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I. Summary

A satisfactory procedure for electroplating ~~tuballoy~~⁴ has been developed. ~~The method~~ involves anodic treatment of the metal in a concentrated solution of trichloroacetic acid prior to plating. Uniform and rapid attack on ~~tuballoy~~, small metal loss and good plate adherence are advantages of the procedure. Consistently good plates have been obtained during the past year on both laboratory and semi-production scale operation. However, a smooth, uniform plate-tuballoy interface completely free of contamination has not been realized. Adherent electroplates of practically all of the platable metals have been deposited on ~~tuballoy~~ using this pretreating procedure. /end

Electroplates appear to be of some value as blocking layers to prevent the inter-diffusion of tuballoy and coating materials. Indications are that chromium plates are effective in preventing tuballoy-aluminum alloy formation during the Al-Si jacketing treatment.

A number of electroplates are suitable for the prevention of oxidation of tuballoy when exposed to ordinary atmospheres. Neither single nor composite "as plated" deposits of allowable thicknesses afford appreciable protection to tuballoy exposed to aqueous media. Composite copper-tin plates heat treated in silicone fluid have shown quite good corrosion resistance in static solutions at moderate temperatures, however, such favorable results have not been obtained with specimens heat treated by other methods. The corrosion resistance of diffused (high temperature) nickel and nickel-molybdenum plates appears to be 10-100 times better than that of unalloyed tuballoy.

Electroplating on aluminum has been of considerable interest and importance, especially so in connection with the zinc canning process.

The electroplating group has cooperated with other groups by doing a considerable volume of service plating.

Approved by:

Frank F. Firth
(Division Director)

Submitted by:

Group Leader

Frank F. Firth
(Section Chief)

II. Introduction

A protective coating for tuballoy is essential for successful operation of reactor units of the present design. The necessity for a protective coating is two-fold (1) prevent oxidation of tuballoy, (2) entrap by products. Electroplating is, in general, the most applicable of the several well-established methods for producing metallic coatings on metals. The amount of protection afforded by electroplates is determined largely by two characteristics of the deposit, (1) adherence and (2) thickness. The degree of adherence is directly related to the condition of the surface and the structure of the base metal. Metal thickness limitations are necessary confinements to the application of electroplating to the coating problem.

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III. Principles of Plating on Tuballoy

Early exploratory work and progress in the development of the fundamentals of electroplating on tuballoy prior to June 1, 1944, are discussed in the Quarterly Record Report on Electroplating. (1)

A. Pretreatment Prior to Plating

As mentioned previously, the condition and cleanliness of the base metal surface determine to a very large extent the amount of protection resulting from the subsequent electroplate. Maximum plate adherence is realized when the fundamental structure of the base metal is continued, at least for the first few atomic layers, in the deposit. A plate-base metal relationship of this type in which there is a gradual change from the structure of the base metal to that of the plate is known as the so-called "chemical bond." The surface of the more active metals usually cannot be kept perfectly clean even for a very short time so that there is always an oxide layer between the plate and the base metal. Knowing and accepting this fact, the other alternative is to deliberately prepare an oxide film of suitable qualities for binding the plate to the base metal. Procedures for plating on aluminum, for example, are based on this principle.

In addition to the usual cleaning and degreasing operations, most metals are given a treatment to remove any oxide which may be present and to etch the surface before plating. The last step is very important in the preparation of tuballoy as a base for electroplates. Methods that do not adequately remove the distorted crystals from the surface of the metal have not proved successful. The dark oxide usually present on tuballoy is soluble in nitric acid. It can also be removed by anodic treatment in suitable electrolytes. (H_2SO_4 , H_3PO_4), however neither of these treatments etch the surface sufficiently to reveal the crystal structure or prepare the surface properly for the deposition of adherent electroplates.

The methods that have proven successful for the deposition of adherent electroplates involve anodic treatment of the tuballoy in solutions containing chloride ion. Hydrochloric acid reacts very violently with tuballoy by simple immersion at room temperature. This characteristic is not shared by the other common chemical reagents. Uninhibited solutions of hydrochloric acid have not proven satisfactory for pretreating purposes for three reasons:

(1) CT-1793 (A-2622)

(1) a very non-uniform surface is produced, (2) the reaction once started is difficult to control (time required to start the reaction varies considerably from specimen to specimen), (3) adherent plates are not obtained on surfaces thus prepared. During the course of a series of experiments to find a chloride compound of more desirable qualities, a solution of trichloroacetic acid was investigated. Anodic treatment of tuballoy in a 15% solution of this acid produced a very voluminous green film on the surface of the specimen. Solution of this green deposit in nitric acid revealed a smooth, uniformly etched surface with the crystalline structure of the metal clearly revealed. The appearance and adherence of the plate deposited on this specimen was the best obtained up to that time. This method, after further investigation which resulted in several modifications, is the most satisfactory pretreating procedure for plating tuballoy developed to date. It has been in operation for more than a year with consistently good results. A large variety of other reagents have been investigated, none of which can be recommended in their present stage of development. Complete operating details of the trichloroacetic acid method are given in a later part of this report. A method (2) involving the use of a phosphoric acid-hydrochloric acid mixture appears promising, however, the results reported are for short time operation.

Although the trichloroacetic acid method is the recommended procedure at the present time, it possesses certain limitations so that a brief discussion of the favorable and unfavorable points is deemed worth while.

Advantages:

1. Rapid, uniform attack. In general, all specimens react immediately and at the same rate regardless of their past history. (The length of time required to initiate the attack in unmodified hydrochloric acid often varies by a factor of ten or more).
2. Good adherence. The large quantity of electroplated tuballoy which has been successfully soldered is indicative of the quality of the plate-base metal bond. True chemical bonding is not claimed, however, it is believed that the adherence is better than that generally associated with mechanical bonds. Alloy formation by high temperature diffusion and the atmospheric corrosion resistance of electroplated tuballoy betoken good adherence.
3. Small metal loss. Specimens pretreated by this method suffer a loss of approximately 1 mil on the radius.

4. The method is simple, rapid, easily controlled, and not hazardous. The general precautions to be observed when working with strong acids must, of course, be adhered to.

Disadvantages:

1. Contamination of plate-base metal interface. Efforts to eliminate completely this "dark component" have not been successful. The amount of this component varies considerably from specimen to specimen and for different areas on a particular slug. The extent of the effect has been greatly reduced so that localized areas are completely clean.
2. Irregularity of the interface. A perfectly smooth plate-base metal interface has not been realized. This condition also varies considerably as some areas are quite good. A further reduction in the magnitude of this jaggedness is necessary before much improvement in the smoothness and imperviousness of the "as plated" deposits can be expected.
3. Thermal and electrical instability of trichloroacetic acid. This subject will be discussed in a later section pertaining to solution control.

The present status of the problem of pretreating tuballoy prior to plating can be summarized briefly by stating that considerable progress has been made and a method has been developed by which consistently good results can be obtained, however, certain aspects of the present procedure must be improved upon before a satisfactory solution to the problem can be claimed.

As a result of the past year of experimentation and semi-production operation, the following pretreating procedure is recommended.

1. Initial Surface - a ground surface is desirable but not essential.
2. Degreasing - vapor degreasing in trichloroethylene is quite satisfactory. Anodic treatment in strong alkaline solution, such as the commercial cleaners used on steel, is also suitable. Cleaners containing soluble chlorides should not be used.

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3. Shot Blasting - this treatment aids rapid and uniform attack by the trichloroacetic acid (immersion in nitric acid removes the surface oxide but tends to passivate the metal).

4. Nitric Acid Treatment - Solution - 35% HNO_3 ; time- 1 min.; temperature - room. This treatment removes iron and loose oxide remaining on the surface after shot blasting.

5. Running Water Rinse

6. Etching - Solution - 500-700 grams of trichloroacetic acid per liter of solution; anodic treatment, current density, 50 amps/ft.²; time - 3-5 minutes; temperature - 50-60°C. Although the metal is attacked by simple immersion the use of current is recommended for speed and uniformity. The rate of attack is accelerated with increased temperature and concentration. Usually 3 minutes is sufficient time for this operation.

7. Running Water Rinse

8. Nitric Acid Treatment - same solution as for step 4. The black deposit on the surface of the metal after the anodic treatment in trichloroacetic acid dissolves rather slowly in more dilute acid (10-15%). Concentrated nitric acid cleans the metal quite quickly (reaction is not violent), but is not recommended because such treatment tends to cause blistering in subsequent electroplates. Hot nitric acid solutions are to be avoided. The reaction reaches quite violent proportions at 50°C.

9. Running Water Rinse - cold water rinse followed by hot water; time - not more than 1 minute.

10. Plating - the metal should be introduced into the selected plating bath as quickly as possible.

B. Solution Control

As mentioned previously trichloroacetic acid is decomposed by heat and/or electrolysis. The major products of this decomposition are chloroform, carbon dioxide and chloride ion. Small amounts of phosgene and carbon monoxide may also be formed. Freshly prepared solutions of trichloroacetic do not etch tuballoy satisfactorily due to the absence of chloride ion. Heat and/or electrolysis liberate the necessary concentrations of chloride ion. The length of time required for this "ageing" process varies inversely with concentration. This plus the fact that uniformity of etch increases with increasing concentration, is the reason for using a concentrated solution of the acid.

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Graph I shows the rate of decomposition of tri-chloroacetic acid by heat and by electrolysis. As indicated in the graph, the acid concentration decreases rapidly at the boiling point of the solution. This temperature is, of course, much higher than that used under actual operating conditions. The solution used for the electrolysis experiments was maintained at a temperature of 25°C. Carbon cathodes and tuballoy anodes were used. The anode current density was 50 Amps/ft.². This subject is being investigated in more detail and the results will be included in a later report.

Two quantitative methods have been used for determining the acid concentration -

1. Titration with sodium hydroxide.
2. Specific gravity measurements.

The relationship between specific gravity and concentration is shown in Graph II. The maximum error by this method is believed to be less than 2-10 grams/liter of solution.

A spongy green film forms on the metal if and when the acid concentration falls below 500 gs/l of solution. At higher acid concentrations, the metal is covered with a thin black deposit.

C. Plating Baths

1. Conventional Baths

Practically all of the platable metals have been deposited on tuballoy. Acidic, basic and neutral baths have all been used successfully. Baths containing high concentrations of chlorides are not applicable. A manual of operating instructions for electroplating tuballoy is being prepared, included in which is a detailed discussion of pretreatment, suitable plating baths, rack design, tank construction and temperature control equipment.*

2. Nickel, Nickel-Molybdenum and Molybdenum Plating Baths

Corrosion data indicate that certain nickel-tuballoy⁽³⁾ and molybdenum-tuballoy⁽⁴⁾ alloys are approximately ten times more corrosion resistant than unalloyed tuballoy.

-
- (3) MUC-JED-28
(4) MUC-NG-15
* CT-C-2116

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CONC. OF CCl_3COOH IN GS./L. OF SOLUTION

GRAPH I

Decomposition of aqueous CCl_3COOH solutions
Effect of electrolysis

Effect of heat (boiling temperature)

456 010

ANODIZING TIME IN MINUTES *** BOILING TIME IN MINUTES

GRAPH II

Density of aqueous CCl_3COOH solutions
Room temperature

CONC. OF CCl_3COOH IN CS./L. OF SOLUTION

456 011

SPECIFIC GRAVITY

Although the high danger coefficients of these elements prohibits the use of uniform alloys, the use of alloy clad slugs is feasible. Experiments were initiated to determine the possibility of producing alloy surfaces by electroplating tuballoy with nickel, molybdenum or an alloy of the two metals. Diffusion and corrosion data will be considered later in this report.

a. Nickel - a modified Watt's bath is recommended for the production of consistently good plates on tuballoy. All of the nickel plates prepared for diffusion studies were plated in a bath of this type, a rather dilute high sulfate solution.

Bath composition and operating conditions:

55 grams/liter $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
52 grams/liter H_2SO_4 , Anhydrous (hydrated salt can be used if allowance is made for water content)
8 grams/liter NH_4Cl
8 grams/liter H_3BO_3
Temperature - 50-55°C
Current Density - 25-30 Amps/ft.²
pH - 5.0-5.5
At 30 Amps/ft.², 0.001" of nickel is deposited per hour.
Cathode rod agitation is required.

b. Nickel-Molybdenum alloy baths:

Ammonical nickel-molybdenum bath:

200 grams/liter $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
7.5 grams/liter H_3BO_3
3 grams/liter MoO_3
pH - 10.3 (NH_4OH)
Temperature - room
Current Density - 30-60 Amps/ft.²
Efficiency is approximately the same as that of the Watt's nickel bath
Deposits are quite brittle
Plate analyses:
Wt. %: 85-90% Nickel
10-15% Molybdenum
0.5% Oxygen

Alkaline pyrophosphate nickel-molybdenum bath:

8 grams/liter $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
80 grams/liter NaHCO_3
40 grams/liter $\text{Na}_4\text{P}_2\text{O}_7$

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20 grams/liter MoO_3
Current Density - 30-50 Amps/ft.²
Temperature - room
This bath was developed by H. S. Myers at
Columbia University (5)

Plate analyses:

Wt. %: 55-40% Nickel
35-50% Molybdenum
10% Oxygen

Attempts are being made to increase the thermal stability of the bath by replacing NaHCO_3 with a more stable buffer. Methods of increasing the efficiency (5-15%) are also being investigated.

c. Molybdenum baths:

Although several baths are reported in the literature as being suitable for the deposition of metallic molybdenum, no plate analyses are given and it is doubtful that the pure metal was obtained. The following patented bath appears to be the most promising of any investigated.

10 grams MoO_3
100 grams $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$
100 grams $\text{K}_2\text{C}_2\text{H}_3\text{O}_2$
100 cc H_2O

pH lowered to 6.2-6.5 with glacial acetic acid
Current Density - 200-500 Amps/ft.²

The conductivity of this concentrated bath is rather low as an applied voltage of 15-20V is required to maintain the necessary current density. Efficient cooling is necessary to prevent overheating (highest optimum temperature - 50°C). MoO_3 is but slightly soluble at the recommended pH. Either no deposit or a black oxide is obtained from solutions of lower pH. Molybdic acid is quite soluble in alkaline solutions but electrolysis yields only an oxide. Current efficiency is very low. The molybdenum content of the deposits is usually about 85% by weight. Molybdenum sesquioxide Mo_2O_3 , which has the highest metal to oxygen ratio of any of the known oxides, contains 80% molybdenum. The deposits have a dull metallic luster. It is quite probable that some metallic molybdenum is being deposited unless a hither-to-unknown

oxide is being obtained. A preliminary X-ray analysis did not reveal the presence of any metallic molybdenum, however, this method is not generally applicable for the detection of minor constituents.

3. Non-Aqueous Media

An investigation of non-aqueous solutions was undertaken with two aims in view - (1) improvement of the electroplate-tuballoy bond; (2) electroplating of aluminum.

a. Liquid Ammonia and Related Solvents -

Copper was the metal selected for studying the effect of the various solvents on plate characteristics. The solvents investigated were liquid ammonia, formamide, acetamide and propionamide. Copper was added in the form of the cyanide, nitrate or sulfate. Although a copper deposit was obtained from most of the solutions tried, none of them can be recommended in their present stage of development. The best plates obtained, plated from a liquid ammonia solution of copper nitrate and ammonium nitrate, were inferior to those deposited from aqueous solutions. The desired improvement in the plate-tuballoy bond was not realized. This work was exploratory in nature and the meager results do not justify more than tentative conclusions.

b. Electroplating of Aluminum -

Due to the fact that aluminum had been chosen as the jacketing material for tuballoy, a few experiments were conducted to investigate the feasibility of plating this metal. Several baths for electroplating aluminum are described in the literature. A bath having the following composition was selected for this work:

Anhydrous AlCl_3 , 66 mole percent

Anhydrous NaCl , 20 mole percent

Anhydrous KCl , 14 mole percent

Temperature - 100°C

Current Density - 10-30 Amps/ft.²

Anodes - 2S Aluminum

Very thin, adherent deposits of aluminum were obtained on copper. Attempts to increase the plate thickness produced treed or spongy deposits. Two attempts were made to deposit aluminum on tuballoy, both were unsuccessful. Aluminum anodes are quite soluble in this melt. In the event that the electroplating of aluminum should become of more interest, it is recommended that this bath be more thoroughly investigated.

IV. Evaluation of Electroplates on Tuballoy

A. Electroplates as "Blocking Layers"

Aluminum-tuballoy, silicon-tuballoy and aluminum-silicon-tuballoy alloys are very brittle. The likelihood of one or more of these alloys being formed during or following the present canning methods is quite good. An investigation of the value of electroplates in preventing this alloy formation was deemed worthwhile.

1. High Temperature Clinton Slugs

The operating level of the X unit could be increased considerably if the interdiffusion of aluminum and tuballoy could be prevented at elevated temperatures. Previous experiments had indicated that certain electroplates might serve this purpose and at the same time not use too much of the excess K.

A number of X size slugs were electroplated, canned (unbonded), and welded by atomic hydrogen. Copper was plated from the pyrophosphate bath, nickel from the modified high sulfate bath and chromium from the concentrated chromic acid bath. The results are recorded in the following tables. The slugs in Table I were heated at 300°C; those in Table II at 400°C; and those in Table III at 500°C. All of the specimens were heated in air. The slugs included in Tables I and II were in test for slightly more than four months. Inadvertently the temperature of the furnace set for 500°C rose to 700°C and consequently all the specimens listed in Table III were ruined after being in test for two months.

Of the 30 specimens tested at 300°C, 14 showed more or less swelling. Two of the 14 failed completely. All of the composite Cu-Ni plates passed the test. Only one of the 18 specimens in test at 400°C showed any indication of failure. Eight of the 21 specimens in test at 500°C showed no indication of failure. Of the 10 plated specimens which showed change, 2 showed pimpling; 3 of the 4 unplated specimens showed pimpling. Pimpling is probably due to alloy formation. As mentioned previously, these specimens in test at 500°C were all lost after two months. Although no definite conclusions are warranted from these results, it is believed that (1) electroplates are of value as blocking layers and (2) the volume of gas released by electroplates at elevated temperatures is not appreciably greater than that obtained from unplated tuballoy under the same conditions.

TABLE I (300°C)

NO.	PLATE	OBSERVATIONS
Unplated 1	None	No change
" 2	"	Bottom* very slightly concave
" 3	"	Bottom slightly concave
" 4	"	Swelling at top after 5 weeks, no further change during remainder of test.
" 5	"	Bottom slightly concave
" 6	"	Rupture of can at weld after 9 days. Specimen removed.
Ni 16	0.001" Ni	Slight swelling at weld after two weeks, no further change during remainder of test.
" 23	" "	No change
" 24	" "	No change
" 25	" "	Slight swelling at welded end after 5 weeks, no further change during remainder of test.
" 26	" "	Same as Ni 25
" 27	" "	Slight swelling at welded end.
Cu 12	0.001" Cu	No change
" 13	" "	No change
" 18	" "	Pimples on the wall of bottom half of specimen after 6 weeks. No further change.
" 30	" "	Bottom slightly concave
" 31	" "	No change
" 34	" "	Bottom slightly concave
Ni 34	0.005" Cu + 0.005" Ni	No change
" 35	" "	No change
" 36	" "	No change
" 37	" "	No change
" 40	" "	No change
" 48	" "	No change
" 49	" "	No change

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TABLE I (Cont'd.)

NO.	PLATE	OBSERVATIONS
Cp 108	0.005"Cu+0.005"Cr	Swelling at welded end after two weeks. No further change during remainder of test.
" 109	" "	No change
" 111	" "	No change
" 112	" "	No change
" 122	0.005"Ni+0.005"Cr	Swelling at both ends after 6 weeks. Can ruptured after three months. Specimen removed.

* Bottom refers to the end of the can opposite the weld.

TABLE II (400°C)

NO.	PLATE	OBSERVATION
Unplated 8	None	No change
" 10	"	No change
" 12	"	No change
" 14	"	No change
Cr 184	0.001"Cr	No change
" 187	" "	No change
Cu 62	0.001"Cu	No change
Ni 59	0.001"Ni	No change
Cr 169	0.005"Cu+0.005"Cr	No change
" 170	" "	No change
" 206	" "	No change
Cr 189	0.005"Ni+0.005"Cr	No change
" 192	" "	No change
" 193	" "	No change
" 211	" "	No change
" 212	" "	No change
Ni 62	0.005"Cu+0.005"Ni	No change
Ni 65	" "	Severe swelling after 2 days. Specimen removed. Can removed. Plate unchanged.

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TABLE III (500°C)

NO.	PLATE	OBSERVATIONS
Unplated 7	None	No change
" 9	None	Pimpling after 2 weeks.
" 11	None	Pimpling after 2 weeks, rupture of can after 4 weeks. Specimen removed.
" 13	None	Pimpling after 2 weeks, rupture of can after 3 weeks. Specimen removed.
Cu 63	0.001"Cu	Pimpling after 9 days.
Ni 58	0.001"Ni	Swelling after 7 days.
" 60	"	No change
Cr 183	0.001"Cr	Swelling at welded end after 2 days. Specimen removed. Can removed. Plate unchanged.
" 185	"	Same as Cr 183
" 186	"	Swelling after 2 days. No further change.
" 195	"	No change
Ni 63	0.005"Cu + 0.005"Ni	No change
" 64	" "	No change
Cr 204	0.005"Cu + 0.005"Cr	Pimpling after 2 weeks.
" 205	" "	Swelling after 7 days.
" 207	" "	No change
Cr 190	0.005"Ni + 0.005"Cr	Swelling after 2 weeks.
" 191	" "	Slight swelling after 2 weeks.
" 194	" "	Swelling after 2 weeks.
" 210	" "	No change
" 215	" "	No change

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TABLE IV
ATMOSPHERIC CORROSION - FOUR MONTHS

NO.	PLATE	PRETREATMENT	OBSERVATIONS
6	0.001" Zn	CCl ₃ COOH	No evidence of failure
2	"	H ₃ PO ₄ -HCl	No evidence of failure
6	0.001" Cd	CCl ₃ COOH	No evidence of failure
6	0.003" Cu	CCl ₃ COOH	No evidence of failure
6	0.003" Ni	"	No evidence of failure
2	"	H ₃ PO ₄ -HCl	No evidence of failure
6	0.003" Cr	CCl ₃ COOH	No evidence of failure
6	0.001" Ni + 0.001" Zn	"	No evidence of failure
2	" "	H ₃ PO ₄ -HCl	No evidence of failure
6	0.001" Cu + 0.001" Zn	CCl ₃ COOH	No evidence of failure
2	" "	H ₃ PO ₄ -HCl	No evidence of failure
6	0.001" Ni + 0.001" Cd	CCl ₃ COOH	No evidence of failure
2	" "	H ₃ PO ₄ -HCl	No evidence of failure
6	0.001" Cu + 0.001" Cd	CCl ₃ COOH	No evidence of failure
2	" "	H ₃ PO ₄ -HCl	No evidence of failure
6	0.001" Cu + 0.001" Pb	CCl ₃ COOH	No evidence of failure
6	0.001" Cu + 0.002" Pb	"	No evidence of failure
6	0.001" Ni + 0.001" Cr	"	All of the specimens showed pit type of corrosion.
6	0.001" Cu + 0.001" Ni	"	No evidence of failure
6	0.001" Ni + 0.001" Cu + 0.001" Ni	CCl ₃ COOH	5 of the specimens showed peeling of the plate at the ends.
6	0.001" Sn *	"	No evidence of failure
6	0.001" Brass *	"	One specimen showed pit type of corrosion.

* Placed in test one month later than the other specimens.

2. Hot Dipping Procedures

Preliminary experiments indicated that nickel or chromium electroplates could be wetted in molten Al-Si (12% Si) with or without a pre-dip in Zn-Al (5% Al). Continuation of this work did not yield consistent results largely due to poor plate adherence and to flaws in the surface of the slugs in the form of cracks, pits and pipes which could not be bridged by the plates. Improvements in plating technique have augmented the quality of the plate-tuballoy bond. The work on hot dipping electroplated specimens has been continued at Cleveland with more promising results. Some improvement in the technique has been made and the results indicate that a chromium plate (0.001") is effective in preventing tuballoy from diffusing into Al-Si, at least during the dipping process. Nickel appears to be somewhat less effective in this regard.

B. Atmospheric Corrosion

The use of electroplates as a means of protecting tuballoy against oxygen pickup when exposed to ordinary atmospheric conditions was investigated. It was necessary that the coating be applied without elaborate mechanical pretreatment or any treatment involving appreciable metal losses.

One hundred and eight X size specimens were plated as shown in Table IV. These specimens were weighed (accuracy $\pm 0.05g.$) and photographed before being placed in specially constructed corrosion racks located on the roof of Site B. After four months' exposure, the specimens were closely examined, weighed and re-photographed. There was no appreciable change in the weight or in the physical appearance of the specimens. As indicated in the table, twelve specimens, representing three types of plates, showed evidence of base metal oxidation. Since no attempt was made to select only the most perfect slugs for this work, some of the failures may be due to flaws in the tuballoy. All of these specimens were plated in Cleveland. Pretreating was done in dilute trichloroacetic acid solution. Better plates could be expected by using the concentrated solution which has been developed more recently.

C. Static Corrosion

Eight X slugs, plated as indicated in Table V, were canned (each can was perforated with 9 No.60 holes) and welded. The specimens were placed in static corrosion in synthetic W water at 70°C. The average rate of increase of diameter of the first six specimens was very nearly the same as the rate observed with canned (unbonded and unplated) W

size slugs while the last two swelled only about one-half as rapidly. The inference being that the straight nickel plate offered some protection, but that the straight copper or the composite Cu-Ni or Cu-Cr plates did not. Longitudinal cracks were observed to start at the pin holes in the aluminum jacket after the diameter had increased about sixty mils. By the time the swelling had caused an increase of seventy to seventy-five mils, the cracks had grown to about an inch in length.

D. Reactor Cartridge

This proposed slug assembly for the another laboratory requires a corrosion resistant coating for the individual slugs during the "cooling" period following their discharge.

It is highly desirable that adequate protection be given the slugs before the unit is assembled. Since the allowable thicknesses of otherwise suitable single metal plates are not sufficient to permit the deposition of impervious plates as such, an investigation of composite, diffused plates was deemed worthwhile. Quite impervious coats have been obtained on steel by plating thin deposits of tin on copper followed by diffusion. Corronizing, another commercial method for protecting steel or brass, consists of plating 0.0002" of Zn over 0.0002" of Ni, and subsequent heat treatment.

The work carried out at Chicago is summarized in Table VI. Due, in part, to the lack of information regarding the composition and temperature of the water to be used in actual operation, corrosion tests were conducted in both synthetic W and distilled water at several temperatures. The small number of specimens tested and the fragmentary nature of the data do not justify any definite conclusions. The results in their present state are included in this report because no further work on this problem is anticipated.

A more detailed investigation of thin diffused plates is being conducted in Cleveland. Composite copper-tin plates, alloyed by heat treatment (300°C) in silicone fluid, have shown very good corrosion resistance at 350°C and 500°C in static distilled water. Specimens diffused by heating in vacuo have not shown such good protection, in fact, the results obtained by heat treating in silicone fluid have not been confirmed by other methods.

E. Diffusion of Electroplates

As mentioned earlier in this report, certain tuballoy alloys, those containing five percent nickel or five percent molybdenum, are approximately ten times more corrosion

TABLE V
STATIC CORROSION

SLUG NO.	INCREASE IN DIAMETER (MILS)				ELECTROPLATE
	24 Hrs.	264 Hrs.	552 Hrs.	984 Hrs.	
9	1.7	17.5	39.0	85.0	0.0005"Cu+0.0005"Ni
10	0.8	12.5	34.8	75.4	0.0005"Cu+0.0005"Ni
13	1.7	13.4	34.4	62.7	0.0005"Cu+0.0005"Cr
14	1.3	15.8	36.8	73.8	0.0005"Cu+0.0005"Cr
1	2.7	18.5	39.5	69.1	0.001"Cu
2	2.5	16.3	43.6	86.3	0.001"Cu
Average	1.8	15.8	38.0	75.4	
5	0.5	4.0	15.3	41.6	0.001"Ni
6	0.8	4.3	16.0	34.0	0.001"Ni
Average	0.6	4.1	15.6	37.8	

TABLE VI CORROSION DATA

NO.	PLATE	HEAT TREATMENT	CORROSION MEDIUM	TIME	RESULT
Sn 2	0.001"Cu+0.001"Sn	In vacuo, 300°C, 18 hrs.	Syn. "W" Water 70°C	6 days	Severe undercutting
Sn 3(1)	" "	" " "	" "	"	" "
Sn 4(1)	" "	In vacuo, 300°C, 125 hrs.	Syn. "W" water 50°C	22 days	" "
Sn 6(1)	" "	" " "	" "	"	Severe undercutting and pitting.
Sn 8	" "	" " "	" "	"	" "
Sn 20	0.0007"Cu+0.0001"Sn	In vacuo, 300°C, 142 hrs.	Distilled water, room temperature	30 days	Several large pits near the ends.
Sn 21	" "	" " "	" "	"	" "
Sn 28	0.001"N1+0.0001"Sn	In vacuo, 300°C, 48 hrs.	Syn. "W" Water 50°C	13 days	Severe pitting
Sn 29	" "	" " "	" "	"	" "
Sn 30	0.0007"Cu+0.0003"Sn	Silicone "500", 300°C, 3 hrs.	Distilled water, room temperature	30 days	Slight pitting on one end.
Sn 32(2)	" "	" " "	" "	"	No evidence of attack
Sn 33(3)	" "	" " "	" "	"	Slight pitting on one end.
Sn 34(2)	" "	" " "	" "	"	Slight pitting on one end.
N1 109	0.001"N1	None	Syn. "W" Water, 50°C	21 days	Very badly pitted
N1 107	"	"	" 70°C	6 days	" "
N1 151	"	"	Dist. Water Rm. Temp.	30 days	Considerable pitting

- (1) 3/8"x1/2" deep hole in ends of slug - no plate in holes.
 (2) CH₃Cl wash after silicone treatment.
 (3) Trichlorethylene wash after silicone treatment.

resistant than the unalloyed metal. The more recently investigated columbium alloys appear to be very inactive.

A report of experiments conducted by the Metallurgy Section on the diffusion of nickel and nickel-molybdenum (10-15% Mo) electroplates is being prepared by B. Nelson.

Although the corrosion data are rather inconsistent, a general lowering of the rate of attack on the diffused plates is apparent. The addition of small percentages of molybdenum to the nickel plate does not produce any marked change in the corrosion resistance.

The future program of the Electroplating Groups calls for the development of a suitable technique for plating and diffusing nickel, molybdenum, and, if possible, columbium and tantalum.

V. Electroplating on Metals Other Than Tuballoy

A. Aluminum

Electroplating on aluminum has been of considerable interest and importance. Copper, nickel, silver, and chromium have been plated on aluminum in cooperation with the various canning groups. Of the various methods tried, one developed by the Aluminum Company of America is considered to be the most generally applicable. The procedure recommended for 2S aluminum is as follows:

1. Cleaner: (immersion)
5% NaOH (by wt.), temp., 65°C, time - 30 sec.
2. Thorough wash in running water.
3. Pretreatment: (anodic)
Solution: 30% H_3PO_4 (by wt.)
Temperature: 30°C (not particularly critical)
Current Density: 10-12 Amps/ft.² - 25V.
Time: 8-12 minutes
Cathodes - Carbon
4. Thorough wash in running water.
5. Plating.

A modification of this process was used for plating the upper inside surface of aluminum cans with chromium for the zinc canning process. A thin plate of moderate adherence was desired as the purpose of the plate was to prevent wetting of the plated portion of the can wall by zinc during the canning operation.

1. Vapor degrease
2. Cleaner: (immersion)
5% NaOH (by wt.)
Temperature - room
Time - 1-2 minutes

3. Thorough wash in running water.
4. Pretreatment: (anodic)
 - Solution - 40% H_3PO_4 (by wt.)
 - Time - 5 minutes
 - Voltage - 25
 - Cathodes - Stainless steel or aluminum
5. Thorough wash in running water.
6. Chromium plating:
 - Solution - 400 grams/liter CrO_3
 - 4 grams/liter H_2SO_4
 - Current Density - 300 Amps/ft.²
 - Temperature - room
 - Time - 10 minutes
 - Anodes - lead + 6% Sb

The tops of approximately 3000 cans were plated by this procedure. Rejects, the percentage of which was quite low, were easily stripped prior to replating by anodic treatment in a 40% H_3PO_4 solution containing 15 cc/liter of concentrated H_2SO_4 .

B. Beryllium

The following procedures were investigated as pretreating media for beryllium.

1. Alternate dips in 1:1 HCl and 1:1 HNO_3 . Reaction with HCl was quite vigorous. The surface is quite deeply etched by this procedure exposing the crystal structure of the metal.
2. Anodic treatment in H_3PO_4 solution (40% by wt.) containing 20 cc/liter concentrated HCl.

The adherence of copper plated to the surfaces thus prepared was only fair, however, it was satisfactory for soldering purposes.

VI.

General Service Work

A. Rapid Corrosion of Aluminum (Weld Testing)

In order to determine the effective depth of weld on canned specimens, it was necessary to have a method for the uniform removal of aluminum from the weld bead. Pits and voids thus exposed could be detected in the vacuum leak tester. A method (6) was developed involving anodization in a nitric acid solution (35% by wt.) containing hydrofluoric acid (10% by vol.) maintained at a temperature of approximately 85°C. Continued use of this method indicated that the attack at the weld bead was not sufficiently uniform for routine testing.

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Another method was developed involving immersion of the welded end of the can in hot sodium hydroxide solution followed by a short dip in nitric acid solution to remove the black surface film remaining after the caustic treatment. Although this method has not been thoroughly tested, the results to date betoken uniform attack on aluminum.

B. Oxide Coats on Aluminum

One of the proposed methods for the detection of swollen slugs in a unit is based on the change in electrical conductance of a suitable assembly inserted between the slugs and the aluminum tube. A suggested assembly consists of an oxide coated aluminum wire enclosed in a thin walled, small bore aluminum tube. Experiments were conducted to investigate the methods of formation and the electrical resistance of synthetic oxide films on aluminum. A method (7) was developed by which it is possible to build up quite thick oxide coats that are uniform and adherent and which exhibit very very high electrical resistance. The procedure involves anodic treatment of aluminum in three percent oxalic acid solution at room temperature and 50 volts D.C. potential. Under these conditions, the rate of oxide formation is approximately 0.1 mil per 10 minutes.

C. Service Plating

The Electroplating Group has cooperated with other groups by doing a considerable quantity of service plating. Continuation of this service is anticipated, especially in regard to aluminum and tuballoy plating.

Written by:

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