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ELECTRODEPOSITION OF ALLOYS

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FIG. 1

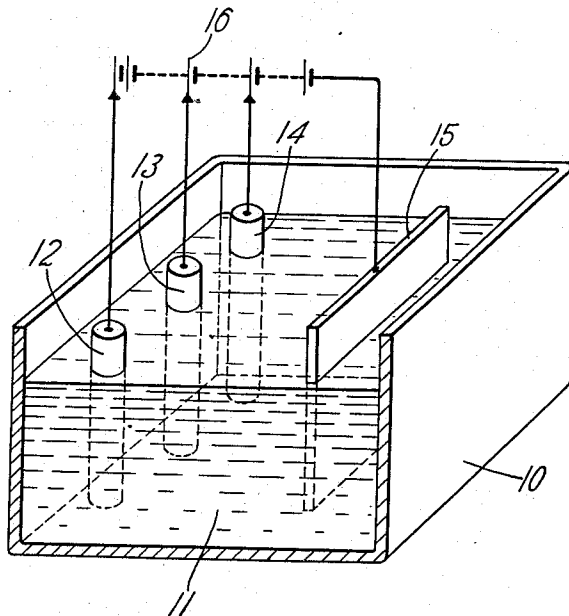
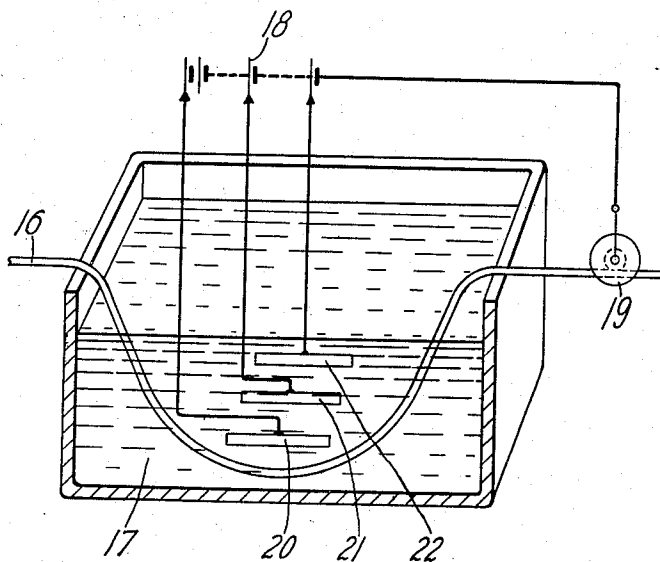


FIG. 2



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ELECTRODEPOSITION OF ALLOYS

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10 Claims. (Cl. 204—2)

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

An object of this invention is to electrochemically deposit from a single electrolyte an alloy of three metals which will have a substantially uniform composition throughout.

A specific object is to deposit an alloy of iron, nickel, and cobalt upon a conductor in any one of a variety of proportions of these metals suitable as a magnetic loading material.

It is generally known in the art of electrodeposition that if two metals are to be electrodeposited simultaneously in definite proportions over a period of time, it is necessary that it be equally easy for each metal to be deposited in its desired proportion. The ease with which ions of a metal in solution leave the solution and deposit on a cathode is measured by the drop of potential at the cathode for the particular solution. If a solution contains ions of two metals in a given proportion and it is desired to deposit them on a cathode in this proportion, then the potential of the cathode with respect to one of the metals in the solution must be the same as the potential of this cathode with respect to the other metal in solution. This is commonly difficult to realize in practice. Thus, when depositing two metals that have similar cathode potentials such as copper and zinc out of a cyanide solution as is normally done in brass plating, the instantaneous cathode potential of the copper in the solution may become different from that of the zinc in the solution, resulting in a brass deposit that is either copper-rich or zinc-rich and correspondingly copper-colored or else more yellow-colored than the average brass deposit. There are several conditions in the electroplating process which may affect the potential of a metal or metals in the solution with respect to the cathode. Such conditions are the concentration of the ions of the metal or metals in solution, the presence of other ions and substances in the electrolyte, the temperature of the electrolyte and the current density. Some of these conditions admit of regulation or control as does temperature, proportion of different metal ions, or presence of other substances, but it is difficult, if not impossible, to maintain the average instantaneous current density in the electrolyte constant. Even if this were possible the current density would still vary for different points on the surface of the cathode, depending on the distance between the anode and various points on the cathode.

When depositing two or more metals simultaneously to obtain an alloy of the metals, the variation in current density usually causes the cathode potential of one of the metals to change in greater or lesser degree than the cathode potential of the other metal or metals, thus varying the composition of the alloy. Even when the rate of change of cathode potential with respect to current density is the same for the two metals at equal cathode potentials, it is found that, in depositing two metals simultaneously, the one having the lower cathode potential deposits in greater proportion than the other metal until the concentration of the ions of the first mentioned metal is considerably reduced, after which the second metal will deposit in greater amounts. In accordance with U. S. Patent 1,837,355 granted to R. M. Burns and C. M. Warner, on December 22, 1931, for given operating conditions nickel and iron are deposited on a cathode as an alloy of uniform composition and each metal is simultaneously deposited in its proper proportion by varying the composition of the electrolyte until the rate of change of the current density-cathode potential characteristics of both metals coincide over a substantial portion of the current density range. In this manner the variation of cathode potential with current density is the same for both nickel and iron in forming the alloy and consequently a deposit of uniform composition is obtained over the entire surface of the cathode, even with appreciable changes in the current density.

According to the present invention, under given operating conditions, an alloy of nickel, iron and cobalt of uniform composition suitable as a magnetic material is electrodeposited over the entire surface of a cathode submerged in an electrolyte which has in solution nickel, iron and cobalt ions in quantities necessary to produce an alloy of some desired composition. The electrolyte may be replenished during operations with the metals of the alloy by providing anodes of one, two or all the metals, together with their ions in solution, or by providing a single inert anode, that is, one which is noncorrosive in the electrolyte, and adding from time to time sufficient ions in solution to replace those deposited at the cathode. The current furnished to the electrolyte is regulated according to the alloy desired and if more than one anode is employed the current is apportioned through each. A smooth flexible alloy of any desired thickness is thus obtained providing the acidity of the electrolyte is maintained within certain narrow limits. In order to produce a brittle alloy, such as is required for making mag-

netic dust, the acidity or current density, or both, may be increased. But the increase should not be carried to such limits as to cause substantial change in the variations of the cathode potentials of the metals deposited, otherwise the proportions of the deposited constituents will be changed. Furthermore, by extending the time of electrodeposition and preparing the surface of the cathode an alloy of sufficient thickness and strength to allow for stripping from the cathode, may be formed.

A feature of the invention consists of a signaling conductor surrounded by a magnetic alloy of nickel, iron and cobalt, electrolytically deposited thereon.

In the following description reference is made to two forms of apparatus which may be employed to electrodeposit an alloy of nickel, iron and cobalt. It is to be understood, however, that the invention is not limited to these particular apparatus nor to the method of making this particular alloy, herein described.

Referring to the drawing, Fig. 1 is a diagrammatic view of the electrodepositing apparatus, with the front of the tank removed, equipped with anodes of the three metals to be deposited and adapted for depositing the alloy in sheets, and Fig. 2 shows diagrammatically the apparatus adapted for producing the alloy as an adhesive coating on a signaling conductor.

In Fig. 1 of the drawing the tank 10 contains an electrolyte 11, the anodes 12, 13 and 14 and the cathode 15. The battery 16 or other suitable source supplies a positive potential to the anodes which may be electrically connected, but means is preferably provided for individually varying the potential applied to each anode so that the currents flowing therethrough may be adjusted to suitable values. The current flowing through each anode is preferably so adjusted that a constant concentration of the ions of each metal is maintained in the electrolyte and the anode areas are preferably such that the current per unit area is the same for each anode. When depositing a nickel-iron-cobalt alloy composed of 40% nickel, 35% iron and 25% cobalt, satisfactory results are obtained by employing anodes of nickel, cobalt and iron, respectively, having surface areas of 40 to 45 units, 25 to 28 units, and 35 to 37 units, respectively, because of the differences in the tendencies of these metals toward solution with normal metal ion concentration. Because of the variations in corrosion efficiency of the metals employed as anodes, it may be preferable to provide anodes of equal surface areas and correct for any corrosion inefficiency of the metals by adjusting the amount of current furnished to each anode. Instead of employing a plurality of anodes, one for each of the metals to be deposited, a single anode composed of the alloy and having suitable proportions of the component metals may be employed where the alloy is desired in thin sheets. In cases where it may be advantageous to employ anodes of one or two of the components, salts, such as the hydroxides, of the remaining component metal or metals, may be added continuously or at regular intervals so as to maintain the concentration of the metal ions in the electrolyte substantially constant. Of the component metals iron and cobalt are preferred for use as anodes in the order mentioned, and in such cases the nickel is added as a compound, such as nickel hydroxides. If only one anode is employed iron is generally selected as the anode

and then both the cobalt and nickel are added in the form of hydroxides.

The cathode 15 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 so treated that the deposited alloy does not adhere firmly to it. When depositing nickel-iron-cobalt alloys, satisfactory results may be 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 may then be removed from the cathode as it leaves the electrolyte and a continuous strip of the alloy may thus be obtained.

An electrolyte for producing an alloy of 40% nickel, 35% iron and 25% cobalt, may be made up from three separate electrolytes, each being prepared as though the component metals are to be separately deposited. Each electrolyte is composed of the sulphate and the chloride of the metal it is prepared to deposit, together with a buffer mixture of boric acid and sodium sulphate, which mixture serves to maintain the acidity of the electrolytes constant over the operating range of current density. The electrolytes are prepared as follows:

		Grams	
No. 1	NiSO ₄ ·7H ₂ O	210	110
	NiCl ₂ ·6H ₂ O	30	
	H ₃ BO ₃	25	
	Na ₂ SO ₄	125	
No. 2	FeSO ₄ ·7H ₂ O	208	115
	FeCl ₂ ·4H ₂ O	30	
	H ₃ BO ₃	25	
	Na ₂ SO ₄	125	
No. 3	CoSO ₄ ·7H ₂ O	211	120
	CoCl ₂ ·6H ₂ O	30	
	H ₃ BO ₃	25	
	Na ₂ SO ₄	125	

Sufficient water is added to each of the above groups of constituents to make one litre of solution for each electrolyte and then the three electrolytes are mixed together in proportions of, No. 1: No. 2: No. 3=4:3½:2½ to form an electrolyte for plating the alloy, composed of

	Grams	
NiSO ₄ ·7H ₂ O	84	130
NiCl ₂ ·6H ₂ O	12	
FeSO ₄ ·7H ₂ O	73	10.5
FeCl ₂ ·4H ₂ O	10.5	
CoSO ₄ ·7H ₂ O	53	7.5
CoCl ₂ ·6H ₂ O	7.5	
H ₃ BO ₃	25	125
Na ₂ SO ₄	125	

Where separate anodes such as 12, 13 and 14 representing nickel, iron and cobalt respectively, are employed in the plating electrolyte the current is adjusted for each anode so that the metal ion concentration in the electrolyte for the three metals, remains constant, and a satisfactory alloy composed of 40% nickel, 35% iron and 25% cobalt may thus be produced by maintaining, first, the electrolyte at a temperature of 50 to 60° C., secondly, the average of the instantaneous values of the current density at about 1.08 amperes per square decimeter, and thirdly, the hydrogen ion concentration (pH) of

the solution at 4. The reason for adjusting the current through the three anodes is to cause corrosion of the anodes in the electrolyte in quantities corresponding to those deposited at the cathode. In electrolytes where a single anode is employed this adjustment of the current is unnecessary because the electrolyte is replenished with metal ions of the component metals by adding hydroxides of the metals in definite proportions directly to the solution.

Nickel-iron-cobalt alloys of a wide range of compositions, particularly those used for magnetic materials, such as disclosed in the Elmer Patents 1,715,646 and 1,715,647, granted June 4, 1929 may be readily obtained by varying the metal ion concentration of the three metals in solution according to the proportions of the component metals in the alloy to be expected. The alloy may be made very brittle to facilitate grinding into dust such as is used in the manufacture of induction coil cores by increasing the acidity of the electrolyte or current density, or both, to a point where the plating potentials of the component metals begin to vary by substantial amounts with variations in current densities. It is well known in the art that it is important in producing an alloy of uniform composition that the cathode potential-current density characteristics of the component metals be maintained substantially equal over the operating range of current density.

Fig. 2 of the drawing illustrates diagrammatically a conductor 16 being passed slowly through a plating electrolyte 17, obtained as described above, of which it forms a cathode. That suitable rollers or other means may be provided for guiding the conductor through the electrolyte will be understood. The conductor is connected to a source of current 18 by means of a roller contact 19. The anodes 20, 21 and 22 of nickel, iron and cobalt are also connected to the source of current 18. In this manner an alloy of definite proportions may be satisfactorily electroplated on a signal conductor. The arrangement shown in Fig. 2 may be varied to provide a single inert anode or a separate anode for the three component metals of the alloy as described above.

What is claimed is:

1. A method of simultaneously electrodepositing nickel, iron and cobalt to form a magnetic alloy of uniform composition which comprises immersing an electrical conductor as a cathode in a composite electrolytic bath consisting of separate electrolytic baths for electrodepositing nickel, iron and cobalt mixed in proportions varying in accordance with the relative percentages of the three metals desired in the alloy, each of said electrolytic baths containing a soluble sulphate and a soluble chloride of each of the metals to be deposited and a buffer mixture, passing a direct current of a value depending on the alloy desired and the number of anodes employed in the composite bath through the composite electrolytic bath and cathode, and replenishing said bath so that the concentration therein of the hydrogen ion and the ions of each metal composing the alloy remain substantially constant during operation to maintain the cathode potential-current density characteristics of said metals substantially coincident over the operating range of current density.

2. A method, according to claim 1, wherein the step of replenishing the electrolytic bath comprises adding iron as an anode in said bath.

3. A method, according to claim 1, wherein the

step of replenishing the electrolytic bath comprises adding iron and cobalt as anodes in said bath.

4. A method according to claim 1, wherein the step of replenishing the electrolytic bath comprises adding iron, cobalt and nickel as the anodes in said bath.

5. A method of simultaneously electrodepositing nickel, iron and cobalt to form an alloy of uniform composition which comprises immersing an electrical conductor as a cathode in an electrolyte including soluble sulphates and chlorides of said metals, which are mixed in proportions varying in accordance with the relative percentages of the three metals in the alloy, a borate, and an alkaline metal, passing a direct current of a value depending on the alloy desired and the number of anodes employed in the composite bath through the electrolytic bath and cathode and replenishing said bath so that the concentration therein of the hydrogen ion and the ions of the three metals composing the alloy remain substantially constant during the operation to maintain the cathode potential-current density characteristics of said metals substantially coincident over the operating range of current density.

6. A method of simultaneously electrodepositing a uniformly composed magnetic alloy of nickel, iron and cobalt in ranges of 10% to 80% nickel, 10% to 60% iron, and 5% to 80% cobalt, which comprises preparing a solution of soluble salts of the three metals selected in such proportions as desired, from the group including sulphates and chlorides, passing through said solution to a cathode a direct current within such ranges of current densities that the cathode potential-current density characteristics of the three metals are substantially coincident over the operating range of current density at the surface of the cathode, and replenishing the ions of the three metals at substantially the respective values of the three metals in the deposited alloy.

7. The method of producing an alloy of approximately 40% nickel, 35% iron and 25% cobalt which consists in simultaneously electrodepositing the three metals in the desired proportions from an electrolyte which contains per liter of water the following ingredients:

	Grams	
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ -----	84	125
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	12	
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ -----	73	
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ -----	10.5	
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ -----	53	
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ -----	7.5	130
H_3BO_3 -----	25	
Na_2SO_4 -----	125	

and is subjected to such operating conditions as a temperature of 50° to 60° C., an average instantaneous current density of 1.03 amperes per square decimeter and a hydrogen ion concentration of 4.

8. In an apparatus for electrodepositing nickel, iron and cobalt alloys, a plurality of anodes comprising one of nickel, another of iron and still another of cobalt, and a cathode immersed in an electrolyte composed of nickelous sulphate, ferrous sulphate, cobalt sulphate, nickelous chloride, ferrous chloride, cobalt chloride, sodium sulphate and boric acid, and means for applying a potential between said cathode and said anodes, the proportions of said constituents of the electrolyte being adjusted so as to make the cathode potentials of the nickel, iron and cobalt substantially

equal over the operating portion of the current density range.

9. In an apparatus for depositing an alloy of approximately 40% nickel, 30% iron and 25% cobalt, an anode of nickel, another anode of iron and still another anode of cobalt, the surface areas of the anodes being 40 to 45% of nickel, 35 to 37% of iron and 25 to 28% of cobalt of the total anode areas, and a cathode immersed in an electrolyte, and means for applying a potential between said cathode and said anode, the composition of said electrolyte being such that the cathode potentials of the metals composing the alloy to be deposited are substantially equal over the operating range of current density.

10. In an apparatus for depositing an alloy of approximately 40% nickel, 35% iron and 25%

cobalt, a plurality of anodes comprising one of nickel, another of iron and another of cobalt, the ratio of the surface areas of the anodes being 40 to 45% nickel, 35 to 37% iron, and 25 to 28% cobalt, and a cathode immersed in an electrolyte which contains per liter of water the following ingredients:

	Grams	
NiSO ₄ ·7H ₂ O	84	
NiCl ₂ ·6H ₂ O	12	85
FeSO ₄ ·7H ₂ O	73	
FeCl ₂ ·4H ₂ O	10.5	
CoSO ₄ ·6H ₂ O	53	
CoCl ₂ ·6H ₂ O	7.5	
H ₂ BO ₃	25	90
Na ₂ SO ₄	125	

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20	95
25	100
30	105
35	110
40	115
45	120
50	125
55	130
60	135
65	140
70	145
75	150