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The Electrolytic Deposition of Chromium Upon Aluminum

By

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of Butte

Butte, Montana
May 10, 1932
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Submitted as a part of the requirements for a degree of

Bachelor of Science

in

Metallurgical Engineering

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Montana School of Mines

by

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of

Butte

Supervised by

Professor J. U. MacEwan

Doctor A. E. Koenig

Doctor C. L. Wilson

Butte, Montana

May 10, 1932

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The Electrolytic Deposition of Chromium Upon Aluminum

Theoretical Considerations

History: Chromium plating from chromic acid baths has been known for 70 years. Only recently has it been used commercially. The first electro-deposition of chromium was made by Dunsen,

but Geuther seems to have been the first to obtain it from chromic acid solutions.

Carveth and Curry made a survey of all work done on chromium plating prior to 1905, and also submitted some new ideas of their own.

In September 1923 Schwartz gave a publication entitled, "Chromium Plating Steel Using Chromium Anodes".

In August 1925 a detailed description of electrodeposited chromium was published.

Usefulness: The prime factors for the use of chromium plate as a substitute for other electro deposited metals are:

1. High polish obtained.
2. Non-corrodibility.
3. Hardness.
4. Resistance to tarnish.

1) B. of S. No. 346 Tech. paper.--1927
5. Color and beauty.

Chromium has at present surpassed other metals in use in plating, because of the above characteristics; and furthermore, because it may be deposited economically for commercial use.

Mechanics of Chromium Plating

In plating tableware of intricate design there are a few difficulties which are not encountered in the laboratory. The articles are nickel plated then buffed and finally chromium plated. Antimonial lead anodes are placed so as to conform to the shape of the work being done. A 6% antimonial lead alloy has been found to make the best anodes.

Conditions for Plating in General

In order to obtain the highest efficiency, the chromic acid bath has to be maintained at a

2) C. A. Vol. 25--pp. 3248
relatively high temperature of 46-52 degrees C. The acid bath concentration has to be accurately controlled, the ratio being chromic acid molarity; sulphate normality :: 50 : 1. The current density also is fairly high, an average being 16 amperes per square decimeter.

Scope of Investigation

The purpose of this investigation is primarily to determine the best conditions for plating chromium on aluminum. The work was carried out with the hope of obtaining coherent deposits, and of determining the conditions under which such deposits may be duplicated. Another object was to obtain good throwing power in order to secure a well distributed deposit.

Experimentation

Mechanical and electrical apparatus are as shown on the diagram in Figure 1. The water in the bath is first heated and then held at a constant temperature by heat supplied from an electric light globe, the current being turned off and on by an electro-magnet in series with a gas-over-mercury thermostat.
Chromium Plating Apparatus

FBLT - Voehrge

Fig 1

Plan View

Dry Cells
Electro-Magnet
Thermostat
Light Globe
Cell
Stipper
Ammeter
Volmetter
SWITCH
Rheostat
End Projection
The electro-plating solution used throughout the work was made up as follows:

250 g. chromic acid per liter.
2.5 g. sulphuric acid per liter.

Plating Directly on Aluminum

As a chromium plate directly on aluminum was the ultimate desideratum, such plating was first attempted. The Aluminum was cleaned with a solution of sodium phosphate and sodium carbonate, after which a suitable deposit was secured. It was noticed that the preparation of the cathode was essential before attempting to plate. If the cathode was not rolled or buffed the deposit would in most instances crack and roll up. The rolling or cracking of the chromium plate tended to take place wherever there was a scratch or indentation. Due to the poor throwing power of the chromic acid solution, scratches and indentations tended to form lines and points of weakness from which the deposit would tend to break away. This is an example of the negative throw-
ing power of chromic acid baths.

In plating directly on aluminum the plating was of course, done over the oxide film which forms as soon as aluminum comes in contact with air or water. The oxide film seemed to be detrimental in making the chromium adhere to the aluminum.

**Plating with Copper**

As copper tends to form a smooth coherent electro-plate, this metal was used as a base, by plating the copper from cuprous cyanide baths. An excess of cyanide was required in the bath in order to deter the formation of copper hydroxide. The solution had an excellent throwing power. Smooth deposits were obtained but they had very poor coherence to the aluminum. The current efficiency in the operation was as low as 12.4%. Because of the difficulties encountered in controlling the formation of the copper oxide, the copper plating on the aluminum was abandoned.
Plating with Nickel

Nickel was found to give the best deposits on aluminum. It had the best coherence and required the least amount of buffing. An ammonium nickel sulphate bath was used with nickel chloride as an addition for the control of the nickel anode passivity. The bath was saturated with nickel ions. Nickel chloride helps control the passivity of the nickel anode and adds nickel ions to the solution and increases the conductivity of the electrolyte. A very low current density of 0.45 amperes per square decimeter was found to give the best deposits at a temperature of 20 degrees C. The solution had an excellent throwing power.

Chromium, plated on the nickel, could be bent about 30 degrees without cracking. Bright deposits of chromium were obtained on the nickel with a current density of 8 amperes per square decimeter at a temperature of about 45 degrees C. The main difficulty found in these plates was not the coherence of the chromium to the nickel, but of the nickel to the aluminum.

An attempt was made to make the nickel more coherent to the aluminum by means of annealing the
nickel plated aluminum at a temperature of 600 degrees C. for various lengths of time. Due to the unequal expansion of the metals and the affinity of nickel for oxygen, this was found to be impracticable. On the plates, where the nickel was not oxidized or peeled off by the unequal expansion of the plates, the nickel adhered very closely to the aluminum.

Plating Aluminum with Another Metal from a Solution

It seems that in order to get a good deposit on aluminum the oxide must first be dissolved off and then another metal plated directly on it before it could oxidize again, hence, an aqueous solution of sodium zincate with an excess of sodium hydroxide was used. The sodium hydroxide tended to dissolve the aluminum oxide off, after which the aluminum replaced the zinc in the solution and made a thin deposit of metallic zinc on the plate. This deposit was almost always obtained in a powdery form, because of the evolution of hydrogen gas about the plate. The hydrogen came from the decomposition of the water by metallic aluminum. It was impossible to get a good plating of chromium on the zinc as
Aluminum plates dipped in a fused sodium zinc-cate bath, made by dissolving zinc oxide in molten sodium hydroxide became coated with a plating of zinc immediately. This zinc plate was very coherent and formed a good base for chrome plating. The aluminum plate was annealed in this operation.

Control and Analysis of the Solutions

Bent cathode test: The bent cathode test was used to determine the sulphate content of the plating solution. A bent cathode is put in the solution and plated for about a minute. If the solution showed a poor throwing power, more sulphate was added. This method is used on a commercial scale by the General Motors Company, but it was not applicable in the present investigation as the plating was on too small a scale and correct use of this method demands an acquired technique.

Sulphate analysis: The reactions necessary for sulphate analysis are as follows:

1. Reduce the chromic to chromous ions.
2. Form chromium acetate.
3. Precipitate the sulphate with barium chloride.

7 cc. of HCl, 25 cc. of acetic acid, and 20 cc. of ethyl alcohol were added to the sample of solution to be analyzed. It was then boiled and the chromic ions were reduced to chromous ions by the alcohol. The sulphate was precipitated with barium chloride.

Determination of the chromic ions: A sample of the solution was titrated with ferrous ammonium sulphate solution, which was made up of 40 g. of ferrous ammonium sulphate and 75 cc. of sulphuric acid per liter. It was standardized against a standard potassium permanganate solution. Potassium ferri-cyanide was used as an outside indicator in order to eliminate the difficulty of distinguishing the end point obtained by titrating back with potassium permanganate solution. It took about 0.3 cc. of the

ferrous ammonium sulphate solution to make a distinguishable end point in a 600 cc. dilution.

Determination of chromous ions: To a sample of the solution, 25 cc. of sulphuric acid and a few drops of a dilute manganese sulphate solution were added. It was then brought to a boil and 10 cc. of silver nitrate solution, containing 2.5 g. per liter of silver nitrate, was added to precipitate chlorides. Then 20 cc. of a 10% ammonium persulphate solution was added to oxidize the chromous ions. The end of the reaction was indicated by the formation of permanganic acid from the manganese sulphate. The addition of 3 cc. of HCl decomposed the permanganic acid. The solution was thoroughly boiled and titrated with ferrous ammonium sulphate solution. By the difference of the chromic ion analysis and the chromous ion analysis, the amount of chromous ions present was found.
Results

A graph illustrating the importance of current density and temperature is reproduced in Fig. 2. The bright deposit is the one desired; the conditions are: 46 to 52 degrees C., 15 to 16 amperes per square decimeter. The control of temperature will be elaborated upon later.

Lifting the cathodes from the baths more frequently than once in every two minutes prevents deposition, wherefore hydrogen is not entirely eliminated. Removal at less frequent intervals mere-

6) E. of S. Tech. Paper No. 346--1927
ly reduces the efficiency of deposition. Stirring decreases current efficiency and vigorous stirring stops deposition entirely. Silica gel was added to decrease convection currents, but the throwing power was affected.

The current efficiency of chromium deposition is low as shown in Table 1.

Table 1: Deposition of Cr on Al sheet cathodes.

<table>
<thead>
<tr>
<th></th>
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<td>15</td>
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<td>1.50</td>
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<td>50</td>
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<td>1.53</td>
<td>1.50</td>
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<td>0.02</td>
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</table>
When 16 amp. per square decimeter is maintained the deposit may be scratched only by hard steel. This degree of hardness is quite desirable, especially on bumpers on automobiles.

Some of the deposits could be bent through an angle of 30 degrees without cracking.

The bright deposits are body centered and vary with increasing amounts of hexagonal close packed to dark deposits which are 85% hexagonal.

Analysis of the chromic acid solutions were made in order to have a control of the sulphate ions, and to maintain the chromic ion concentration, table 2.

<table>
<thead>
<tr>
<th>Plate</th>
<th>CrO$_3$ per L.</th>
<th>Chromous /L.</th>
<th>SO$_4$ /L.</th>
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<td>18</td>
<td>2.64</td>
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<tr>
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<td>199</td>
<td>10.8</td>
<td>2.49</td>
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<tr>
<td>6</td>
<td>186.4</td>
<td>12.4</td>
<td>2.69</td>
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<tr>
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<td>208</td>
<td>17</td>
<td>2.58</td>
</tr>
<tr>
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<td>204</td>
<td>19</td>
<td>2.71</td>
</tr>
<tr>
<td>9</td>
<td>196</td>
<td>15</td>
<td>2.64</td>
</tr>
</tbody>
</table>

Table 2.

The best deposits were obtained when two anodes were used, due to the negative throwing power of chromium.
Conclusions

1. The best deposits are obtained when the temperature is about 47 to 50 degrees C. with corresponding current density of 14 to 17 amperes per square decimeter. The efficiencies are relatively low ranging from 7.25% to 13.2%.

2. Lead anodes are used not only because of their suitability, but because of their low cost.

3. The anodes should have a large area in comparison with the cathodes. A ratio of 3:1 improves the uniformity of the deposits.

4. With lead anodes the ratio of the chromous ions to the chromic ions remains almost a constant. This is due to high oxygen over voltage on them.

5. Zinc from molten baths of sodium zinicate gave the most coherent deposit on the aluminum. This coherent deposit was not always reproducible, and in forming it the aluminum plate was annealed.

6. From observations obtained, the nickel did not cohere any better than the chromium to the aluminum. The nickel gave a smooth surface on which to plate the chromium and therefore the chromium did not require as much buffing, but aside from that, it did not present any advantage.
7. The chief function of the sulphate was found to be to increase the throwing power of the solution.