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ELECTRICALLY DEPOSITED CORE IRON

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This invention relates to thin magnetic material. In particular, it relates to thin, electrodeposited metal having improved magnetic properties.

Iron, nickel, cobalt, and their alloys are known to possess the electromagnetic properties necessary in many types of electrical equipment. Customary methods known to metallurgists have continuously improved magnetic materials through special alloying, melting, and rolling techniques. The advent of higher frequency applications has produced a demand for thinner materials, so that the eddy current losses are not excessive. Thus, 0.014-inch or heavier material is used at low frequencies, 0.005-inch to 0.007-inch material at frequencies around 400 cycles per second, 0.005-inch material at 800 cycles, and 0.002-inch material for higher frequencies. Economic considerations and production difficulties have prevented the large-scale production of thinner material, which is needed before advances can be made in new high-frequency equipment. Thinner material, to 0.0001-inch in thickness, is produced by special rolling techniques at high cost.

Commercial hot-rolled, silicon steels are used in low-frequency, gross magnetically active equipment. Special alloys of much greater cost, such as the commercial Deltamax, Hypersil, and HCR, have superior magnetic properties and are produced in relatively thin gauge down to a thickness of approximately 0.00025-inch or less. These special thin-gauge alloys are very expensive, and to obtain improved magnetic behavior at high frequencies not heretofore accomplished, results in their cost being out of the range that would make them economically suitable for broad use in totally new and superior magnetic equipment.

In order that preferred magnetic behavior can be obtained, the iron or iron alloys must have special orientations which are favorable for magnetization. The cold-rolled material of the presently available thinnest gauges is easy to magnetize in one direction, namely, the direction of rolling. In other directions, it is not nearly so readily magnetized. Therefore, an improved and highly desirable magnetic material would result if it could be produced in thicknesses less than 0.001-inch and be magnetized with equal ease in any direction in the surface.

It has been discovered that, under specially defined conditions of electrolysis, iron sheet or strip can be produced with very superior magnetic properties because, under the special conditions to be disclosed hereinafter, the iron sheet or strip has a highly preferred crystal orientation with the (110) plane parallel to the surface. This preferred orientation must be present in order to obtain magnetic properties not heretofore attainable. Furthermore, there is no prior indication that electrodeposited iron has even been produced with the highly preferred (110) orientation in the thickness ranges exceeding 0.00001-inch. References to the technical literature on iron plating are summarized in an article by Finch and Sun, Trans. Faraday Soc., 32, 852–63, 1936, reporting many investigations of the structure of electrolytic iron, and none of them show an orientation other than (111) crystallographic plane parallel to the surface, except that, thin iron films of thicknesses less than 0.000008-inch have been observed to have the (110) or (100) orientation, which, as greater thickness is applied, change to the (111) orientation.

That mechanical work, such as rolling, forging, or drawing, produces a totally different structure than electrodeposition, is clearly disclosed by Young, U. S. Patent 2,128,389. Young discloses that a rolled sheet of iron or steel, as a consequence of the rolling operation, has a crystalline structure greatly elongated in the direction of rolling or of extension of the sheet. The sheet has a fibrous, stringy structure. Electrolytically deposited sheet is also of fibrous crystalline structure, but the fibers or crystals lie not in the direction of the surface and are not parallel to the surface, but are perpendicular to the surface. Thus, any electrolytic sheet which had the characteristic electrodeposited structure would obviously be altered in structure by rolling or forging so that the crystals were changed to be elongated in the direction of mechanical deformation. Furthermore, Young discloses that heat treating of the electrodeposited iron provides ductility without substantial change in the crystalline structure and that this is made possible because of iron oxide occluded in the grain boundaries, and freedom from impurities of a reducing nature, and that it is the iron oxide content which prevents grain growth at heat-treating temperatures and insures the continuance of the crystalline structure that is characteristic of the electrolytically deposited sheet. He also discloses that the reducing impurities in the iron are too small in quantity to reduce all the iron oxide during normalizing.

It has been found that heat treating, under conditions to be defined hereinafter, of the new electrolytically produced iron having highly preferred orientation in the (110) direction improves the magnetic properties of the material because, in a hydrogen atmosphere, impurities including oxides are eliminated. Such heat treatment does not alter the high degree of preferred orientation and, thus, contrary to the material made by Young, iron oxides are substantially eliminated, and, even then, the as-electrodeposited material is not crystallographically changed in a manner unfavorable for superior magnetic properties.

It is, therefore, an object of this invention to provide a new and novel material having superior magnetic properties.

It is another object of this invention to produce electrodeposited iron with a highly preferred orientation with the (110) plane parallel to the surface of the sheet or strip.

It is a further object of this invention to provide a method by which improved magnetic iron or iron alloys can be manufactured.

In obtaining the objectives of this patent disclosure, iron is electrodeposited in thicknesses less than 0.002-inch and as thin as 0.0001 inch in continuous form without holes or visible physical defects from a solution containing 630 g./l. of ferrous chloride ($FeCl_2.4H_2O$), 120 g./l. of sodium chloride, and sufficient hydrochloric acid to provide a pH of 2. The iron plate having the improved magnetic properties is electrodeposited at 100 amp./sq. ft. in a temperature range of 95 to 110° C. at a rate of 0.0001-inch per minute. In order to obtain the novel magnetic properties, it is essential that there be ferric iron in the plating bath.

An important and novel feature of the process is the use of a suitable basis-metal surface on which to electrodeposit the iron. An improper basis metal will lead to orientation in some other crystallographic plane or, at best, provide a very weak degree of orientation in the (110) direction. It has been found that chromium is particularly suitable for receiving electrolytic iron which will assume a high degree of the (110) preferred orientation.

Furthermore, it has been discovered that the deposition of iron with the (110) orientation in a high degree is critically dependent upon the pH, and current density. Thus, the obtaining of superior magnetic properties is dependent upon maintaining the deposition conditions within close tolerances, which, however, are not impracticably narrow. In addition to affecting the magnetic properties, the conditions of deposition, as is well known to those skilled in the art, also influence the mechanical properties of the plate.

For example, ductile, nonadherent iron with (110) orientation can be electroformed continuously and be

stripped to produce an improved and superior magnetic foil, under the following electrodeposition conditions:

$FeCl_2 \cdot 4H_2O$ conc	450–700 g./l. in the bath.
NaCl conc	60–120 g./l. in the bath.
Ferric iron (Fe^{+++})	0.1–200 g./l. in the bath.
Temperature	80° C. to boiling.
Current density	75 to 125 amp./sq. ft.
pH	Less than 4.

The electrodeposition is made on a basis metal surface of either hard chromium, low contraction chromium, or decorative chromium plate on nickel, or decorative chromium plate on copper. The basis metal must be cold when entering the bath, below 66° C. Otherwise, stripping is difficult.

When the NaCl concentration exceeds 120 g./l., the electroformed iron has a (111) orientation. Also, when the current density is less than 75 amp./sq. ft. or greater than 125 amp./sq. ft., the electroformed iron has a (111) orientation which is not conducive to good magnetic properties.

A stainless steel basis material causes the iron electroformed on it under the cited electrodepositing conditions to be randomly oriented in structure as does also a copper basis surface. A nickel basis surface with (110) orientation causes the iron plate to have a (110) orientation but the iron electroform is firmly adherent and is not detachable without damage to produce the electroformed iron foil of this invention.

When the ferric iron concentration is as shown, the (110) oriented iron is electrodeposited at pH up to 4. Maintenance of ferric iron concentration is difficult at pH above 2, because of hydrolysis to precipitate basic ferric compounds. Thus, operation is preferred at pH of 2 or lower.

The novel feature of using chromium-plated basis-metal surface on which to electroform the desired magnetic iron sheet is not obvious to one skilled in the art and is contrary to disclosures in the technical literature on iron plating. Finch and Sun, loc. cit., show that, regardless of the orientation of the basis-metal surface, in their iron plate, when the thickness exceeded 0.000008-inch, the orientation was with the (111) plane in the surface. Furthermore, in 1939, Wasserman ("Terturen Metallischer Werkstoffe," Springer, Berlin, 1939) provides a summary of X-ray studies of iron electroplates and shows that only the (111) and (112) orientations have ever been observed. Thus, a high degree of orientation in the (110) direction, which is most desirable for superior magnetic uses, would not be expected by one skilled in the art of iron plating simply by changing the electrolyte composition and plating conditions.

Previously, the orientation of a deposit has been shown to be influenced by the basis metal in only initial low thicknesses. Thicker deposits were believed to be oriented only as determined by the plating bath and plating conditions.

One skilled in the art would conclude that plating iron, nickel, or other magnetic alloy on a basis metal in which the surface has a preferred (110) orientation in the plane of the surface will produce thin plate of preferred orientation in the (110) direction. Indeed, it has been found that iron electrodeposited 0.001-inch under the cited conditions on a nickel basis metal with (110) orientation also has (110) orientation in the preferred direction, but the plate is not strippable, whereas iron less than 0.000008-inch thick on the same nickel surface is oriented (100). The (100) orientation for iron is even more desirable than (110) for magnetic material, but there is as yet no process for electrodepositing iron with (100) orientation in thickness exceeding 8 millionths of an inch. However, the (110) orientation of the basis-metal nickel is not the controlling factor per se, because the same iron deposition conditions on copper with a (110) orientation produced iron sheet 0.001-inch thick having no orientation at all but a random structure. Furthermore, on a stainless steel surface, the iron plate deposited from the cited conditions showed no orientation and only a random structure.

As a further example of our discovery of the novel behavior of chromium plate in causing the high degree of

preferred orientation (110), it has been discovered the following bath and plating conditions:

50 oz./gal. ferrous ammonium sulfate,
Sulfuric acid to pH 2,
100° C.,
100 amp./sq. ft.

also produces, on a chromium basis surface, a strippable iron plate over 0.00001-inch in thickness with high degree of preferred orientation with the (110) plane parallel to the sheet surface, when the ferric iron (Fe^{+++}) concentration is in the range of 0.2 to about 50 g./l. Orientation of the iron electroformed foil is (111) when ferric iron is less than 0.2 g./l. and is random when ferric iron concentration exceeds 50 g./l.

Thus, a chromium basis surface and plating conditions at pH 2 or less are preferred to obtain the novel result of the invention.

Extreme thinness and the high degree of preferred orientation in the (110) plane are simultaneously necessary for producing material of superior magnetic properties not heretofore obtained.

In an electrodeposit, the orientation is such that a crystal axis stands perpendicular to the surface or parallel to the direction of current flow, and there is rotational symmetry about the axis. Thus, it will be obvious that the novel product of the invention will be magnetized with equal ease in any direction in the plane of the electroformed sheet or strip and, thus, is a superior material for magnetic uses. Furthermore, since this preferred orientation can be produced in extremely thin material, equipment of magnetic design not heretofore possible is now within reach because of the technical improvement accomplished as well as the economical advantages of the method for producing extremely thin metal.

It is believed that the mechanism by which the novel process achieves the product claimed is related to the fact that chromium and iron have the atomic dimension "*a*" nearer the same than other pure metallic elements. Electrodeposited iron under certain conditions of deposition on chromium plate, assumes a (110) orientation, and other metals such as chromium, cobalt and nickel for which the "*a*" dimension approaches in value close to that of iron, can be codeposited with the iron in providing a thin magnetic foil.

Having thus disclosed the invention, what is claimed is:

1. Thin iron sheet having a thickness of at least 0.0001 inch and not greater than 0.002 inch and having substantially entirely preferred orientation with the (110) crystallographic plane parallel to the surface of the sheet and rotational symmetry about the fiber axis which is perpendicular to said surface.

2. As an article of manufacture, a chromium surface and a layer of iron on said surface, said iron layer having a thickness of at least 0.0001 inch and not greater than 0.002 inch, and characterized by having substantially entirely preferred orientation with the (110) crystallographic plane parallel to the surface thereof and rotational symmetry about the fiber axis which is perpendicular to said surface.

3. The process of making electrodeposited magnetic iron foil which comprises the steps of forming a bath comprising from 450 to 700 g./l. ferrous chloride, 60 to 120 g./l. sodium chloride and sufficient hydrochloric acid to provide a pH of not greater than 4, maintaining said bath at a temperature of from 80° C. to boiling, and passing a current of from 75 to 125 amp./sq. ft. through the bath to a chromium surface serving as a cathode.

4. The process of making electroformed magnetic iron foil comprising the steps of forming a bath comprising from 450 to 700 g./l. ferrous chloride, 60 to 120 g./l. sodium chloride and sufficient hydrochloric acid to provide a pH of not greater than 4, maintaining said bath at a temperature of from 80° C. to boiling, passing a current of from 75 to 125 amp./sq. ft. through the bath to a chromium surface serving as a cathode, and mechanically removing the iron foil from the chromium surface.

5. The process of making electroformed magnetic iron foil comprising the steps of forming a bath comprising from 450 to 700 g./l. ferrous chloride, 60 to 120 g./l. sodium chloride and sufficient hydrochloric acid to provide a pH of not greater than 4, maintaining said bath at a temperature of from 80° C. to boiling, passing a current of from 75 to 125 amp./sq. ft. through the bath to a chromium surface serving as a cathode, mechanically

removing the iron foil from the chromium surface, and heating the electroformed iron foil in a hydrogen atmosphere to a temperature above 650° C. for 1 to 60 minutes.

6. An electrolyte for electrodepositing magnetic iron foil which comprises from 450 to 700 g./l. of ferrous iron chloride, 60 to 120 g./l. of sodium chloride, and sufficient hydrochloric acid to provide a pH not greater than 4.

7. An electrolyte for electrodepositing magnetic iron foil which comprises from 450 to 700 g./l. of ferrous iron chloride, 60 to 120 g./l. of sodium chloride, and sufficient hydrochloric acid to provide a pH not greater than 2.

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