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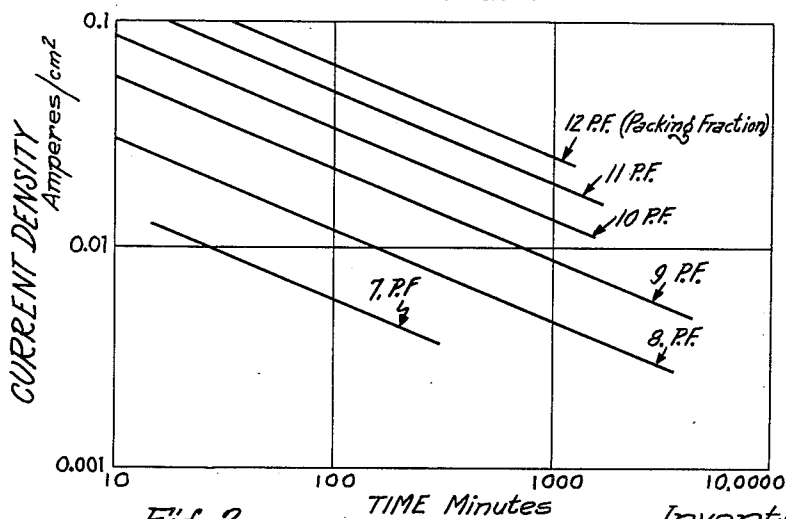
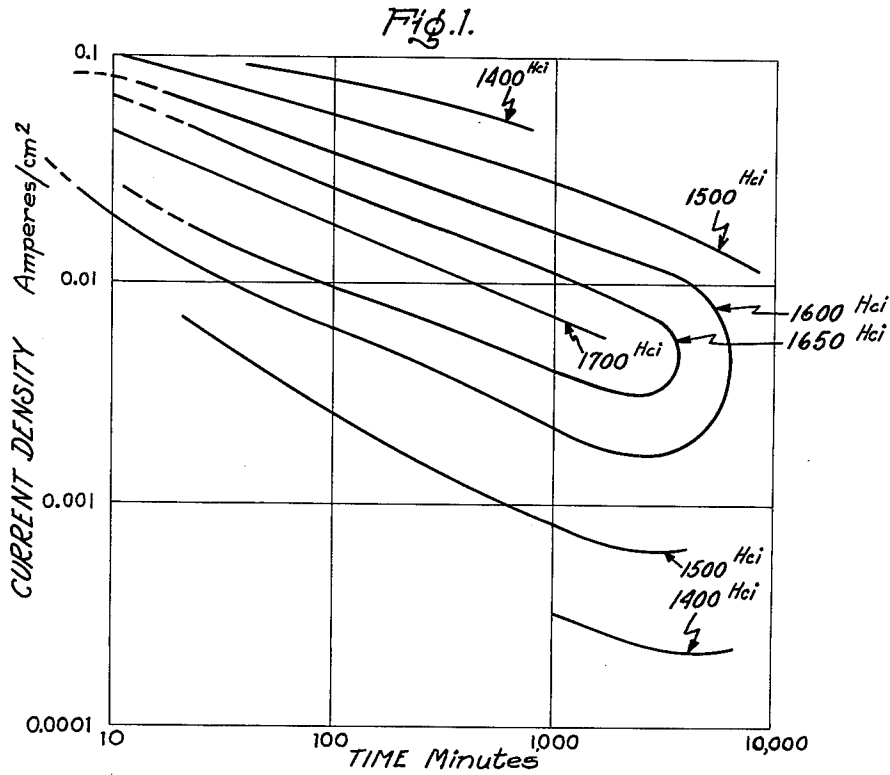
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3,198,716

MAGNETIC MATERIAL AND METHOD OF PREPARING THE SAME

Filed Dec. 21, 1961

2 Sheets-Sheet 1



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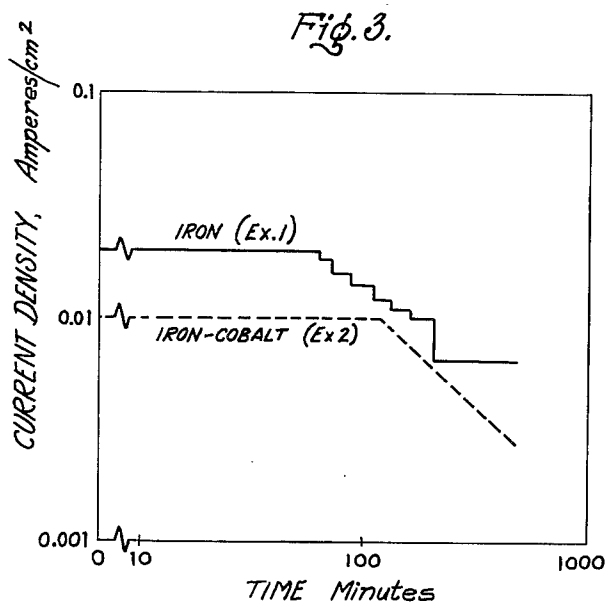
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MAGNETIC MATERIAL AND METHOD OF PREPARING THE SAME

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2 Sheets-Sheet 2



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MAGNETIC MATERIAL AND METHOD OF PREPARING THE SAME

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6 Claims. (Cl. 204-10)

This invention relates to permanent magnet materials comprising elongated, single domain particles having greater structural uniformity and higher magnetic quality than has heretofore been possible and to a process for preparing said magnetic material.

U.S. Patent 2,974,104, Paine et al., assigned to the same assignee as the present invention, discloses magnetic materials composed of elongated, single domain particles, exhibiting very high energy products. These magnetic materials are prepared by electrolytically depositing, at a constant optimum current density, particles of iron or iron-cobalt alloys into a liquid metal cathode, such as mercury, under quiescent interface conditions between the liquid cathode and the electrolyte.

Such magnetic materials have been found to have a wide distribution of particle structures, a characteristic which results in a decrease in the magnetic quality of the assembly of particles. To produce magnetic material of the greatest possible total magnetic energy, it would be desirable to produce particles of the optimum shape and, consequently, particles whose structures or shapes are as nearly uniform as possible.

It is a principal object of this invention to provide a process for electrolytically depositing elongated, single domain, magnetic particles possessing a high degree of structural uniformity. It is an additional object of this invention to provide elongated, single domain, magnetic materials having greater total magnetic energy than has heretofore been possible.

Briefly described, the present invention involves the discovery that particles of substantially uniform structure may be produced if, during at least a portion of the electrodeposition cycle of the fine particles, the cathode current density is progressively lowered to maintain a substantially constant maximum coercive force in the electrodeposited particles. By so lowering the current density, it has been found that particles of nearly constant structure and of significantly improved magnetic properties are obtained. In accordance with a further aspect of the invention, it has been found that particles of even greater structural uniformity may be obtained if a purified electrolyte is used in the foregoing electrodeposition procedure. By a "purified" electrolyte is meant an electrolyte specially treated to remove organic impurities in a manner more fully set out hereinafter.

The invention will be understood more clearly by reference to the following description taken in connection with the accompanying drawing wherein:

FIGURE 1 shows the intrinsic coercive force values of particles electrodeposited at constant current as a function of current density and time;

FIGURE 2 shows the packing fraction values of particles electrodeposited at constant current as a function of current density and time; and

FIGURE 3 illustrates graphically two schedules for progressively lowering the current density to maintain

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a nearly constant coercive force and packing fraction in the electrodeposited particles.

While not intending to be limited to any specific theory, it is believed that the invention is based upon the following considerations. During electrodeposition of iron, or other ferromagnetic particles, into a liquid metal cathode, the iron atoms condense into particles in a closely packed ordered array at the interface between the liquid cathode and the electrolyte. When the particles are deposited at constant current, a gradual change in the particle shape takes place as deposition proceeds. This variation in particle shape is believed to be due to gradual changes in the environment of the growing particle or fiber as the electrodeposition proceeds. This results in part from an increase in the thickness of the mass of particles formed by the elongated iron fibers. The increasing mass of particles near the surface of the mercury reduces the rate of flow of mercury to the surface where the fibers are growing. Consequently, the greater mass of iron particles tends to push upward toward the interface because of its greater buoyancy as compared with mercury. On the other hand, the rate of iron deposition is dependent on the current density, and if this current density is kept constant in the face of the changing environment at the point of electrodeposition, the fiber structures will not grow uniformly. The present invention compensates for this changing environment by progressively lowering the current density and hence the rate of iron deposition.

In addition to the foregoing, it has been found that hydrogen gas bubbles and adsorbed impurities form on the surface of the mercury cathode during electrodeposition and create microscopic variations in current density at the point of electrodeposition. By treating the electrolyte with, for example, activated charcoal, the formation of hydrogen bubbles and adsorbed impurities is inhibited and thus uniformity of current density on a microscopic scale is provided. Whereas, in the absence of such treatment, the iron formed during electrodeposition is in the form of a loose dispersion in mercury, with the use of treated electrolyte the elongated iron particles deposit in the form of a solid gel in the mercury. In the former case, the loose dispersion contains a wide distribution of particle shapes including spherical particles. In the latter case, the gel contains only elongated fibers while under the gel in the fluid mercury phase some essentially spherical particles are normally present. The better quality elongated particles in gel form may then be relatively easily separated and removed from the poorer quality spherical particles.

It can thus be seen that a progressive lowering of the current density during electrodeposition results in particles of greatly increased structural uniformity. By combining this procedure with the use of a purified electrolyte, the structural uniformity is enhanced to an even greater extent and in addition the separation of higher quality from lower quality magnetic particles is made possible.

A further advantage of the progressive decrease of the current density is a resulting increase of two to three-fold in the production rate of the fine particles. For example, to make a magnet having a total energy product of 6.0 million gauss-oersteds from deposition at constant current, requires deposition at 0.005 amp./cm.² for 500 minutes or

0.0025 amp./cm.² for 1000 minutes, or equivalent combinations, resulting in 0.05 gram of iron per cm.² of mercury surface in 1000 minutes. The same or better quality material has been made by starting deposition at 0.01 amp./cm.² for 120 minutes and then progressively dropping the current density of 0.005 amp./cm.² for 360 minutes. This produced about 0.065 gram of iron per cm.² of mercury in only 480 minutes. This corresponds to a three-fold increase in yield per unit time.

The foregoing, and particularly the manner in which the current is lowered, will be more clearly understood by reference to the drawings. FIGURE 1 plots the contour lines of constant intrinsic coercive force (H_{ci}) in oersteds of iron particles deposited at constant current with a charcoal-treated electrolyte. The intrinsic coercive force values of the iron particles were measured at -196° C. in their dilute state after optimum aging and tin treatment. It can be seen from FIGURE 1 that at a given constant current the coercive force of the deposited particles progressively changes during the electrodeposition procedure.

FIGURE 2 corresponds to FIGURE 1 except that the contour lines are those of constant packing fraction (P.F.) in percent rather than coercive force. The contour lines of FIGURE 2 represent the packing fraction of iron particles in the gel phase deposited from a charcoal-treated electrolyte. It can be seen that as deposition continues at constant current, the packing fraction increases. It can also be seen from FIGURES 1 and 2 that the slope of the contour lines of constant coercive force and the slopes of the contour lines of constant packing fraction are approximately the same.

The rate at which the cathode current density should be progressively lowered to achieve optimum structural uniformity and magnetic properties can be determined by following along the slope of the best magnetic properties. The slope for intrinsic coercive force will be about the same as that of total magnetic energy but the former is more conveniently measured and hence is used herein to determine the schedule for lowering the current density. This slope will correspond to the constant coercive force contour line (see FIGURE 1) having the highest value.

In addition, if the density or packing fraction of the solid gel formed with the use of a purified electrolyte is maintained constant during electrodeposition, it has been found that structurally uniform particles are obtained. By a progressive lowering of the current density during electrodeposition, a nearly constant packing fraction may be obtained. (The packing fraction is a measure of the volume density of the particles and specifically, the volume of electrodeposited particles per total volume of a given sample.) Thus, a proper schedule for lowering of the current density may be relatively easily determined by following that contour line of constant packing fraction (FIGURE 2) corresponding to the best magnetic properties.

FIGURE 3 illustrates a program or schedule for progressively lowering the current density by following a constant maximum coercive force contour line (FIGURE 1) during electrodeposition of iron and iron cobalt, respectively. It will be seen from FIGURE 3 that the current density is maintained constant until the line of optimum coercive force is reached and then progressively lowered either uniformly, or stepwise, during substantially the remainder of the electrodeposition procedure to follow the slope of the contour line of FIGURES 1 and 2. During the initial period of deposition, the current density need not be maintained constant until the line of optimum coercive force is reached, but this has been found to achieve optimum results.

The electrodeposition procedure of the present invention may be carried out in the same manner set forth in the above Paine et al. Patent 2,974,104 except that the current density is progressively lowered during electrodeposition to maintain a constant particle structure. As

there disclosed, the process comprises electrolytically depositing ferromagnetic particles into a liquid metal cathode, preferably mercury, from an acidic electrolyte comprising ions of the ferromagnetic material while maintaining a quiescent interface between the cathode and the electrolyte. The electrolyte or plating solution consists of the soluble salts of the ferromagnetic metals in the form of, for example, sulfates or chlorides. The pH of the electrolyte is made acidic with, for example, sulfuric or hydrochloric acid, a preferred pH being about two. A consumable anode is used of either the pure ferromagnetic metal or alloys of several ferromagnetic metals. A non-consumable anode of an inert material, such as platinum or graphite, may also be used. A current density between 0.001 amp./cm.² and 0.1 amp./cm.² may be used although values around 0.01 amp./cm.² are preferred. Ordinarily, the electrolyte will be at room temperature of $20-30^{\circ}$ C. during the electrodeposition although other electrolyte temperatures may be used if suitable adjustments are made in current density and time of deposition.

After electrodeposition is completed, the electrodeposited particles are removed as a mercury slurry. If the electrolyte has been treated so as to inhibit hydrogen evolution, the electrodeposited particles in the gel only are removed to obtain the best and most uniform particles. The particles are then heat-treated, to optimize their physical shape and produce maximum coercive force, for from 5-20 minutes at temperatures up to 300° C. and preferably at about $150-200^{\circ}$ C. and then cooled. If desired, the fine particles may be coated with, for example, tin or antimony, the latter in accordance with U.S. Patent 2,999,778, assigned to the same assignee as the present invention. Lead, as a matrix, is then added in elemental form as chunks or pellets of lead as set forth in U.S. Patent 2,999,777, assigned to the same assignee as the present invention. The particles are then aligned and compressed and the remaining mercury removed as, for example, by vacuum distillation at an elevated temperature. The mercury-free mixture of aligned particles and matrix is then ground into a powder and may be either hot or cold pressed and realigned into their final magnet structure.

For purposes of determining properties, the particles, subsequent to the coating step with tin or antimony, may be aligned in a mold by a magnetic field and compressed to any desired packing fraction. The resulting magnets are suitable for evaluation of their magnetic properties but contain from 20 to 90 percent mercury.

The following examples illustrate the preparation of elongated magnetic particles in accordance with the practice of the present invention.

EXAMPLE 1

Iron particles were deposited using an electrolyte of approximately 2 molal FeSO_4 in distilled water. The electrolyte was treated with roughly an equal volume of activated coconut charcoal (6-14 mesh) overnight, filtered into a circulating system containing a pump, a cotton filter cylinder, additional activated coconut charcoal, a temperature controller and the deposition cell. The pH was adjusted to 2.13. The cell was assembled on a shock mounted platform using an iron anode and a stainless steel screen, with $\sim 1/8$ " openings, beneath the mercury pool. After some preliminary deposition to remove depositable impurities, deposition into fresh mercury was then performed following the current density-time schedule depicted in FIGURE 3. The particular current density variation with time was chosen so as to approximate the deposition of the best particles at all times as indicated by the property contour lines shown in FIGURE 1 and corresponding to uniform packing density lines as shown in FIGURE 2. The electrolyte was slowly circulated at the rate of 0.15 liter/min. and maintained at $25^{\circ}\text{C.} \pm 2^{\circ}\text{C.}$ The gel structure was then removed as a single unit by lifting it out on the screen. A suitable portion was then aged

for 20 minutes at 170° C., treated with excess saturated tin-mercury amalgam, placed into a mold, aligned and compressed to 50,000 pounds per square inch.

Table I compares the room temperature properties (column 3) of magnets prepared as set forth in Example 1 with the corresponding properties (columns 1 and 2) of the best iron particle magnets prepared by electrodeposition at 25° C. at constant current with untreated and charcoal-treated electrolyte.

Table I

	(1)	(2)	(3)
Electrolyte.....	Untreated	Charcoal Treated	Charcoal Treated
Current Density, amps./cm ² ..	0.030	0.007	0.020 plus 0.020 to 0.007
Time, minutes.....	54	390	60 plus 440
(BH) _{max} , gauss-oersteds ¹ ..	3.2×10 ⁸	4.0×10 ⁸	4.2×10 ⁸
H _{ci} , oersteds ²	680	790	800
B _r , gauss ³	8,700	8,750	9,090
B _r /B _i @10,000 oersteds ⁴	0.88	0.88	0.91

¹ (BH)_{max} is the maximum energy product.
² H_{ci} is the intrinsic coercive force.
³ B_r is the residual induction.
⁴ B_r/B_i is the ratio of residual to saturation induction.

EXAMPLE 2

Iron-cobalt alloy particles were deposited using the procedures set forth in Example 1 for pure iron particles, except that the electrolyte had a pH of 1.8 and contained 15.45 percent Co⁺⁺ by weight as determined by chemical analysis. The anode was an alloy of 37.5 percent Co—62.5 percent Fe and the particles deposited contained 37.7 percent Co—62.3 percent Fe by weight. The sample was aged at 200° C. for 40 minutes, tin-treated as before and then further aged at 180° C. for 20 minutes. The different aging treatment reflects the change in growth characteristic with changing cobalt alloy composition. The particular current density time program is also plotted in FIGURE 3, and was carried out by means of a suitably shaped motor driven cam to obtain the smoother variation in current with time shown. It should be noted that because the current density changes, the cobalt content of the particles also changes. This cobalt content is calculated to change from about 32 percent cobalt at the beginning of the deposition to about 44 percent cobalt at the end of the deposition. This change does not significantly change the magnetic properties of the particles.

Table II below summarizes the room temperature properties (column 3) of magnets prepared in accordance with Example 2 and compares these properties with the properties (columns 1 and 2) of the best iron-cobalt particles prepared at constant current with untreated and with charcoal-treated electrolyte.

Table II

	(1)	(2)	(3)
Electrolyte.....	Untreated	Charcoal Treated	Charcoal Treated
Current Density, amps./cm ² ..	0.008	0.005	0.010 plus 0.010 to 0.003
Time, minutes.....	560	960	120 plus 355
(BH) _{max} , gauss-oersteds ¹ ..	5.0×10 ⁸	6.1×10 ⁸	6.6×10 ⁸
H _{ci} , oersteds ²	1,050	930	900
B _r , gauss ³	9,050	10,300	10,800
B _r /B _i @3,500 oersteds ⁴	0.88	0.91	0.93

Although the coercive force of the particles made from untreated electrolyte (column 1) shows a higher value than from the treated electrolyte (columns 2 and 3), the coercive force in the dilute state was higher for the particles from the treated electrolyte. The difference results from the fact that the packing fraction for the best magnets (highest (BH)_{max}) occurred at a higher packing fraction for the treated particles than the untreated particles.

This invention is particularly useful in the electrodeposition of particles of iron or iron-cobalt alloys. However, it is also useful with other known ferromagnetic materials including iron, cobalt, nickel and alloys of iron, cobalt and nickel with each other or with other ferromagnetic alloying constituents or with minor amounts of non-ferromagnetic constituents such as manganese or platinum.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. In a process of preparing fine particle magnetic material comprising electrolytically depositing fine particles into a liquid metal cathode during an electrodeposition cycle sufficiently long to produce elongated single-domain magnetic particles from an electrolyte comprising ions selected from the class consisting of iron ions, cobalt ions, nickel ions and combinations thereof, while maintaining a quiescent interface between the cathode and the electrolyte, the improvement which comprises progressively lowering the cathode current density during a major portion of the electrodeposition cycle within the range from a maximum of 5 amps./cm.² to a minimum of 0.001 amp./cm.² to maintain a substantially constant maximum coercive force in the electrodeposited particles.

2. Magnetic material comprising elongated, single domain particles selected from the class consisting of iron, cobalt, nickel and alloys of iron, cobalt and nickel, produced in accordance with the process of claim 1.

3. A process of preparing fine particle magnetic material comprising electrolytically depositing fine particles in the form of a gel into a liquid metal cathode during an electrodeposition cycle sufficiently long to produce elongated single-domain magnetic particles from a purified electrolyte comprising ions selected from the class consisting of iron ions, cobalt ions, nickel ions and combinations thereof, while maintaining a quiescent interface between said cathode and said electrolyte,

the cathode current density during a major portion of said electrodeposition cycle being progressively lowered within the range from a maximum of 5 amps./cm.² to a minimum of 0.001 amp./cm.² to maintain a substantially constant maximum coercive force in the electrodeposited particles.

4. The process of claim 3 in which the electrolyte is purified with activated charcoal.

5. A process of preparing fine particle magnetic material comprising electrolytically depositing fine particles in the form of a gel into a liquid metal cathode during an electrodeposition cycle sufficiently long to produce elongated single-domain magnetic particles from a purified electrolyte comprising ions selected from the class consisting of iron ions, cobalt ions, nickel ions and combinations thereof, while maintaining a quiescent interface between said cathode and said electrolyte,

the cathode current density during a major portion of said electrolytic deposition being progressively lowered within the range from a maximum of 5 amps./cm.² to a minimum of 0.001 amp./cm.² to maintain a substantially constant packing fraction in the gel of fine particles, said packing fraction corresponding to that producing the highest magnetic properties.

6. A process of preparing fine particle magnetic material comprising electrolytically depositing fine particles into a liquid metal cathode during an electrodeposition cycle sufficiently long to produce elongated single-domain magnetic particles from a purified electrolyte comprising ions selected from the class consisting of iron ions, cobalt ions, nickel ions, and combinations thereof, while maintaining a quiescent interface between said cathode and said electrolyte, to form a gel phase of electrodeposited elongated particles and a fluid phase comprising electrodeposited essentially spherical particles,

the cathode current density during a major portion of said electrolytic deposition being progressively low-

ered within the range from a maximum of 5 amps./cm.² to a minimum of 0.001 amp./cm.² to maintain a substantially constant maximum coercive force in the electrodeposited particles and recovering the gel phase only of electrodeposited elongated particles.

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