

UNITED STATES PATENT OFFICE

2,131,427

PROCESS OF ELECTROLYTICALLY DEPOSITING IRON AND NICKEL ALLOY

William A. Crowder, Newark, N. J., assignor to
Pyrene Manufacturing Company, Newark,
N. J., a corporation of Delaware

No Drawing. Application November 19, 1935,
Serial No. 59,547

5 Claims. (Cl. 204-2)

The present invention relates in general to electrodeposition of metals, and has for an object to produce homogeneous deposits of iron and nickel alloy not substantially exceeding 5% nickel.

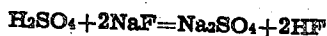
Another object of the invention is to produce deposits of iron and nickel not substantially exceeding 5% nickel alloyed in definite proportions, i. e., in the proportions in which these metals are present in the solution from which the deposits are produced.

Still another object of the invention is to produce deposits of iron and nickel alloy not substantially exceeding 5% nickel in ductile form, i. e., in a form which can be machined as it leaves the electrolyte without prior annealing.

In accordance with the invention, the above objects are attained by the use of an electrolyte having several important operating characteristics, all of which will hereinafter appear.

The deposits produced from this electrolyte, besides their homogeneity, ductility, and capability of production in definite proportions of iron and nickel, are of a suitable crystal structure that will firmly adhere to the base metal as is necessary in building up worn machine parts, and may be satisfactorily produced on aluminum, aluminum alloys, cast iron, zinc, zinc alloys, lead, lead alloys, steel, copper, brass, and graphite or carbon surfaces, for the purpose of electroforming and for use as a base for other types of plating. Moreover, they may be satisfactorily produced for electroforming of tubes, cylinders or other parts requiring high tensile strength, deposits containing as much as 5% nickel being permitted by the invention.

In accordance with the process of the present invention, iron and nickel alloy not substantially exceeding 5% nickel is electrodeposited through a heated solution of ferrous sulphate and nickel sulphate, in which solution hydrofluoric acid and sodium fluoride are both present. Preferably the hydrofluoric acid is formed in situ by causing part of the sodium fluoride to react with sulphuric acid, sodium sulphate being also formed by the reaction shown in the following equation:



In preparing the solution, ferrous sulphate and nickel sulphate are employed in such relative quantities as to cause the ratio of nickel to iron to be the same as in the desired alloy not substantially exceeding 5% nickel to be deposited. The quantity of hydrofluoric acid to be either added or formed in situ should be such as to cause the

solution to be operated at a pH not exceeding 5.0, preferably at a pH between 3.0 and 5.0. The quantity of sodium fluoride should be such as to cause the solution to be substantially saturated therewith. For producing the hydrofluoric acid in situ, the sodium fluoride should be in excess of the quantity required for its reaction (with sulphuric acid), the excess being such as to enable such saturation to be obtained.

The preferred temperature of operation of the solution is substantially 70° centigrade, above which the solution need not be heated for its satisfactory operation, maximum solubility of ferrous sulphate being reached at 70° centigrade.

Preferably, ferrous sulphate should be employed in quantity sufficient to bring the solution, at the temperature of operation, to a specific gravity of substantially 1.25 (referred to water at 20° centigrade). Analysis of the iron content of the solution is then made, and nickel sulphate is added in the amount corresponding to the desired alloy not substantially exceeding 5% nickel to be deposited, the usual amount added being such as to produce an alloy of from 3% to 5% nickel, which range conforms with specifications for nickel steel of high tensile strength. At the stated preferred solution concentration corresponding to a specific gravity of 1.25 (referred to water at 20° centigrade), 25 grams of sodium fluoride and approximately 2 cubic centimeters of concentrated sulphuric acid (66° Baumé), both per litre of water, have been found satisfactory for producing the hydrofluoric acid in situ. With the sodium fluoride and sulphuric acid employed in such amounts, the hydrofluoric acid formed by reaction is the principal agent effecting anode corrosion during electrolysis. That is, it is the hydrofluoric acid, and not so much the sulphuric acid, which causes the iron and nickel at the anodes to pass into solution. The sodium fluoride and sulphuric acid should both be added prior to the ferrous sulphate and nickel sulphate.

If the nickel content of the solution does not exceed the limit permitted by the invention (corresponding to an alloy not substantially exceeding 5% nickel), iron and nickel are deposited at the cathode substantially in the same ratio as these metals occur in the solution. This is deemed one of the important aspects of the invention and has been found to be due to the use of hydrofluoric acid and sodium fluoride in the solution, particularly when that acid is formed in situ. It is quite possible that a complex salt of iron (ferrous fluorosulphate) and a complex

salt of nickel (nickel fluorosulphate) are produced in the solution, which salts may act to effect the equalization of the cathode potentials with respect to the iron and nickel in solution, enabling these metals to be deposited in any ratio of nickel to iron desired no greater than the limit contemplated by the invention (corresponding to an alloy not substantially exceeding 5% nickel).

Another important feature of the invention resides in the stated preferred solution concentration corresponding to a specific gravity of 1.25 (referred to water at 20° centigrade), which concentration is exceptionally high and is made possible essentially by the high activity of fluorine, which prevents passivity at the anodes. At this concentration, it has been found that the osmotic pressure in the solution is such as to insure its most satisfactory operation. Substantially constant conditions are maintained in the solution, secondary anode corrosion being reduced to a minimum. That is, little iron and nickel are dissolved at the anode when the solution is not in service, and little iron and nickel over the amounts necessary to produce the deposit at the cathode are dissolved under operating conditions. This even and quantitative solution at the anodes at a concentration corresponding to a specific gravity of 1.25 (referred to water at 20° centigrade) acts to maintain the solution at that concentration.

The stated preferred solution concentration corresponding to a specific gravity of 1.25 (referred to water at 20° centigrade) is a critical value. Thus, if at the temperature of operation the concentration of the solution is reduced to, say, the degree corresponding to a specific gravity of 1.2 (referred to water at 20° centigrade), the osmotic pressure is correspondingly reduced to a point where too rapid anode corrosion takes place, thereby causing rapid changes in the acidity of the solution, which in turn not only necessitates pH measurements at short intervals, but also exerts a detrimental effect on the ductility of the deposit. If, on the other hand, at the temperature of operation the concentration of the solution is increased to, say, the degree corresponding to the specific gravity of 1.3 (referred to water at 20° centigrade), the osmotic pressure is increased to a point where all anode corrosion substantially ceases, which not only increases the acidity of the solution, but also lowers the cathode efficiency or rate of deposit at the cathode, the deposit here again being adversely affected in character.

At the stated preferred solution concentration corresponding to a specific gravity of 1.25 (referred to water at 20° centigrade), the large amount of ferrous sulphate in the solution renders it extremely conductive to electric current. The solution may thus be satisfactorily operated employing current densities as high as from 15 to 30 amperes per square decimeter. At these high current densities the rate of deposit is considerably accelerated, and the tendency toward "treeing" or rough deposits is considerably reduced, which is especially desirable when thick deposits are being produced. Moreover, even at those high current densities, variation in rate of deposit is effectively prevented because of the substantially constant conditions maintained in the solution. It has been found that as the proportion of sodium fluoride is increased above 25 grams per litre, the solubility of the ferrous sulphate is correspondingly reduced, which has the

effect of diminishing the range of current densities that may be satisfactorily employed.

Because of the presence of hydrofluoric acid in the solution, any ferric salt with which the ferrous sulphate employed may have been contaminated, is immediately dissolved by reduction to the ferrous state, and during electrolysis any ferric salt which, because of oxidation of ferrous iron, may tend to precipitate out of the solution, is also reduced to the ferrous state, whereby the solution is maintained clear at all times. Hitherto the precipitation of basic iron salts has been the source of considerable difficulty in some electrolytes. Thus, these insoluble salts, if allowed to accumulate in the solution, cause rough deposits, as well as inclusions in such deposits, and must therefore be removed as fast as they are formed, as by continuously circulating the electrolyte through a suitable filter. Not only is the solution of the invention free from suspended particles and sediment at any time, but the necessity of continuous filtration is entirely eliminated.

As already stated, the solution of the invention is preferably operated at a pH ranging between 3.0 and 5.0. These low acidities are made possible because of the use of hydrofluoric acid as the active acid reagent, complex ions being formed in the solution. And they may be used even when high densities of current are passed through the solution. Satisfactory deposits have thus been obtained from electrolytes operated within the preferred range of pH values specified and at a current density of 30 amperes per square decimeter.

Several advantages are obtained as a result of the low acidity values of the solution which may be employed. One advantage is that the amount of hydrogen generated at the cathode is reduced to a minimum, which prevents the formation of brittle deposits normally caused by absorption of hydrogen. Another advantage is that the use of expensive diaphragms, such as asbestos bags or specially made porous pots, which has hitherto been required for collecting the insoluble impurities, such as graphitic carbon, from the anodes, is eliminated. That is, simple canvas bags may be used to enclose the anodes, the collected impurities of course settling to the bottom of such bags so that they in no way hinder anode corrosion. Moreover, the use of elaborate ventilating systems and of expensive containers for containing the solution is also eliminated.

It is well known that the pH of an electrolyte is apt to change due to varying anodic conditions or other causes, such as accidental contamination or other causes, such as accidental contamination with alkali or acid, and that such changes have a marked effect on the current efficiency and the quality of the deposits. These changes are greatly minimized by the invention, there being several factors contributing to this effect. One factor has already been stated, namely, the even and quantitative solution at the anodes when operating at a solution concentration corresponding to a specific gravity of 1.25 (referred to water at 20° centigrade), which factor maintains the solution at that concentration. Another factor is the action of the sodium fluoride in the solution. That is, the sodium fluoride acts as a buffer salt controlling the pH of the solution against any great variation due to any cause. It is to be particularly noted, however, that this buffer action is almost entirely eliminated in solutions having a degree of concentration appreciably less than that corresponding to a specific gravity of 1.25 (referred to water at 20° centigrade).

In the practice of the invention, it has been found that, due to the fact that the iron and nickel in the anodes is completely dissolved, periodic cleaning of the anodes is unnecessary, there being no formation of insoluble coatings on their active surfaces.

The following procedure may be followed for producing an iron and nickel deposit not substantially exceeding 5% nickel in accordance with the invention:

A lead-lined tank suitably equipped with heating facilities is filled approximately three-quarters full of water, which water is heated to a temperature of 70° centigrade. The precalculated amount of sodium fluoride, in the proportion of 25 grams per litre of water, is then added to the water and dissolved therein; and, for the purpose of forming hydrofluoric acid, there is admixed with the resulting solution an amount of concentrated sulphuric acid (66° Baumé) precalculated in the approximate proportion of 2 cubic centimeters per litre of water. Bags of ferrous sulphate are then suspended in the solution and are maintained therein until sufficient ferrous sulphate has been dissolved to bring the specific gravity of the solution to 1.25 (referred to water at 20° centigrade), at the temperature of 70° centigrade. Upon removal of the ferrous sulphate bags, the solution is analyzed for its iron content, and the required amount of nickel sulphate based on this analysis is added to cause the ratio of nickel to iron in the solution to be the same as in the desired alloy not substantially exceeding 5% nickel to be deposited. Thereafter, iron and nickel anodes each containing these metals in the proper ratio of nickel to iron (also the same as in the desired alloy not substantially exceeding 5% nickel to be deposited) are suspended in the solution, canvas bags being employed to enclose the anodes. The object or objects to be electroplated are likewise operatively positioned in the solution; and, at the temperature of 70° centigrade, the anode and cathode terminal bars are connected to an electroplating generator of suitable capacity.

A pH test of the solution should then be made in order to determine whether it is necessary to add so-called addition reagents to correct the solution to the pH value desired. That is, an acidic correcting substance should be added if the acidity of the solution is to be increased, and an alkaline correcting substance should be added if the acidity of the solution is to be decreased. By this means, if necessary, the pH of the solution is preferably adjusted to substantially 3.4, as measured by colorimetric methods, this pH value having been found most satisfactory when the solution is operated at the temperature of 70° centigrade and the specific gravity of 1.25 (referred to water at 20° centigrade).

Sulphuric acid may be used as the acidic correcting substance, and sodium or ammonium hydroxide as the alkaline correcting substance. As to the current density which may be employed, 15 amperes per square decimeter will produce satisfactory deposits of iron and nickel alloy not substantially exceeding 5% nickel for building up worn machine parts and for electroforming.

When it is necessary to employ correcting substances, it has been found that if they are added to the solution by merely pouring them into the tank, they do not mix satisfactorily, thereby causing a detrimental localized condition to exist until the solution is stirred thoroughly. This difficulty can be overcome by employing a lead pipe

for adding the correcting substances to the solution, in which pipe perforations have been provided at regular intervals. This pipe is placed in the corner of the tank, and is so formed as to also extend along the bottom of the tank. When the correcting substances are poured through the upper end of the pipe, they are distributed through the perforations at several points in the solution, which insures their mixing with the solution before coming in contact with the object or objects being electroplated. This method of adding the correcting substances eliminates the necessity of removing the object or objects being electroplated for the purpose of adjusting the solution.

Whereas the electrodeposition of iron and nickel alloy according to the process of the present invention has been herein described as being carried out from anodes each containing both iron and nickel, it is understood that the iron may be deposited from separate anodes containing iron, and the nickel from separate anodes containing nickel. Moreover, it is possible to employ iron anodes only and maintain the nickel content of the solution substantially constant by adding nickel sulphate thereto at regular intervals, or to employ nickel anodes only and maintain the iron content of the solution substantially constant by adding ferrous sulphate thereto at regular intervals. Still another possibility would be to employ non-corrosive electrodes as the anodes, the iron and nickel contents of the solution being then maintained substantially constant by addition of both ferrous sulphate and nickel sulphate at regular intervals.

None of the procedures described in detail should be interpreted as limiting the invention, these procedures being capable of being modified in many ways without departing from its spirit.

What is claimed is:

1. The process of electrolytically depositing iron and nickel alloy not substantially exceeding 5% nickel, which comprises electroplating through a heated solution of iron and nickel salts consisting of ferrous sulphate and nickel sulphate, said solution containing hydrofluoric acid and sodium fluoride, the relative quantities of ferrous sulphate and nickel sulphate present in said solution being such as to cause the ratio of nickel to iron present in said solution to be the same as in the desired alloy not substantially exceeding 5% nickel to be deposited, the quantity of ferrous sulphate present in said solution being sufficient to bring it at the temperature of operation to a specific gravity of substantially 1.25 referred to water at 20° centigrade, the quantity of hydrofluoric acid present in said solution being such as to cause it to be operated at a pH not exceeding 5.0, and the quantity of sodium fluoride present in said solution being such as to cause it to be substantially saturated therewith.

2. The process of electrolytically depositing iron and nickel alloy not substantially exceeding 5% nickel, which comprises electroplating through a heated solution of iron and nickel salts consisting of ferrous sulphate and nickel sulphate, said solution containing hydrofluoric acid formed by reacting sodium fluoride and sulphuric acid therein, the sodium fluoride being employed in excess of the quantity required for the reaction, the relative quantities of ferrous sulphate and nickel sulphate present in said solution being such as to cause the ratio of nickel to iron present in said solution to be the same as in the desired alloy not substantially exceeding 5% nickel to be

deposited, the quantity of ferrous sulphate present in said solution being sufficient to bring it at the temperature of operation to a specific gravity of substantially 1.25 referred to water at 20° centigrade, the quantity of hydrofluoric acid formed in said solution being such as to cause it to be operated at a pH not exceeding 5.0, and the excess of sodium fluoride present in said solution being such as to cause it to be substantially saturated therewith.

3. The process of electrolytically depositing iron and nickel alloy not substantially exceeding 5% nickel, which comprises electroplating through a heated solution formed by adding to water sodium fluoride in the proportion of 25 grams per litre of water, sulphuric acid in amount to form by reaction with sodium fluoride sufficient hydrofluoric acid to cause the solution to be operated at a pH ranging between 3.0 and 5.0, ferrous sulphate in amount to bring the solution at the temperature of operation to a specific gravity of substantially 1.25 referred to water at 20° centigrade, and nickel sulphate in amount to cause the ratio of nickel to iron present in the solution to be the same as in the alloy not substantially exceeding 5% nickel to be deposited.

4. The process of electrolytically depositing iron and nickel alloy substantially not exceeding 5% nickel, which comprises electroplating through a heated solution formed by adding to water sodium fluoride in the proportion of 25 grams per litre of water, concentrated sulphuric acid sub-

stantially in the proportion of 2 cubic centimeters per litre of water, ferrous sulphate in amount to bring the solution at the temperature of operation to a specific gravity of substantially 1.25 referred to water at 20° centigrade, and nickel sulphate in amount to cause the ratio of nickel to iron present in the solution to be the same as in the desired alloy not substantially exceeding 5% nickel to be deposited, said solution being maintained during operation at a pH of substantially 3.4.

5. The process of electrolytically depositing iron and nickel alloy not substantially exceeding 5% nickel, which comprises electroplating through a heated solution formed by adding to water sodium fluoride in the proportion of 25 grams per litre of water, concentrated sulphuric acid substantially in the proportion of 2 cubic centimeters per litre of water, ferrous sulphate in amount to bring the solution at the temperature of operation to a specific gravity of 1.25 referred to water at 20° centigrade, and nickel sulphate in amount to cause the ratio of nickel to iron present in the solution to be the same as in the desired alloy not substantially exceeding 5% nickel to be deposited, said solution being operated at a temperature of substantially 70° centigrade, at a pH ranging between 3.0 and 5.0, and at a current density ranging between 15 and 30 amperes per square decimeter.

WILLIAM A. CROWDER.