

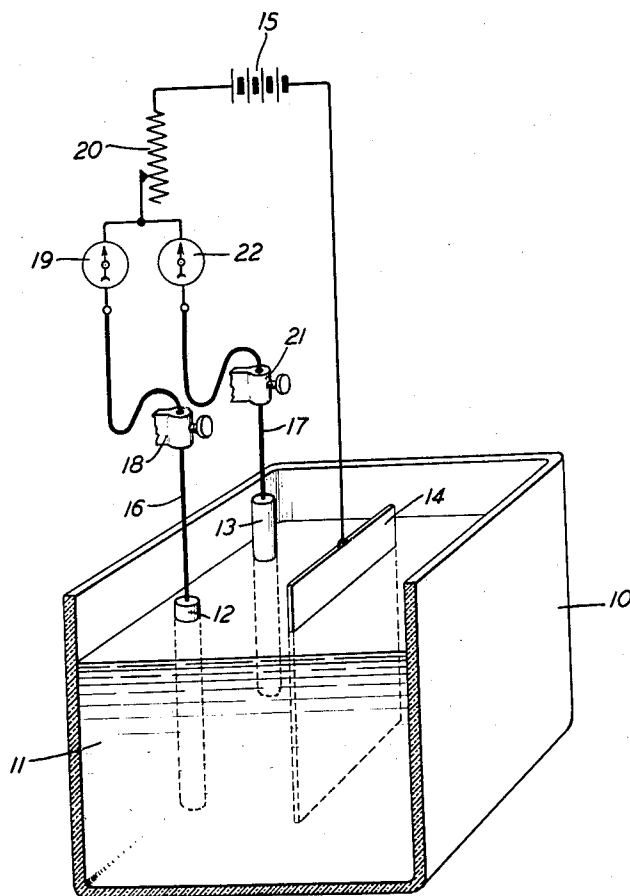
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ELECTRODEPOSITION OF ALLOYS

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ELECTRODEPOSITION OF ALLOYS

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This invention relates to electrochemical processes and more particularly to the electrodeposition of alloys.

An object of this invention is to electrochemically deposit a nickel-iron alloy which will have a substantially uniform composition throughout and be tougher and more flexible than heretofore known.

Another object is to maintain the separate anodes of the nickel and iron, that is, their surfaces exposed to the electrolytic solution, at the same potential during the operation of electrodepositing.

Heretofore in processes of electrodepositing, the texture of the alloy deposited, particularly when deposited in the form of thin sheets, was too brittle for satisfactory handling. This is due primarily to the use of certain salts in the electrolyte which form complex ions which in turn tend to increase the hardness and strength of the deposit. Some of the salts commonly used are those of sodium and ammonium and in solutions containing either of these salts complex ions are readily formed. Furthermore, in electrochemical processes heretofore developed wherein separate anodes of nickel and iron were employed in electrolytic baths, current was supplied over each anode during operation but no attempt was made to maintain the anodes at zero potential with respect to each other. This resulted in the formation of a deposit of metal from one anode on the anode of a lower potential.

According to the present invention an alloy of nickel and iron is electrodeposited in a manner similar to that described in United States Patent 1,837,355, granted to R. M. Burns and C. W. Warner on December 22, 1931, with the exceptions that magnesium sulphate is used in place of sodium sulphate and that improved means are employed for maintaining the ratio of the alloying metals in solution constant and for adjusting the anode areas exposed to the solution so that the anode areas are maintained at zero potential with respect to each other. The magnesium sulphate forms no complex salts with the sulphates or chlorides of either nickel or iron and therefore does not form any complex ions in solution. Furthermore, the magnesium sulphate in solution has, because of its high solubility in water, a less tendency to form precipitates, thereby producing alloy deposits of strikingly less internal tension as evidenced by the tendency of the deposit to coil up when stripped from the cathode. The ratio of the metals to be deposited in the alloy is maintained constant in the solution by providing sepa-

rate anodes of nickel and iron and adjusting the anode areas in the solution so that the current flows through said anodes in the proper amount to replace the metal removed from the solution at the cathode.

The principal features of the present invention resides in the use of magnesium sulphate in place of sodium sulphate in the electrolyte described in United States Patent 1,837,355, supra, and in the methods of adjusting the current flows in the anodes and adjusting the anode areas in solution so that the ratio of alloying metals in solution remains constant and that the anode areas in solution are maintained at a zero potential with respect to each other.

An embodiment of apparatus for practicing the present invention is shown in the single figure of the drawing.

In the following description reference is made to one form of apparatus and one set of operating conditions which may be employed to deposit an alloy composed of 79% nickel and 21% iron. It is understood, however, that the invention is not limited to this particular apparatus nor to making the particular alloy. Other nickel-iron alloys such as those mentioned in United States Patent 1,837,355, supra, may be similarly electrodeposited by substituting in the electrolytic bath magnesium sulphate in place of sodium sulphate to produce results equally as well as that of the invention disclosed therein.

Other objects and features may be had by referring to the following detailed specification taken in conjunction with the accompanying drawing:

Referring to the drawing a diagrammatic view of the electrodepositing apparatus is shown with the front portion of the vat removed. The vat 10 contains an electrolyte 11, the anodes 12 and 13 and the cathode 14. The battery 15 supplies a positive potential to the anodes over circuit paths 16 and 17. The anodes are preferably connected to the battery 15 in the manner shown in the drawing, for example, path 16 includes an ammeter 19 and a suitable device such as that represented by a clamp 18 for holding the anode 12 in a raised or lowered position in the electrolyte 11 so that the anode area in the solution may be varied at will. The path 17 includes elements designated 21 and 22 which respectively correspond to those included in path 16. A rheostat 20, common to both, connects these paths to battery 15. The currents flowing through the anodes are adjusted by means of the rheostat and any variation in the readings on the ammeter is

adjusted by raising and lowering either anode by means of devices 18 or 21 so as to maintain a constant ratio between the readings. In this way a constant concentration of the ions of each of the alloy metals is maintained in the electrolyte and the anode areas in solution are preferably such that the current per unit area is the same for each anode. When depositing a nickel-iron alloy composed of 79% nickel and 21% iron, satisfactory results have been obtained by employing anodes having surface areas in the solution in a ratio which will give the desired current distribution through the anodes. This ratio may be, for example in the alloy just mentioned, 75% to 95% nickel to 5% to 25% iron because of the differences in the tendencies of these metals toward solution with normal ion concentration. The means described herein for adjusting the current and the anode surface areas in the solution are particularly satisfactory because anodes of equal size may be employed and any variation in the corrosion efficiency of the metals employed as anodes can be compensated for by raising or lowering the anodes during operation thereby varying the surface areas in the solution.

The cathode 14 may be of any suitable composition and form, but where it is desired to strip the deposit from the cathode, it is preferable to employ a flat cathode of a metal which may be stainless steel or of a material so treated that the deposited alloy does not adhere firmly to it. In depositing nickel-iron allows satisfactory results have been obtained by employing a cathode of brass which has been treated either by dipping in selenic acid or by coating electrolytically in a solution of ammonium molybdate. The adhesion of the deposited alloy to the cathode may also be prevented by coating the cathode with graphite. Another form of cathode which may be employed is a large slowly rotating cylinder having a portion of its surface submerged in the electrolyte. The deposited alloy is removed from a cathode of the cylinder type as it leaves the electrolyte and a continuous strip of the alloy may thus be obtained. The product of the present invention is particularly desirable where it is preferred to produce the alloy in long continuous strips.

A satisfactory electrolyte for producing an alloy of approximately 79% nickel and 21% iron may be made by mixing the following ingredients:

	Grams
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ -----	212
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ -----	22
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	18
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ -----	2.5
H_3BO_3 -----	25
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ -----	125

and adding sufficient water to make one liter of solution. This electrolyte may be used satisfactorily in an electroplating process wherein is maintained, first, the electrolyte at a temperature of 50 to 60° C., secondly, the average of the instantaneous values of the current density at a point as high as 300 amperes per square foot, thirdly, the hydrogen ion concentration (pH) of the solution between 3 and 4. The ratio of the anode surface areas exposed to the solution is that required to give satisfactory current distribution through the anodes. The electrolyte and conditions of operation may be suitably modified for other proportions of iron and nickel.

The scope of the present invention includes replacing the sodium sulphate with magnesium sul-

phate in the electrolyte employed in U. S. Patent 1,920,964, granted to R. M. Burns on August 8, 1933, to produce a tougher and more flexible nickel-iron-cobalt alloy. It also includes for the purpose of producing a tougher and more flexible deposit the use of magnesium sulphate in an electrolyte for electrodepositing iron, nickel or cobalt separately or magnetic alloys of these elements.

It will be found in using the above-mentioned electrolyte when subjected to the conditions set forth above that the cathode potential-current density characteristics of the two metals to be deposited will be substantially coincident over the operating range of current densities. The cathode potential-current density characteristics are defined in United States Patent 1,837,355, supra.

What is claimed is:

1. The method of electrolytically depositing a metallic substance consisting of elements of the iron-nickel-cobalt group which comprises precipitating said metallic substance upon a cathode from a solution including magnesium salts.

2. The method of electrolytically depositing a magnetic alloy of iron and nickel which comprises precipitating iron and nickel together upon a cathode from a solution including magnesium salts.

3. The method of electrolytically depositing a magnetic alloy of iron and cobalt which comprises precipitating said metal upon a cathode from a solution including magnesium salts.

4. The method of electrolytically depositing a magnetic alloy of iron, nickel and cobalt which comprises precipitating said metals together upon a cathode from a solution including magnesium salts.

5. A method according to claim 2 wherein the salts used in the solution is magnesium sulphate.

6. A method according to claim 2 wherein the solution includes nickel, iron and magnesium sulphates.

7. The method of electrolytically depositing a magnetic alloy of nickel, iron and cobalt which comprises precipitating a separate electrolytic bath for each of said metals, adding magnesium salts to each of said electrolytic baths, mixing said electrolytic baths in proportions depending on the proportions of said metals desired in the alloy and passing a direct current through the composite electrolytic bath to precipitate an alloy of said metal substantially free from other materials present in the composite electrolytic bath.

8. The method of simultaneously electrodepositing a magnetic alloy of metals of the nickel-iron-cobalt group of uniform composition and of a tenacious texture which consists in immersing anodes of the metal constituting the alloy in an electrolytic bath containing a soluble sulphate and a soluble chloride of each of the metals to be deposited, and a buffer mixture comprising a boric acid and magnesium sulphate, passing through the anodes in parallel, the electrolytic bath and cathode, direct current of values depending on the alloy desired and the number of anodes employed in the solution, and adjusting said current to a definite ratio so that the concentration in the solution of the ions of each of the metals composing the alloy remain substantially constant during operation, and varying at will during operation the anode surface areas exposed to the solution so as to maintain said surface areas at zero potential with respect to each other.

9. A method according to claim 8 wherein the anode surface area exposed to the solution is varied by raising or lowering one or all of said anodes in or out of the solution.

- 5 10. The method of producing an alloy of approximately 79% nickel and 21% iron which consists in simultaneously electrodepositing the two metals in the desired proportion from an electrolyte which contains per liter of water the following ingredients:

	Grams
15 $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ -----	212
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ -----	22
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	18
15 $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ -----	2.5
H_3BO_3 -----	25
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ -----	125

and is subjected to such operating conditions as a temperature of 50 to 60° C., an average instantaneous current density up to 300 amperes per square foot, and a hydrogen ion concentration between 3 and 4.

- 20 11. In an apparatus for electrodepositing alloys comprising nickel and iron, a plurality of anodes comprising one of nickel and another of iron and a cathode immersed in an electrolyte containing nickelous sulphate, ferrous sulphate, nickelous chloride, ferrous chloride, magnesium sulphate and boric acid, means for applying po-

tentials at a certain ratio to said anodes, and means for varying at will during operation the anode surface areas in the electrolyte to maintain said surface areas at zero potential with respect to each other.

12. In an apparatus for depositing an alloy of approximately 79% nickel and 21% iron, an electrolytic bath, an anode of nickel and another anode of iron in said bath, a source of current, means for applying current from said source to said anode and adjusting said current at will during operation to maintain the ratio of the nickel ions and iron ions in the solution constant, and means for varying at will during operation the respective surface areas of said anodes in the solution of said bath to maintain said areas at a ratio required to give satisfactory current distribution through the anodes, and a cathode immersed in said electrolytic bath which contains per liter of water the following ingredients:

	Grams
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ -----	212
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ -----	22
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	18
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ -----	2.5
H_3BO_3 -----	25
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ -----	125

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