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THE ELECTRODEPOSITION
OF
IRON-MANGANESE 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
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Abstract

An electrodeposition of an iron-manganese alloy was made from the same conditions determined by previous research. Various addition agents were experimented with in an attempt to produce better conditions for electrodeposition. It was found advantageous to add small amounts of sodium lauryl sulfate and ammonium sulfite to the electrolyte. Further experimentation revealed that the use of an insoluble anode and increased distances between the electrodes produced undesirable results.

Introduction

This thesis is primarily concerned with work carried out in connection with the codeposition of two metals. Codeposition may be defined as the simultaneous deposition of two metals, brought about by passing an electric current through a solution containing the ions of both metals. Codeposition of two metals may take place only when their equilibrium potentials in a given electrolyte are relatively close.

Alloy deposition by electrolytic means has received considerable attention in recent years, and a great many different combinations of metals have been successfully deposited. The principal alloy commercially electrodeposited on an industrially important scale is brass; however, there are indications that other such alloys will become equally important. A number of other alloys are now plated, some to a considerable commercial extent, and others only in very limited amounts. Important among these are the nickel-iron alloys (particularly the valuable Permalloy), copper-tin alloys (bronze), and also certain alloys of the precious metals, which are plated for reflectors.[1]

Electrodeposited metals usually have extraordinarily fine grain size and uniformity of structure. They, therefore, produce surfaces which may have properties, for instance hardness, superior to those of similar surfaces produced by other means.

The object of the work here described is, by experimental work in the laboratory, to determine the factors which improve the conditions of deposition of iron-manganese alloys as they have been determined by previous research.[2] In the present study, experiments have been made with the use of addition agents, with variations in bath temperature, with changes in the distance between the electrodes, and with the effects of using an insoluble anode.

Theory of Codeposition of Metals

When a current is passed through a solution, part of the current is carried by migration of the negative ions present, and part by the positive ions. The result is that the negative ions are precipitated or positive ions are dissolved at the anode, and positive ions are deposited at the cathode. In the case of a metal-ion bearing solution, the metal will be plated out on the cathode. It must be understood that a definite minimum potential or voltage (the decomposition voltage) must be maintained befor an appreciable current will flow, the potential required varying with the nature of the salt present in the solution, and with the concentration of the salt in the solution.

When salts of two different metals are present in a solution being electrolyzed at a given voltage, the salt having the lower decomposition potential will decompose first, and, when the deposition of the metal from that salt is complete, the current flow will practically cease. Then, if the applied voltage is raised sufficiently to exceed the decomposition potential of the second salt, the second metal will be deposited. Codeposition of the two metals may occur only when their equilibrium potentials in a given electrolyte are very nearly the same; this is accomplished chiefly by altering the concentrations of the two salts which are the sources of metal-ions in the solution.

The theoretical voltage required to deposit a metal from a solution of a given concentration may be calculated from the following equation:

$$E = E^{\circ} + \frac{RT}{NF} \ln A$$ [3]

Where:

E - theoretical decomposition potential

E° = single electrode potential of the metal

R = gas constant expressed in calories (1.985)

T = absolute temperature

F = current required to deposit one equivalent of metal (96,500 coulombs)

N = valence change which takes place in deposition

$\ln A$ = natural logarithm of metal-ion activity

At 25° C:

$$E = E^{\circ} + \frac{0.0592}{N} \ln A$$

To determine the ion-activity theoretically necessary for the deposition of an alloy the following method of calculation is used:

First, the electromotive force (E) is determined by use of the above equation for one of the metal ions, assuming a given activity of that ion, preferably a unit activity.

The electromotive force thus found necessary for deposition of the first metal is then substituted for (E) in the equation for the second metal:

$$E = E^{\circ}_{2} + \frac{0.0592}{N_2} \ln A_2$$

Since (E) has already been determined and $E^o{}_2$ and N_2 have known values for the second metal, this equation may now be solved for A_2. A_2 represents the activity of the second metal ion which must be present to allow deposition of that metal by an applied potential (E).

Therefore, with the metal ions present in solution in activities A (assumed) and A_2 (calculated) for the first and second metals respectively, application of a potential (E) to the electrolytic cell should cause both metals to deposit on the cathode simultaneously.

Unfortunately, the metal ion activities calculated by the above method are usually erroneous. Values of the single electrode potentials for a given metal are different for acetates, cyanides, chlorates, or other anions than for sulphates, for which the values are usually determined. Also, the simultaneous presence in the solution of another salt may change conditions, because of secondary reactions, so that values so calculated are far from correct. Therefore, the equation is of little practical value.

Actually, the determination of the activity or concentration of salts and of the voltage required for codeposition of two metals is accomplished entirely by trial and error, rather than by the theoretical calculations described. The latter are, however, of interest in illustrating the principles involved in alloy deposition.

Previous Work Done

As a thesis problem, E. C. Roberts in 1942 - 1943[4] carried out a program of research to determine the optimum cell conditions for deposition on an iron-manganese alloy. Previous to Roberts' work, Fink and Kolodney[5] had done considerable work on this problem, and were able to deposit such an alloy from a bath containing salts of ferrous ammonium sulfate, manganous sulfate, and ammonium sulfate. This was fundamentally the same solution as that used by Roberts, his differing from it only in concentration.

Roberts' data reveals, however, that electrodeposition for a longer period than three minutes produced a poorly adherent deposit.

Roberts' best results were obtained by the use of the following bath conditions:

Bath solution:

$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$----------------100g/1.
$MnSO_4 \cdot 2H_2O$--------------------------190g/1.
$(NH_4)_2SO_4$-------------------------- 40g/1.

pH---------------------------------- 1.5
Current density ----------- 6 amps/sq. dm.
Temperature ---------------------- 20° C.
Separation of electrodes ----------1 inch.
Time -------------------------------15 Min.
Voltage drop --------------------1.6 volts.
Area of anode and of cathode ---15 sq. cm.

Results:

Weight of deposit ---------------------0.2264 g.

Percent manganese in alloy ----------- 51.5 %

Current efficiency ------------------- 87.5 %

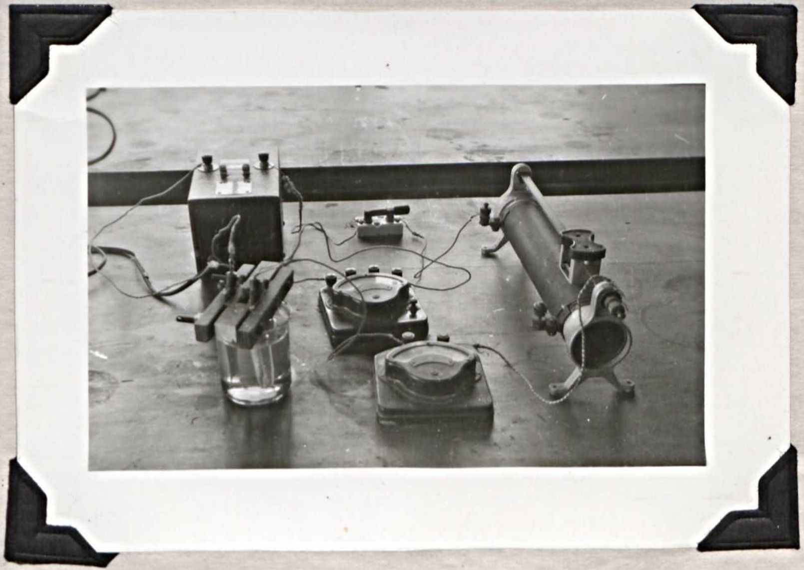
Laboratory Apparatus Used

The apparatus used is as follows:

1 Cenco Transformer-Rectifier set.
1 Weston Ammeter.
1 Weston Voltmeter.
1 Rheostat.
A Beckman pH meter.

At first a 150 cc. beaker was used for the cell, but later a 250 cc. beaker was used because the throwing power was much better. A steel anode and copper cathode were used; both were 3½ centimeters wide and were immersed to a depth of 5 centimeters in the bath, giving anode and cathode areas equal to 17.5 square centimeters. An amperage of 3 amps per square decimeter was used.

Below is a picture of the apparatus.



Experimental Results

In the first experimental electrolysis, an attempt was made to reproduce the results obtained by Roberts. A copper cathode and an iron anode were used, in a solution containing the following:

$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$-------------------100g/1.
$MnSO_4 \cdot 4H_2O$----------------------------227g/1.
$(NH_4)_2SO_4$---------------------------- 40g/1.

The solution was adjusted to pH of 1.5 by adding sulfuric acid. The electrodes were placed one inch apart and the applied voltage was regulated by means of a rheostat to maintain a current density of 3 amperes per square decimeter of electrode surface.

The resulting deposit was bright and fine-grained; however, near the edges of the cathode, the deposited metal was flaky and non-adherent. A heavy coating of MnO_2 was formed on the anode, indicating the need for a diaphragm to prevent the contamination of the catholyte if electrolysis is to be carried on over a period of time. A qualitative analysis indicated the presence of manganese in the electrodeposit.

Varying the pH of the Solution

Keeping the concentration of the solution, the current density and the electrode spacing constant, the pH of the solution was varied to determine at what pH the best deposition would take place.

Time = 30 min.; C.D. = 3 amps/sq.dm.; Cathode area = 17.5 sq.cm.; $MnSO_4 \cdot 4H_2O$ ---227 g/l.; $(NH_4)_2SO_4$---40 g/l.; $FeSO_4.(NH_4)_2SO_4.6H_2O$---100g/l.

pH	Volts	Wt. of Dep.	Curr.Eff.	Remarks
1.0-1.3	1.05	0.0152	5.9%	Deposit was bright and poorly distributed; poor eff.
1.5-1.9	1.25	0.1189	46.2%	Deposit was bright and adherent; good throwing power; flaky in places.
2.0-2.4	1.30	0.1193	46.3%	Deposit was bright but was flaky at the bottom of cathode.
2.5-2.9	1.32	0.1183	45.8%	Deposit was grayish and poorly adherent.

The best deposition is obtained by maintaining a pH between the limits of 1.5 and 2.0. A great deal of care must be taken in cleaning the cathode and removing any oxidized coating before electroplating is attempted; otherwise, the coating produced will be faulty, and erroneous conclusions will be drawn concerning the effect of other conditions.

In every case a qualitative test showed manganese to be present in the cathode deposit.

These determinations were made as follows:

Because the electrodeposit usually adhered closely to the cathode and was difficult to remove by mechanical means, the deposited alloy was taken into solution by dipping the coated electrode into HCl, this acid being used because it would not attack the copper cathode after the plated coating had been dissolved. The solution so produced was then boiled dry to remove all chloride ions; otherwise if the removal of chlorides was not complete, the test would not work. The residue from this evaporation was taken up with HNO_3, and this solution was poured into a test tube containing lead dioxide. The test-tube was then heated slightly and allowed to stand until the solids settled. A pink supernatant solution indicated the presence of manganese.

The approximate current efficiency was determined as follows:

In electrolysis, 96,500 coulombs of electricity will deposit one gram-equivalent of any metal.

An approximate value for the gram-equivalent of an iron manganese alloy would be 27.7, when iron is deposited from the ferrous ion, and manganese from the manganous.

The amount of alloy that should be deposited in thirty minutes with a current of one ampere, assuming 100% efficiency, is, therefore:

$$\frac{96,500}{30 \times 60 \times 1} = \frac{27.7}{X}$$

$$X = 0.516 \text{ grams.}$$

The actual weight of the cathode deposit produced per ampere divided by this number gives the approximate current efficiency for each electrolysis.

Effect Of Using An Insoluble Anode

It was thought that the use of an insoluble anode might produce an alloy deposit having better physical properties. The fact that an insoluble anode would not have to be replaced might also prove advantageous in certain plating operations. A steel anode, made passive by dipping it in concentrated nitric acid, was used.

Results:

Time = 15 min.; C.D. = 3 amps/sq.dm.; cathode area = 17.5 sq. cm.; $MnSo_4.4H_2O$---227 g/l.; $(NH_4)_2SO_4$---40g/l.; $FeSO_4\cdot(NH_4)_2SO_4.6H_2O$---100 g/l.

pH	Volts	Wt. of Dep.	Curr. Eff.	Remarks
1.6-1.75	3.4	0.0632	48.8%	Deposit bright but rough. Poor throwing power.

From the above data, it is evident that the use of an insoluble anode is impracticable.

Addition Agents

In commercial practice, it has often been found advantageous to add colloidal or reducible substances to the electrolytic bath, to improve the quality of the cathode deposit. A wide range of high molecular weight organic products has been found to give smoother and finer grained deposits in certain specific cases.

Mantell's "Industrial Electrochemistry" states,[6]

> "Substances which increase the weight of the cathode deposit, i.e., are adsorbed, tend to reduce the size of the crystals in the deposit, whereas substances which do not vary the crystal size cause no increase in the weight of the deposit for the same amount of current."

In an attempt to improve the physical nature of the alloy deposit from the sulphate iron-manganese bath, several addition agents were tried.

Gelatin was added to the electrolyte in small quantities, but produced no noticeable change in the deposit. The amount used was two grams per liter of solution. The voltage drop across the cell was smaller than when the gelatin was not present but this was probably due to the fact that the temperature of the bath was higher.

Dreft (sodium lauryl sulfate) in a small amount, two grams per liter, was added to the electrolyte, and the following was observed:

1. The hydrogen bubbles passing off at the cathode were much smaller than when no such addition was made.
2. The alloy coating produced was smoother and seemed to be brighter.
3. There was no change in the voltage drop across the cell.

Due to lack of time, it was impossible to make a more thorough investigation of the effects of Dreft additions on the deposit. However, it appears to be a promising "brightener."

In the electrodeposition of manganese alone,[7] sulfite ions are added to the catholyte to increase the purity of the deposit, to improve its texture, and to reduce the tendency toward formation of nodular surfaces on the deposited metal. The presence of the sulfite ion in the anolyte eliminates the formation here of flocculent brown manganese-oxide hydrates, and the amount of adherent oxide formed on the anodes can be controlled by careful sulfite additions.

Since sulfite additions are so helpful in electrodepositing manganese alone, it seemed possible that similar additions might be beneficial in depositing iron and manganese together. Usually, in practice, the sulfite ion is added by passing sulphur dioxide through the solution. However, in the laboratory study of the effect of this addition, the use of ammonium sulfite was more convenient. The conditions and results of test electrolysis using this addition are outlined below:

Solution Concentration:

172g/l.----$MnSO_4 \cdot H_2O$
50g/l.----$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
40g/l.----$(NH_4)_2SO_4$
4g/l.----$(NH_4)_2SO_3$
C.D.-------3.amps/sq.dm.
V.D.-------0.9 volts.
pH-------1.5

Electrodes were one inch apart.

Results:

H_2S passed off at the cathode.
A brown precipitate formed in the solution.

Cathode deposit was black.
Some MnO_2 formed an anode.

From the above results, it was concluded that too much ammonium sulfite had been added. Therefore, in a second test the same concentrations given above were used, except that only one gram of ammonium sulfite per liter was used. Here the pH range was 1.8-2.0.

Results:

Voltage Drop was 1.17 volts.
Some H_2S gas passed off.
Throwing power was poor.
Some MnO_2 formed at the anode.

Again the same conditions were maintained using a concentration of one gram of ammonium sulfite per liter, but with a pH range of 1.3 to 1.5.

Results:

Voltage Drop was 1.22 volts.
No H_2S passed off.
Throwing power was the same as when sulfite ion was absent.
Some MnO_2 formed on anode, but no flocculent MnO_2 was present in the solution, even after electrolysis had been carried on for a considerable length of time (1 hour).
There was good deposition.

From the above results it seems desirable to add a small concentration of sulfite ions to the electrolyte to reduce or prevent contamination of the bath by MnO_2. This might allow continuous and effective operation of the cell for longer periods than had previously been possible.

Increasing The Distance Between The Electrodes

It seemed worthwhile to try electrolysis with an increased distance between the electrodes, in view of the possibility that a better deposit might result from this wider spacing.

Results:

Time = 30 min.; C.D. = 3 amps/sq.dm.; pH = 1.4 to 1.65; $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$---100g/l.; $(NH_4)_2SO_4$---40g/l.; $MnSO_4 \cdot H_2O$---172g/l.

Dist.	Volts	Wt. of Dep.	Curr. Eff.	Remarks
1 inch	1.25	0.1189	46.2%	Good deposit, slightly flaky only at edges.
1¼ inch	1.35	0.1140	44.2%	Small amount of scaling, throwing power quite poor.

From the above data it is evident that increasing the anode to cathode distance to one and one-quarter inches decreased the current efficiency, and the properties of the cathode deposit were inferior to those produced when the electrodes were more closely spaced. Since no advantages appeared to balance these effects, no further increase in electrode separation were attempted.

Summary Of Results

The experimental research outlined above revealed the following facts concerning codeposition of iron and manganese:

1. A pH in the range of 1.4 to 1.8 gives best conditions for deposition from the $MnSO_4$- $FeSO_4$ - $(NH_4)_2SO_4$ bath.
2. The use of an insoluble anode is undesirable, since it results in a cathode deposit of poor properties, and also increases the power requirement of the process.
3. An increase in distance between the electrodes reduced the efficiency of deposition, gave a less desirable cathode deposit, decreased throwing power and increased voltage drop. The desirability of close electrode spacing is, therefore, evident.
4. The presence of additions of sodium lauryl sulfate in the electrolyte seemed desirable in brightening and improving the physical nature of the deposit.
5. The addition of sulfite ions to the electrolyte offers promise in preventing contamination of the solution by the MnO_2 otherwise formed in large amounts.

Since the time available for research was very limited, it was impossible to determine exactly the amounts of $(NH_4)_2SO_3$ and Dreft which give the best results.

Applications And Suggestions For Further Investigation

A possible application of the electrodeposition of iron-manganese alloys would be to the build-up of worn parts or parts accidentally made undersize. Chromium is now commonly used for this purpose. However, if iron could be used in its place, the iron would have the advantage of cheapness (significant in large scale operations), and could subsequently be carburized and heat treated to the appropriate hardness.

In carburizing practice, manganese up to 1.5% is added to plain carbon steel to induce hardness or wear resistance in the carburized surface, and to increase the rate of carbon penetration.[8] The manganese lowers the transformation point of austenite and renders this transformation extremely sluggish. It, therefore, allows a better, more easily controlled case hardening operation, increases the depth of the hardened coating, and improves the hardness and wear resistance of the carburized surface.

To produce these particular effects, the manganese must be present only in small amounts--up to about 1.5%. An electrodeposit of this composition could probably be obtained by altering the concentration of the individual salts in the electrolyte.

In building up worn gears, this process would probably be very useful. Chromium plating is extremely brittle and in such applications can not stand the shocks encountered in use, whereas a carburized steel would give good service.

Other applications are:

1. Buildup of Hadfield steels (high Mn) in bulldozer parts, bucket lips, and other parts subject to extremely great wear conditions.
2. Ferromanganese alloys.

Because of the possible applications discussed above, it is apparent that the electrodeposition of iron-manganese alloys deserves further study. On the basis of the author's research, the following points seem to merit investigation:

1. The effect on bath conditions of increasing the temperature of the electrolyte.
2. Further investigation of the effects of addition agents in the electrolyte.
3. The use of two or more anodes to overcome the rather poor throwing power of the electrolyte.
4. Development of a continuous purification system for the electrolyte to provide a constant flow of solution free from impurities---This would probably make possible continuous operation of a given cell for much longer periods.
5. A further study of the deposition of low manganese alloys for such applications as electroplating worn parts to be subsequently case hardened---This could probably be accomplished by altering the concentrations of the individual salts in the solu-

tion, possibly accompanied by a variation of the pH of the bath.

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