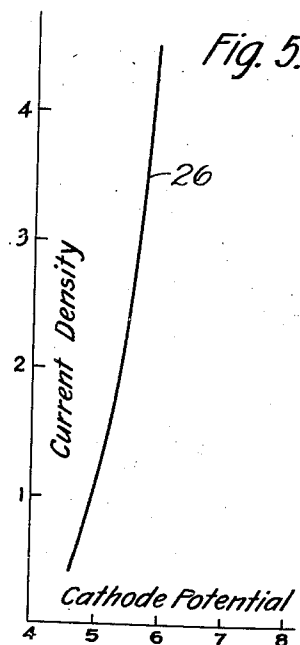
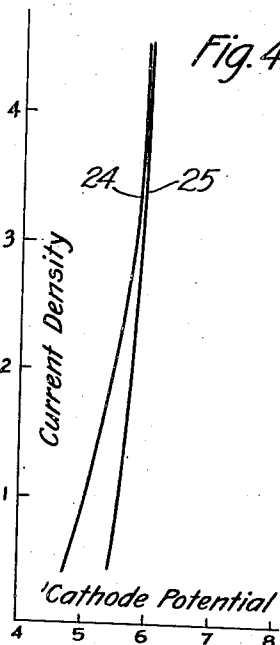
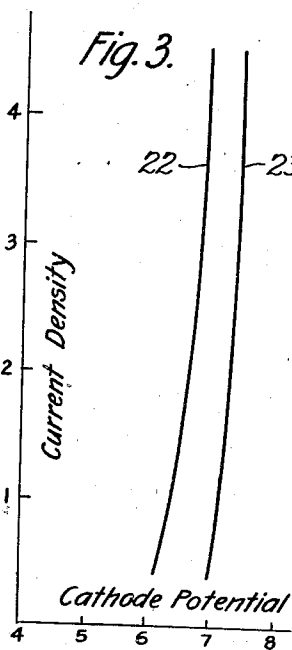
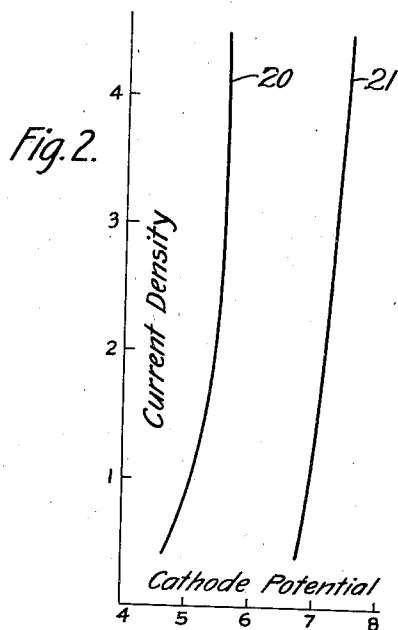
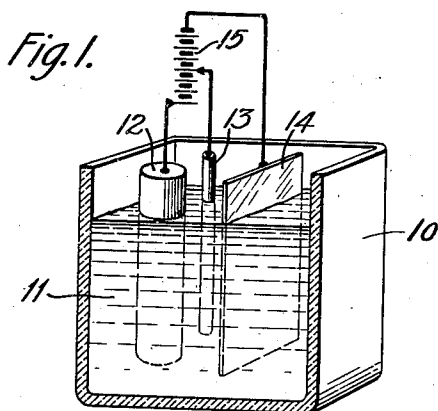


Dec. 22, 1931.

R. M. BURNS ET AL
ELECTRODEPOSITION OF ALLOYS

1,837,355

Filed Sept. 8, 1926



Inventors:
Robert M. Burns
Clarence W. Warner
by *John R. Palmer* Atty.

UNITED STATES PATENT OFFICE

ROBERT M. BURNS, OF BROOKLYN, NEW YORK, AND CLARENCE W. WARNER, OF GLEN RIDGE, NEW JERSEY, ASSIGNORS TO BELL TELEPHONE LABORATORIES, INCORPORATED, OF NEW YORK, N. Y., A CORPORATION OF NEW YORK

ELECTRODEPOSITION OF ALLOYS

Application filed September 8, 1928. Serial No. 134,165.

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

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

In accordance with one embodiment of this invention there are produced smooth, flexible deposits of an alloy of uniform composition throughout, in the form of thin sheets which have sufficient strength to withstand stripping from the cathode on which they are formed.

If, over a period of time, two metals are to be electrodeposited simultaneously in a definite proportion, 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 the cathode is measured by the potential of the cathode against the 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 the 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 it 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 an 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 the solution, the presence of other ions and substances in the electrolyte, the temperature of the electrolyte and the current density. Many 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, a 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 where 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 amount.

In accordance with the present invention, for given operating conditions, the slope and the axial displacement of the current density-cathode potential curves for the metals composing an alloy are changed by varying the composition of the electrolyte until the curves for the several component metals coincide over a substantial portion of the current density range. Under these conditions, the variation of cathode potential with current density is the same for each metal composing the alloy, and consequently, a deposit of uniform composition is obtained over the entire surface of the cathode even with appreciable changes in current density. Moreover, the deposit is smooth, flexible and of sufficient strength to withstand stripping from the cathode. In order to avoid brittleness in the deposited alloy, the acidity of the electrolyte is maintained within certain narrow limits.

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 to be understood, however, that the invention is not limited to this particular apparatus nor to the method of making this particular alloy.

Referring to the drawings, Fig. 1 is a diagrammatic view of the electrodepositing apparatus with the front portion of the vat removed. Figs. 2 to 4, inclusive, show current density-cathode potential curves for the deposition of iron and nickel when employing electrolytes of various compositions and indicate how the curves for the deposited metals may be moved into proximity by changing the composition of the electrolyte. Fig. 5 shows a similar curve for the simultaneous electrodeposition of iron and nickel in accordance with the present invention.

In Fig. 1 of the drawings, the vat contains an electrolyte 11, the anodes 12 and 13 and the cathode 14. The battery 15 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 current flowing therethrough may be adjusted to a suitable value. 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 alloy composed of 79% nickel and 21% iron, satisfactory results have been obtained by employing anodes having surface areas in the ratio of 85% nickel to 15% iron. Instead of employing a plurality of anodes, one of each metal composing the alloy, a single anode composed of the alloy and having suitable proportions of the component metals may be employed. In some cases it may be advantageous to employ anodes of one or more of the component metals of the alloy and a chemical compound, such as the hydroxide, of the remaining component metals. For instance, when depositing a nickel-iron alloy, a nickel anode may be employed and ferrous hydroxide may be added to the electrolyte continuously or at regular intervals so as to maintain the concentration of the ferrous ions substantially constant.

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 so treated that the deposited alloy does not adhere firmly to it. When depositing nickel-iron alloys, 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 using the

metal as a cathode. 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 the cathode as it leaves the electrolyte and a continuous strip of the alloy may thus be obtained.

Curve 20 of Fig. 2 shows the relation which exists between cathode potential and current density when nickel is deposited from an electrolyte composed of nickelous sulphate and nickelous chloride, while curve 21 of the figure shows the relation when iron is deposited from an electrolyte of ferrous sulphate and ferrous chloride. In Fig. 3, curve 22 is a cathode potential-current density curve for the deposition of nickel from an electrolyte composed of nickelous sulphate, nickelous chloride and boric acid, while curve 23 of this figure shows, on the same coordinates, the operating conditions for depositing iron from an electrolyte composed of ferrous sulphate, ferrous chloride and boric acid. Curves 24 and 25 are obtained by employing electrolytes composed of the same ingredients as employed in obtaining curves 22 and 23 respectively, of Fig. 3, with the addition in each case of sodium sulphate. Curve 26 of Fig. 5 shows the conditions for depositing an alloy of nickel and iron from an electrolyte having the combined ingredients used in obtaining curves 24 and 25, namely, nickelous sulphate, ferrous sulphate, nickelous chloride, ferrous chloride, sodium sulphate and boric acid. The temperature of the electrolyte in obtaining all of these curves was maintained at approximately 50° C.

These curves indicate that, for given operating conditions, their slopes and positions depend largely on the composition of the electrolytes. When employing the electrolytes here used in obtaining the data shown plotted in Fig. 4, it is seen that curves for the two metals are made to practically coincide over a substantial portion of the current density range. For this condition a deposit of uniform composition is obtained, when the metals are deposited simultaneously, since any change in current density will cause an equal change in the cathode potential for each of the metals composing the alloy and therefore an equal change in the amount of each metal deposited.

In obtaining the curves of Fig. 5, the proportions of the constituents of the electrolyte were such that an alloy of approximately 79% nickel and 21% iron was deposited. The size of the anodes and the spacing between the anodes and the cathode were such that the concentration of the ions of both metals remained constant. The electrolyte was maintained at a temperature of 50° C.

and the average of the instantaneous values of current density was about 4 amperes per square decimeter. The ratio of the surfaces of the anodes was about 85% nickel to 15% iron and the currents flowing through the anodes were in about the same ratio. The amounts of the various constituents of the electrolyte employed in depositing this alloy were as follows:

	Grams
10 $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ -----	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
15 $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ -----	180

Sufficient water was added to the above constituents to make one liter of solution.

In accordance with the invention, the deposit can be made of any desired thickness depending only on the time during which the operation is carried on. A cathode may be employed to which the deposited alloy will adhere firmly, or it may be one which permits the stripping of the deposited alloy from the cathode. The invention is especially useful, however, in obtaining the deposited alloy in the form of sheets which can be stripped from the cathode and which are thinner than can be conveniently obtained by rolling. Sheets as thin as .0003" have been successfully made electrolytically. Even where a thicker sheet of alloy is required, it is found that rolling causes strains in the material which often give it undesirable electrical or mechanical properties. The strains introduced when employing the electrolytic method are of small order and this method, therefore, may simplify the heat treatments of the alloy.

What is claimed is:

1. In an apparatus for electrodepositing nickel-iron alloys, an anode of nickel, a second anode of iron and a cathode immersed in an electrolyte composed of nickelous sulphate, ferrous sulphate, nickelous chloride, ferrous 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 and iron substantially equal over the operating portion of the current density range.

2. In an apparatus for depositing an alloy of approximately 79% nickel and 21% iron, an anode of nickel, a second anode of iron, the surface areas of the anodes being approximately 85% nickel and 15% iron, and a cathode immersed in an electrolyte and means for applying a potential between said cathode and said anodes, the composition of said electrolyte being such that the cathode potentials of the metals composing the alloy to be de-

posited are substantially equal over the operating range of current density.

3. In an apparatus for depositing an alloy of approximately 79% nickel and 21% iron, an anode of nickel, a second anode of iron, the ratio of the surface areas of the anodes being approximately 85% nickel and 15% iron, and a brass cathode which has been treated by dipping in selenic acid, immersed in an electrolyte and means for applying a potential between said cathode and said anodes, the composition of said electrolyte being composed of

	Grams per liter	
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ -----	212	80
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ -----	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	
$\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ -----	180	85

In witness whereof, I hereunto subscribe my name this 28th day of August, A. D. 1926.

ROBERT M. BURNS.

CLARENCE W. WARNER.