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DIFFUSION OF ELECTROPLATES

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DIFFUSION OF ELECTROPLATES

Summary

Tuballoy slugs have been electroplated with nickel, copper over nickel, chromium over nickel and molybdenum with nickel. The electroplates were diffused by heating in rotating tube furnaces or by high frequency induction. The corrosion rates of these coated slugs was determined in synthetic W-water at 90°C.

The alloyed surface appeared to be attacked only slightly but localized corrosion at imperfections in the surface resulted in an overall corrosion rate for 1000 hours which was only 10 to 100 time less than that of pure tuballoy.

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Introduction

The diffusion study of electroplates has been carried on from the standpoint of obtaining a corrosion resistant layer on the surface of tuballoy slugs. As other investigations (MUC-JED-28) have indicated that the Ni-Tu alloys have higher corrosion resistance than tuballoy, the protective action of both nickel surfaces and nickel alloy surfaces has been studied. Most of the work was done on Ni plates, but Ni-Cu, Ni-Cr, Ni-Ag and Ni-Mo composite plates have been studied. As electroplates on tuballoy are, in the main, porous and do not have sufficient bonding to the tuballoy beneath, it seems likely that bonding may be improved by a diffusion treatment of some sort.

The Tu-Ni diagram shows the formation of a peritectic compound, Tu_2Ni , at about $780^{\circ}C$ with low nickel concentrations, and further, the formation of a eutectic at about $740^{\circ}C$ with higher nickel concentrations. Since the compound would effectively block further diffusion, it becomes necessary, for appreciable diffusion to occur, to heat the specimen to a temperature high enough to decompose this compound, and in this temperature range the eutectic is molten.

Experimental Procedure

It was decided, from a study of the Tu-Ni diagram, that for appreciable diffusion of nickel plates, and presumably, nickel alloy composite plates, a temperature above $815^{\circ}C$ must be used, and further it was thought that by rotating a tube containing the plated slug, the liquid eutectic film would be carried by centripetal forces along the side of the slug as it rotated against some ceramic material. It was further thought that this movement of the film would have a tendency to wash out oxides or other impurities which might be on the surface of the tuballoy; unfortunately, no direct evidence that this was accomplished was ever obtained.

Various times and methods of heating were used in this study. Two general methods of heating were used - (1) A relatively slow type of heating in a resistance furnace where the tube was rotated during the heating and cooling cycle, and (2) A fast type using high frequency inductive heating. Figure 1 shows schematically the set-up used for the rotating tube treatment, and Figure 2 that used for the inductive heating treatments in which the slug remained stationary.

The scheme of using a rotating evacuated tube needs to be examined in some detail. A fused silica tube was used at first, but because of its brittleness was later superseded by one of stainless steel; it was also becoming evident that smooth rotation was desirable and this was more easily obtained using a steel tube. The plated slug was loaded into a ceramic liner inside the diffusion tube together with suitable dummy slugs or ceramic spacers to hold the plated slug in the desired place, the tube closed with a gasket seal, evacuated, and closed off with a valve. The loaded assembly was placed in the furnace, heated until a recorder showed that a predetermined temperature, indicative of a temperature of $815^{\circ}C$ inside the tube, had been,

obtained, and further heated for a desired period at which time heating was discontinued. The tube was rotated usually during the heating and cooling cycle above 700°C. Due to the total weight of the assembly, including tube, slugs, liner, etc., a long period of heating was necessary to obtain the desired diffusion temperature. Under these conditions of heating the time actually at diffusion temperature loses much of its significance, being in the order of 1/2 to 2 hours, as compared with a total heating and cooling cycle of 14 to 18 hours.

The methods of heating and cooling employed when using the resistance furnace and a rotating evacuated tube are summarized here.

1. The loaded assembly put into a cold (i.e. 200°C or lower) furnace, the total unit heated to the desired temperature for the desired time and then slowly cooled.
2. The loaded assembly put into a hot (700°C approx.) furnace, heating continued to the desired point, and upon furnace cooling to 700°C, rotation stopped, the tube removed from the furnace and air cooled.
3. Various combinations of the two methods above, such as slow heating and fast cooling, or fast heating and slow cooling as well as intermediate rates of heating or cooling were also used. Because of other adverse conditions, no hard or fast conclusions could be drawn from a study of the heating and cooling rates, although it did seem that the method of slow heating and slow cooling would result in a slug with a somewhat better surface in cases where other factors remained substantially the same.

The use of a rotating tube with ceramic liners does not look promising because of contamination of the surface of the slug with refractory material. Graphite, sillimanite (Al_2SiO_5), zircofrax (ZrSiO_4) and alundum (Al_2O_3), the latter both unlined and lined with BeO, were used as a ceramic lining for the rotating tube. Graphite was quickly eliminated as a suitable material because of carbon pick-up. The silicate minerals were unsuitable because of silicon pick-up after reduction by the tuballoy. The use of the unlined or the BeO lined alundum likewise had its drawbacks, as due to the friable nature of these materials debris from the ceramic would inevitably be found pitting the slug or being stuck into it. Alundum liners must not be wholly discounted, however, as the use of some which had been fired at a higher temperature might have been entirely satisfactory. In the absence of such evidence, however, it may be strongly suspected that any moving tube containing a ceramic material would prove troublesome.

Attempts to diffuse plated slugs by rotating them in space, clamping them in a cradle having ceramic plugs at the ends and loading in the evacuated tube, were unsuccessful; the difficulty was that the liquid film would drop onto the stainless steel tube and eat through it rapidly or freeze the whole assembly, or else the cradle would come apart and let the entire slug roll haphazardly against the steel tube.

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Since the method of heating in space seemed to show some promise, it was decided to heat the slugs by an inductive method. This method was to place the slugs in an upright position on a ceramic block inside a glass cylinder, the assembly being tied to a vacuum pump and pumped continuously. A thermocouple in close proximity to the slug actuated a controller for an Ecco oscillator. The controller was calibrated with an optical pyrometer when the slugs were in the liminous range. With this type of set-up the desired temperatures were attained very quickly, and the degree of temperature control was very close. Some flowing of the diffusion coat was observed, as measured by dimensional changes, these changes in diameter being in the order of one mil, but a tendency for pores to be filled up was noticed; in itself a desirable attainment.

Metallographic Study of Diffused Electroplates

The metallographic studies of diffused electroplates as originally planned were not carried out because of time limitations. Somewhat scattered metallographic evidence which has been obtained in the course of corrosion work does allow some general conclusions to be drawn but since the evidence is rather fragmentary, conclusions must be drawn with some caution.

A. Studies on Plates Heated in Wire Wound Tube Furnaces.

1. For straight nickel plates alone, a temperature of 820°C or higher is required for appreciable diffusion to occur. Figure 3A shows the structure obtained at a temperature below that of the first eutectic. No portion of the specimen became molten and as would be expected from the phase diagram, at least two compounds have formed and these seem to have effectively blocked further diffusion. Figure 3B shows the structure obtained by heating above the eutectic temperature but below the peritectic temperature. This shows the eutectic and the first compound, Tu_6Ni , as would be expected. Both of these slugs were heated without rotation, and in the second case part of the film flowed away from the slug.
2. In general, at temperatures of 825°C or higher diffusion is rapid. The diffusion structure appears as solid eutectic or eutectoid for an appreciable distance, and, extending nearly as far again into the specimen, scattered diffusion is noted as though associated with grain boundary penetration. Figures 4A and 4B clearly illustrate this point. It is significant that even in the unetched condition, the penetration was visible often to the extent of 1/16" to 1/8".
3. While variations in time and temperature have an effect on the extent of diffusion, no definite conclusion regarding the extent of penetration of the diffusing element can as yet be drawn from the experiments so far performed. However, an analysis of Figures 4B, 5A and 5B may lead to these conclusions. The effect of small changes in temperature and time during a long heating and cooling cycle is rather small. As shown in both Figures 4B and 5A, the general type of diffusion structure consists of a solid eutectic or eutectoid band near the surface and the scattered stringers extending

far into the specimen. However, the effect of a long period at the diffusion temperature, during a long heating and cooling cycle, produces quite a change in the structure noted. As shown in Figure 5B the solid diffusion structure near the surface seems to be slightly broken up and the extent of penetration into the specimen is much greater.

4. The formation of a composite Ni-Cu plate, by adding the Cu as a flash over the Ni plate, seems to decrease the extent of diffusion. The diffusion structure appears more continuous near the edge and the scattered diffusion structure does not penetrate as deeply into the sample. A comparison of Figure 6A with Figures 4A and 4B shows that there is a marked decrease in the extent of diffusion when Cu was added to form a composite plate. Figure 6B which shows the structure obtained at a slightly lower temperature, shows substantially the same features, viz. that the diffusion structure seems to be concentrated near the edge of the specimen and that its extension into the sample is slight.
5. The addition of Cr to the Ni plate, to form a composite plate, has little, if any, influence on the diffusion process. If any conclusion is to be drawn, it is that it acts as does Cu in decreasing the extent of diffusion and resulting in a more nearly continuous diffusion structure near the surface. Figure 7 illustrates this point.
6. It is to be noted that both Ni-Cr alloys and Ni-Cu alloys are solid solutions in the temperature range employed, a fact which may explain their inhibiting effects on the diffusion process.

It might be well at this time to consider what effect the initial interface might have upon the problem of diffusion of these electroplated slugs. We may postulate that during heating brittle compounds form first and if the temperature becomes high enough, a liquid eutectic forms and these compounds decompose. To obtain smooth diffusion coats, it becomes necessary for the diffusion process to repair the damage done to the initial surface by the formation of these compounds and later the eutectic film. We may postulate three conditions under which the repairing of this damage might be difficult, if not impossible, and which would result in a poor surface on the diffused slug.

1. An imperfect electroplate due to poor adherence of the plate to the base metal. Figure 8A shows the structure of a tight plate and Figure 8B shows the structure of a poorly adherent plate.
2. A poor vacuum in the diffusion tube.
3. A condition in which the slug was not at the temperature expected due to its displacement in the tube during rotation.

Figure 11 shows the appearance of a slug which had a very poor surface after the heat treatment. This is, in general, the appearance of all slugs which show some type of loose coat after treatment. It may be of significance that oxide was always found underneath these loose flaky plates, even eliminating the cases where the tube remained evacuated, indicating the presence of oxide at the original interface.

B. Metallographic Studies on Plates Heated by Induction

Slugs which were plated with Ni and with Ni-Mo were sectioned and polished. Figures 8A and 8B show the appearance of undiffused Ni plated slugs. Figure 8A shows a plate which has relatively good adherence although there is some debris at the interface. Figure 8B shows a plated slug in one section of which extremely good adherence was obtained and adjacent to this, a section where considerable dirt was trapped beneath the plate. As previously stated, one objective in the diffusion operation was an attempt to wash out this debris during the diffusion treatment.

Figure 9 shows the structure obtained when a Ni-Mo plated slug was heated by induction for a relatively long time and Figure 10 that obtained after heating by induction for a relatively short time, the approximate times being 2 hours and 0.25 hours at temperature respectively. The apparatus was not calibrated for accurate temperature measurements and the temperature was estimated at $775^{\circ} - 250^{\circ}\text{C}$. Figure 9 shows that tuballoy has diffused outward while the nickel has gone inward, and the original interface is still discernable. Note the presence of what may be oxide at the interface boundary. This may be base metal oxide or an oxide of molybdenum. A structure due to molybdenum cannot be distinguished. In addition to the general diffusion which extends approximately 8-10 mils past the interface, there is shown another diffusion structure preferentially arranged, possibly at grain boundaries.

Figure 10 shows that with short heating times the diffusion structure does not appear as stringers extending into the tuballoy base metal but as a thin continuous band; the situation is somewhat analogous to that shown in Figures 4B, 5A and 5B.

The influence of molybdenum as a component of an alloy plate with nickel is not yet clear. It is to be remembered that molybdenum plates out with difficulty, and although a promising technique was developed by Mr. Rebol of the electroplating section, it has not yet been investigated thoroughly; it is entirely possible that the same difficulty is being experienced as has been shown before, namely, that an oxide of molybdenum is being laid down instead of molybdenum metal.

Corrosion Rates of Diffused Electroplates

Certain of the diffused plates were tested in static corrosion using a synthetic "W" water containing 1×10^{-4} H_2O_2 , 2-3 ppm Cl^- and temperature of 90°C . Table I gives a summary of corrosion rates for diffused nickel and nickel-copper composite plate. Table II gives similar data for codeposited Ni-Mo plates which were heated by induction. It cannot be too highly emphasized that these rates must be used only for comparison purposes, since we are often dealing with localized corrosion due to damaged plates,

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debris in the coat or thin spots in the coats. Nevertheless, the following observations seem to be of interest.

1. A diffused nickel coat increases the static corrosion resistance by a factor of 10 to 100 times over that of pure tuballoy.
2. The addition of copper or chromium as a component of a composite coat, in general decreases the static corrosion resistance over that of the diffused nickel coat by a factor 2 or 4, while still being higher than that of an uncoated slug.
3. Although it was expected that the Ni-Mo plates would have a higher static corrosion resistance than would Ni plates, because of the corrosion resistant natures of Ni-Mo alloys, the data does not show any marked increase in the static corrosion resistance of these diffused plates over that of Ni coats. We may postulate three reasons why these slugs should be no better than the slugs plated with Ni alone.
 - (a) The ternary Ni-Mo-Tu may be no more corrosion resistant than the Ni-Tu alloys.
 - (b) Since in the temperature and composition range employed the Ni-Mo alloys are alpha solid solution, the extent of diffusion may be decreased by the same factor which acted in the case of Ni-Cu or Ni-Cr.
 - (c) It may be that no metallic molybdenum was present in the plate, molybdenum being a difficult element to plate and, as mentioned previously, may have been in the form of an oxide.

The corrosion of all these slugs was very erratic, usually being by pinhole corrosion where the corrosion rates were low until the diffused plate was corroded through exposing the raw tuballoy below, at which point the rate increased by a large factor. Swelling of these slugs sometime occurred and portions of unattacked coats frequently scaled off.

An examination of Figures 11 through 13B gives a rather complete picture of how slugs which had been heated for relatively long periods stood up in the static corrosion tests. The attack was in two general phases; an overall corrosion of the diffused coating, and a specific attack which manifested itself in pinholing or local attack. The generalized corrosion at one end is believed to have been caused by increased aeration of the water at the surface, the slugs being suspended in water with a portion being above the surface. Particular attention is called to Figure 13B showing a corroded slug which developed a large cavity. Indeed, this slug practically exploded at this point and its effective diameter increased by some 25 to 30%. No satisfactory explanation can be given for this action, although it has been suggested that the formation of corrosion products in deep seated cracks may give rise to forces great enough to rupture the base metal.

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Examination of Figures 14A through 16 gives an indication of how corrosion occurred in coated slugs which had been heated for relatively short periods by induction. Figures 14A and 14B show the general nature of the corrosion of these slugs, where we have, in addition to the generalized attack, a type of corrosion in which pieces of material seem to be broken out as though the attack were associated with a channelling under the surface until a piece was free to fall out of the slug. Because of this tendency, corrosion rate studies do not have the significance they would otherwise have if the general overall type of attack was the only one present. Figure 16 shows the appearance of a slug which did not have good protection on one end, probably by a flowing downward of the liquid diffusion film. After corrosion, swelling and deep channeling in this area had occurred, and it is apparent that in a few places the interchannelling type of corrosion had also occurred as evidenced by the deep irregular holes. This picture seems to indicate clearly the absolute necessity of obtaining smooth diffused coats and of keeping dimensional changes during the heating to a minimum.

The diffusion problem as it has been studied so far seems to resolve itself into this statement: the diffusion process must result in a slug in which the dimensional changes are slight and constant, the diffused coat is adequately bonded to the slug, is free of pinholes, thin spots or other damage, and furthermore is highly corrosion resistant in itself.

References:

MUC-JED-28

Notebooks

42-B
837-B
1232
250-B

Prepared by _____

Submitted by _____

Section Chief

Approved by:

Division Director

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Associate Division Director

TABLE I

Corrosion Data on Diffused Nickel and Nickel-Copper Electroplates

No.	Plate	Diffusion Temp ^{OC}	Time (hrs.)	Corrosion Time (hrs.)	Corrosion Rate mg/cm ² /hr.
Raw Tu Slug	None			114 456	.9 1.1
D-21	Ni	856	4½	314 643 1011 1366	.18 .46 .41 .50
D-27	Ni	834	.56	334	.006
D-29	Ni	829	.67	334 726 1081	.012 .02 .28
D-19	Ni Cu	840	3	314 643 1011 1366	0.07 .05 .12 .14
D-20	Ni Cu	850	4½	314 643	.14 .40
D-26	Ni Cu	839	0.56	334 726 1081	.17 .08 .13
D-28	Ni Cu	829	.67	834 702 1057	.022 .06 .15
D-24	Ni Cu	848	3	317 643 1011 1366	.16 .37 .35 .28

TABLE II

Corrosion Studies on Diffused Ni/Mo Coplates

No.	Temp°C	Time (hrs.)	Corrosion Time (hrs.)	Corrosion Rate mg/cm ² /hr.
121	725	.08	936	.165
123	800	1.25	600	.075
124	775	.16	888	.085
125	815	.25	840	.136
126	815	.20	840	.145
127	775	2.0	600	.123
128	775	2.	600	.088
129	740	1.	504	.001
141	725	0.25	600	.355
146	740	1.	504	.120
152	740	1.33	600	.544
153	725	.33	600	.016

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ROTATING TUBE DIFFUSION

FIG. 1

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INDUCTION DIFFUSION FURNACE

FIG. 2

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Figure 3 Diffused Nickel Electroplate

A. Micro #1594 500 X

Tu

1st Compound $Tu_6Ni?$ 2nd Compound $TuNi?$

Ni.

Diffused 16 hours at $700^{\circ}C$ - No Rotation.

B. Micro #1177 500 X

Tu

Compound Tu_6Ni

Eutectic

Specimen #399 - Diffused $15\frac{1}{2}$ hours at $756^{\circ}C$
No Rotation.

Figure 4 Diffused Nickel Electroplate

Micro #2074 100 X

Specimen D-31
Diffused 40 Minutes at 835°C
Rotated Inside Zircofrax

Micro #2094 100 X

Specimen D-27
Diffused 35 Minutes at 838°C
Rotated Inside Sillimanite

Figure 5 Diffused Nickel Electroplate

A. Micro #2362 100 X

Specimen D-39
Diffused 45 Minutes at 850°C
Rotated Inside Zircofrax

B. Micro #3182 100 X

Specimen D-21
Diffused 4½ hours at 856°C
Rotated Inside Zircofrax

Figure 6 Diffused Ni/Cu Composite Electroplates

A. Micro #2090 100 X

Specimen D-26
Diffused 35 Minutes at 834°C
Rotated Inside Sillimanite

B. Micro #2095 100 X

Specimen D-28
Diffused 40 Minutes at 829°C
Rotated Inside Sillimanite

Figure 7 Diffused Ni/Cr Composite Electroplates

Specimen D-30
Diffused 40 Minutes at 835°C
Rotated Inside Zircofrax

Figures 8A - 8B Nickel Electroplates

A. Micro #2022 500 X

Rough Nickel Plate on Tuballoy

B. Micro #2016 500 X

Smooth Nickel Plate on Tuballoy

Figure 9 Diffused Ni/Mo Coplated Electroplate

Micro #3051

100 X

Tu

Diffusion Structure

Interface
Plate

Diffused Approximately 2 hours at
 $775 \pm 25^\circ\text{C}$ by Induction.

Figure 10 Diffused Ni/Mo Coplated Electroplate

Micro #3049

100 X

Tu

Diffusion Band

Diffused Approximately 0.25 hours
at $775 \pm 25^\circ\text{C}$ by Induction.

Figure 11 Diffused Nickel Electroplate

A. Macro #1304 1 1/3 X

B. Macro #1305 1 2/5 X

Specimen D-44
Diffused 20 Minutes at 852°C
Rotated Inside Ceramic Cradle

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Figure 12 Diffused and Corroded Nickel Electroplate

A. Macro #1295 1 1/3 X

Specimen D-27
Diffused 35 Minutes at 834°C
Rotated Inside Sillimanite
Corroded 334 hours at 90°C

B. Macro #1299 1 1/3 X

Specimen D-21
Diffused 4 1/2 hours at 850°C
Rotated Inside Zircofrax
Corroded 1366 hours at 90°C

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Figure 13 Diffused and Corroded Ni/Cu Composite Plate

A. Macro #1303 1 1/3 X

Specimen D-29
Diffused 0.56 hours at 834°C
Rotated Inside Sillimanite
Corroded 1081 hours at 90°C

B. Macro #1296 1 1/3 X

Specimen D-20
Diffused 4 1/2 hours at 856°C
Rotated Inside Zircofrax
Corroded 643 hours at 90°C

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Figure 14 Diffused and Corroded Ni/Mo Coplate

A. Macro #1316 1 X

Specimen 126
Diffused 0.2 hours at
815°C by Induction
Corroded 840 hours at 90°C

B. Macro #1314 1 X

Specimen 128
Diffused 2 hours at
775°C by Induction
Corroded 600 hours at 90°C

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Figure 15 Diffused and Corroded Ni/Mo Coplate

Macro #1313 1 X

Specimen 129
Diffused 1 hour at 741°C by Induction
Corroded 504 hours at 90°C

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Figure 16 Diffused and Corroded Ni/Mo Coplate

A. Macro #1317 1 X

B. Macro #1321 1 X

Specimen 125
Diffused 0.25 hours at 815°C by induction
Corroded 840 hours at 90°C

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