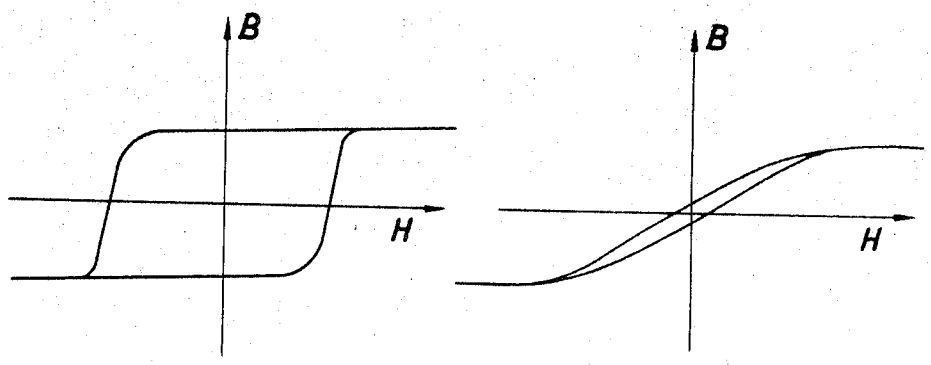
July 20, 1971 J. JOSTAN 3,594,290

PROCESS OF MAKING THIN FERROMAGNETIC FILMS AND ELECTROLYTE THEREFOR

Filed Nov. 27, 1967 2 Sheets-Sheet 1

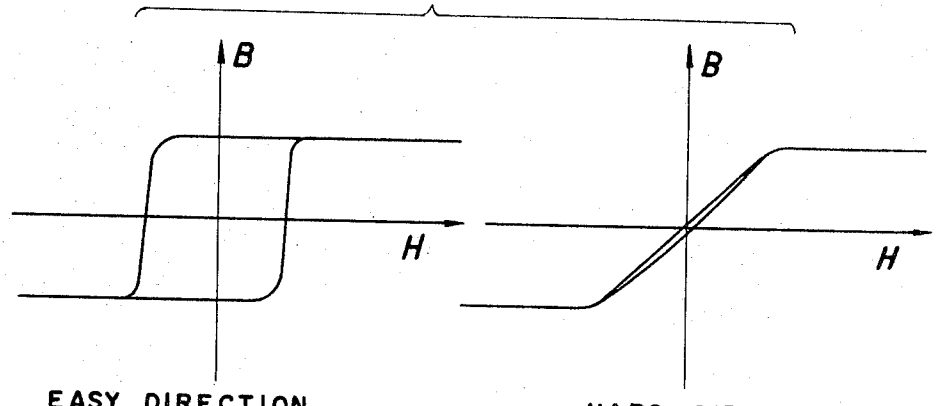
Fig. 1



EASY DIRECTION HARD DIRECTION

WITHOUT Se-ADDITIVE (FIELD STRENGTH: 8 Oe)

Fig. 2



EASY DIRECTION HARD DIRECTION

WITH Se-ADDITIVE (FIELD STRENGTH: 8 Oe)

INVENTOR
Josef Jostan

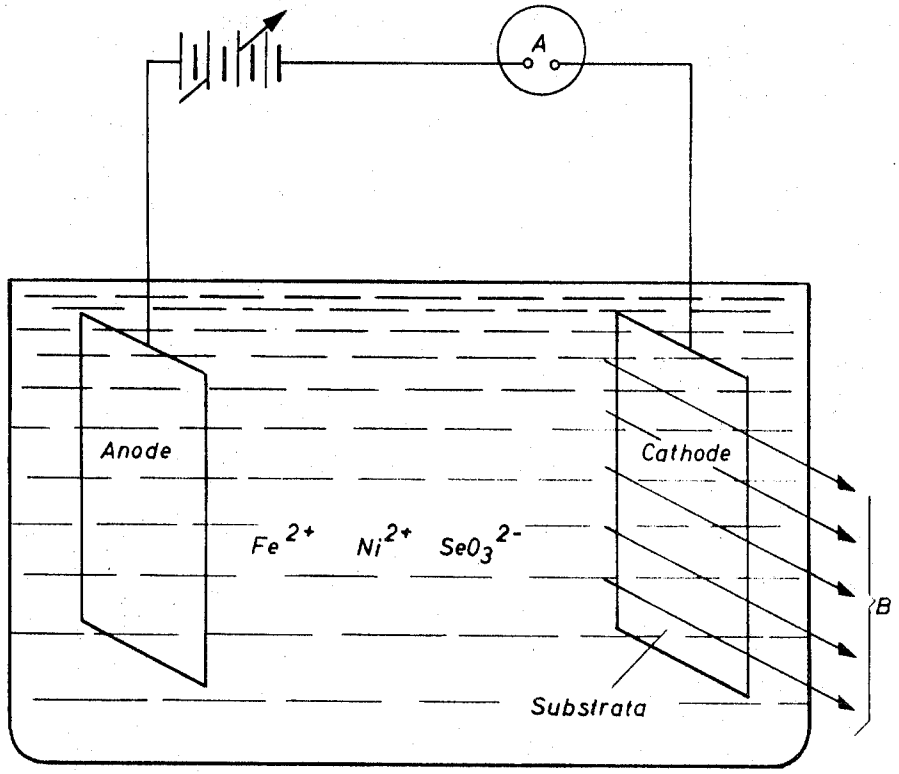
BY Spencer & Kaye
ATTORNEYS

July 20, 1971 J. JOSTAN 3,594,290

PROCESS OF MAKING THIN FERROMAGNETIC FILMS AND ELECTROLYTE THEREFOR

Filed Nov. 27, 1967 2 Sheets-Sheet 2

Fig. 3



INVENTORS
Josef Jostan

BY Spencer & Kaye
ATTORNEYS

United States Patent Office 3,594,290
Patented July 20, 1971

3,594,290

PROCESS OF MAKING THIN FERROMAGNETIC FILMS AND ELECTROLYTE THEREFOR

Josef Jostan, Ulm, Germany, assignor to Telefunken Patentverwertungsgesellschaft m.b.H., Ulm (Danube), Germany

Filed Nov. 27, 1967, Ser. No. 685,895
Claims priority, application Germany, Nov. 26, 1966, T 32,595
Int. Cl. C23b 5/32
U.S. Cl. 204—43 7 Claims

ABSTRACT OF THE DISCLOSURE

An improvement in a process for making thin ferromagnetic films and an electrodeposition bath for use in the process. The process involves the electrodeposition of nickel and iron onto a cathode substrate from a bath containing nickel and iron salts. The improvement comprises the steps of adding selenium compounds to the bath and maintaining the pH of the bath at less than 3. The bath for use in the process contains selenium compounds in addition to the nickel and iron salts and has a pH which is less than 3.

BACKGROUND OF THE INVENTION

The present invention relates to a method of making thin ferromagnetic films by electrodeposition.

Because of their high switching speeds, thin magnetic films are useful in a wide range of switching applications; they are especially suitable, for example, as information storage devices in electronic data processing equipment. In order to use such films in practice it is necessary to have a preferred direction of magnetization; that is, an as close as possible approximation to a rectangular hysteresis loop in an easily magnetizable direction, also called an easy direction, and an as close as possible approximation to a closed hysteresis characteristic in a hard magnetizable direction, also called a hard direction. It is also required that such films be switchable with but a low coercive force and, above all, that they be capable of production with reasonable economy.

Of the prior art processes for producing thin nickel-iron alloy films, which preferably have a composition of 81% nickel and 19% iron, only the vacuum deposition process and the electrodeposition process yield usable thin films. Since the vacuum or vapor deposition method requires costly apparatus and since large surfaces or cylindrical substrata can be coated with a uniform film thickness and a homogeneous composition only with difficulty, this process is uneconomical and unsuitable for fabricating storage matrices with continuous production line techniques.

The galvanic deposition of permalloy films, on the other hand, exhibits a number of advantages from the technological standpoint. The problem of producing a metallic conducting extremely flat substrata, as is required for the electrolytic fabrication of memory films, can be easily solved, if this process is employed, either by chemically coating a piece of glass with metal or by using the glass as a mother matrix and reproducing its surface by an electroplating technique.

Thin permalloy films which have been coated on such flat substrata by means of the electrodeposition usually do not, however, possess the desired magnetic characteristics. Since the baths employed in the electroplating

process contain iron and nickel in a specific quantity ratio as cations, the composition of permalloy films produced by electrodeposition varies with the film thickness. Every inhomogeneity of the film effects a change, however—and usually for the worse—of its magnetic behavior. Attempts have been made in the past, therefore to produce thin nickel-iron films with reproducible magnetic characteristics, by improving the electrolyte and by exactly controlling the conditions of deposition.

It has been possible to produce substantially homogeneous films with improved magnetic characteristics by means of certain electrolyte additives such as thiocarbamide, alkalihypophosphite and alkaliarsenite, which influence the deposition mechanism of nickel and iron as complex forming substances or reducing agents. Similar results have been achieved through the simultaneous deposition of small amounts of copper, cobalt or molybdenum from an electroplating bath containing copper salts, cobalt salts or molybdate in addition to nickel and iron salts. The results of these attempts have been less than completely satisfactory, however, since these baths are unstable; their individual constituents are subject to oxidation with the air and make necessary a continuous control of the bath. Furthermore, the permalloy films which include small percentages of sulphur, phosphorus and other elements that have been used in the prior art are very susceptible to corrosion and are, therefore, strongly subject to aging effects.

SUMMARY OF THE INVENTION

An object of the present invention, therefore, is to find a way, requiring no additional expenditure of labor, of making thin ferromagnetic films of nickel-iron alloy so that the films will have good magnetic characteristics and will be strongly resistant to corrosion and have, therefore, a longer useful life.

This and other objects which will become apparent in the discussion that follows are achieved, according to the present invention, by employing an electrodeposition bath which contains selenium compounds in addition to nickel and iron salts. The process according to the present invention not only serves to avoid the disadvantages of the prior art processes mentioned above but also possesses the advantage, first, that only very small quantities of additives containing selenium are sufficient and, second, that it effects a considerable stabilization of the electrolytic bath.

Thin films, which are made in accordance with the present invention, are distinguished from thin films of the same thickness which are made without selenium additives by a nearly quadratic hysteresis loop in the easy direction, a nearly closed hysteresis characteristic in the hard direction, switching times in the nanosecond region, a low coercive force H_c and by a low anisotropic magnetic field strength H_k. The films produced by the method according to the present invention are also considerably more resistant to corrosion.

According to a preferred embodiment of the present invention the selenium added to the bath is in its tetravalent form. The process according to the present invention is carried out with the pH value of the bath below 3; preferably in the range of 2.0 to 2.8 pH units. A preferred form in which the selenium may appear in the bath is as a selenite ion SeO_3^{2-}. The selenium can be added to the electrolyte as selenium dioxide, selenious acid H_2SeO_3, or as one of its salts, for example, sodium selenite $Na_2SeO_3 \cdot 4H_2O$. It is possible, however, to employ other compounds of selenium as well.

According to a further feature of the present invention either the electrolytic current intensity or the deposition potential can be held constant during the deposition process; that is, the process can be carried out either galvanostatically or potentiostatically. This does not mean, however, that a desired change in the cathode current intensity or the cathode potential can not be made during the electrolysis.

It is of adavntage, also, to expose the cathode to a strong homogeneous magnetic field during the electrodeposition process, the lines of force of which are directed parallel to the cathode surface. This magnetic field will insure that the deposited thin film will possess a high degree of uniaxial magnetic anisotropy.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagram of the hysteresis curves of a thin film produced without a selenium additive as proposed by the present invention.

FIG. 2 is a diagram of the hysteresis curves of a thin film produced with a selenium additive in accordance with the present invention.

FIG. 3 is a schematic diagram of the equipment used to produce ferromagnetic thin films in accordance with the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will now be described in further detail with reference to a non-limitative example.

A solution is employed as an electrodeposition (electrolytic) bath which contains 0.02 to 2.00 grams of sodium selenite. Optimum results are obtained with concentrations of 0.08 to 1.50 grams of sodium selenite per liter of solution. This corresponds to a selenium concentration in the bath of between 0.025 and 0.47 grams selenium per liter of solution. The pH value of the bath is maintained below the value 3, and preferably between 2.0 and 2.8. The bath temperature is constant and lies at the ambient temperature. Ferromagnetic thin films having favorable values for the applied magnetic field H and the magnetic induction B may be obtained potentiostatically with a cathode potential, taken with respect to a normal hydrogen electrode, of between 850 and 900 millivolts and galvanostatically with cathode current densities which lie between 5 and 7 ma./cm^2. Under these conditions films with a thickness of approximately 800–1000 A. will be deposited within 110 seconds.

Nickel-iron films which contain selenium are very resistant to the influences of corrosion. For example, and in contrast to pure nickel-iron films, they are scarcely corroded at room temperature by 5% nitric acid. This is not to say, however, that the thin films made according to the present invention are less capable of being etched. They may be etched without difficulty, for example, with a 5% solution of iron (valence 3)-chloride.

The characteristics of thin magnetic films are quite strongly dependent upon the film thickness. The switching behavior may under certain circumstances be better, for example, with very thin films than with thicker ones. Whereas pure nickel-iron films made by the electrodeposition process produced good results only with thicknesses above approximately 1200 A., comparable characteristics are possessed by thin films made in accordance with the present invention over a wide range of film thicknesses: from approximately 500 A. to 2000 A.

The ratio of nickel to iron in the film varies according to the concentrations of the two cations in the electrolytic bath. The best magnetic characteristics of deposited thin films made in accordance with the present invention are obtained when the ratio of Ni^{2+}:Fe^{2+} lies between 98:2 and 97:3. This nickel-iron ratio produces an iron content in the deposited thin film of between 16 and 23%.

In a special exemplary embodiment of the present invention the electrodeposition bath used to make thin films contains the following compounds:

TABLE I

Compound:	g./l.
Nickel sulfate ($NiSO_4 \cdot 6H_2O$)	218
Ammonium iron (2)-sulfate ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$)	6.8–10.5
Boric acid (H_3Bo_3)	10–30
Sodium chloride (NaCl)	10–30
Saccharin ($C_6H_4SO_2NHCO$)	0.8
Sodiumlaurylsulfate ($CH_3(CH_2)_{11}OSO_3Na$)	0.4
Sodiumselenite (31% Se) ($Na_2SeO_3 \cdot 4H_2O$)	0.08–1.5

The electrodeposition process using this bath is carried out at a pH value of between 2.0 and 2.8, preferably at 2.5. The bath temperature equals a constant 20° C.; motion of the bath electrolyte or the cathode is avoided. Plates of platinum, nickel or nickel and iron are employed as an anode. A small glass plate having a surface area of approximately 4 cm.^{2}, which has layers first of chrome and then gold vapor-deposited thereon in a vacuum, serves as the cathode and as the substrate for the ferromagnetic film.

Good results may also be obtained with very smooth substrata which are made according to the following process. A glass plate, sensitized in a tin (2)-chloride solution and activated in a palladium (2)-chloride solution, is coppered non-electrically, reinforced with electroplated copper and coated with a film of glass fiber-laminated epoxy resin. This copper-plastic sheet is removed from the glass plate and the surface which originally faced the glass given a corrosion-protective coating of gold either non-electrically or by electrodeposition. This extremely flat surface of this sheet then serves as a support for the thin permalloy film. Substrata consisting of polished metals, or glasses or plastics metallized chemically or by electrodeposition may also be used instead of this described sheet.

The deposition is carried out at a cathode potential of 1125 mv. relative to a saturated calomel electrode; that is, at a cathode current density of about 6 ma./cm.^{2}. The exposure time which is in the range of 60 to 200 seconds yields films with thicknesses between 500 and 2000 A. During the electrodeposition, a magnetic field of approximately 150 oersteds is placed on the cathode oriented so that its lines of force are parallel to the surface of the substrate.

The dependence of the measured coercive force H_c and the anisotropy magnetic field strength H_k upon the selenium concentration of the bath for a completely permalloy film having a thickness of 1000 A. is summarized in the following table.

TABLE II

Se concentration of the bath (g./l.)	Oersteds	
	H_c	H_k
0	4.0	5.0
0.065	2.4	3.2
0.130	2.6	3.0
0.190	3.0	2.6
0.255	3.1	2.5
0.320	2.8	2.3
0.480	2.8	2.3

As may be seen in Table II, as the selenium concentration increases, H_k becomes smaller than H_c; that is, the thin films become inversed. The switching times of the films containing selenium, in accord with the present invention, measured in a switching field of 10 oersteds at an angle of 45° from the preferred axis, are in the range of

a few nanoseconds and are thus somewhat shorter than the switching times of pure nickel-iron films.

Another characteristic of the thin films produced according to the present invention is that the nickel and iron concentration of the film can vary over a considerable range without any substantial unfavorable influence on the properties of the film. It is therefore unnecessary, in making films according to the present invention, that the composition of the bath, the bath temperature, and the cathode current density or the cathode potential be adjusted with extreme accuracy.

FIGS. 1 and 2 illustrate the hysteresis loops of thin films manufactured according to the prior art method and the method according to the present invention, respectively. As may be seen from FIG. 2, the thin films with the selenium additive exhibit a more rectangular hysteresis loop in the easy direction of magnetization and a more nearly closed loop in the hard direction than do the pure nickel-iron films of the prior art. The coercive force property of the selenium additive films is also not as great as the coercive force of the films of the prior art.

FIG. 3 illustrates, in schematic form, the equipment employed to carry out the process of making thin films according to the invention. There is shown an anode and a cathode connected to an adjustable source of electrical power and immersed in an electrolytic bath. The bath there shown comprises a water solution of nickel and iron cations and, as an example of one of the possible selenium additives, selenite ions. The cathode, which forms the substrate for the nickel and iron deposits, is placed in a magnetic field B directed parallel to the electrode position surface. This magnetic field may be generated in the usual manner by magnetic poles arranged externally to the bath. It is possible, too, to use a cathode of large or vaulted surface or of cylindrical form.

It will be understood that the above description of the present invention is susceptible to various modifications, changes, and adaptations, and the same are intended to be comprehended within the meaning and range of equivalents of the appended claims.

I claim:

1. In a process for manufacturing thin ferro-magnetic films of nickel-iron alloy by electrodeposition using an aqueous bath containing nickel salts and iron salts and a cathode, immersed in said bath and including a plane surface, connected to a source of electricity, the improvement comprising the steps of adding selenium compounds

to said bath, maintaining the pH of said bath at less than 3, maintaining the ratio of Fe^{+2}:Ni^{+2} at at least about 2:98, maintaining the selenium concentration at at least about 0.025 grams per liter, and exposing said cathode to a strong homogeneous magnetic field, the lines of force of which are arranged parallel to said cathode surface.

2. The process defined in claim 1, wherein the selenium in said selenium compounds is in the tetravalent form.

3. The process defined in claim 1, wherein said pH of said bath is in the range of 2.0 to 2.8.

4. The process defined in claim 1, wherein said selenium compounds are selected from the group consisting of selenium dioxide and sodium selenite.

5. The process defined in claim 1, further comprising the step of maintaining a potential on said cathode which is a constant.

6. The process defined in claim 1, further comprising the step of maintaining a current at said cathode which is a constant.

7. An aqueous bath for use in electroplating nickel-iron magnetic films comprising approximately 218 g./l. of nickel sulfate hexahydrate, approximately 6.8 to 10.5 g./l. of ammonium iron (2)-sulfate hexahydrate and approximately 0.08 to 1.5 g./l. sodium selenite tetrahydrate, and wherein the bath pH is less than 3.

References Cited

UNITED STATES PATENTS

2,125,229	7/1938	Harshaw et al.	204—49
2,338,529	1/1944	Mougey et al.	204—49
3,027,309	3/1962	Stephen	204—43
3,141,837	7/1964	Edelman	204—43

FOREIGN PATENTS

1,474,163	2/1967	France	204—43

OTHER REFERENCES

M. R. Thompson et al., Transactions of the American Electrochemical Society, vol. 42, pp. 79–82 (1922).

M. R. Thompson et al., Transactions of the Electrochemical Society, vol. 42, pp. 88–89 (1922).

GERALD L. KAPLAN, Primary Examiner

U.S. CL. X.R.

29—194, 195, 196, 199; 75—170; 148—31.55; 340—174