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The Electrodeposition of Copper-Cobalt Alloys

Richard L. Dunn

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Dunn, Richard L.

THE ELECTRODEPOSITION
of
COPPER-COBALT ALLOYS

A Thesis
Submitted to the Department of Chemistry
in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

by
Richard L. Dunn

MONTANA SCHOOL OF MINES
BUTTE, MONTANA
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ABSTRACT

An attempt was made to deposit a 50:50 copper-cobalt alloy from various sulfate electrolytes. No true 50:50 alloy was obtained but various mixtures of cobalt and copper rich crystals were deposited.

INTRODUCTION

"The codeposition of two or more metals so as to form a coat of alloy is an old art but a new science. Thirty years ago, two alloys were being plated on steel; today a wide variety of different alloys are commercially plated on a half dozen basis metals. Application of alloy plating includes decorative and protective finishes; linings for bearings; making special alloys which are too costly, or too difficult, or even impossible to prepare otherwise; making bonding layers to act as solder; electroforming thin sheets and thermopiles; special surfacing; etc.

"Alloy deposition is entering a period of increasing commercial interest. Many thousand pounds of useful alloys are being electrodeposited in decorative and protective finishing of metals and in engineering application. Alloy deposition in practice and research has shown some definite advantages. In general, one may expect alloy plates to be denser and harder than plates of the single metals involved. In certain composition ranges, alloy deposits have been found more corrosion resistant; more protective for the basis metal; brighter than either metal alone; more readily buffed; tougher and more suitable for subsequent plates; and deposited satisfactorily over a wider range of operating conditions than can one or both of the individual metals. In several instances current effi-

ciency has been improved and actual deposition of a metal such as tungsten, or deposition of nickel and iron from cyanide baths, has been made possible by codeposition with a second metal. Electrodeposited alloys usually have extraordinarily fine grain size, uniform structure, and are amenable to the customary metallurgical heat-treatments. The alloys are produced cold, hence need not be subjected to undesirable heating.¹

The above mentioned circumstances explain the growing interest in alloy plating and the great amount of research now being done on the subject. Probably the main alloys now being deposited commercially are brass^{1, 2, 3, 4, 5} and nickel-cobalt^{6, 7}. In addition to these two, many others are being plated out at least on a laboratory scale. These include Cu-Sn, Pb-Ti³, Ni-Cu,³ Ni-Fe,³ Cu-Ni-Zn,⁸ Au alloys,⁹ Ag-Pb, Fe-W,¹¹ Ni-W,¹² Co-W,¹³ Ni-Zn,¹⁴ Fe-Mn,¹⁵ in addition to many others.

For the above reasons, alloy plating was chosen as the field for this thesis. Copper-cobalt deposition was singled out because no successful alloy of 25 to 75% copper and the balance cobalt had ever been made by this or any other means so far as could be determined in the available literature.

THEORY

Success in alloy deposition depends on an empirical knowledge of the effect of the several variables on the plate deposition.¹⁷ Following is a list of the common variables in alloy plating and their general effect on the deposits.

Current Density: An increase in current density tends to increase the proportion of the less noble metal in the alloy plate.¹⁸ Also it will cause an increase in hydrogen evolution, thus cutting down on the efficiency and perhaps resulting in a porous and poorly adherent deposit.

Agitation: Increasing the agitation will usually increase the proportion of the more noble metal in the deposit.¹⁹

Temperature: Higher temperatures normally favor the deposition of the more noble metal and the evolution of more hydrogen. It decreases the electrical resistance of the bath and therefore may improve the efficiency of the operation.

pH: Decreasing the pH will cause an increase in the evolution of hydrogen with the accompanying ill effects. This also usually affects the composition of the cathode deposit one way or another. This is usually the result of its effect on other variables.¹⁹

PREVIOUS ATTEMPTS TO MAKE A 50:50 COPPER-COBALT ALLOY

To prepare a workable alloy of equal parts of copper and cobalt has so far not met with success when resorting to ordinary fusion methods.¹⁶ Attempts by Fink and Hutton to produce one by the electrolysis of sulfate solutions also failed,¹⁶ as did trials by Fink and Delisle with powder metallurgy.¹⁶

In the summary of their paper on the codeposition of copper and cobalt, Fink and Hutton made the following statements:

"In spite of wide variation of plating conditions in the sulfate bath no true alloy (of say 25 to 75% of copper by weight and the balance cobalt) was obtained by codeposition. It was found that the deposit was either substantially cobalt or substantially copper, depending upon relatively slight variations in pH, current density, bath temperature, and metal ion concentration and proportion. It is indicated that the cathode product is largely a matter of cathode film pH and proportion of cobalt to copper ion concentration. It would seem possible to obtain by codeposition a true cobalt-copper alloy, of say equal parts by weight, provided the cathode film pH and the cobalt to copper ion proportion were closely regulated and controlled.¹⁶"

METHOD

The electroplating was done in a 250 cc. beaker with graphite electrodes. These had a diameter of 0.6 cm. and a length of about 12 cm. Current was supplied by lead storage batteries. The current density was controlled by regulating the number of cells connected in the circuit and by a rheostat connected in series with the electrolytic cell. The cathode was rotated by means of an automatic stirrer which ran on 110 volt, 60 cycle alternating current.

Three different solutions were prepared in the course of the work. These were stored in 500 cc. bottles and used as needed. The various electrolytes were made by mixing these in various proportions always maintaining a total bath volume of 100 cc. The three solutions are listed below with their compositions.

- | | |
|------------|--|
| Solution A | 200 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per L. |
| Solution B | Saturated with CoSO_4 and 40 g. boric acid per L. |
| Solution C | Saturated with CoSO_4 . |

The solutions were made by dissolving the salts and the acid in boiling hot water. The stock supply of

cobalt sulfate was partially dehydrated so the exact composition of solutions "B" and "C" could not be readily determined. These two solutions were saturated at room temperature due to the excess salt crystallizing out as the bottles cooled.

The apparatus was set up and then connected to the batteries. When cathode rotation was used, the stirrer was set in action before applying the current. The rheostat was adjusted so as to get the desired current density. Deposition was continued just long enough for a substantial coating to form. The cathode speed, ammeter reading, relative speed of the cathode, etc. were recorded. After this the cathode was dipped into nitric acid until the coating dissolved and then was rinsed twice in successive beakers of distilled water. The deposition was then repeated with the same cathode and the desired changes in conditions.

At first difficulty arose due to nitric acid collecting in the porous core of the electrode, but this was overcome by dipping the tip of each cathode used in molten parafin and allowing it to harden. This filled the pore spaces and no further trouble due to nitric acid contamination of the electrolyte was encountered.

The compositions of the deposits were estimated by the color of the plates and lay the relative number of white and copper colored crystals.

RESULTS

At first some of the work already done by Fink and Hutton at Columbia University, New York City, was repeated.¹⁶ Various mixtures of "A", the CuSO_4 solution, and "B", the CoSO_4 and H_3BO_4 solution, were made up and tried. No appreciable amount of cobalt was deposited until the mixture was cobalt rich to the extent of about 70% "B". Then an irregular mixture of cobalt and copper plated out on the side of the graphite cathode facing the anode, and essentially copper on the opposite side.

With cathode rotation and various current densities, it was found that electrolytes containing from 93 to 97% "B" or "C" and the balance "A", gave the most promise of depositing a 50:50 copper-cobalt alloy.

Effect of Cathode Rotation

No definite bearing of cathode speed on the relative amounts of the two metals deposited was established. However it was noticed that with rotation a stronger relative cobalt ion concentration was necessary in order for a noticeable amount of cobalt to show. This might have been due to the unreliability of the sight method of determining the composition instead of to less cobalt actually depositing.

The effect of cathode speed on the character of the deposit was very apparent. At slow speed the deposits were in streaks, and at high speeds they were poorly adherent and lacking in luster. The most desirable rate seemed to be about 600 r. p. m.

Effect of Current Density

As would be expected, higher current densities favored the deposition of greater amounts of cobalt at the expense of copper. Various current densities from 2 amp./dm² to 40 amp./dm² were tried. However, on the basis of the results obtained, no generalities could be made as to the effect of current density on the character of the deposits. The best results were gotten at about 17 amp./sq. dm., although some promising results were obtained with about 10.

Effect of Temperature

In the electrolytes where the pH was regulated by boric acid, higher temperatures favored the deposition of cobalt; whereas in electrolytes using citric acid, the opposite effect was indicated.

At higher temperatures, the coatings were dull and poorly adherent. The best results were obtained at about room temperature or slightly warmer.

Effect of Additions

Various addition agents were tried including nickel sulfate, citric acid (to the boric acid bath), sodium citrate, gelatin, and dupinol.

The nickel ion seemed to favor the deposition of cobalt but was harmful to the character of the coating. It probably had this effect because of its favoring the evolution of more hydrogen and thus causing pit formation and poor adherence.

Citric acid, 10 g. per L. was added to the boric acid bath in an effort to prevent the formation of a blue precipitate (probably hydroxides) which had been giving trouble. No hydroxides precipitated in this bath but the deposits were poorly adherent. Addition of sodium citrate (10 g./L) resulted in a fairly good deposit of coarse cobalt and copper crystals, about 50-50. See Bath "1" on Page 10.

The addition of a small amount of gelatin had no noticeable effect on the deposit, but dupinol seemed to improve the luster and adherence while reducing the pitting. This was probably due to its being a wetting agent and thus causing the hydrogen to be rapidly removed from the cathode.

Effect of Agitation

Due to the formation of the hydroxide precipitate mentioned above, agitation with a stirring rod in addition to cathode rotation was resorted to during electrolysis in order to decrease the pH of the cathode film. This prevented the formation of the damaging precipitate. It also reduced the pitting and improved the properties of the deposit in general.

Use of Copper Cathodes

It was thought likely that deposition might be better on copper than on graphite. As no suitable copper cathodes were available, a coating of copper was first put on a graphite electrode and this was used before having a chance to oxidize.

This resulted in improved deposits which were probably due to the overvoltage of hydrogen being greater on copper than on graphite, and thus reducing its evolution and accompanying ill effects.

Use of a Citric Acid Bath

In an effort to improve the deposits, electrolytes containing various amounts of citric acid were tried. The resulting coatings seemed to be more fine grained, less pitted, and smoother than the plates obtained from the boric acid baths. Also no hydroxide precipitates were formed. This effect was probably due to the change in the pH which resulted from the change in buffers.

Some Promising Baths and Conditions

Fairly good deposits of a mixture of cobalt and copper grains were obtained with the baths and conditions listed below. All deposits would probably have been improved by the use of a copper or copper plated cathode instead of a graphite one. The listed compositions of the deposits are estimates based on the appearance of the plates.

1. Bath:

97 cc. cobalt, boric acid solution (B).

3 cc. copper solution (C).

1 g. citric acid.

1 g. sodium citrate

0.1 g. nickel sulphate.

Conditions:

Temperature 25° C.
Current density 15 amp./sq. dm.
Cathode speed 300 r. p. m.

Deposit:

Coarse dull crystals which were about 50:50
copper and cobalt.

2. Bath:

94 cc. "B".

6 cc. "A".

Conditions:

Temperature 25° C.
Current density 17 amp./sq. dm.
Cathode speed 600 r. p. m.

(Also brisk agitation.)

Deposit:

Fine grained cobalt with similar copper grains
imbedded in it. It appeared to be about 30% copper.
The plate was rather dull but adherent.

3. Bath:

95 cc. concentrated CoSO_4 solution (C).

5 cc. "A".

2 g. citric acid.

Conditions:

Temperature 52° C.
Current density 26 amp./sq. dm.
Cathode speed 600 r. p. m.

Deposit:

Fine grained and adherent but with a dull luster.
The color indicated that both copper and cobalt were
present.

CONCLUSIONS

No deposit which could possibly be a good cobalt-copper alloy having a composition of 25 to 75% copper was obtained. It seems probable, that with the proper conditions, a fine-grained aggregate of copper and cobalt, crystals could be plated from a sulfate bath. However, even then it seems unlikely that the plate would have such value commercially.

The effect of pH and various addition agents should be investigated more thoroughly.

BIBLIOGRAPHY

1. Faust, Charles L., Special Vol., Modern Electroplating, Electroches. Soc., 59, (1942).
2. Coats, H. P., Sp. Vol., Modern Electroplating, Electroches, Soc., 87, (1942).
3. Mantell, C. L., Industrial Electrochemistry, Sec. Ed., 206 to 209, (1940).
4. Monaweck, J. H., Trans. Electrochem, Soc., 82, 59, (1942).
5. Thompson, Maurice de Kay, Theoretical and Applied Electrochemistry, 154, (1939).
6. Soderberg, Pinner, and Baker, Sp. Vol., Modern Electroplating, Electroches, Soc., 145, (1942).
7. Weiseberg, L., Trans. Electroches, Soc., 73, 145, (1935).
8. Faust and Montillon, Trans. Electrochem. Soc., 73, 417, (1938).
9. Weisberg, L. Trans. Electrochem. Soc., 73, 431, (1938).
10. Faust and Thomas, Trans. Electrochem. Soc., 73, 431, (1939).
11. Holt and Black, Trans Electrochem. Soc. 82, 205, (1942).
12. Holt and Nielson, Trans. Electrochem. Soc., 82, 193, (1942).
13. Holt and Black, Trans. Electrochem. Soc., 84, 353, (1943).
14. Lustman, Benjamin, Trans. Electrochem. Soc., 85, 363, (1943).
15. Roberts, Earl C., A Thesis on the Electrodeposition of Iron Manganese Alloys, Montana School of Mines, Butte, Montana, (1943).
16. Fink and Hutton, Trans. Electrochem. Soc., 85, 191, (1944), (Breprint).
17. Faust, C. L., Electrochem. Soc., Special Edition, Modern Electroplating, 61, (1942).
- 18 & 19. See 17, pages 78 & 79.

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