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NASA CR-54610



N67-32158

FACILITY FORM 608

(ACCESSION NUMBER)

42

(PAGES)

CR-54610

(NASA CR OR TMX OR AD NUMBER)

(THRU)

1

(CODE)

17

(CATEGORY)

DEVELOPMENT OF DISPERSION STRENGTHENED CHROMIUM ALLOYS

by

E. F. Abrams, J. A. Alexander
R. G. Shaver, and J. C. Withers

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-7606

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) 3.00

Microfiche (MF) 65

ff 653 July 65

GENERAL TECHNOLOGIES CORPORATION

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SUMMARY REPORT

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CHROMIUM ALLOYS

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March 15, 1967

CONTRACT NAS 3-7606

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ABSTRACT

The preparation of dispersion strengthened chromium having minimal quantities of interstitial impurities was investigated using aqueous and fused salt electrodeposition techniques. With the aqueous bath, nitrogen interstitial contents of less than 5 ppm were obtained in "as deposited" chromium and oxygen interstitial contents were reduced to 30 ppm by heat treatment with ultrapure hydrogen. Promising microstructures were obtained with the aqueous electrodeposition approach, but were not reproducible. The main problem in preparing dispersion strengthened chromium by this technique was found to be the inclusion of insufficient quantities of alumina or thoria dispersoid. No usable electrodeposits were made with the fused salt bath techniques studied.

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SUMMARY

This report covers the work accomplished during fifteen months of effort on Contract NAS 3-7806, the Development of Dispersion Strengthened Chromium Alloys. The principle objective of the program was to develop a technique for producing by electrodeposition a stable dispersion strengthened chromium with a specific microstructure of dispersoid particles and then processing the deposited structure into consolidated samples having a minimum of 98 percent of theoretical density. Aqueous and fused salt electrodeposition techniques were studied, and the dispersoids used were particles of Al_2O_3 , MgO , and ThO_2 . A secondary objective of the program was to control the level of interstitial impurities such as oxygen, nitrogen, carbon and sulfur in the consolidated samples to within specified maximum values.

The initial phase of the program involved establishing the levels of plating parameters of both the aqueous and fused salt approaches which would yield the purest chromium. Difficulties encountered in the fused salt electrodeposition approach resulted in this system being dropped in favor of the aqueous electrodeposition procedure. In the aqueous system a range of deposition conditions was studied and nitrogen contents as low as 1 part per million (ppm) and oxygen contents as low as 230 ppm were obtained in "as deposited" chromium. Optimum plating parameters from standpoints of purity and rate of deposition were determined to be as follows:

33 oz/gal CrO_3
0.46 oz/gal sulfate catalyst
185-212°F plating temperature
864 amps/ft² current density

Oxygen contents were reduced from 2000 ppm to 30 ppm by treatment of the deposited chromium with ultrapure hydrogen at elevated temperature.

Ultrasonic agitation was demonstrated to yield de-agglomerated suspensions of Al_2O_3 in chromic acid plating solutions. Preliminary electron micrography established the feasibility of producing dispersion strengthened chromium by electrodeposition techniques. Problems were encountered in establishing metallographic techniques to yield reproducible results in studying the microstructure of "as deposited" chromium containing codeposited dispersoids.

Parameters affecting the volume fraction of included dispersoid oxide during electrodeposition were studied and it was found that volume percents of dispersoid were below 0.3 at all conditions studied except one; this was with the use of a silicofluoride catalyst which yielded 0.91 volume percent of dispersoid. Since 2 to 8 volume percent dispersoid is required for proper dispersion strengthening, one of the major problems in producing dispersion-strengthened chromium by this process is the difficulty of obtaining sufficient amounts of dispersoid.

INTRODUCTION

The attributes of a dispersion strengthened alloy are well known. Dispersion strengthened chromium would be a significant advancement in structural materials. The development of chromium alloys as structural materials has been deterred by chromium's extreme sensitivity to oxygen and nitrogen interstitial impurities which result in embrittlement so extensive that its use as a structural component is prevented. Therefore, any technique which is used to produce dispersion strengthened chromium must, of necessity, be capable of controlling the embrittling interstitial impurities.

Electrodeposition was the technique employed in this program to produce dispersion strengthened chromium. Chromium can be electrodeposited from both aqueous and fused salt baths. Proper selection of plating parameters can be used to control the concentrations of embrittling interstitial impurities in the deposited chromium. The present state-of-the-art of electrodepositing chromium has yielded metal having nitrogen and oxygen interstitial impurity contents of 10-40 ppm and 200-400 ppm respectively (1,2,3,4).

The objective of this program was to form a dispersion strengthened chromium product from both aqueous and fused salt plating baths. Al_2O_3 and ThO_2 were the dispersoids investigated in the aqueous system and MgO and ThO_2 were the dispersoids selected for the fused salt approach.

The pieces of electrodeposited chromium containing the included dispersoids were to be further processed by crushing and by using techniques such as gas pressure bonding, hot pressing, or canned extrusion to consolidate the particles into approximately 1/2" diameter by 1/2" long cylinders. These cylinders were then to be evaluated for dispersoid particle size, interparticle spacing, purity, stability of dispersion at elevated temperatures in atmospheres of argon and air, volume fraction of dispersoid, density, hardness and phase identification where necessary.

It was required that the process produce, in unalloyed chromium, a dispersion microstructure having the following parameters as a consolidated specimen:

- Volume percentage of dispersoids: less than 8 v/o
- Dispersoid particle size: less than 0.1 micron
- Interparticle spacing: less than 1.5 microns

The overall program was subdivided into the following areas of effort:

- Establishing aqueous and fused salt plating parameters which optimize chromium purity
- Developing techniques for oxide dispersion and inclusion
- Consolidating the electrodeposited chromium containing several volume fractions of dispersoids
- Testing and evaluating the consolidated samples

TECHNICAL PROGRAM

AQUEOUS ELECTRODEPOSITION

Background . Past effort has shown that it is possible to electrodeposit high purity chromium from aqueous solutions with relatively low oxygen and nitrogen contents ^(1,2,3,4). It was found that oxygen content in the deposits varies markedly with temperature of the electrolyte and catalyst/CrO₃ ratio. Two typical graphs are shown in Figure 1. It was also found that nitrogen content in chromium, electrodeposited from aqueous solutions, depends primarily on the purity of the CrO₃ used to form the plating bath. If the oxygen content versus temperature graph shown in Figure 1 were extrapolated to high plating temperatures, one would expect a further reduction in oxygen content. The lowest value of oxygen reported in chromium made by this process was 50 parts per million (0.0050 percent) ⁽¹⁾. In general, the values of oxygen content reported using this process are in the range of 100 to 200 parts per million (0.01 to 0.02 percent).

While the oxygen content of the chromium electrodeposit is a function of temperature and catalyst/CrO₃ ratio, the plating current efficiency is also dependent on these variables. The already low current efficiency (7-15 percent) associated with commercial type chromium baths is further reduced by increasing the plating bath temperature. It was also reported that current efficiency could be increased to as high as 30 to 40 percent by the use of silicofluoride-type catalysts ⁽³⁾. However, the use of this type catalyst did not yield chromium as pure as that obtained with sulfate catalysts. The use of potassium silicofluoride as a catalyzing agent has been shown to produce deposits with the lowest nitrogen content ⁽²⁾, but the oxygen content was higher in these particular investigations than with a sulfate catalyst.

Experimental Procedures .

CrO₃ and Materials Purity

The main source of nitrogen impurity has been shown to be due to residual nitrate from the manufacture of chromic acid ⁽²⁾. This problem was attacked in two different ways. The first method involved the elimination of residual nitrate by either recrystallization or solvation of the chromic acid. The second was to locate a source of purer chromic acid.

Attempts to remove or lessen the amount of NO₃ in the CrO₃ were made by solvent extraction with methanol, diethyl ether, and acetone. CrO₃ is reported to be soluble in these solvents. Alkali nitrates were reported to be either slightly soluble, or very slightly soluble in alcohol and either very slightly soluble or insoluble in ether ⁽⁵⁾. Eight attempts were made to purify CrO₃ by solvent extraction: two with diethyl ether,

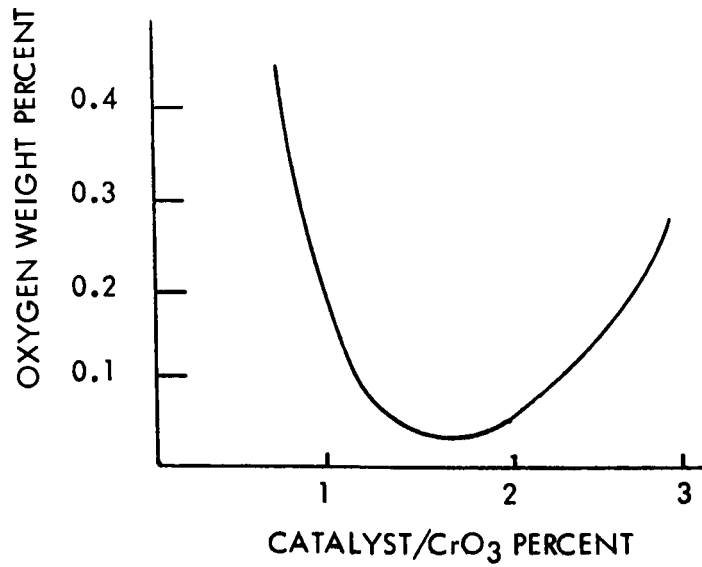
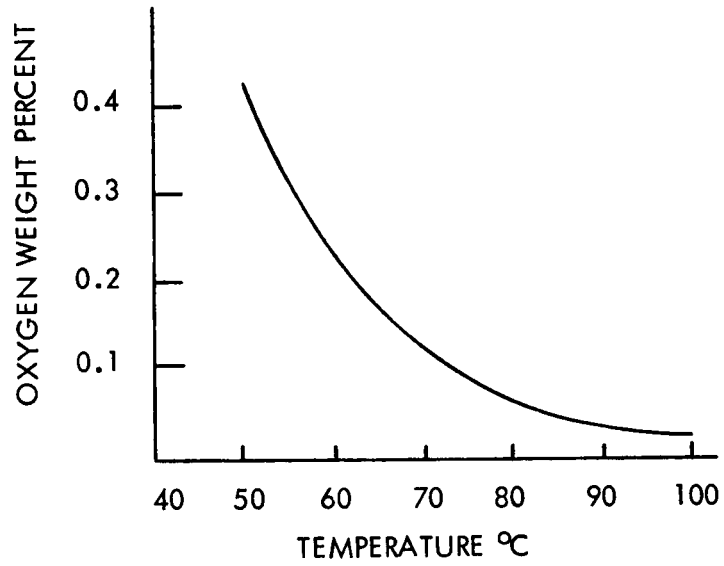


Figure 1. Effect of Temperature and Catalyst on Oxygen Content in Chromium Deposits (ref. 3)

one with acetone, and five with methanol. It was concluded that the further purification of CrO_3 by solvent extraction was not feasible.

Concurrent with the above effort, attempts were made to locate a source of CrO_3 which was relatively free of nitrate contamination. Investigation narrowed down possible sources of pure CrO_3 to Baker reagent grade CrO_3 (99.3% pure) and Allied Chemical technical CrO_3 flake (99.9% pure). Samples of each were analyzed and the results, listed in Table 1, showed the Allied material to be less contaminated with nitrogen than the Baker reagent grade (10 parts per million compared to 39 parts per million). Allied CrO_3 was selected for use throughout this program.

The CrO_3 solution was further purified by passing it through a cation exchange resin column to remove contaminating cations. Amberlite 200 cation exchange resin was recommended by the Rohm and Hass Company for use with a strongly oxidizing solution such as the chromic acid plating solution. A glass ion exchange resin column was fabricated and the CrO_3 solution which was passed through the resin was analyzed along with a control solution which was not treated. The results, also listed in Table 1, show the benefit obtained by this purification step. For example, sodium ion was reduced from over 1 percent to 15 ppm. All plating solutions prepared for this program were treated by Amberlite 200.

Table 1 also lists the purity of the lead and carbon anode materials used throughout the program. No contamination problems were anticipated with these materials.

All reagents and materials such as the sulfuric acid and potassium silicofluoride catalysts were purchased chemically pure and not treated.

Plating Parameter Study

Since the various plating parameters, such as temperature, catalyst type, catalyst concentration and current density affect the purity and quantity of chromium deposited from an aqueous plating bath, a study was started to optimize these parameters before the large scale preparation of chromium containing dispersoids was scheduled to begin.

Initially a lead-lined recirculating plating cell and a high pressure cell were constructed to investigate deposition parameters from room temperature to above 212°F . Figure 2 is a photograph of the lead-lined recirculating cell. Considerable difficulty was encountered in its fabrication and ultimately it was abandoned because of continual leaking of the lead lining. Another cell with structural modifications was made from rigid polyvinyl chloride (PVC). This cell is shown in Figure 3. Both of these cells were jacketed so that either hot or cold liquids could be circulated around them to maintain plating solution temperature. The PVC cell (500 ml. capacity) proved adequate for small-scale work and was replaced later in the program with a larger cell (3000 ml. capacity) of glass construction, shown in Figure 4. The new cell capacity was necessary to meet the demands of the program. Two such cells, working simultaneously, were required for adequate production due to the low

Table 1. Chemical Analyses of Materials
Elements Reported in P.P.M.

Sample Description	N	C	S	F	Cl	K	Li	Si	Al	Mg	Th	Ba	Cu	Fe	Nb	Ni	Ca	Ti
Allied Technical CrO ₃ Flake	10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Reagent Baker CrO ₃ Powder	39	-	-	-	-	40	10	10	10	10	N.D.	10	10	10	1000	20	N.D.	N.D.
Reagent Baker 250 g/l CrO ₃ Sol.	3.9	80	<50	-	-	L-M	25	<10	<10	45	<200	N.D.	N.D.	N.D.	M-H	N.D.	N.D.	N.D.
Reagent Baker 250 g/l CrO ₃ Sol. Amberlite 200 Purified	4.5	1.6	50	-	-	10	<10	<10	<10	<10	<200	N.D.	N.D.	N.D.	15	N.D.	N.D.	N.D.
Lead Anode	-	16	<10	<10	<4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Graphite Anode	-	<999K	<10	N.D.	10	<10	<10	20	10	N.D.	N.D.	N.D.	N.D.	N.D.	<10	N.D.	70	80

N.D. = Not Detectable
L = Low 0.1 - 1%
M = Medium 1 - 10%

H = High 10 - 100%
- = Not Analyzed

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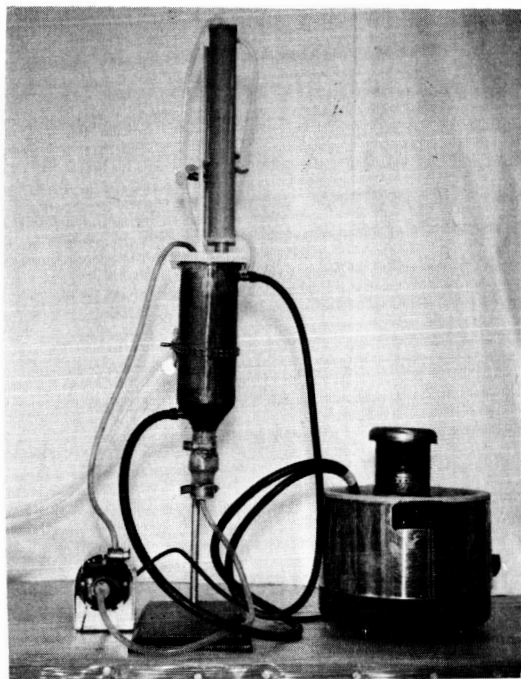


Figure 2. Lead-Lined Recirculating Aqueous Cell

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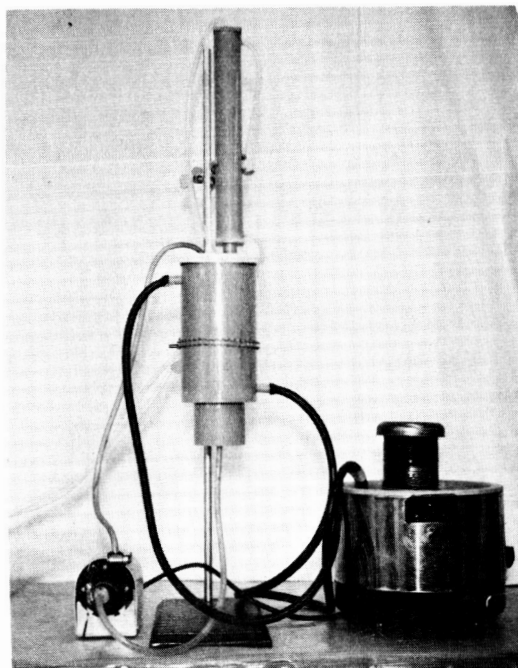


Figure 3. Polyvinyl Chloride Recirculating Aqueous Cell

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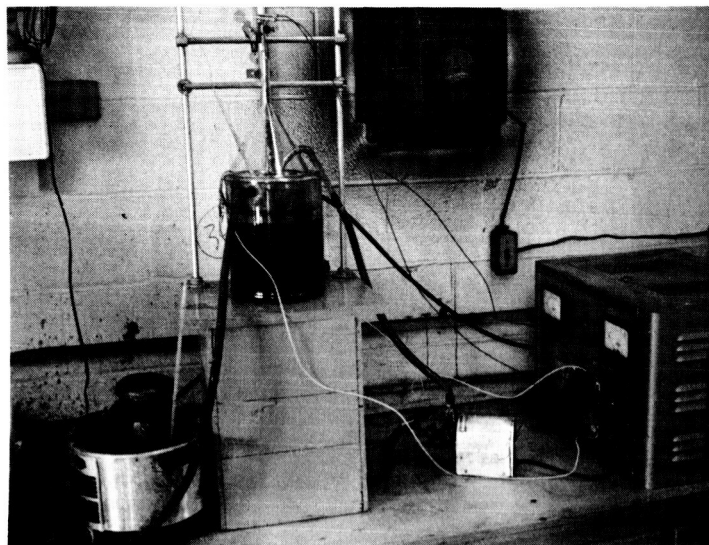


Figure 4. Three-Liter Glass Cell

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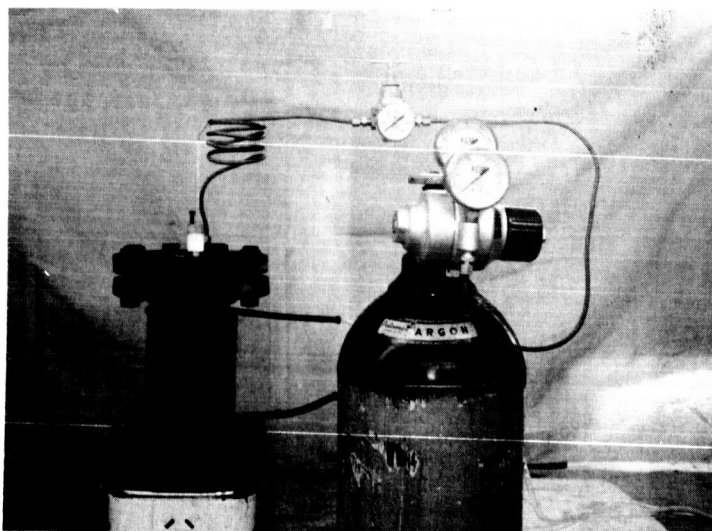


Figure 5. Teflon-Lined High Pressure Cell

current efficiency inherent in electrodepositing chromium.

A high pressure cell was constructed from a standard flanged welding neck. A standard blind flange was used as a lid. The welding neck rated for 150 psi use had an inside diameter of 4 inches and was 12 inches long. This cell was coated internally with polyvinyl chloride and heated by means of a standard hot plate from the bottom and by circulating hot oil through copper coils along the side. The operating temperature was maintained at an elevated boiling point under pressure, which was controlled by a pressure regulator between the cell and an argon cylinder. The PVC lining showed a deterioration after use, probably due to the attack of the hot chromic acid on the small amount of plasticizer present in the lining material. This problem was solved by obtaining a Teflon-lined flanged pressure vessel which is illustrated in Figure 5. This vessel worked as well as the first and eliminated the plating bath contamination because of the inertness of the Teflon lining. It was used on all deposition runs above 212°F.

A parametric plating study using the levels of parameters shown in Table 2 was carried out. The parameters were: plating bath temperature of 158°F, 185°F, 212°F, and 257°F; catalyst concentrations ranging from 0.22 ounces per gallon to 0.67 ounces per gallon; and current densities of 288, 576, 864 and 1152 amperes per square foot of cathode surface. The CrO_3 concentration was held constant at 33 oz/gal.

Discussion of Results

Table 3 lists all the tests performed with the plating parameters used and the resulting oxygen and nitrogen contents. The analyses were conducted by Ledoux and Company, Teaneck, New Jersey and were limited to oxygen and nitrogen in most cases since these were the critical interstitial impurities and had to be kept to low values.

Results from the early runs, in which an aluminum cathode was used, show the nitrogen content to be independent of the plating temperature and catalyst type, and that the oxygen content is not further reduced at elevated plating temperatures but is strongly affected by the type of catalyst used. Since the potassium silicofluoride catalyst yielded higher oxygen content, work was discontinued on this catalyst. Based on the low nitrogen contents obtained from these early runs, the effort was continued to optimize the plating parameters to obtain the lowest oxygen content in the chromium plate with the sulfate catalyst.

It was also evident that some method other than varying plating conditions would be necessary to further reduce the oxygen impurity in the deposited chromium. The method selected was to treat the deposited chromium with hydrogen at elevated temperature. The process is discussed in detail in the description of the hydrogen reduction apparatus.

Table 2. Aqueous Cell Chromium Deposition

Preliminary Test Plan

<u>Test No.</u>	<u>Temperature (°F)</u>	<u>Catalyst Conc. (oz/gal)</u>	<u>Current Density (amp/ft²)</u>
A1	158	0.33 SO ₄	576
A2	185	"	"
A2b	185	0.46 SO ₄	"
A3	212	0.33 SO ₄	"
A4	257	"	"
A5	158	0.33 SiF ₆	"
A5a	158	0.67 SiF ₆	"
A6	185	0.33 SiF ₆	"
A6a	185	0.67 SiF ₆	"
A7	212	0.33 SiF ₆	"
A7a	212	0.67 SiF ₆	"
A8	257	0.33 SiF ₆	"
A8a	257	0.67 SiF ₆	"
A9	212	0.22 SO ₄	"
A9b	185	0.46 SO ₄	864
A10	212	0.67 SO ₄	576
A11	185	0.22 SiF ₆	"
A12	"	0.67 SiF ₆	"
A13	"	0.33 (50/50 SO ₄ /SiF ₆)	"
A13b	"	0.46 (50/50 SO ₄ /SiF ₆)	864
A14	"	0.33 SO ₄	288
A15	"	0.33 SO ₄	864
A15b	"	0.46 SO ₄	864
A16	"	0.33 SO ₄	1152
A16b	"	0.46 SO ₄	1152

About midway through the electrodeposition study, the cathode was changed from aluminum to copper because the adhesion of the chromium to aluminum cathodes was not good, causing loss of deposit during the run. Also, the aluminum cathodes were adversely affected by the silicofluoride catalyzed plating solutions. Since the chromium had to be further treated as an integral cylinder to remove the oxygen, copper cathodes were used for the improved adherence. The copper was removed by dissolving in nitric acid, leaving a hollow cylinder of chromium which was washed several times in deionized water. However, as indicated in Table 3, all tests performed with a copper cathode yielded higher values of nitrogen and oxygen content in the chromium. Nitric acid contamination was suspected. It has been reported⁽²⁾ that nitric acid removal of a copper cathode does not affect the measured quantity of nitrogen impurity in the deposited chromium. Nevertheless, it was thought advisable to investigate this possibility further. Sample A15BR-3 was prepared and boiled several times in distilled water after dissolving the copper cathode. The high nitrogen and oxygen contents of this sample (nitrogen-45 ppm, oxygen-216 ppm) showed that either the nitric acid is not affecting the interstitial impurity contents or that boiling the sample in distilled water is not a suitable method of removing the trace quantities of nitrate if present. Additional samples were prepared and boiled in 25 percent sodium bicarbonate solution followed by repeated treatments in boiling distilled water to see if this procedure would further reduce the nitrogen level.

From the results obtained on tests A16BR-1 and A2B, it was found that no reduction in nitrogen interstitial content was achieved and that carbon interstitial content was increased by the sodium bicarbonate treatment. Tests A15BR-6 and A15BR-7 were performed to establish the effect of dissolving an aluminum cathode in a 25 percent sodium hydroxide solution on the interstitial oxygen content of the chromium. The results showed that sodium hydroxide treatment had no deleterious effect on the interstitial oxygen content and very low (<5 ppm) interstitial nitrogen was measured as in previous cases where an aluminum cathode was used. Since nitrogen interstitial content appeared to increase when the copper cathodes were used, it was thought advisable to recheck the purity of the raw chemical because its arrival was coincidental with the use of copper cathodes. The sample of CrO₃ flake from a second lot was analyzed to contain 19 ppm of nitrogen impurity, which is acceptable in the undiluted chemical.

Based on the foregoing results, it is concluded that high purity electrodeposited chromium can be achieved by:

- Using an aluminum cathode to eliminate nitric acid contamination
- Using chromium trioxide with minimum nitrogen impurity
- Using an ion exchange resin to reduce cation contamination of the plating solution
- Using a sulfate catalyzed plating solution

Table 3. Aqueous Deposition Results

Test No.	Nominal Plating Temp. (°F)	Catalyst Conc. (oz/gal)	Current Density (amp/ft ²)	Cathode Material	Average Plating Rate (gm/hr/in ²)	Results		Remarks
						Oxygen Content (ppm)	Nitrogen Content (ppm)	
A1	158	0.33SO ₄	576	Al	0.053	250	<10	
A2	185	"	"	"	0.188	250	2	
A3	212	"	"	"	0.0785	230	1	
A4	257	"	"	"	0.0722	560	2	
A5	158	0.33SiF ₆	"	"	0.212	960	19	
A5a	"	0.67SiF ₆	"	"	0.100	700	<5	Very low chromium yield
A6	185	0.33SiF ₆	"	"	<0.0106	---	---	
A6a	"	0.67SiF ₆	"	"	0.0680	1000	4	
A7a	212	"	"	"	0.0403	1000	1	
A8	257	0.33SiF ₆	"	"	---	---	---	No deposition
A8a	"	0.67SiF ₆	"	Cu	0.144	>1000	16	Possible HNO ₃ contamination
A9	212	0.23SO ₄	"	"	<0.0088	---	---	Very low chromium yield
A9b	185	0.46SO ₄	864	"	0.123	471	14	Possible HNO ₃ contamination
A10	212	0.67SO ₄	576	"	0.0446	4600	17	Possible HNO ₃ contamination
A13b	185	0.23SO ₄	864	"	<0.0083	---	---	Very low chromium yield
A15B-1	"	0.23SiF ₆	"	"	0.089	1700	35	Possible HNO ₃ contamination
A15B-2	"	0.46SO ₄	"	"	"	74	1136	Treated with H ₂ at TkF, 5 hrs, 1300°C
A15B-3	"	"	"	"	"	90	182	Treated with H ₂ at TkF, 10 hrs, 1300°C
A168	"	"	1152	"	0.0783	---	---	Sample used to find suitable cathode solvent
A15BR-1	"	"	864	"	0.100	33	220	H ₂ treated at 1100°C for 2 1/2 hrs
A15BR-2	"	"	"	"	0.111	---	---	Collected for H ₂ treatment
A15BR-3	"	"	"	"	0.0823	216	45	Boiled in distilled H ₂ O
A15BR-4	"	"	"	"	0.0648	---	---	Collected for H ₂ treatment
A15BR-5	"	"	"	"	0.0587	---	---	Collected for H ₂ treatment
A15BR-6	"	"	"	Al rod	0.0675	437	<5	Sample chipped off
A15BR-7	"	"	"	Al tube	0.0513	273	<5	Al dissolved in NaOH
A28	"	"	576	Cu	0.069	170	11	Boiled in distilled H ₂ O; Sample contained <50 ppm sulfur
A168R-1	"	"	1152	"	0.129	237	68	NaHCO ₃ treated, then boiled in distilled H ₂ O

FUSED SALT ELECTRODEPOSITION

In a fused salt electrodeposition system the plating bath is composed of the halide of the metal to be plated plus alkali metal halides to lower the melting point. Graphite or Inconel is most frequently used as the crucible material, and operation is normally in an inert atmosphere. Three series of tests were performed to establish fused salt plating parameters.

The first series of tests were conducted using a eutectic containing 42 percent LiCl and 58 percent KCl, which has a melting point of 671°F. Chromium shot having 99.999 percent purity was added to the eutectic so that after solution the bath would contain 10 mole percent of CrCl₂. The first series of tests were conducted at 842°F with current densities of 10, 50, and 100 amperes per square foot of stainless steel cathode surface for periods of one to two hours. No plating occurred since the chromium shot did not go into solution.

A second series of tests were conducted at 1652°F and 100 amps/ft² current density using a carbon cathode and either chromium shot or chemically pure CrCl₂ as the cation source. Only a slight amount of chromium shot was dissolved and therefore only a slight amount of chromium was deposited. The low melting eutectic had too high a vapor pressure at 1652°F which resulted in a substantial loss of salt bath. Severe corrosion of the carbon cathode and furnace parts were noted.

In the third series of tests, the melt formulation was changed to 90 percent KCl and 10 percent CrCl₂ which has a low vapor pressure at the 1650°F operating temperature. The negative results in this series and the previous series led to the discontinuance of effort in the fused salt approach.

OXIDE DISPERSION AND INCLUSION

Dispersoid Materials. The refractory oxides selected for use as dispersoids in the aqueous system were aluminum oxide and thorium oxide. Magnesium oxide and thorium oxide were selected for the fused salt approach. Early in the program, Linde B Al₂O₃, having an average particle size of 0.05 micron, was used in preliminary tests. The dispersoids used throughout the program were as follows:

<u>Dispersoid</u>	<u>Particle Size</u>	<u>Supplier</u>
Al ₂ O ₃ (Alon C)	0.01 - 0.05 micron	Cabot Chemical
MgO (Marinco OL)	0.04 micron (average)	Whittaker, Clark
(Marinco OH)	0.08 micron (average)	and Daniels
ThO ₂	0.005 - 0.015 micron	Thorium Limited,
	0.01 - 0.03 micron	England

Dispersion Techniques. A preliminary study was conducted early in the program with Linde B Al_2O_3 , having an average particle size of 0.05 micron, in varying concentrations of 3.3, 6.6, 13.2 and 26.4 ounces per gallon of chromium plating solution. The solutions consisted of 33 ounces per gallon of CrO_3 and 0.33 ounces per gallon of H_2SO_4 and were operated in the temperature range of 149 to 158°F at current densities of 288 and 576 amperes per square foot of cathode surface. A total of eighteen runs were made which included all the concentrations of dispersoid. Initially, the Al_2O_3 was placed in suspension by the use of an electric stirring motor and kept in suspension during plating by recirculating the plating solution through a centrifugal pump. The 6.6 and 13.2 ounces-per-gallon particle concentration appeared to produce the best results. However, none of the deposits were considered satisfactory because of obvious particle agglomeration and non-uniformity of particle spacing.

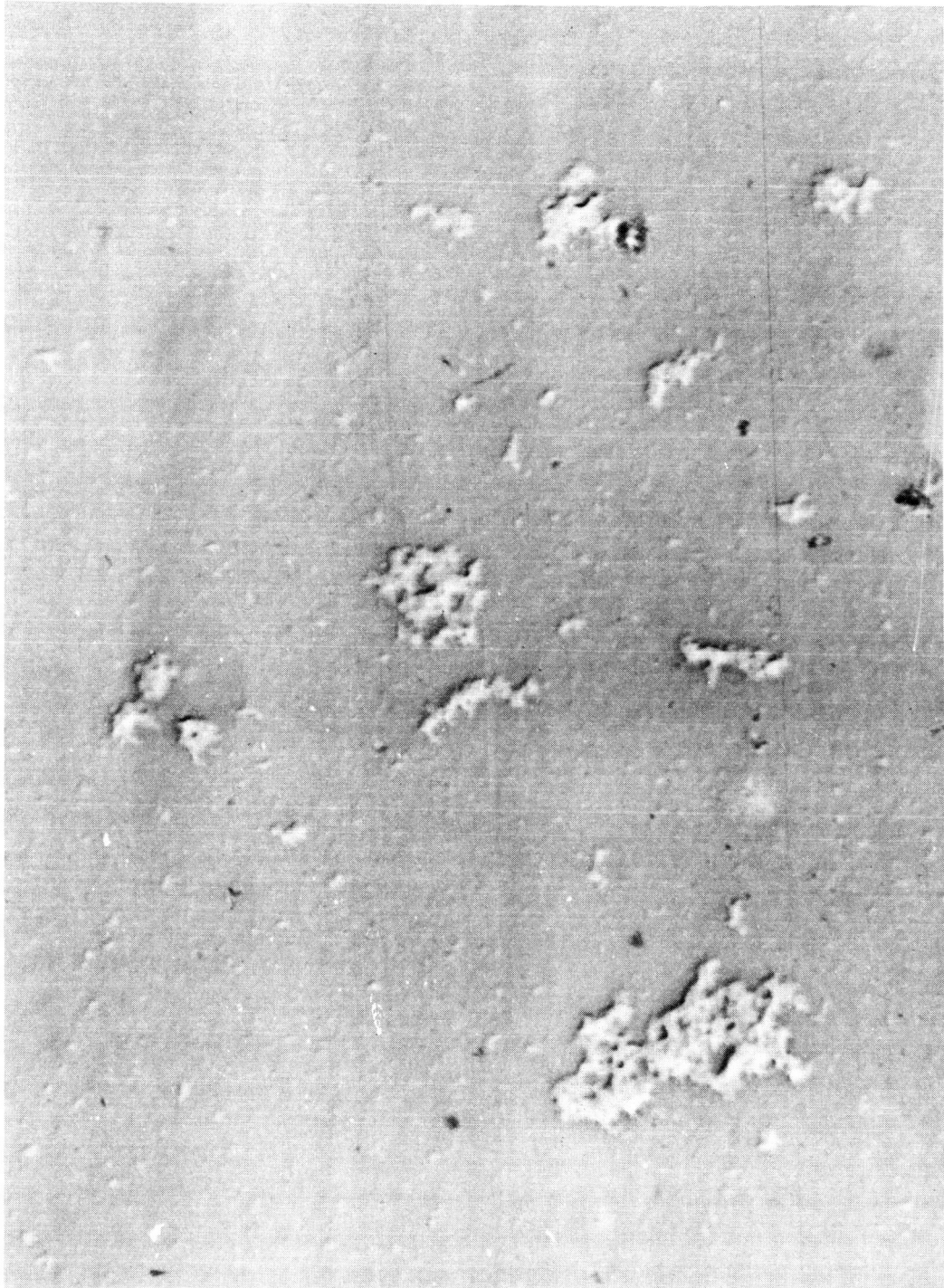
Further work was necessary to eliminate the agglomerates of Al_2O_3 being included in the deposited chromium. Another series of ten tests were performed under the following conditions:

33 oz/gal CrO_3
0.33 oz/gal H_2SO_4
6.66 oz/gal Al_2O_3 (Alon C)
576 amps/ft²
155°F

Of the ten tests, the first four were deposited on copper cathodes and the remainder on nickel cathodes. The solutions were premixed at 1800 rpm for varying lengths of time, ranging from 2 minutes to 1 hour. All the tests were conducted in a small glass recirculating cell. The cathodes were changed to nickel because the copper substrate interfered with metallographic preparation. Subsequent examination showed that agglomerates of Al_2O_3 were still present. Figure 6 is a representative electron micrograph at 28,000X showing the agglomerates in sample No. 28 of this test series. Although the dispersion shown in Figure 6 is partially agglomerated, it contained many small particles of interest and appeared to establish the feasibility of producing dispersion strengthened chromium by electrodeposition. Several samples were prepared using ultrasonic deagglomeration and were submitted to Micro-Met Laboratories, Inc., West Lafayette, Indiana for evaluation. Difficulties were encountered in establishing metallographic preparation techniques to yield reproducible results.

Dispersion Deposition Results. In accordance with program requirements, pre-production lots of alumina- and thoria-dispersed chromium product were to be evaluated in consolidated form at a single volume fraction of dispersoid. If these proved to be satisfactory, then production lots containing three volume fractions of both oxides were to be further evaluated in consolidated form.

Nine deposition runs were made to complete the pre-production lot of alumina-dispersed chromium product. These runs were made using the following conditions, which were previously determined to be optimum with respect to deposition rate, in the apparatus shown in Figure 7:



← 1 μ →

Figure 6. Alumina-Dispersed Chromium Showing Particle Agglomeration (28,000X)

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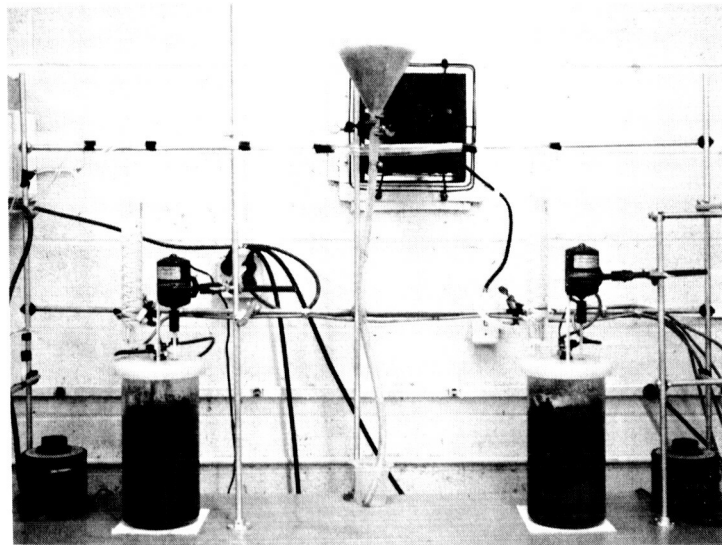


Figure 7. Pre-production Apparatus

Bath size	-	3 liters
CrO ₃ concentration	-	33.0 oz/gal
H ₂ SO ₄ concentration	-	0.46 oz/gal
Al ₂ O ₃ concentration	-	3.3 oz/gal
Average plating temperature	-	190°F
Current density	-	864 amps/ft ²
Deposition run time range	-	10-21 hours
Cathode material	-	copper tube

The total yield of chromium was 61.2 grams. The entire yield was treated with ultrapure hydrogen (99.9994%) at 1100-1400°C for 4 hours. This treatment changed the appearance of the chromium from a dull grey matte finish to a shiny "decorative-type" chromium finish. The treatment also increased the ductility of the chromium as evidenced by the difficulty encountered in grinding the material to minus 100 mesh particles with a high density alumina mortar and pestle. Before the hydrogen treatment, the "as deposited" chromium was considerably easier to crush to this mesh size.

A pre-production lot of 63 grams of thoria-dispersed chromium product was made using the same conditions as the alumina-dispersed lot with the exceptions that aluminum cathodes were used and the concentration of thoria was 6.6 oz/gal. This lot was heat treated in the hydrogen reduction apparatus at 1300-1600°C for 4 hours. Two samples of thoria-dispersed chromium product were measured for microhardness. One sample was in the "as deposited" state and the other was from the same lot but heat treated at 1300-1600°C in pure hydrogen. The results were as follows:

<u>Preproduction Lot Product</u>	<u>Load (grams)</u>	<u>Knopp Hardness No.</u>	<u>Rockwell Hardness</u>
TDCr (as dep.)	100	573	53C
TDCR (H. T.)	100	181	90B

Thus there was a significant reduction of hardness after heat treating with hydrogen.

The grinding of the preproduction lot of alumina-dispersed chromium product was done in a U. S. Stoneware "high alumina" ball mill jar with 1/2 inch diameter alumina balls. The 58-gram lot was reduced in particle size to minus 100 mesh by grinding for 48 hours, separating the minus 100 mesh material, then grinding the residue an additional 24 hours. Alumina contamination from the ball mill was suspected and upon analysis the contamination was verified as 9.3 v/o Al₂O₃. The ball mill was not ruled out as a grinding aid since this was the first sample of chromium ground. The mill jar and balls became impregnated with chromium which should have reduced or eliminated further contamination. However, when the thoria-dispersed chromium product was crushed to minus 100 mesh the sample was still contaminated with over 5 v/o Al₂O₃. It was obvious that other crushing techniques had to be employed. A sample of the "as deposited" chromium was crushed in the high density alumina mortar and pestle while a sample of heat-treated chromium was filed with a chromized file. These samples were analyzed for alumina and iron contamination with the following results:

<u>Grinding Aid</u>	<u>Percent Contamination</u>
Mortar and pestle	0.21 v/o Al ₂ O ₃
Chromized file	1.85 Iron

The crushing of heat treated chromium was very difficult and it was decided to crush "as deposited" chromium, consolidate, and heat treat the consolidated samples for removal of interstitial oxygen. The crushing of "as deposited" chromium to avoid contamination is a problem but with proper equipment it is believed that the contamination could be held to an acceptable limit.

Upon examination of the heat treated alumina- and thoria-dispersed chromium product at 500X, particles ranging in size from $< 1\mu$ to 8μ were observed (see Figure 8). It was decided to postpone consolidation of the preproduction lots to establish the reason for the larger particles to identify them. To establish the optimum heat treating temperature at which oxygen interstitial content is reduced and particle agglomeration does not occur, the following study was started:

Electrodeposit a cylinder of alumina-dispersed chromium product with a minimum wall thickness of 30 mils.

At the same time, electrodeposit a similar cylinder of chromium as a control.

Analyse the chromium for oxygen and nitrogen content and examine the microstructure of a section of the alumina-dispersed chromium product.

Heat treat the remaining cylinders at 1100°C in a pure hydrogen atmosphere.

After heat treating, analyse and examine each cylinder as before to establish changes in purity and/or microstructure.

If no particle agglomeration has occurred and the oxygen interstitial content has not been reduced sufficiently, electrodeposit another pair of cylinders and heat treat at 1200°C for similar evaluation.

Repeat this procedure until an optimum heat treating temperature can be determined.

After several tests were performed in which cylinders of pure chromium and alumina-dispersed chromium product were made, heat treated and examined metallographically (see the following section on metallographic examination), it was determined that the particles were not agglomerates of aluminum oxide, but were chromic oxide (Cr_2O_3), since the same particle morphology was in both deposits. Therefore, this investigation was discontinued.

The thoria sol with a particle size range of 0.005-0.015 microns was used. The sol was very stable in distilled water but when added to the chromic acid plating solution it flocculated and did not remain in suspension unless the solution was well agitated. The Alon C alumina was in the slightly larger particle size range of 0.01 to 0.04 micron and formed a more stable dispersion in the chromic acid plating solution. Thoria sol having a particle size range similar to that of the Alon C alumina

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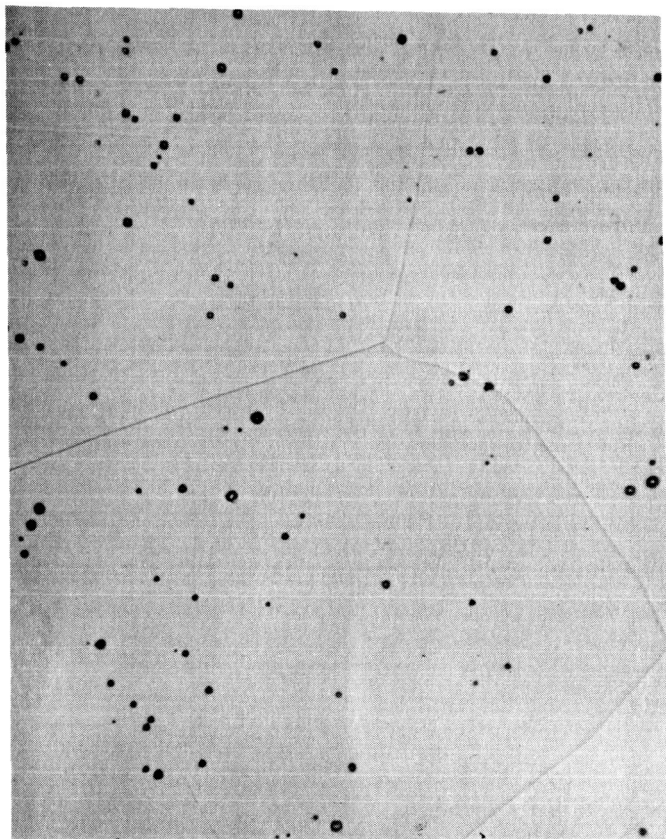


Figure 8. Cr_2O_3 Particles in Alumina-
Dispersed Chromium (500X)

also flocculated when added to the plating solution.

Concurrently with the manufacture of the pre-production lots of alumina- and thoria-dispersed chromium, a series of experiments were conducted to determine the effect of dispersoid concentration in the plating bath on the volume percent of dispersoid in electrodeposited chromium. Deposition runs were made containing four different bath concentrations of alumina and thoria at two current densities. The volumetric percent of oxide in each run is given below:

<u>Condition</u>	<u>Concentration of Oxide in Bath (oz/gal)</u>	<u>Nominal Current Density (amps/ft²)</u>	<u>Volume Percent of Oxide in Cr Sample</u>
As Deposited	1.3 Al ₂ O ₃	864	0.23
"	3.3 Al ₂ O ₃	864	0.10
"	6.6 Al ₂ O ₃	864	0.23
"	1.3 Al ₂ O ₃	864	0.0007
"	1.3 ThO ₂	864	0.014
"	6.6 ThO ₂	864	0.17
Cathode	6.6 Al ₂ O ₃	288	0.003
Dendrite	6.6 Al ₂ O ₃	288	0.057
As Deposited	13.2 Al ₂ O ₃	288	0.017
Ball Milled	3.3 Al ₂ O ₃	864	9.3
Ball Milled	6.6 ThO ₂	864	>5.0 Al ₂ O ₃ 0.29 ThO ₂

These results show that dispersoid contents of less than 0.3 v/o are achieved in the chromium deposited on the cathode at the conditions with which the pre-production lots were made.

Subsequent electron microscopy substantiated the low volume fraction of included oxides and further efforts were made to reproduce the promising earlier results shown in Figure 6. Tables 4, 5, 6, 7 and 8 list all the dispersion deposition runs and their results.

The following points are noted from the results in Tables 4 and 5 and previously listed analytical data:

The ratio of cathode chromium to dendrite chromium decreases with increasing current density.

Nitric acid removal of copper cathodes definitely causes an increase of nitrogen content in the chromium deposit. The amount of nitrogen present is not significantly affected by heat treating with ultrapure hydrogen at 1100-1200°C.

Table 4. Deposition Runs during April 1966

Test No.	Dispersoid Concentration (oz/gal)	Current Density (amp/ft ²)	Average Temp. (°C)	Cathode	Deposition Rate (g/hr/in ²)	Results
V1	3.3 Al ₂ O ₃	864	89	Al	0.040	Cathode Cr contained 0.10 v/o Al ₂ O ₃ .
V2	1.32 Al ₂ O ₃	864	90	Al	0.055	Cathode Cr contained 0.23 v/o Al ₂ O ₃ .
V3	6.6 Al ₂ O ₃	864	90	Al	0.031	Cathode Cr contained 0.23 v/o Al ₂ O ₃ .
V4	1.32 ThO ₂	864	85	Al	0.091	Cathode Cr contained 0.007 v/o ThO ₂ .
V5	6.6 ThO ₂	864	80	Al	0.060	Cathode Cr contained 0.17 v/o ThO ₂ .
V6	3.3 ThO ₂	864	81	Al	0.051	Cathode Cr contained 0.014 v/o ThO ₂ .
1	6.6 Al ₂ O ₃	864	95	Al	0.011	Very low deposition rate on Al cathode.
2	none	864	72	Cu	0.043	Hollow cylinder formed ranging .032-.048 thick.
3	none	288	40	Cu	0.068	Hollow cylinder formed ranging .020-.038 thick.
4	6.6 Al ₂ O ₃	288	44	Cu	0.034	Cathode Cr contained < 0.003 v/o Al ₂ O ₃ . Dendrite Cr contained 0.057 v/o Al ₂ O ₃ .

All plating baths were formulated to 33 ozs/gal CrO₃ and 0.47 ozs/gal H₂SO₄.

Table 5. Deposition Runs during May 1966

Test No.	Dispersoid Concentration (oz/gal)	Current Density (amps/ft ²)	Average Temp. (°C)	Run Time (hours)	Cathode	Agitation	Results
5	none	288	38	71.5	Al	Stirrer	Cylinder 18-25 mils thick heat treated 2 hrs at 1110-1150°C. Cylinder cracked during heat treatment. 19 gms on cathode, 15 gms dendrites, N ₂ content < 5 ppm.
6	6.6 ThO ₂ 0.005-0.015 microns	216	33	48.3	Al	Stirrer	Cylinder 15 mils thick heat treated 2 hrs. at 1110-1150°C. Cylinder cracked during heat treatment.
7	6.6 Al ₂ O ₃	288	37	43.8	Al	Recirc. Pump	Pump seal failed. Al ₂ O ₃ began to settle out after 24 hrs.
8	6.6 Al ₂ O ₃	576	-	-	Cu	Stirrer	Test failed during weekend - no results.
9	13.2 Al ₂ O ₃	576	-	-	Cu	Stirrer	Test failed during weekend - no results.
10	none	576	55	47.8	Cu	none	19 gms Cr on cathode, 28 gms dendrite.
11	13.2 Al ₂ O ₃	288	34	118.3	Cu	Stirrer	54.5 gm cylinder 60 mils thick heat treated 5.3 hrs at 1080 - 1200°C - 0.017 v/o Al ₂ O ₃

Table 5 (cont.) Deposition Runs during May 1966

Test No.	Dispersoid Concentration (oz/gal)	Current Density (amps/ft ²)	Average Temp. (°C)	Run Time (hours)	Cathode	Agitation	Results
12	none	288	41	70.7	Cu	none	40.5 gm cylinder 50 mils thick heat treated 5.3 hrs at 1080 - 1200°C. Before H. T. O ₂ 2000 ppm N ₂ 57 ppm. After H. T. O ₂ 33 ppm N ₂ 71 ppm.
13	13.2 ThO ₂ 0.015 - 0.03 microns	144	35	68.3	Cu	Stirrer	No results - cathode seal failed
13A	13.2 ThO ₂ 0.015 - 0.03 microns	144	30	141.3	Cu	Stirrer	50 mil cylinder - scheduled for heat treatment.
14	none	288	37	119.2	Cu	none	55 mil cylinder - scheduled for heat treatment.
15	26.2 Al ₂ O ₃	288	43	120.8	Cu	Stirrer	Cr cracked off cathode during run. Cathode Cr had <0.003 v/o Al ₂ O ₃ . Dendrite Cr had 0.17 v/o Al ₂ O ₃ .
15A	26.2 Al ₂ O ₃	288	40	137.5	Cu	Stirrer	Cr continued to flake off cathode during run.
16	none	288	36	117	Cu	none	Uneven cylinder formed and flaking off cathode continued.

All plating baths were formulated to 33 ozs/gal CrO₃ and 0.47 ozs/gal H₂SO₄.

Dendrite chromium has a significantly larger amount of occluded oxide dispersoid than cathode chromium from the same run. The data show an apparent dependency of oxide inclusion rate on current density which seems to be overriding the effect of initial oxide concentration in the plating bath.

At constant current densities, there is an increasing amount of thoria content in the deposit with increasing initial concentrations of thoria in the plating bath.

Ball mill grinding of thoria-dispersed chromium product caused excessive contamination of the sample with alumina from the mill jar.

In Table 6, test numbers 17 and 18 were conducted with aluminum cathodes at low current density and, as expected, the chromium did not adhere to the cathode. During these runs, it was discovered through metallographic examination that previous samples prepared at 288 amps/ft² current density yielded little or no dispersoid oxide inclusion. Tests 19 and 20 were performed at higher current densities of 576 and 864 amps/ft² because the data at that time indicated an increase in oxide inclusion with an increase in current density. Test 21 was run under the same conditions as test 19 to obtain additional cathode chromium necessary for consolidation. Test 22 was conducted to obtain additional oxide inclusion data at 1152 amps/ft² current density. Subsequent analyses of samples 19 and 20 indicated that more oxide was deposited than at 288 amps/ft² current density.

The phenomenon of low oxide inclusion rate in chromium plating baths appears to be related to deposition rate which in turn is related to plating bath efficiency. It is felt that electrophoresis does not influence the rate of oxide inclusion since the high electrolyte content of the plating bath and resulting low pH yields an unstable colloid and consequent precipitation of agglomerated particles. Without a stable colloid, electrophoresis is greatly suppressed. However, it is believed that the inherent inefficiency associated with chromium plating baths is the more important factor determining the rate of oxide inclusion. In the aqueous chromium plating bath a considerable amount of hydrogen is liberated at the cathode which may be preventing the oxide particles from entering the cathode-plating bath interface, which would be necessary for particle entrapment during chromium deposition. The samples prepared early in the program which showed promising oxide dispersions were prepared using a recirculating pump to keep the oxide particles in suspension and had a steady stream of plating solution impinging on the cathode surface. It was felt that this steady stream of plating solution containing dispersoid particles on the cathode was forcing particles on the cathode-plating bath interface, thereby displacing the hydrogen gas and allowing inclusion of particles with chromium deposition. Unfortunately, the concept of agitation by recirculation was set aside because of difficulties associated with chromic acid attack of the recirculating pump which caused frequent shut-downs and maintenance of equipment.

In Table 7, tests 23 and 24 were performed to study the effect of cathode geometry on inclusion rate of the oxide dispersoid. All plating conditions were the same on these tests and it appears that the tubular cathode yielded both a higher de-

Table 6. Deposition Runs during June 1966

Test No.	Cathode	Current Density (amps/ft ²)	Dispersoid	Length of Run (hours)	Weight on Cathode (gms)	Weight of Dendrites (gms)	Deposition
17	Al	288	100 g/l Al ₂ O ₃	77 3/4	40.3	did not adhere	
18	Al	288	100 g/l Thoria	76 1/2	39.5	did not adhere	
19	Cu	864	100 g/l Al ₂ O ₃	166	34.1	87.4	Crushed to 100 mesh.
20	Cu	576	100 g/l Al ₂ O ₃	165 1/2	50.3	120.4	44.7 crushed to 100-mesh.
21	Cu	864	100 g/l Al ₂ O ₃	69 3/4	27.6	49.6	Crushed to 100-mesh. Cathode Cr contained 0.17 v/o Al ₂ O ₃ .
22	Cu	1152	100 g/l Al ₂ O ₃	22	11.8	12.8	Cathode Cr contained 0.033 v/o Al ₂ O ₃ . Dendrite Cr contained 0.23 v/o Al ₂ O ₃ .

All plating baths were formulated to 33 ozs/gal CrO₃ and 0.47 ozs/gal H₂SO₄.

Table 7. Deposition Runs during July 1966

Test No.	Current Density (amps/ft ²)	Cathode	Deposition Rate (g/hr/in ²)	Al ₂ O ₃ Included (v/o)	Remarks
23*	576	Tubular Cu	0.051	0.11	0.43 ozs/gal K ₂ SiF ₆ catalyst; No plating Increased concentration of K ₂ SiF ₆ to 1.59 ozs/gal chromium obtained contained black oxide. Recirculating pump broke down during run. Cr sample sent to NASA Lewis.
24*	576	Flat Cu	0.023	0.013	
25**	864	Tubular Cu	---	---	
25A***	864	Tubular Cu	---	0.91	
26****	576	Flat Cu	---	---	
27****	864	Flat Cu	0.033	0.023	New Manostat pump used. Sample sent to NASA Lewis.
28****	288	Flat Cu	0.049	0.033	
29****	288	L shaped	0.045	0.003	Sample sent to NASA Lewis.
		Flat Cu			
		L shaped			

* 33 ozs/gal CrO₃, 0.47 ozs/gal H₂SO₄
 ** 33 ozs/gal CrO₃, 0.43 ozs/gal K₂SiF₆
 *** 33 ozs/gal CrO₃, 1.59 ozs/gal K₂SiF₆
 **** 33 ozs/gal CrO₃, 0.33 ozs/gal H₂SO₄

position rate and a higher oxide inclusion rate. Both effects are probably due to lower dendrite formation on the tubular cathode, dendrites being sloughed from the surface and lost in the bath. Tests 24 and 25A were made to determine the effect of using a silicofluoride catalyst on the inclusion rate of alumina in a chromium bath. No sulfate catalyst was present in these tests. Test 25 yielded no chromium deposition at a K_2SiF_6 concentration of 0.57 oz/gal and test 25A yielded black chromium when the concentration of K_2SiF_6 was increased to 1.6 ounces per gallon. However, subsequent analysis showed the highest concentration of dispersed oxide yet obtained, 0.91 volume percent. The use of a silicofluoride catalyst, which had been reported to increase the efficiency of chromium electro-deposition, appeared to be a promising approach to increase the rate of inclusion of oxide dispersoids.

A Manostat recirculating pump was obtained so that longer runs could be made without danger of pump failure. Test 27 was made using this pump to impinge the recirculating solution directly on the cathode surface. An aluminum analysis showed the inclusion of only 0.023 volume percent of alumina in the cathode chromium. As usual, the dendrite chromium from this test had a significantly larger amount of included alumina (0.23 v/o). Test 28 was performed using an "L" shaped cathode with the plating surface perpendicular to the anode and facing up. Only intermittent stirring agitation was employed, thereby allowing the alumina particles to settle toward the cathode plating surface. Test 29 had identical plating conditions except the Manostat pump was used to impinge the bath on the plating surface. No difference in dispersoid inclusion was found.

As can be seen from Table 7, a silicofluoride catalyzed plating bath yielded the highest volume percent (0.91 v/o) of included aluminum oxide. Therefore, in Table 8, runs 30 through 33 were made using a catalyst mixture of K_2SiF_6 and H_2SO_4 . Both analytical and metallographic results indicate that the inclusion of sufficient amounts of dispersoid oxide remains to be the major problem area in the preparation of dispersion strengthened chromium by electrodeposition techniques.

Table 9 summarizes all the alumina dispersoid inclusion data. From these results it can be seen that dendrites contain more oxide dispersoids than cathode chromium, and that the use of a silicofluoride catalyst appears to be the best approach studied for achieving significant quantities of included dispersoid.

The total chromium collected both as dendrites and as adherent cathode coating in these runs averaged as 8% of Faraday's Law yield for the sulfate catalyst and as 16% for both the mixed sulfate-silicofluoride catalyst and the pure silicofluoride catalyst. This verifies that silicofluoride-catalyzed baths are more efficient than sulfate-catalyzed baths. The amount of chromium adherent to the cathode in these runs averaged 30% of the total, the remainder being dendritic growth that sloughs from the cathode.

Table 8. Deposition Runs during August 1966

<u>Test No.</u>	<u>Current Density (amps/ft²)</u>	<u>Cathode</u>	<u>Anode</u>	<u>Deposition Rate (g/hr/in²)</u>	<u>Al₂O₃ Included (v/o)</u>	<u>Remarks</u>
30*	288	L-shaped Cu	Pure Pb	-----	-----	No plating.
31*	288	L-shaped Cu	Comm. Pb	0.038	0.023	2 gms on cathode - 6 gms dendrites.
32*	576	L-shaped Cu	Comm. Pb	-----	-----	Pump line failure - no results.
33*	576	L-shaped Cu	Comm. Pb	0.015	0.13	1.3 gms on cathode - 8.2 gms dendrites.
34**	864	Tubular Cu	Comm. Pb	-----	-----	Duplicate to 25A. No plating, black oxide only formed on cathode.

* 33 ozs/gal CrO₃, 0.33 ozs/gal H₂SO₄, 1 49 ozs/gal K₂SiF₆

** 33 ozs/gal CrO₃, 1.59 ozs/gal K₂SiF₆

Table 9. Alumina Dispersoid Inclusion Data

<u>Test No.</u>	<u>Al₂O₃ (v/o)</u>	<u>Bath Conc. of Al₂O₃ (oz/gal)</u>	<u>Bath Catalyst (oz/gal)</u>	<u>Current Density (amps/ft²)</u>	<u>Deposition Rate (g/hr/in²)</u>
V1	0.10	3.3	0.47 SO ₄	864	0.040
V2	0.23	1.32	0.47 SO ₄	864	0.055
V3	0.23	6.6	0.47 SO ₄	864	0.031
4 (cathode)	<0.003	6.6	0.47 SO ₄	288	0.034
4 (dendrite)	0.057				
11	0.017	13.2	0.47 SO ₄	288	0.056
15 (cathode)	<0.003	26.4	0.47 SO ₄	288	
15 (dendrite)	0.17				
21	0.17	13.2	0.47 SO ₄	864	0.049
22 (cathode)	0.003	13.2	0.47 SO ₄	1152	0.089
22 (dendrite)	0.23	13.2			0.097
23	0.11	6.6	0.33 SO ₄	576	0.051
24	0.013	6.6	0.33 SO ₄	576	0.023
25A	0.91	6.6	1.59 SiF ₆	864	
27 (cathode)	0.023	6.6	0.33 SO ₄	864	0.033
27 (dendrite)	0.23	6.6			0.13
28	0.033	6.6	0.33 SO ₄	288	0.049
29	0.003	6.6	0.33 SO ₄	288	0.045
31	0.023	6.6	0.33 SO ₄ , 1.49 SiF ₆	288	0.038
33	0.13	6.6	0.33 SO ₄ , 1.49 SiF ₆	576	0.015

Metallographic Examination. The dispersoid-containing samples must be examined metallographically to determine the particle size and extent of dispersion accomplished as a function of deposition parameters. It was intended that early deposition runs would be examined optically at 1800X to assess the degree of agglomeration of dispersed particles in the deposited layer whereas the final evaluations would be made by electron microscopy to resolve the ultimate particles of dispersoid. Metallographic samples were prepared by a variety of standard mechanical polishing, electropolishing and etching techniques.

Inquiries were made of a number of electron metallographic facilities to ascertain whether reliable techniques for resolving dispersoids in chromium existed. Micro-Met Laboratories, in West Lafayette, Indiana, indicated interest in attempting to solve this problem and a series of samples were sent to this laboratory. Their microscopist had reservations about the accuracy of the representation of particle size, shape and distribution.

The metallographic problems existent with the electrodeposited specimens are multiple and interrelated. Polishing would be an ideal preparation except for the existence of cracks. The cracks are the result of electrodeposition stresses and cannot be overcome while maintaining optimum deposition parameters for high purity and dispersion. Obtaining a reliable replica from this craze-cracked surface for electron microscopic examination is a significant obstacle to analysis of the as-deposited chromium product. A two stage replication technique was attempted but the artifacts associated with multiple surface treatments and replica handlings place doubt on the reproducibility of photomicrographic results.

When metallographic examination of the pre-production lots of alumina- and thoria-dispersed chromium product revealed apparent dispersoid agglomeration (see Figure 8), investigations were initiated to determine whether or not the large particles were indeed agglomerates of dispersoid. To accomplish these, specimens of chromium produced with no dispersoid were given identical processing and examined at 800X together with the dispersoid-containing chromium. The appearance of large particles in both samples led to the conclusion that Cr_2O_3 or Cr_3O_4 particles were precipitating during the heat treatment. Dispersoid agglomeration could not account for the presence of the particles in the plain chromium sample.

After chemical analysis revealed the low volume fraction of included dispersoid in the electrodeposited chromium, the four specimens listed below were subjected to electron microscopy and X-ray diffraction analysis.

<u>Sample No.</u>	<u>Dispersoid</u>	<u>Condition</u>	<u>Electron Microscopy</u>	<u>X-ray Analysis of Particles</u>
11	Al_2O_3	as deposited	X	X
11 Heat treated	Al_2O_3	H_2 annealed	X	
12 Heat treated	none	H_2 annealed	X	
13A Heat treated	ThO_2	H_2 annealed	X	

Electron microscopic examination of the specimens indicated the presence of a coarse precipitate in all the specimens characteristic of Cr_2O_3 . The precipitates became larger after heat treatment. Some fine particles could be resolved in the samples submitted, but X-ray diffraction of the residue from the Al_2O_3 heat-treated specimen resulted in the identification of only Cr_2O_3 in both a fine and a coarse particle separation.

HYDROGEN REDUCTION APPARATUS

As previously discussed, it became apparent that the reduction of the oxygen content of electrodeposited chromium by means of plating parameter control to the contract requirement of less than 20 parts per million was not feasible. It therefore became necessary to consider other methods to accomplish this objective. Greenaway⁽⁷⁾ was successful in reducing the oxygen impurity content of electrolytic chromium to less than 50 parts per million by treating the deposited metal with pure hydrogen at 1500°C for not less than 4 hours. Sample 15B was prepared and divided into three equal parts. Two of the parts were subjected to hydrogen treatment in a furnace. The other part was sent to Ledoux for nitrogen and oxygen analyses as a control sample. The heat treatment was carried out with hydrogen containing less than 4 parts per million H_2O at 1300°C in an electrically heated tube furnace. The results of this experiment showed oxygen reduction and are listed below:

<u>Sample No.</u>	<u>Length of H₂ Treatment (hrs)</u>	<u>Oxygen Content (ppm)</u>	<u>Nitrogen Content (ppm)</u>
15B-1	none	1700	35
15B-2	5	74	1136
15B-3	10	90	182

The increase in nitrogen content after hydrogen treatment may have been caused by nitrogen in the hydrogen gas (99.3% purity). Greenaway's more elaborate equipment and process yielded lower values of nitrogen content as well as oxygen content. His purification train included treatment to remove nitrogen from the gas stream. Based on these results it was decided to construct an apparatus at GTC similar to the one used by Greenaway. Figure 9 shows this apparatus. The following items form the train in this apparatus:

- Hydrogen tank and flow meter
- Caustic soda gas dryer
- P_2O_5 gas dryer
- $\text{Mg}(\text{ClO}_4)_2$ gas dryer
- Copper turning furnace at 400°C
- $\text{Mg}(\text{ClO}_4)_2$ gas dryer
- Dry ice-acetone freeze trap at -78°C
- High frequency induction furnace
- H_2SO_4 gas bubbler

GTC 68-8

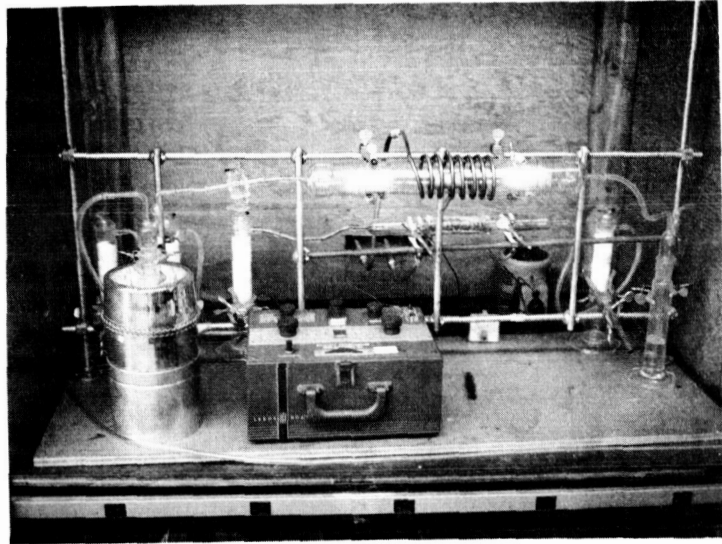


Figure 9. Hydrogen Reduction Apparatus

Sample A 15B-R-1 was treated at 1100°C with -68°F dew point H₂ for 2 1/2 hours. Sample A 15B-R-3 was not treated with H₂ but both samples were boiled several times in distilled water after removal from the copper cathode. The treated chromium changed appearance significantly from a dull gray finish to a bright metallic finish. The results of the analyses are as follows:

<u>Sample No.</u>	<u>H₂ Treatment</u>	<u>Oxygen Content (ppm)</u>	<u>Nitrogen Content (ppm)</u>
A 15B-R-1	yes	33	220
A 15B-R-3	no	216	45

The oxygen impurity content of only 33 parts per million was very encouraging, especially since the samples only reached 1100°C due to furnace operating difficulties. Because of the increased nitrogen content after hydrogen treatment, ultrapure hydrogen (99.9994 percent) was used thereafter.

Both the pre-production lots of chromium product were heat treated in the hydrogen reduction apparatus for four hours. The lot made with alumina reached 1100°-1400° and the lot with thoria reached 1300°-1600°C. The 300° range in temperature was a temperature gradient within the sample with the center of the sample the hottest and the outside diameter the coolest. The temperature gradient should be minimized by either using a stainless steel susceptor to heat the chromium particles by radiation or by heating a uniform cross-section hollow cylinder of "as deposited" chromium. In this latter case the whole surface area is exposed to hydrogen flow, and cooling should be uniform.

A 30-mil seamless stainless steel tube (1 3/8" diameter) was tested as a susceptor for the high frequency induction furnace. After one hour at 1100°C the tube split longitudinally and the temperature dropped to below the red heat. However, when samples 11 and 12 were heat treated, the 50-60-mil-thick cylinders maintained their integrity throughout the five-hour run. The 300° range in temperature of the randomly packed mass of chromium was reduced by two-thirds in heating a uniform cylinder (1080°-1200°C).

Sample 12 before heat treatment contained 2000 ppm of interstitial oxygen and 57 ppm of interstitial nitrogen. After heat treatment the oxygen interstitial content was reduced to 33 ppm and the nitrogen interstitial content was 71 ppm.

The deposited cylinders from tests 13A (ThO₂ dispersed) and 14 (plain Cr) were heat-treated in ultrapure hydrogen at an average temperature of 1130°C for three hours. After three hours the samples cracked and the test was aborted.

It can be concluded that:

"As deposited" chromium cylinders above 60 mils thick can be successfully heat treated by high frequency induction while cylinders below this thickness

crack longitudinally during treatment causing rapid reduction in sample temperature.

Heat treating electrodeposited chromium with ultrapure hydrogen at 1100-1200°C for five hours causes a reduction of interstitial oxygen from 2000 ppm to 33 ppm.

CONCLUSIONS

Based on the results obtained in this program the following conclusions were reached:

1. Nitrogen content in aqueous electrodeposited chromium can be kept below 10 ppm by controlling plating parameters and the purity of the plating solution.
2. Oxygen content in aqueous electrodeposited chromium does not appear to be further reduced by plating at temperatures above 212°F, but shows a tendency to increase. The oxygen content of aqueous electrodeposited chromium can be reduced to acceptable levels by treatment of the deposit with ultrapure hydrogen at elevated temperatures for several hours.
3. Chromium electroplated with sulfate catalyst has less oxygen content than chromium electroplated with silicofluoride catalyst.
4. Nitrogen content is not affected by either catalyst type or temperature in the range studied.
5. Ultrasonic agitation appears to deagglomerate Al_2O_3 particles in the size range of 0.01 to 0.05 micron and create relatively stable suspensions in chromium plating baths. Thoria in the size ranges of 0.005 to 0.015 micron and 0.01 to 0.03 micron flocculates in chromium plating baths.
6. Using plating parameters optimum for chromium purity, very low (less than 0.30 v/o) volume fractions of dispersoid oxides are included in the electrodeposit. Dendrite chromium always contains a significantly larger amount of oxide than cathode chromium.

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