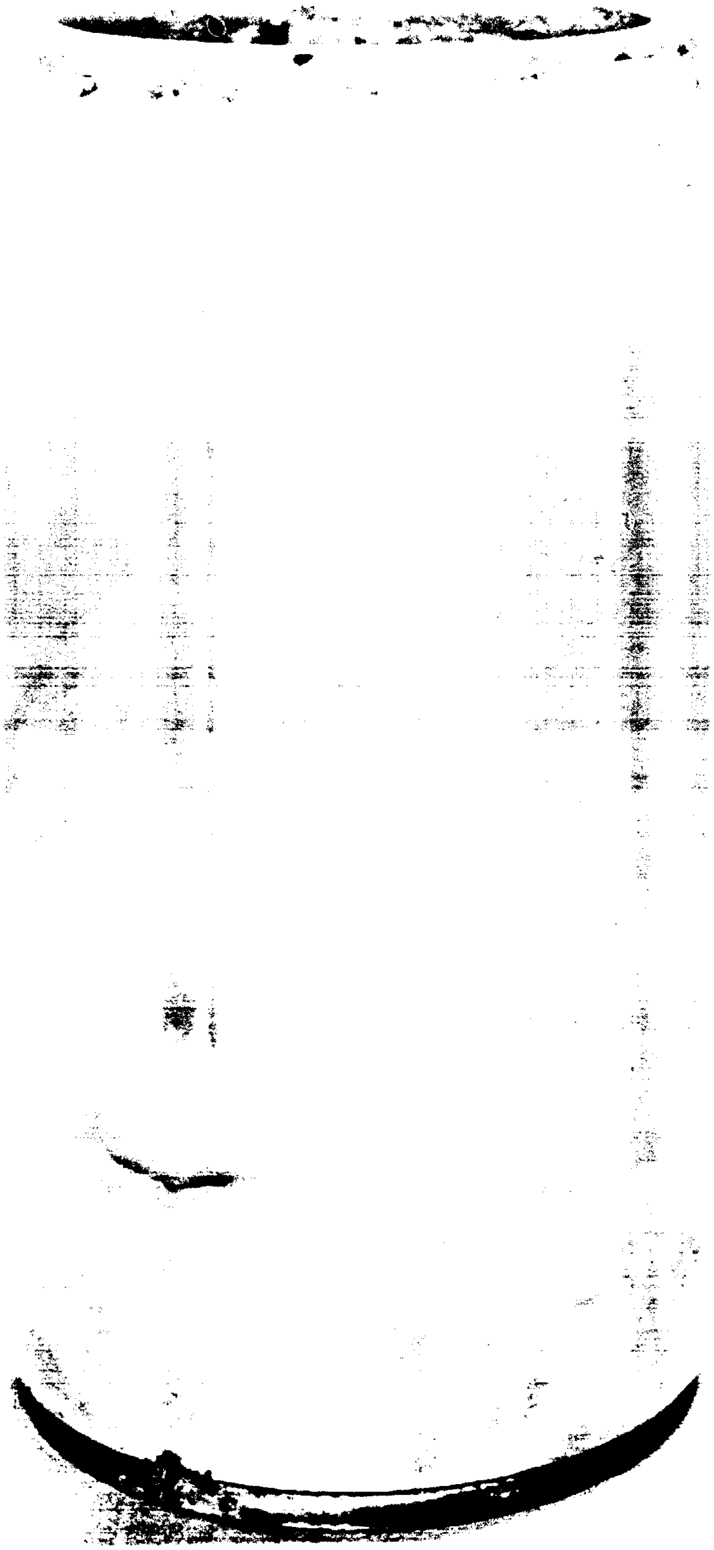


Figure 40. Typical Failure Pattern in Cylinders Electroformed with Copper Outer Shells

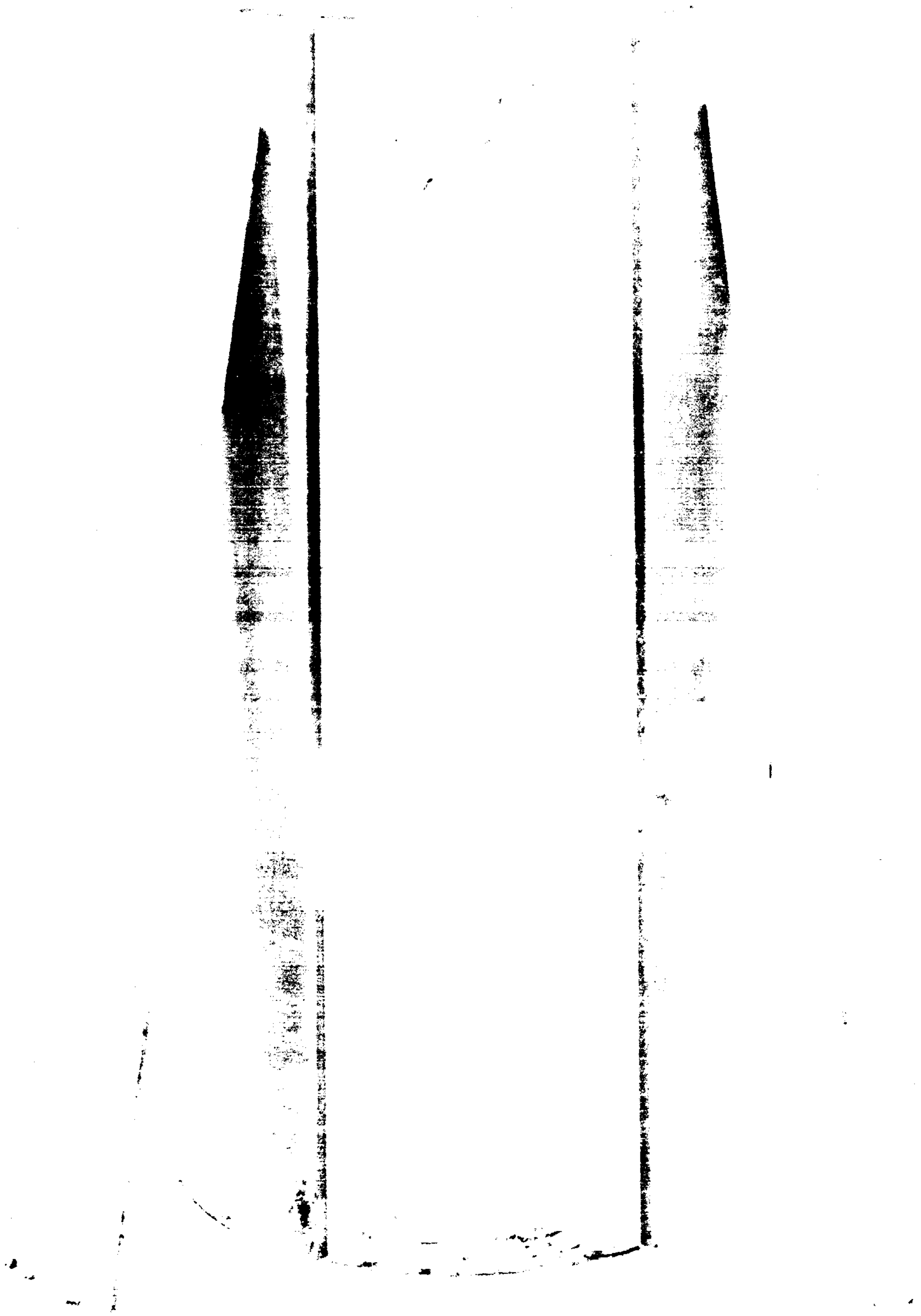


Figure 41. Removal of Mechanical Property Test Strips from Electroformed Outer Shell

Table XIII shows the results of mechanical property testing of all of the metals composing the test cylinders. The shells of the unwelded nickel electroformed cylinders exhibited excellent consistency in mechanical properties from one specimen to another as was expected. The decrease in ultimate and yield strengths of the TIG welded outer shell is normal for high quality electroformed nickel subjected to thermal treatments sufficient to cause metal recrystallization. The percent of elongation in a 25.4 mm (1 in.) gauge length did not increase because the girth weld (zone of maximum metal recrystallization and expected highest ductility) was very narrow with respect to the test gauge length.

Only the tensile test specimens from Cylinders C-2 and C-3 appeared to afford reliable mechanical property results representative of the electroformed copper outer shells. The other cylinder shell specimens were damaged in variable degrees during removal from the Amzirc forgings. The high yield strength and lower than expected elongation of test pieces from Cylinders C-1, C-4, and C-5 reflect the cold work which occurred in the removal of these strips and subsequent attempts to straighten them for test. Although specimens from Cylinders C-1, C-4, and C-5 suffered adverse mechanical property changes during the retrieval operations, they still afford a worthwhile comparison, since Cylinder C-5 had been TIG welded. The lack of significant differences in tensile strength and ductility in these samples indicates that short, severe thermal excursions (typical of welding) may not seriously degrade copper electrodeposits produced by the periodic current reversal technique. All copper electrodeposited outer shells exhibited excellent ductility as will be evident from the shell bulging at the time of joint failure as shown in subsequent photomacrographs.

The mechanical properties of the Amzirc forgings were considered normal for this material and more representative of the desired properties than was found in the Amzirc forgings used to fabricate baseplates for the flat test specimens investigated in the development phase of this work. From these test results it was concluded that the cylinders with electroformed nickel outer shells should fail in the Amzirc bonding ribs during destructive test, and the cylinders with electroformed copper outer shells should fail in the copper shells.

The mechanical properties of the electroformed copper outer shells were lower than those determined for specimens produced under the same conditions of electrolyte composition, electrolyte temperature, and current density in the development phase of this work (Table V). This difference can only be attributed to the change in the periodic current reversal cycle employed for electroforming the outer shells on the cylinders. It was not expected that this ratio of cathodic to anodic current would promote such a significant change in mechanical properties. However, had the same periodic current reversal cycle used in the development effort been applied to the cylinder shell electroforming, it would still be expected that destructive test failure would occur in the copper outer shell.

H. TEST CYLINDER BOND STRENGTH CALCULATIONS

The bond strength of each destructively tested cylinder was determined from the formula:

$$S = P \times \frac{A_c}{A_r}$$

The definition of the terms of this formula are the same as previously presented in Section IV, Electroforming Development. Since minor buckling (bulging) of the outer shells prior to joint failure

TABLE XIII
MECHANICAL PROPERTY TEST RESULTS - ELECTROFORMED OUTER SHELLS AND AMZIRC FORGINGS

Liner Stock or Electroformed Metal	Cylinder Number	Specimen Thickness		Mechanical Properties				
				Ultimate Strength		Yield Strength		Elongation % in 1 in.
		in.	mm	Kpsi	MN/m^2	Kpsi	MN/m^2	
Nickel	N-1	Test specimens could not be separated from this cylinder.						
	N-2	0.042	1.067	114.0	786.0	75.4	519.9	18
		0.042	1.067	113.4	781.9	78.6	541.9	15
	N-3	0.046	1.168	59.1	407.5	46.1	317.9	15
	(TIG Welded)	0.045	1.143	57.3	395.1	44.1	304.1	15
	N-4	0.047	1.194	109.1	752.2	76.2	525.4	16
		0.046	1.168	106.4	733.6	93.2	642.6	13
	N-5	0.049	1.245	111.9	771.6	85.8	591.6	19
		0.049	1.245	111.3	767.4	82.1	566.1	20
Copper	C-1*	0.049	1.245	32.2	222.0	30.7	211.7	13
		0.049	1.245	32.6	224.8	29.5	203.4	12
	C-2	0.056	1.422	29.9	206.2	19.9	137.2	30
		0.055	1.397	29.9	206.2	18.5	127.6	33
	C-3	0.055	1.397	27.4	188.9	17.2	118.6	22
		0.055	1.397	27.4	188.9	16.0	110.3	20
	C-4*	0.054	1.372	34.3	236.5	31.7	218.6	12
	C-5* (TIG Welded)	0.055	1.397	33.4	230.3	31.2	215.1	12
Amzirc	N-2	0.178	4.521	53.1	366.1	46.6	321.3	28
	C-1	0.200	5.080	52.5	362.0	44.4	306.1	29
	C-3	0.179	4.547	49.0	337.9	41.2	284.1	18

*Test strip was severely deformed, scratched, or torn in small areas during removal from the cylinder. Attempts to straighten or repair the specimens probably introduced various degrees of cold work.

occurred only on the copper electroformed cylinders, the area A_c (area of the electrodeposited coverplate over the pressurized channels) was greater for copper shell cylinders than for nickel shell cylinders. This permanent deformation in the copper shells, Figure 40, was conservatively estimated to increase the shell area under pressure by ten percent.

Table XIV presents the calculated bond strengths for each destructively tested channel pattern for each cylinder and provides the test data by which these calculations were made. The values of the calculated bond strengths for all test sections of the cylinders with nickel electrodeposited outer shells were in close agreement with the tensile strength values of the Amzirc forgings reported in Table XIII. Failure would thus be expected to occur in the Amzirc bonding ribs, and this was what actually happened as the metallographic examination disclosed, Figure 42. The photomacrographs in this figure illustrate the strain "necking" of the Amzirc bonding ribs before material stress failure. One photomicrograph in Figure 42 confirms that Amzirc is still bonded to the nickel shell after the joint failed. The remaining photomicrograph shows the nickel shell rupture after the joints had failed. This rupture occurred parallel to a string of pin-holes in the electroformed nickel; these are also discernable in the photomacrographs of Figure 42. This phenomenon occurred on at least two of the cylinders with nickel shells and one of the cylinders with a copper shell.

It was suspected that the formation of pin-holes was related to the silver conductivizing operation. The Amzirc cylinders afforded a larger heat sink than the flat panels in the development program. When the wax-filled channels were heated in an oven prior to application of the silver powder, the Amzirc did not have sufficient time to thermally stabilize at the melt temperature of the channel-filling compound. When the cylinders were removed from the oven and conductivized, the Amzirc bonding ribs absorbed sufficient heat at the wax interface to prevent optimum bonding of the silver powder to the edges of the wax surfaces. In processing Cylinder N-5 for electroforming, the Amzirc liner was intentionally heated for an insufficient period prior to conductivizing. After electroforming the shell for a sixteen hour period, the deposition process was stopped and the shell examined. Numerous tiny pin-holes were present in the deposit and all were in alignment with the channel-bonding rib interface. The pin-holes were all closed mechanically and electroforming resumed after reactivating the nickel surface. Similar pin-holes were also evident in the copper shell of Cylinder C-1 (Figure 43). Photographs showing where these holes were initiated in the nickel shell of Cylinder N-5 are found in Appendix B, Figure 50. Such defects possibly contributed to outer shell rupture before all of the joints failed in destructive test. The liner preparation specification in Section V has been modified to require a more rigid control of thermal stabilization in the chamber liner prior to conductivizing.

The photomicrographs and low magnification photographs of Figure 43 illustrate joint failure in Cylinder C-1 as having occurred in the copper outer shell. From Table XIV, the calculated bond strength for Test Area B of Cylinder C-1 would indicate failure in the electrodeposited copper. Unlike Test Area B, Test Area A of Cylinder C-1 was not constrained in the areas of the cross-manifolds connecting the channels. This, combined with the pin-hole defects previously noted in the copper shell of this particular cylinder, possibly decreased the buckling (bulging) resistance at the ends of the bonding ribs, and this is where joint failures occurred. The low calculated bond strength for Test Area A in Table XIV is possibly in error on this basis, since the photomacrograph in Figure 43 confirms electrodeposited copper to still be attached to the Amzirc ribs at the failed joints. Of the nineteen test areas on the ten cylinders destructively evaluated, the calculated bond strength for Area A

TABLE XIV
DESTRUCTIVE TEST DATA AND BOND STRENGTH CALCULATIONS - TEST CYLINDERS

Cylinder and Test Section	Outer Shell Thickness		Hydrostatic Press. to Fail		Bonding Rib Area in²	Channel Area in²	Calculated Bond Strength		Remarks
	in.	mm.	kpsi	MN/m²			kpsi	MN/m²	
N-1 A	0.042	1.067	14.8	102.0	0.70	2.20	46.5	320.6	Cylinder high pressure
B	0.042	1.067	14.5	100.0	0.70	2.20	45.6	314.4	cycled twice (Note 1).
N-2 A	0.042	1.067	16.8	115.8	0.70	2.20	52.8	364.1	
B	0.042	1.067	16.8	115.8	0.70	2.20	52.8	364.1	
N-3 A	0.046	1.168	14.8	102.0	0.70	2.20	46.5	320.6	TIG welded.
B	0.045	1.143	15.4	106.2	0.70	2.20	48.4	333.7	TIG welded.
N-4 A	0.047	1.194	16.3	112.4	0.70	2.20	51.2	353.0	
B	0.046	1.168	16.0	110.3	0.70	2.20	50.3	346.8	
N-5 A	0.049	1.245	16.2	111.7	0.70	2.20	50.9	360.0	Cylinder shell contained
B	0.049	1.245	16.0	110.3	0.70	2.20	50.3	346.8	two plating restarts.
C-1 A	0.049	1.245	7.2	49.6	0.70	2.41	24.8	171.0	Differing manifold
B	0.049	1.245	10.7	73.8	0.70	2.31	35.3	243.4	constraints (Note 2).
C-2 A	0.056	1.422	8.5	58.6	0.70	2.41	29.3	202.0	
B	0.055	1.397	8.6	59.3	0.70	2.41	29.6	204.1	
C-3 A	0.055	1.397	8.4	57.9	0.70	2.41	28.9	199.3	Cylinder repaired for
B	0.055	1.397	8.0	55.2	0.70	2.41	27.5	189.6	leaks (Note 3).
C-4 A	0.054	1.372	8.9	61.4	0.70	2.41	30.6	211.0	
B	0.052	1.321	8.8	60.7	0.70	2.41	30.3	208.9	
C-5 A	Section A not tested due to shell melt through in TIG welding.								TIG welded.
B	0.055	1.397	11.4	78.6	0.70	2.41	39.2	270.3	TIG welded.

Notes:

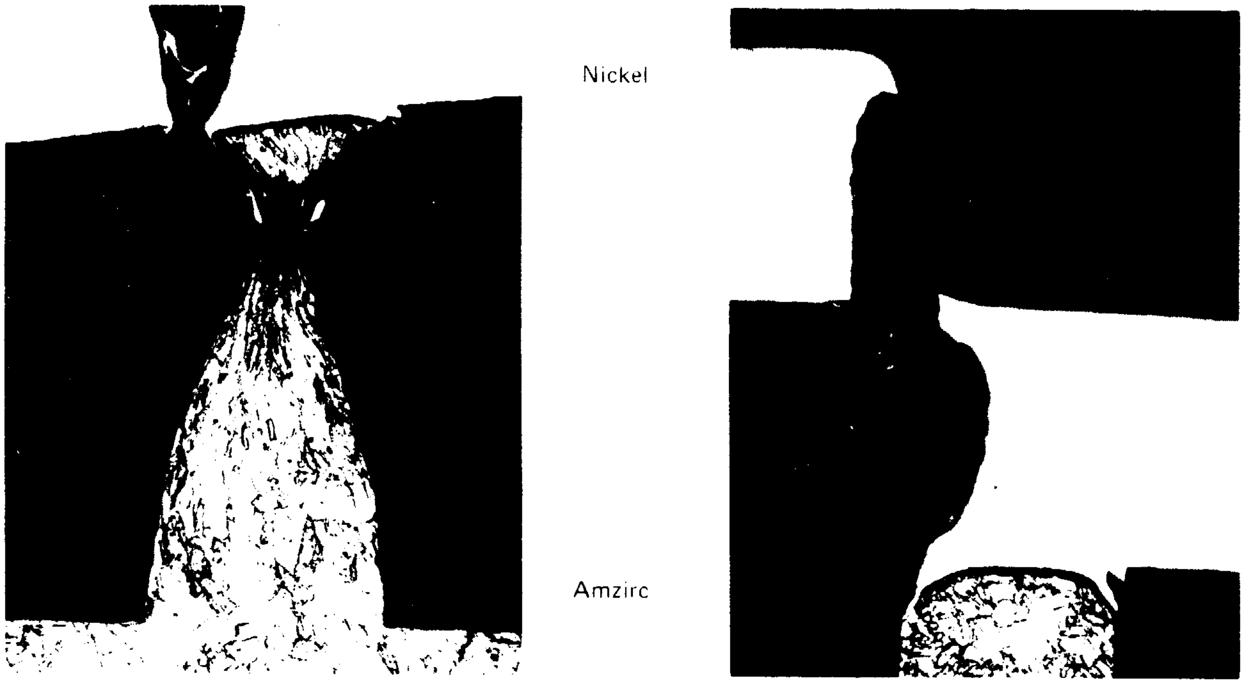
(1) Both sections pressurized in excess of 12 Kpsi (82.7 MN/m^2) during first test attempt. Joints holographically examined, pin-hole leaks repaired, and cylinder retested.

(2) The channels cross-manifolds were constrained on Test Section B but not on A.

(3) Pin-hole leaks closed by vibratory peening and shell over-plated with copper.

Cylinder N-1
Test Area A
Magnification 4X

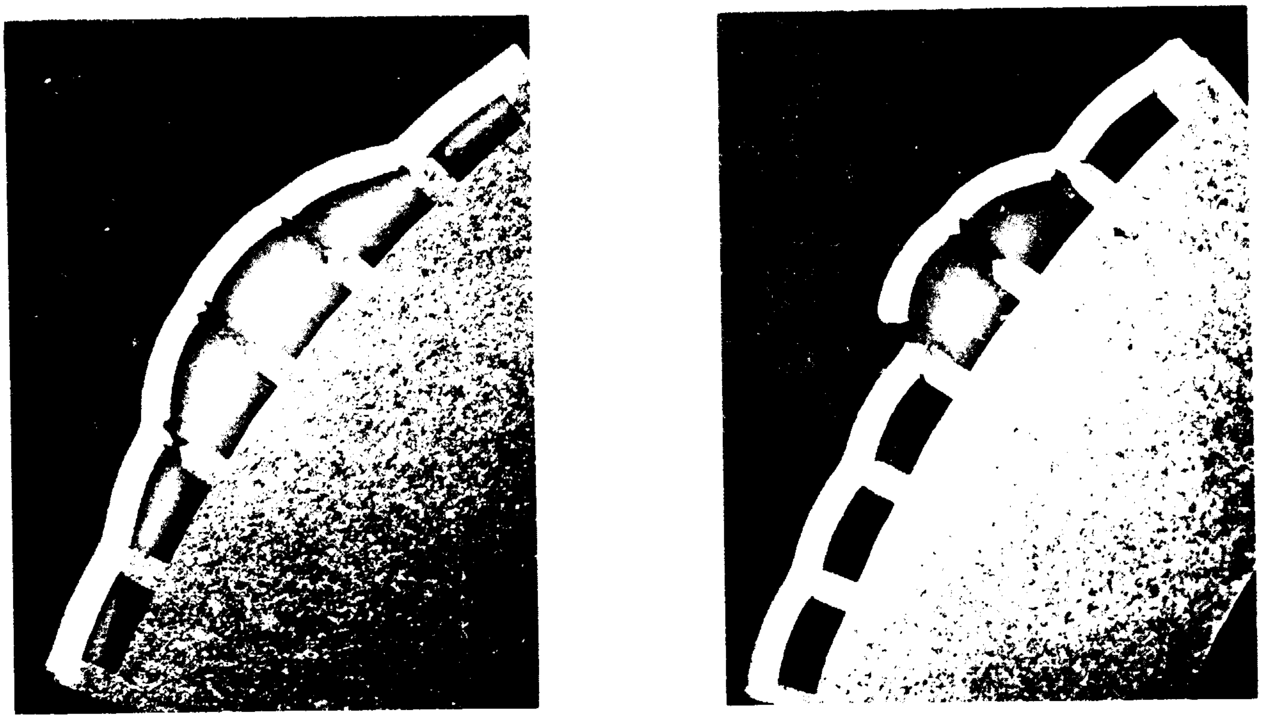
Cylinder N-1
Test Area B
Magnification 4X



Cylinder N-1
Test Area B
Magnification 32X

Cylinder N-1
Test Area B
Magnification 32X

Figure 42. Metallographic Examination Results for Nickel Electroformed Test Cylinder N-1 after Failure



Cylinder C-1
Test Area A

Magnification 4X

Cylinder C-1
Test Area B

Magnification 4X

Electroformed Copper Failure

Electroformed Copper Shell

Amzirc Rib

Cylinder C-1
Test Area B

Magnification 32X

Amzirc Rib

Cylinder C-1
Test Area B

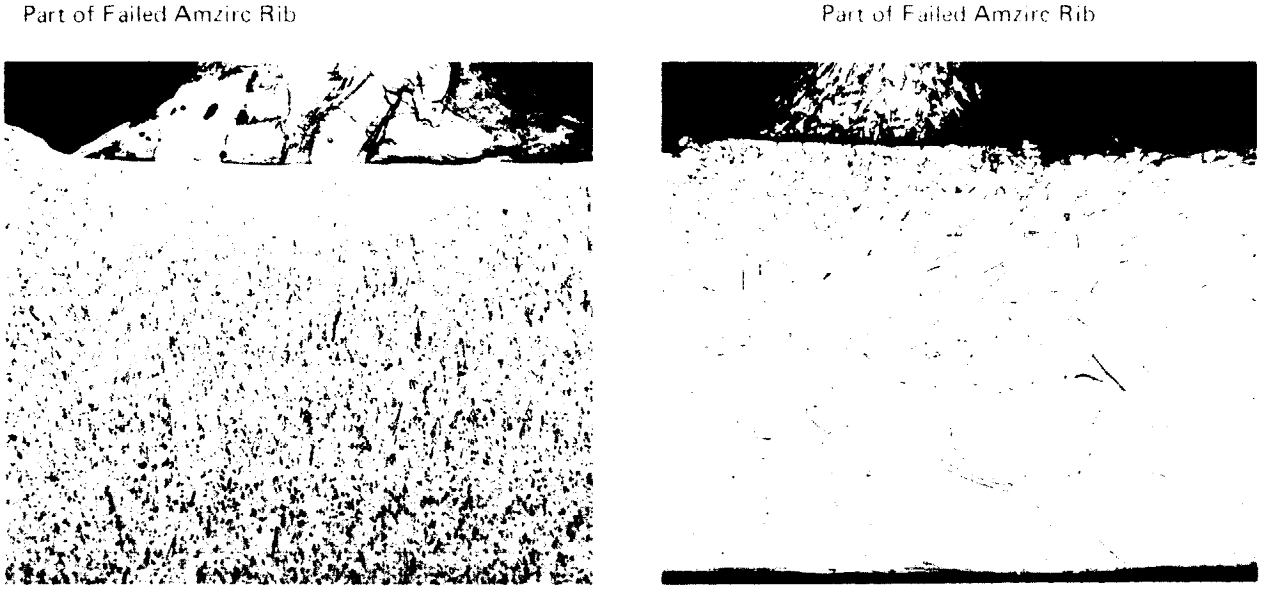
Magnification 32X

Figure 43. Metallographic Examination Results for Copper Electroformed Test Cylinder C-1 after Failure

of Cylinder C-1 was the only value which did not appear valid when compared to the mechanical property test data of Table XIII and the metallographic evidence.

Figure 44 presents typical microstructures observed in the nickel and copper outer shells from the two cylinders submitted to TIG welding. Large grain growth is evident in the electroformed nickel where the weld created a severe thermal environment. The nickel grains are smaller near the bonding rib, indicating this material acted efficiently as a heat sink. No failure at the electroform bondline is evident. In the copper shell, recrystallization occurred, as was expected. The columnar grain structure, typical of periodic reversed deposits of copper, was converted to equi-axed grains of finer size than was anticipated. This structure somewhat resembles that of copper pyrophosphate deposits and may possibly account for the higher pressure required to fail the TIG welded copper cylinder.

Results of the metallurgical examination of the remaining test cylinders will be found in Appendix B. All bonds were judged to have a strength of at least 100 percent of the mechanical strength of the weaker component metal, since no failures were detected in the electroform bondline.

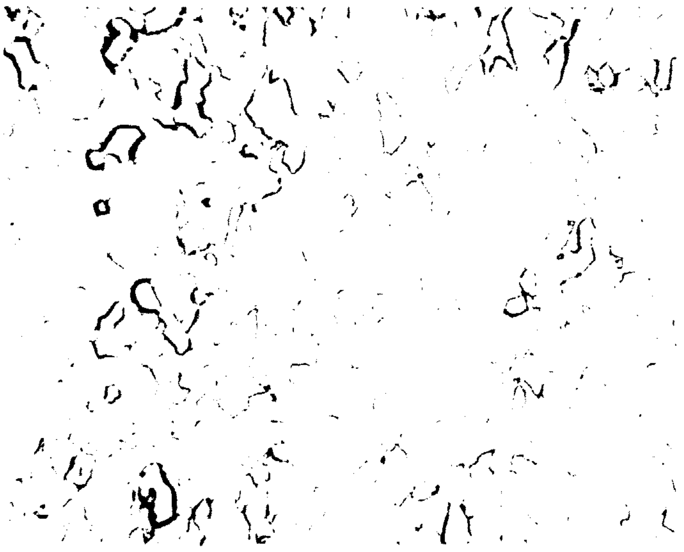


Electroformed Nickel, As Deposited

Cylinder N-5
Test Area A
Magnification 100X

Electroformed Nickel, After TIG Weld

Cylinder N-3
Test Area B
Magnification 50X



Cylinder C-5
Test Area B
Magnification 100X

The area shown in the adjacent photograph illustrates the recrystallization which occurred in the electroformed copper outer shell as a result of TIG welding the test cylinder. This section was located approximately 19.1 mm (0.75 in.) from the TIG girth weld since this is where failure occurred.

Figure 44. Photomicrographs Showing TIG Weld Effects on the Microstructures of Electrodeposited Nickel and Copper Outer Shells

VII. CONCLUSIONS AND RECOMMENDATIONS

It has been demonstrated in this work that reproducible mechanical properties can be obtained in nickel and copper electrodeposits from the nickel sulfamate and acid copper sulfate electrolytes. It has also been shown that copper and nickel electroform bonds can be made on copper and copper alloy substrates with consistently reliable joints resulting. The results of testing and metallographic examination of the Amzirc cylinders with nickel and copper outer shells verified that the specifications developed led to the fabrication of consistently reliable electroformed structures.

The use of periodic current reversal appears to enhance the uniformity of the grain structure in acid copper sulfate electrodeposits. It enables the electroformer to produce good mechanical properties, regardless of the deposit thickness. Current density and the periodic current reversal cycle selection appear to have significant affects on the mechanical properties. A current density of about 4.84 A/dm^2 (45 A/ft^2) and a periodic current reversal cycle with a cathodic to anodic ratio of 2:1 resulted in the most satisfactory mechanical properties in this study. Variation of these parameters makes a wide range of mechanical properties possible. Use of the recommended current density and periodic reversal ratio will result in copper deposits with mechanical properties at least equivalent to those of the wrought annealed copper counterpart.

Copper sulfate electrodeposits produced with periodic current reversal appear to have excellent thermal stability. Exposure of these deposits to high temperature for short periods, such as the TIG welding, resulted in recrystallization as would be expected. However, the new structure retained good mechanical properties and the electrodeposit exhibited no evidence of voids or porosity.

Pyrophosphate copper electrolytes were also shown to be capable of producing deposits with excellent mechanical properties. Under optimum plating conditions, pyrophosphate copper deposits exhibited slightly better mechanical properties than could be obtained from the acid sulfate bath using periodic current reversal. The yield strength of copper was particularly enhanced by deposition from the pyrophosphate solution. The unusual microstructure of these deposits may contribute to this phenomenon. The pyrophosphate electrolyte is very difficult to control and maintain in comparison with the acid copper sulfate bath. Producing deposits consistently within a specific range of mechanical properties may prove difficult unless the electroformer has considerable experience with the pyrophosphate bath and the many pecularities associated with it.

Nickel electrodeposits from the sulfamate bath exhibited excellent mechanical properties over a current density range of 2.15 to 4.30 A/dm^2 (20 to 40 A/ft^2) and an electrolyte temperature of 44.4 to 51.7°C (112 to 125°F). The range of tensile strength was 634.3 to 792.9 MN/m^2 (92 to 115 Kpsi) and the elongation in 25.4 mm (one inch) varied from 10 to 20 percent for these electrodeposition parameters. Wrought annealed Nickel 200 is reported [9] to have typical properties as follows:

Ultimate Strength		Yield Strength		Elongation
Kpsi	MN/m^2	Kpsi	MN/m^2	% in 2 inches
67.0	462.0	21.5	148.2	47

The ductility of the wrought nickel cannot be duplicated in the electroformed counterpart. However, the "as deposited" mechanical strength is superior and the elongation in a given guage length is satisfactory for most structural applications. This difference is attributed to microstructure and the fact that Nickel 200 contains trace malleabilizing elements promoting good ductility over a wide test temperature range by chemically compounding any sulfur present.

After TIG welding, the nickel electrodeposits retained good mechanical properties - even though recrystallization had significantly changed the microstructure.

The results of bonding studies and tests indicated the copper and copper alloy activating procedures were adequate for producing high integrity joints. In all tests on Amzirc cylinders (simulated thrust chamber liners), the bond strengths were equivalent to 100 percent of the mechanical strength of the weaker metal comprising the joint. The program objective of attaining at least 80 percent of this strength was exceeded.

Pin-hole leakage paths in electroformed nickel outer shells had previously presented a serious problem in producing high quality structures. The investigation of these defects indicated the problem could be circumvented by special precautions in conductivizing the wax-filled coolant passages.

Applying the processes and procedures developed in this program, components for two low cycle thermal fatigue study engines were electroformed to produce outer shells for internally cooled structures. Figures 45 and 46 illustrate the parts. These engines will be used by NASA-Lewis Research Center for thermal fatigue evaluation of electroformed copper deposited by the periodic reversal process.

It was apparent from the results and observations of this program that a more detailed investigation of several processes and procedures would be desirable. This was not possible due to the already broad scope of the project and the specific objectives to be met. It is anticipated that further investigation in the following areas would be valuable in improving the capability of electroforming to produce high quality thrust chambers for use under high pressure and severe thermal service:

- Continue the study of periodic current reversal deposition from the copper sulfate electrolyte to determine the quantitative effects of cathodic-anodic cycle ratio and cycle length on mechanical properties. Include the variation of electrolyte temperature in this study.
- Investigate improved electrolyte agitation techniques in the pyrophosphate copper electrolyte and determine the effects on mechanical properties, particularly on ductility.
- Conduct a study to determine the effects of thermal treatments on the mechanical properties of pyrophosphate copper and periodically reversed copper sulfate electrodeposits. Subject specimens to tensile test at elevated temperature.
- Produce and test low cycle thermal fatigue study spools from pyrophosphate copper and acid copper sulfate electrolytes controlled to the optimized parameters obtained in the above studies.
- Investigate the effects of dispersion strengthening copper electrodeposits by codeposition of thermally stable dispersoids of small particle diameter.

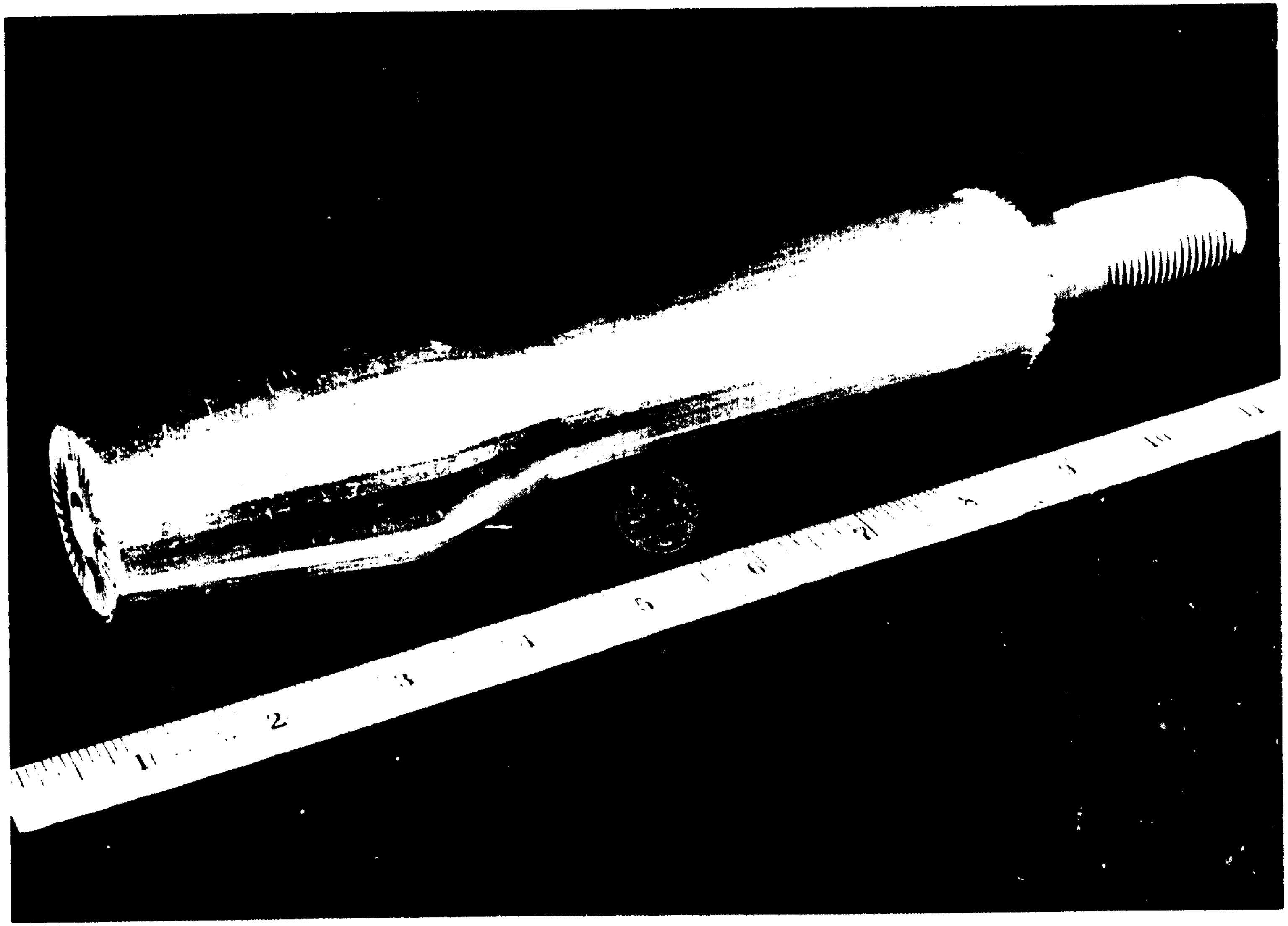


Figure 45 Internally Cooled Plug Section of NASA Low Cycle Thermal Fatigue Study Engine - Copper Electrodeposited Outer Shell Prior to Machining

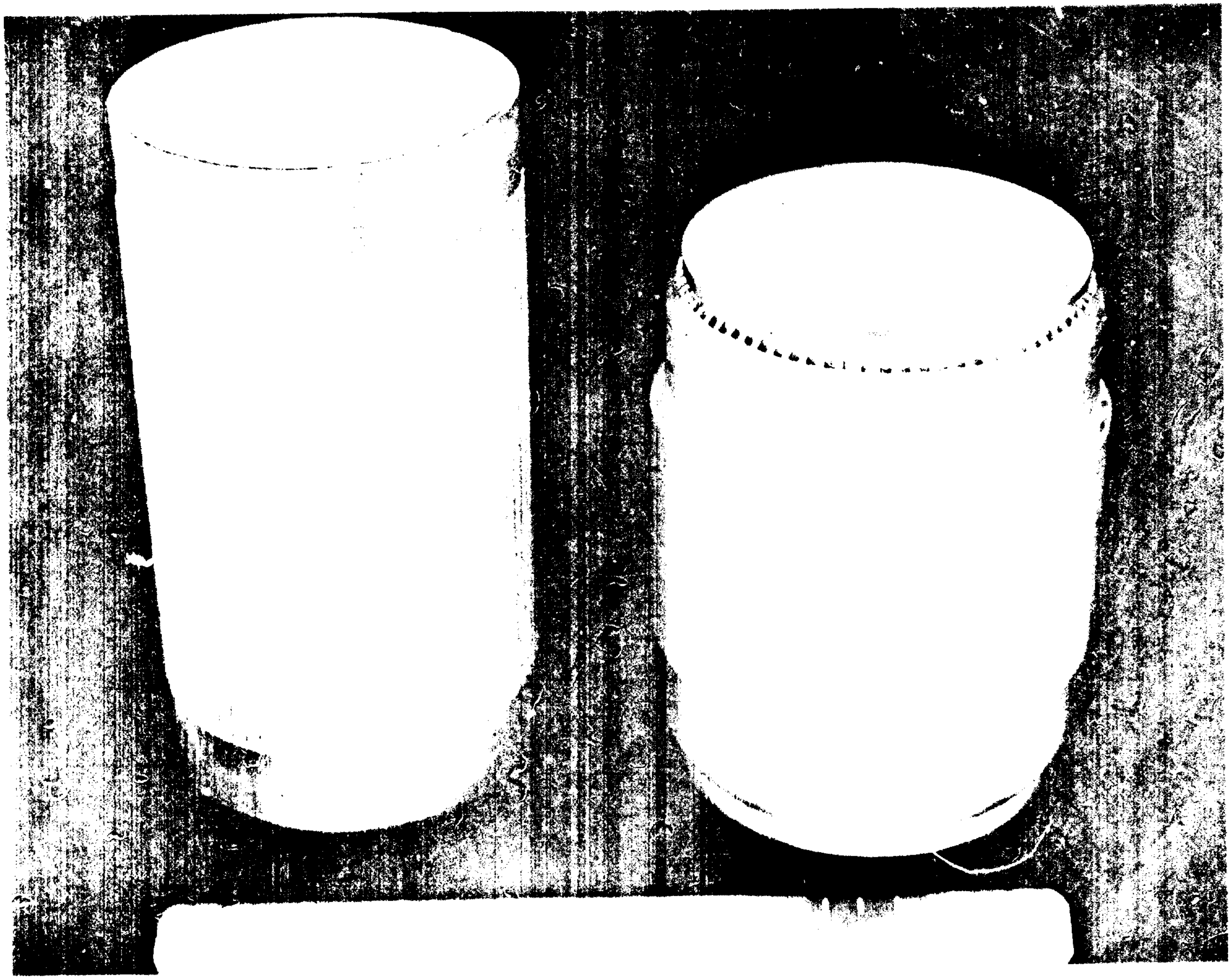


Figure 46. Regeneratively Cooled Spool Section of NASA Low Cycle Thermal Fatigue Study Engine - Amzirc Liner Before and After Electroforming the Copper Outer Shell (Machined)

VIII. REFERENCES

[1] G.A. Malone, "Investigation of Electroforming Techniques", Report NASA CR-134776 April 1975.

[2] James A. Pope, "Electroforming of Linear Accelerator Structures", Plating, 44, pp. 1291-1296 (1957).

[3] Vernon A. Lamb, Christian E. Johnson, Donald R. Valentine, "Physical and Mechanical Properties of Electrodeposited Copper", Journal of the Electrochemical Society, 117 (9), September 1970, pp. 291C-318C.

[4] Alloy Digest, "OFHC Copper", p. Cu-144, Engineering Alloys Digest, Inc., August 1964.

[5] M&T Chemicals Inc. Bulletin P-C-10-X6, "Unichrome Pyrophosphate Copper Plating Process", M&T Chemicals, Inc., Rahway, N.J. (1970).

[6] Vernon A. Lamb, Christian E. Johnson, Donald R. Valentine, "Physical and Mechanical Properties of Electrodeposited Copper", Journal of the Electrochemical Society, 117 (11), November 1970, pp. 381C-404C.

[7] ASTM Committee B-8, "Recommended Practice for Preparation of Copper and Copper-Base Alloys for Electroplating", American Society for Testing and Materials B281-58 (1958).

[8] G.A. Malone, L. Vecchies, R. Wood, "Nondestructive Tests of Regenerative Chambers", Report NASA CR 134656, June 1974.

[9] "Handbook of Huntington Alloys", Huntington Alloys Division, International Nickel Company, Inc., Huntington, W.V. (1965).

APPENDIX A

TEST DATA FROM 56.8 LITER (15 GALLON) PYROPHOSPHATE COPPER ELECTROLYTE STUDY

TEST DATA FROM 56.8 LITER (15 GALLON) PYROPHOSPHATE COPPER ELECTROLYTE STUDY

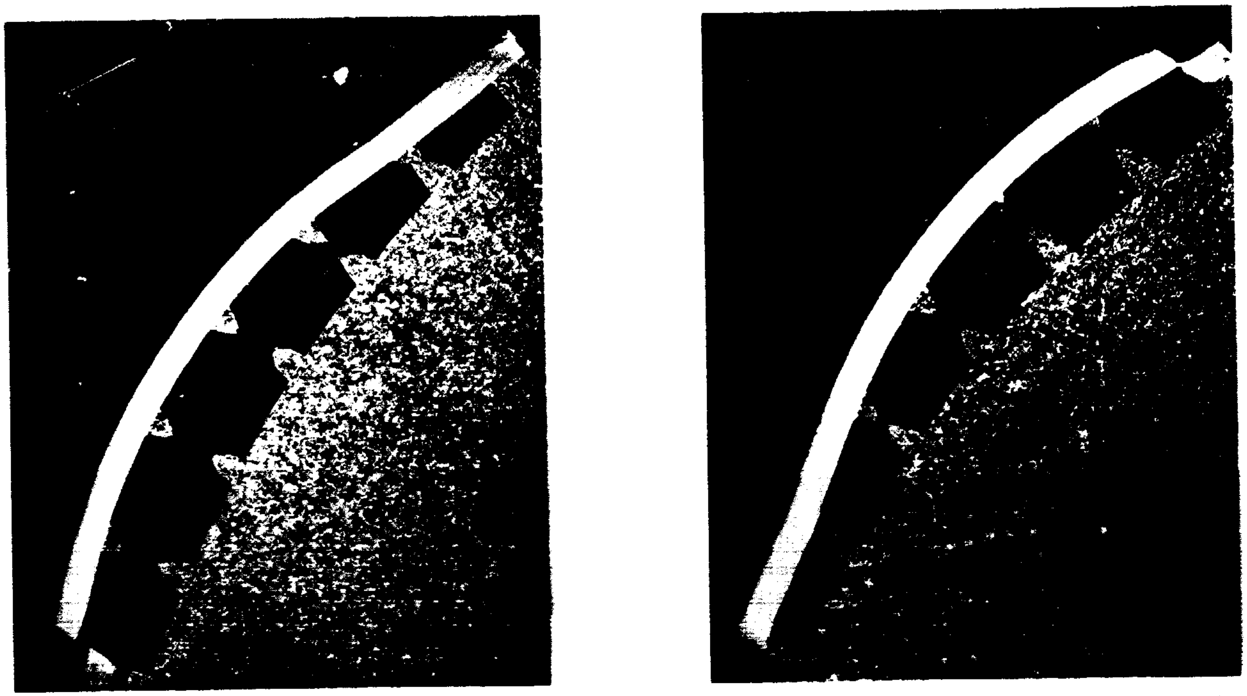
Panel No.	Electrolyte Chemistry and Operating Data	Specimen Thickness		Mechanical Strength				Elongation, %
				Ultimate Strength		Yield Strength		
		in.	mm	Kpsi	MN/m^2	Kpsi	MN/m^2	2 in. (50.8 mm)
1	Copper metal 29.2 g/l., Pyro/Cu Ratio 8.1:1, Ammonia 12.7 g/l, 47.2 to 51.1°C, pH 8.2, current density 2.15 A/dm^2 (20 A/ft^2) low air agitation, no filtering, OFHC Cu anodes (2.5 times cathode area)	0.020	0.508	83.0	572.3	59.3	408.9	9
		0.020	0.508	78.3	539.9	55.6	383.4	12
				(Residual stress 3,580 psi compressive)				
6	Copper metal 26.2 g/l., Pyro/Cu Ratio 7.6:1, Ammonia 13.5 g/l., temp. 51.1°C to 53.9°C, pH 8.0, current density 4.30 A/dm^2 (40 A/ft^2), low air agitation, no filtering, OFHC Cu anodes (2.5 times cathode area).	0.013	0.330	83.8	577.8	64.5	444.7	5
		0.014	0.356	83.2	573.7	68.5	472.3	5
7	Copper metal 26.2 g/l., Pyro/Cu Ratio 7.6:1, Ammonia 1.18 g/l., temp. 51.1°C to 54.5°C, pH 8.3, current density 4.30 A/dm^2 (40 A/ft^2), low air agitation, 10 micron filters in use, OFHC Cu anodes (2.5 times cathode area)	0.027	0.686	72.3	498.5	53.6	369.6	6
		0.028	0.711	76.2	525.4	46.7	322.0	6
		0.027	0.686	73.8	508.9	49.8	343.4	7
8	Copper metal 26.2 g/l., Pyro/Cu Ratio 7.6:1, Ammonia 1.35 g/l., temp. 51.1°C to 54.4°C, pH 8.2, current density 4.30 A/dm^2 (40 A/ft^2), low air agitation, 10 micron filters in use, reduced anode cathode ratio to 1:1.	0.018	0.457	56.7	390.9	35.0	241.3	4
		0.017	0.432	61.3	422.7	37.3	257.2	5
9	Copper metal 28.2 g/l., Pyro/Cu Ratio 7.5:1, Ammonia 1.35 g/l., temp. 50°C to 51.7°C, pH 8.3, current density 4.30 A/dm^2 (40 A/ft^2), improved air agitation, installed 2 micron filtration and continuous carbon treatment	0.021	0.533	47.4	326.8	29.8	205.5	20
		0.020	0.508	43.2	297.9	27.8	191.7	21
		0.018	0.457	45.1	311.0	29.4	202.7	17
		0.018	0.457	40.7	280.6	25.3	174.4	23*
			*Last sample heat treated at 176.7°C (350°F) for 1 hour					
10	Copper metal 30.4 g/l, Pyro/Cu Ratio 6.9:1, Ammonia 1.27 g/l., temp. 55.6°C, pH 8.3 current density 4.30 A/dm^2 (40 A/ft^2), improved air agitation, 2 micron filtration, but high copper content and low pyrophosphate-copper ratio. OFHC Cu anode.	0.011	0.279	77.9	537.1	40.9	282.0	8
		0.012	0.305	77.9	537.1	44.0	303.4	7
		0.011	0.279	41.1	283.4	24.7	170.3	15*
			*Last sample heat treated at 176.7°C (350°F) for 1 hour					
12	Copper metal 28.4 g/l., Pyro/Cu Ratio 7.6:1, Ammonia 1.45 g/l., temp. 53.3°C, pH 8.2, current density 4.30 A/dm^2 (40 A/ft^2), vigorous air agitation, 2 micron filtration, good Pyro/Cu Ratio. OFHC Cu anode	0.025	0.635	43.6	300.6	24.5	168.9	36
		0.023	0.584	45.9	316.5	25.7	177.2	27
		0.029	0.737	43.3	298.6	25.5	175.8	37
15	Copper metal 28.3 g/l., Pyro/Cu Ratio 7.6:1, Ammonia 1.69 g/l., temp. 52.2°C, pH 8.2, current density 4.30 A/dm^2 (40 A/ft^2), air agitation system misaligned. OFHC Cu anodes (2)	0.028	0.711	38.7	266.8	22.7	156.5	14
		0.022	0.559	46.1	317.9	26.5	182.7	14
		0.023	0.584	46.3	319.2	25.6	176.5	17
		0.022	0.559	39.6	273.0	21.9	151.0	20*
			*Last sample heat treated at 176.7°C (350°F) for 1 hour					
16	Copper metal 28.3 g/l., Pyro/Cu Ratio 7.6:1, Ammonia 1.88 g/l., temp. 51.1°C to 54.4°C, current density 4.30 A/dm^2 (40 A/ft^2), added filter aid (Solka-Floc) to filter	0.029	0.737	44.5	306.8	29.3	202.0	8
		0.029	0.737	43.7	301.3	27.5	189.6	10

TEST DATA FROM 56.8 LITER (15 GALLON) PYROPHOSPHATE COPPER ELECTROLYTE STUDY (CONT'D)

Panel No.	Electrolyte Chemistry and Operating Data	Specimen Thickness		Mechanical Strength				Elongation, %
				Ultimate Strength		Yield Strength		
		in.	mm	Kpsi	MN/m^2	Kpsi	MN/m^2	2 in. (50.8 mm)
20	Copper metal 28.6 g/l., Pyro/Cu Ratio 7:1, Ammonia 0.89 g/l., temp. 51.1°C to 54.4°C, current density 3.87 A/dm^2 (36 A/ft^2), high air agitation, low Pyro/Cu ratio, low ammonia, OFHC copper anodes	0.020 0.022	0.508 0.559	53.3 46.6	367.5 321.3	36.4 29.6	251.0 204.1	17 21
25	Copper metal 22.4 g/l., Pyro/Cu Ratio 7.9:1, Ammonia 0.75 g/l., temp. 48.3°C to 52.2°C, current density 3.87 A/dm^2 (36 A/ft^2), high air agitation, new 1 micron filter in use	0.061	1.549	42.2	291.0	27.2	187.5	28

APPENDIX B

METALLOGRAPHIC EXAMINATION RESULTS OF JOINT FAILURES IN NICKEL ELECTROFORMED SHELL CYLINDERS N-2 THROUGH N-5 AND COPPER ELECTROFORMED SHELL CYLINDERS C-2 THROUGH C-5



Cylinder N-2
Test Area A
Magnification 4X

Cylinder N-2
Test Area B
Magnification 4X

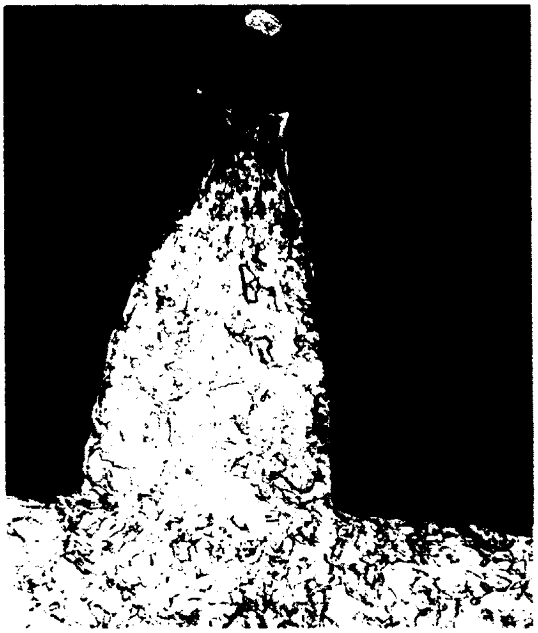
The mode of the joint failure typical in the cylinders with electroformed nickel outer shells is illustrated in the adjacent photomicrograph. The Amzirc bonding rib has failed in an ideal "neck-down" and shear pattern typical of a ductile metal. The electroformed bond appears undisturbed. The bondline is accented by the preferential grain etch used to display the copper microstructure.

Cylinder N-2
Test Area A
Magnification 32X

Figure 47. Metallographic Examination Results for Nickel Electroformed Test Cylinder N-2 After Failure

Cylinder N-3
Test Area A
TIG Weld Zone
Magnification 4X

Cylinder N-3
Test Area B
TIG Weld Zone
Magnification 4X



Amzirc Bonding Rib

Photomicrograph showing the joint failure as occurring in the Amzirc bonding ribs.

Cylinder N-3 (TIG Welded)
Test Area B
Magnification 32X

Figure 48. Metallographic Examination Results for Nickel Electroformed Test Cylinder N-3 After Failure

Cylinder N-4
Test Area A

Magnification 4X

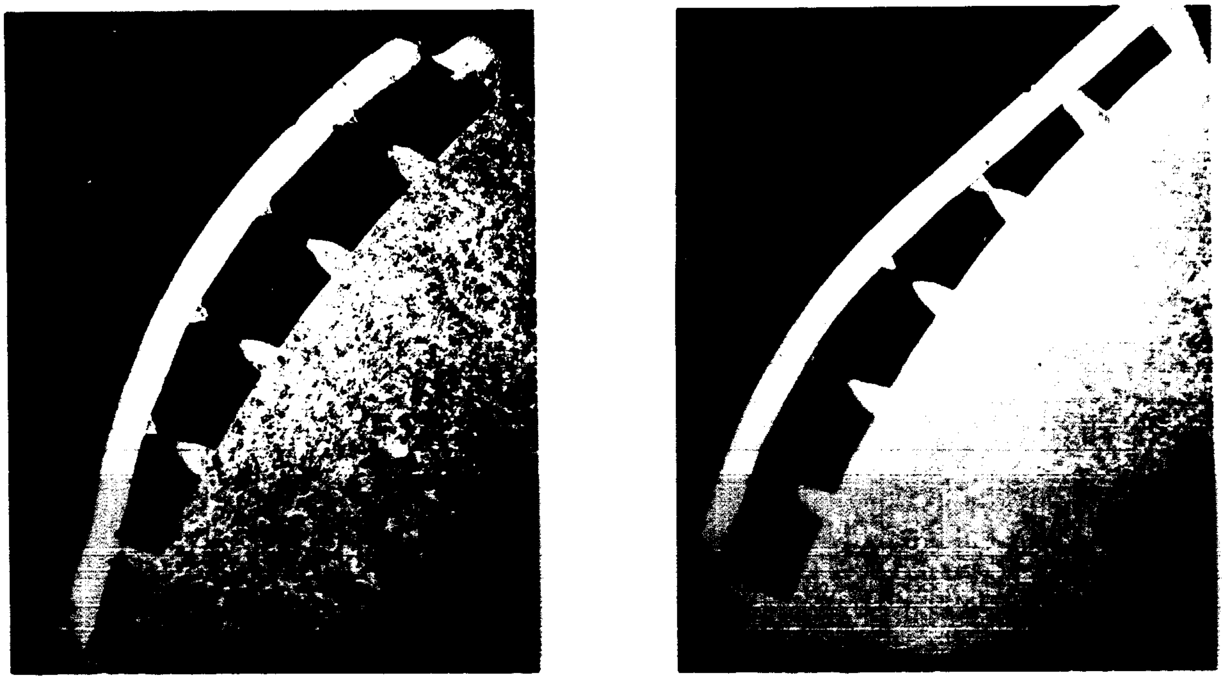
A section from the failed area of Test Section A disclosed all Amzirc bonding ribs contained tensile failures typical of ductile metals. Portions of each of the bonding ribs are securely attached to the bulged electroformed outer shell.

Cylinder N-4
Test Area B

Magnification 4X

The manner of joint failure in Test Area B was almost identical to that shown for Test Area A. Only one Amzirc bonding rib has not failed, but it has been strained to a point of impending failure.

Figure 49. Metallographic Examination Results for Nickel Electroformed Test Cylinder N-4 After Failure



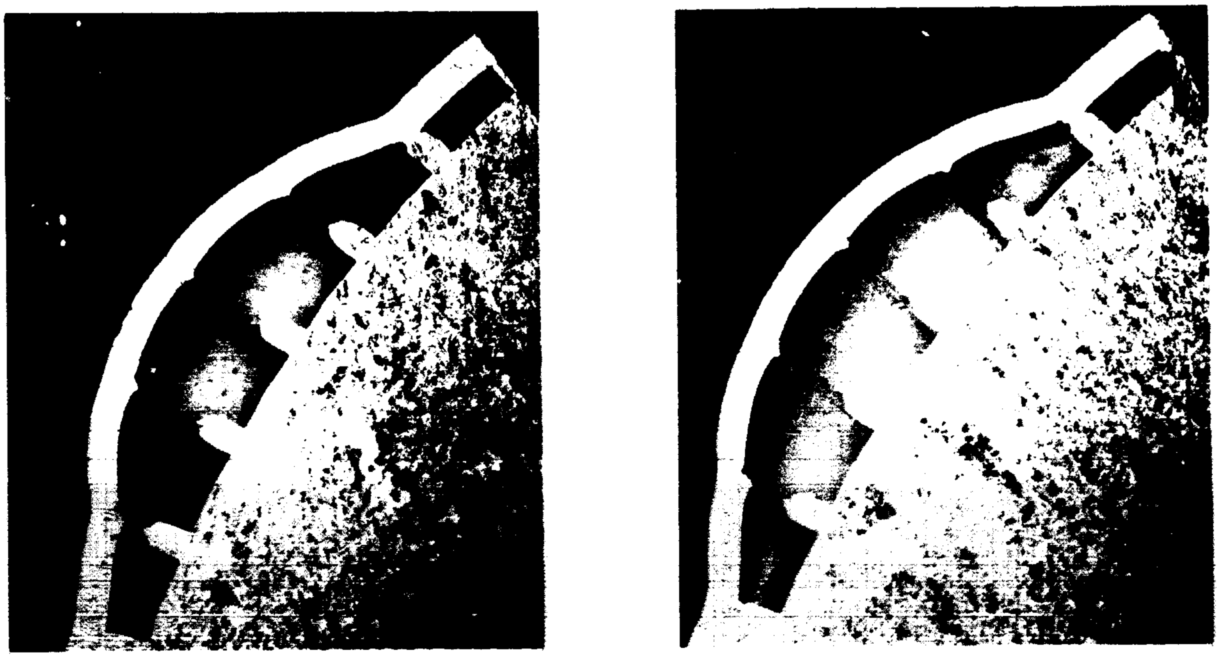
Cylinder N-5
Test Area A
Magnification 4X

Cylinder N-5
Test Area B
Magnification 4X

This section shows a typical Amzirc bonding failure resulting from destructive testing of the cylinder. Note the "pin-hole" defects adjacent to the portion of the Amzirc rib still attached to the electroformed nickel shell. These defects were intentionally produced and repaired by peening them closed after the electroform build-up was about 0.305 mm (0.012 in.) thick. In addition to the plating stop required to make this repair, one other stop and restart was made to examine the build up over the repaired area.

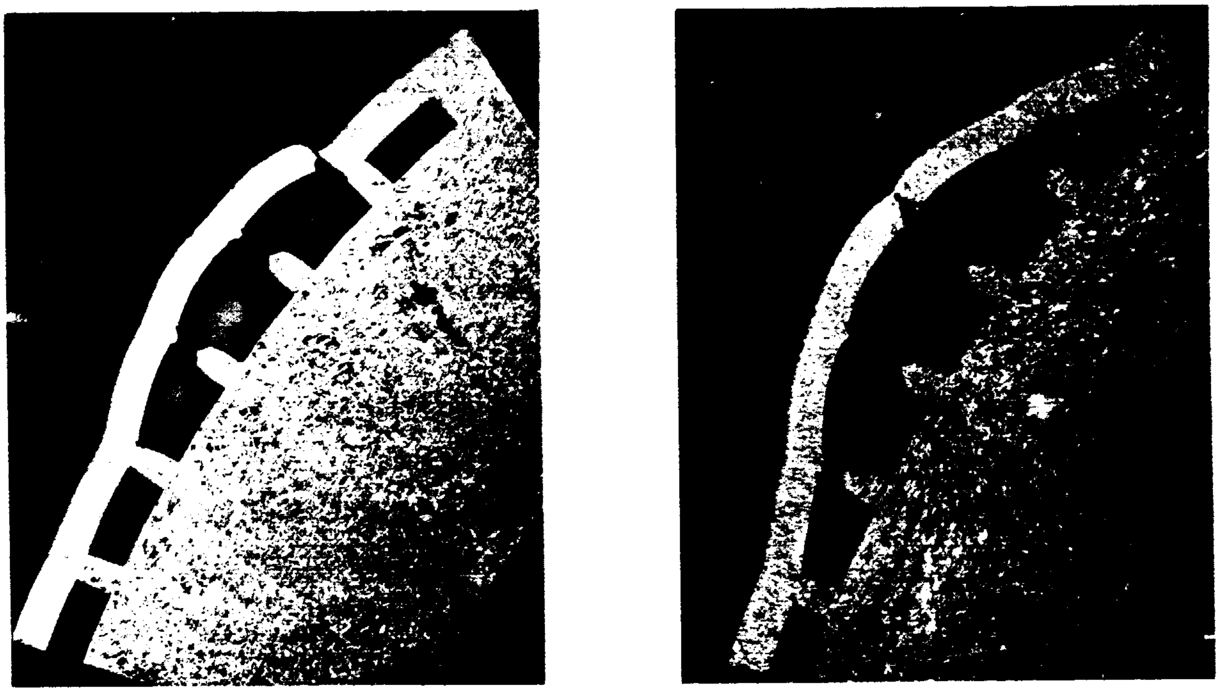
Cylinder N-5
Test Area A
Magnification 32X

Figure 50. Metallographic Examination Results for Nickel Electroformed Test Cylinder N-5 After Failure



Cylinder C-2 Magnification 4X
Test Area A

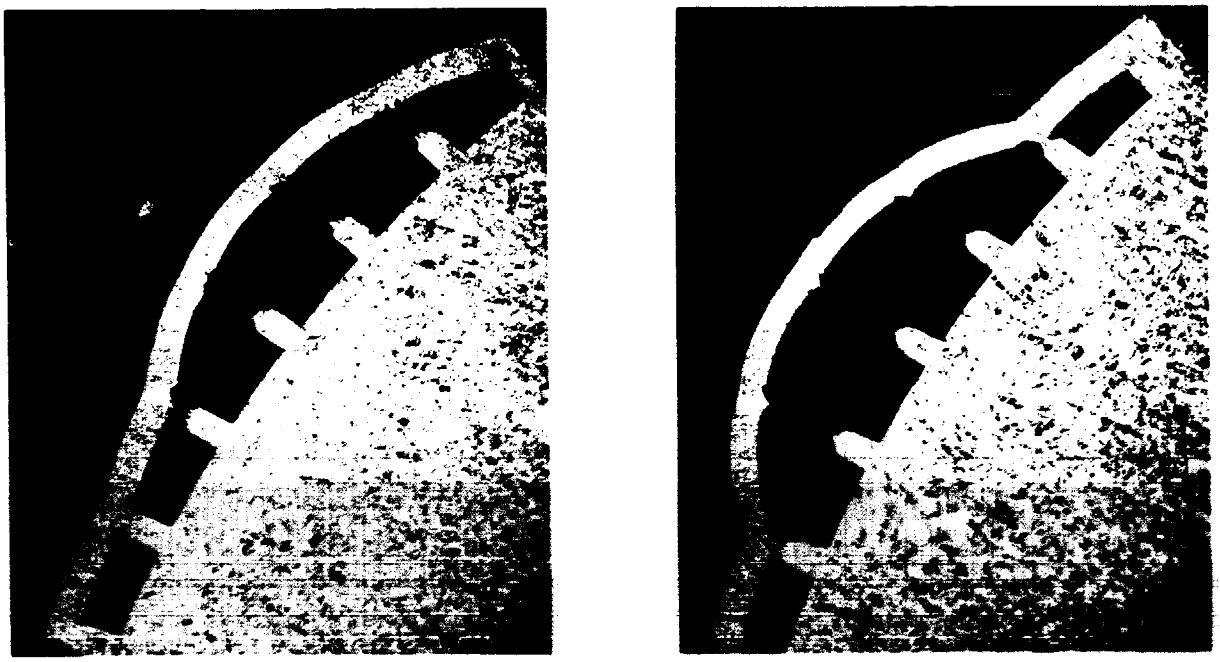
Cylinder C-2 Magnification 4X
Test Area B



Cylinder C-3 Magnification 4X
Test Area A

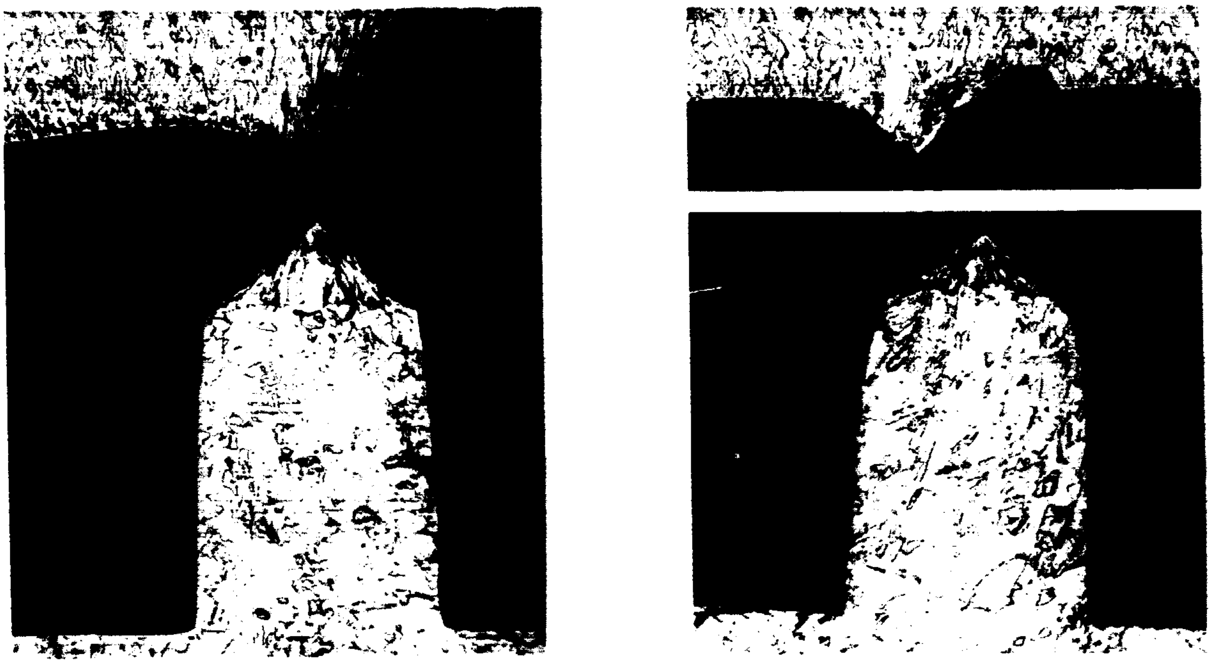
Cylinder C-3 Magnification 4X
Test Area B

Figure 51. Metallographic Examination Results for Copper Electroformed Test Cylinders C-2 and C-3 After Failure



Cylinder C-4 Magnification 4X
Test Area A

Cylinder C-4 Magnification 4X
Test Area B



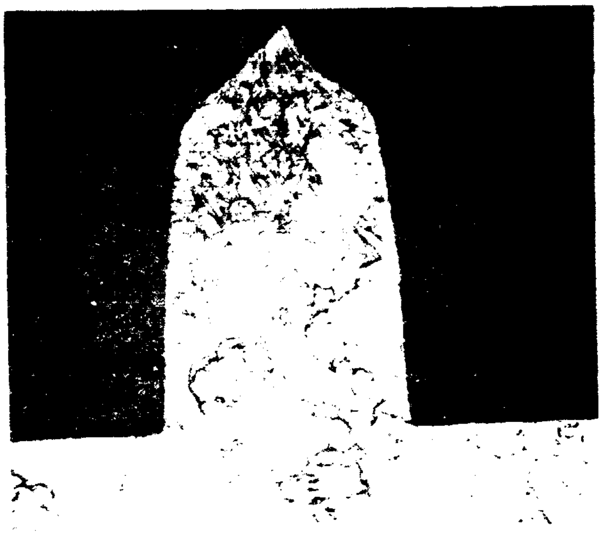
Cylinder C-4 Magnification 32X
Test Area A

Cylinder C-4 Magnification 32X
Test Area B

Figure 52. Metallographic Examination Results for Copper Electroformed Test Cylinder C-4 After Failure

Cylinder C-5 Magnification 4X
Test Area B
Section 19.1 mm (0.75 in.) from TIG Weld

[illegible]



Across Bend [illegible] Pit

Cylinder C-5 Magnification 32X
Test Area B
TIG Welded Cylinder

Figure 53. Metallographic Examination Results for [illegible] TIG Welded Test Cylinder C-5 After Failure