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3,027,309

METHODS OF DEPOSITING NICKEL-IRON FILMS

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No Drawing. Filed Oct. 5, 1959, Ser. No. 844,205

Claims priority, application Great Britain Oct. 9, 1958

5 Claims. (Cl. 204—43)

This invention relates to methods of depositing nickel/iron films and relates particularly to a process for electrodepositing approximately 80/20 nickel/iron thin films having substantially rectangular hysteresis loop onto cylindrical formers from an aqueous solution of nickel and ferrous sulphamates.

Thin films of approximately 80/20 nickel/iron composition have been deposited by various methods for use in magnetic switching and memory devices, the film thickness varying from 1000 Å. to over 10,000 Å. depending on the application. The films can be made to have an "easy" direction of magnetisation which is established by carrying out the deposition in a magnetic field which aligns the film as it is deposited. Films so produced have hysteresis loops in the direction of easy magnetisation which are rectangular with a high degree of remanence, making them very suitable for storing information.

Methods used for depositing such films have included evaporation, chemical deposition, and electrodeposition. In the case of electrodeposition, an aqueous solution of mixed nickel and ferrous sulphates has been used as the electrolyte. Unfortunately films deposited from sulphate solutions are in a highly stressed (tensile) condition, which affects the magnetic characteristics and may cause the film to peel from the substrate. Iron is in fact normally removed from conventional nickel sulphate plating baths because its presence adds to the stress in the plated film.

The present invention provides a process for electrodepositing 80/20 nickel/iron films having the required magnetic characteristics in a relatively unstressed condition, and comprises electrodepositing from an aqueous solution of mixed nickel and ferrous sulphamates under carefully controlled conditions.

According to the present invention, in a process for electrodepositing an approximately 80/20 nickel/iron thin film having a substantially rectangular hysteresis loop on to a former in an aligning magnetic field, the former is made the cathode in an electrolytic cell containing a solution of nickel and ferrous sulphamates, the concentration of nickel ions in the solution is made greater than 100 gm./litre, the ratio of nickel ion concentration to ferrous ion concentration is made between 35:1 and 40:1, the pH is made between 2 and 3.5, the solution temperature is maintained below 30° C., the deposition current is regulated such that the deposition potential lies above 890 mv., and the solution concentration is maintained substantially constant over the surface of the cathode.

The solution temperature is preferably maintained in the range 18° to 22° C., the deposition current being regulated such that the deposition potential is between 920 and 950 mv.

Preferably the cathode surface is initially "struck" by passing a deposition current sufficiently large to deposit a nickel foundation on the cathode.

With the cylindrical former the solution concentration may be maintained substantially constant over the surface of the cathode by rotating the cathode on its own axis aligned substantially vertically and releasing a stream of gas bubbles below the cathode.

Also according to the present invention an apparatus for use in a process as aforesaid comprises a vessel for containing an electrolyte, means for suspending a cylin-

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dricathode vertically in the electrolyte adapted to rotate said cathode on its own axis, and a duct having an orifice for releasing a stream of gas bubbles below said cathode.

Also according to the present invention an electrolyte for use in a process as aforesaid comprises an aqueous solution of nickel and ferrous sulphamates where the nickel ion concentration is greater than 100 gm./litre, the ratio of nickel ion concentration to ferrous ion concentration is between 35:1 and 40:1, and the pH is between 2 and 3.5.

By way of example the deposition of a 1.6 micron (16,000 Å.) film onto a former consisting of a copper rod 4 cm. long and 0.228 cm. in diameter will now be described.

The surface of the rod is prepared for deposition by degreasing in concentrated sulphuric acid and etching for 30 seconds in a nitric acid polishing bath. The rod is then electropolished for 15 minutes in an orthophosphoric acid bath, and the polished rod washed four times with distilled water. The polished surface must support a water film and is not allowed to dry before inserting in the electrolyte. Polyethylene masks may be slipped onto the rod after polishing if it is desired to restrict the length of the magnetic film.

The electrolytic cell is a cylindrical glass container 6.5 cm. in diameter and 12 cm. high. The anode, of pure nickel sheet, is cylindrical and fits closely the inner surface of the container. The polished rod forms the cathode and is suspended vertically in the centre of the cell from the shaft of an electric motor which rotates at one revolution per second. At the bottom of the cell immediately below the cathode is the orifice of a small capillary tube through which nitrogen gas (oxygen-free) is blown at 10 lbs./sq. in. to produce a stream of bubbles which rise past the rod.

To provide an aligning magnetic field along the length of the rod, a 16-turn coil of copper tube is wound round the outside of the glass container. The coil is excited at 50 c./s. with a current of 100 a. (R.M.S.) to produce a peak field of 250 gauss. The coil is cooled by passing water through it.

The electrolyte consists of an aqueous solution of nickel sulphamate ($\text{Ni}(\text{NH}_2\text{SO}_3)_2$) and ferrous sulphamate ($\text{Fe}(\text{NH}_2\text{SO}_3)_2$), plus boric acid (H_3BO_3). Boric acid in concentrations approaching saturation is a normal constituent of nickel plating solutions.

The nickel ion concentration is 113 gm./litre, the ferrous ion concentration is 2.82 gm./litre, and the boric acid concentration is 30 gm./litre. The pH of the solution is adjusted to 2.5 by adding sulphamic acid ($\text{H}(\text{NH}_2\text{SO}_3)$). The pH must be adjusted during the life of the solution as must the nickel and iron concentrations.

The electrolyte temperature is 18°–22° C., i.e. room temperature. The potential which exists between the cathode and the solution during deposition depends on the deposition current and is measured using a saturated calomel reference electrode. The electrode is connected to the cell via a salt bridge comprising a first tube containing KCl solution connected between the calomel electrode and one arm of a two-way stop-cock, and a second tube containing nickel sulphamate solution connected between the other arm of the stop-cock and the cell. In this way the KCl and the nickel sulphamate solutions only make contact in a thin film at the stop-cock, and contamination of the electrolyte by chloride, which would lead to the deposition of stressed films, is prevented. The end of the salt bridge in the cell is placed as close to the cathode as possible without masking it.

The deposition current is obtained from a constant-current electronic circuit, the value of the current being controlled by feedback from the measured deposition potential in a sense to keep the latter constant.

The actual deposition is carried out as follows. Before the cathode is placed in the electrolytic solution the current source is set to supply 0.5 ma., which flows immediately the cathode is immersed and so prevents the newly polished copper surface from dissolving. The magnetic field, the nitrogen bubbler and the motor are set into operation.

A current of 150 ma. is first passed for approximately 5 seconds to "strike" the cathode surface. This has the effect of raising the deposition potential and so depositing a layer of almost pure nickel on the copper. This layer is sufficiently thin not to affect the magnetic properties of the final film, but provides a uniform foundation for the film. The current is then reduced to 25 ma. (current density approximately 10 ma./sq. cm. of cathode area), at which current the deposition potential is 950 ± 10 mv. When a total charge of 16 coulombs has passed, as measured by a coulombmeter, the current is reduced to 0.5 ma. and the cathode, now coated with a nickel/iron film approximately 1.6 microns thick, is removed from the electrolyte. After washing first in distilled water and then in alcohol (iso-propyl and ethyl have been used) the rod is dried under an infra-red lamp.

For thicker or thinner films the total charge passed is varied accordingly.

Films deposited by the above-described process have rectangular hysteresis loops with high remanence and a coercive force of about 3 ± 1 oersteds.

The magnetic aligning field may be either A.C. or D.C. The alignment can be other than axial as in the described example; for example a current passed along the axis of the rod will produce circumferential magnetic alignment, and a combination of axial and circumferential fields will produce helical alignment.

The conditions under which deposition takes place have been found to be rather critical if satisfactory films are to be produced:

(a) The ratio of the concentration of nickel ions to ferrous ions in the solution must be between 35:1 and 40:1. Above and below this range the deposited alloy becomes nickel-rich and iron-rich respectively.

(b) The concentration of nickel ions must be greater than 100 gm./litre to keep the deposition potential sufficiently low.

(c) As is well known in the electrochemical art, the composition of the deposited film depends on the temperature and the deposition potential. To maintain a constant composition the deposition potential must be reduced as the temperature is increased, and vice versa. However it has been found that as the temperature is increased the hysteresis loop tends to become less rectangular, the effect becoming very noticeable above 30° C. At this temperature the corresponding deposition potential to maintain the required composition is about 890 mv.

Satisfactory films having rectangular hysteresis loops can be produced in the region below 30° C. and above 890 mv., the required combination of temperature and potential being a matter of experiment. However it has been found preferable to operate in the temperature range 18° to 22° C. (room temperature), in which range satisfactory films are produced at deposition potentials of between 920 and 950 mv.

(d) The solution concentration must be kept uniform over the cathode surface. As deposition proceeds, nickel and iron are removed from the solution in the vicinity of the cathode, resulting in the less dense liquid rising. The

lower end of the cathode thus receives fresher electrolyte than the upper end, and this results in a change in the composition and magnetic properties along the rod. Rotating the cathode on its own axis helps to break up this upward flow of liquid over the rod, while the gas bubbles produce a rapid upward movement in the liquid of a more or less random kind.

(e) The pH must be maintained in the range 2 to 3.5. Below 2 excessive hydrogen is evolved, while above 3.5 the oxidation of the ferrous ion to ferric is quite rapid.

(f) Although satisfactory films have been produced without initially "striking" the cathode surface with nickel as described above, it is preferred to include this step to ensure uniform deposition. However, in the deposition of very thin films the step must be omitted to prevent affecting the magnetic properties.

Additional stress-reducing agents, such as sodium saccharin or sodium naphthalene trisulphonate can be added to the solution. Their effect becomes greater with thicker films.

In the described example the film was deposited on a copper rod. Satisfactory films have also been deposited on to nickel, iron, brass, beryllium copper, molybdenum, chromium, palladium and silver.

I claim:

1. An electrolyte for the electrodeposition of an approximately 80/20 nickel/iron film on a former consisting essentially of an aqueous solution of nickel and ferrous sulphamates wherein the nickel ion concentration is greater than 100 gm./litre, the ratio of nickel ion concentration to ferrous ion concentration is between 35:1 and 40:1, and the pH is between 2 and 3.5.

2. A process of electrodepositing an approximately 80/20 nickel/iron film on a former comprising introducing nickel and ferrous sulphamates to an electrolyte cell to form a solution thereof having a nickel ion concentration greater than 100 gm./l. and a pH of about 2.0-3.5, extending the former as a cathode within the solution and subjecting it to an aligning magnetic field, maintaining the ratio of nickel ion to ferrous ion concentration at about 35:1-40:1, the solution temperature below 30° C., the deposition current at a value such that the deposition potential is greater than 890 mv., and the solution concentration substantially constant over the surface of the cathode.

3. A process according to claim 2 wherein the solution temperature is maintained at about 18-22° C. and the deposition current is maintained at a value such that the deposition potential is about 920-950 mv.

4. A process according to claim 2 wherein the cathode surface is initially "struck" by passing a deposition current in the solution of such a value as to deposit a nickel foundation on the cathode surface.

5. A process according to claim 2 wherein the former is cylindrical and is extended substantially vertically in the solution as the cathode, and the solution concentration is maintained substantially constant over the surface of the cathode by rotating it on its cylindrical axis and introducing a stream of gas bubbles into the solution below the cathode.

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