United States Patent Office

2,812,276

Patented Nov. 5, 1957

2,812,276

HIGH FREQUENCY CORES

De Witt H. West, Port Eynon, Swansea, and David M. Llewelyn, Clydach, Swansea, Wales, and Ronald W. Floyd, Hall Green, Birmingham, England, assignors to The International Nickel Company, Inc., New York, N. Y., a corporation of Delaware

No Drawing. Application June 29, 1954, Serial No. 440,244

Claims priority, application Great Britain June 29, 1953

6 Claims. (Cl. 148—31.55)

The present invention relates to a special carbonyl iron powder of improved electromagnetic properties for use in high frequency cores and, more particularly, to a method for producing the special powder.

Attempts have been made in the art to improve the electromagnetic characteristics of carbonyl iron powder (produced by the decomposition of iron pentacarbonyl in a free space) for utilization in the production of magnetic cores in high frequency coils and the like. When cores comprising carbonyl iron powder are coupled with high frequency coils, they impart to the coils additional inductance and also additional series resistance. For optimum core-coil efficiency, it is essential that the iron powder employed in the core assure a high Q value which is defined for a core-coil assembly as the ratio of $2\pi fL$ (inductive reactance) to R (series resistance), wherein f is the frequency, L is the inductance measured in henries and R is the resistance measured in ohms. It is desirable that the inductance of the core assembly be as high as possible in contradistinction to the resistance which should be as low as possible so that optimum Q values can be obtained. Generally, when the core-coil resistance is high, eddy current losses are considerable.

A method which has been employed in an attempt to improve the electromagnetic characteristics of carbonyl iron powders has been to heat treat the powders in hydrogen at temperatures up to about 400° C. and higher. While this treatment has been indicated to improve, to a certain extent, the electromagnetic properties of iron powders, it was found that the powders were generally rendered magnetically soft due to a reduction in carbon content, usually substantially below 0.1%, resulting from the hydrogen treatment. Such soft materials were found not to have adequate Q values at high frequencies of the order of about 20, 30 and even 50 megacycles when employed in cores. Although many attempts were made to overcome the foregoing difficulties and disadvantages, none, as far as we are aware, was entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that magnetic core material can be produced with a consistently high Q value by subjecting a carbonyl iron powder of controlled carbon content to nitriding in an atmosphere containing nitrogen in a reactive form.

It is an object of the present invention to provide an improved process of treating carbonyl iron powder whereby substantially increased Q values are obtained.

Another object of the invention is to provide a treated carbonyl iron powder characterized by improved electromagnetic properties at high frequencies of the order of 20, 30 and even 50 megacycles.

The invention also contemplates a magnetic core characterized by high Q values in combination with low eddy current losses when employed at high frequencies.

Generally speaking, the present invention contemplates an improved nitriding process for treating carbonyl iron powder of controlled carbon content whereby the powder

resulting from the treatment is characterized by markedly improved Q values when employed in magnetic cores. The improved results of the invention are achieved when ammonia is employed as the nitriding medium and when the carbonyl iron powder employed in the nitriding treatment contains controlled amounts of carbon ranging from about 0.1% to 0.9%, preferably in amounts ranging from about 0.5% to 0.85%.

In order to obtain the results of the invention, the carbonyl iron powder is heated in ammonia gas to 300° C. or above, generally to 350° C. or above and preferably to 400° C. to homogenize the powder. The ammonia treatment may be carried out at temperatures ranging from about 250° C. to about 550° C. The rate of nitriding in a given furnace is affected by the specific surface of the powder, the rate of flow of the ammonia over the charge and the temperature. The nitriding time decreases as the temperature is increased and for a charge weight of 300 gms. in a bed 5" x 1½" x ½" treated in a 2" diameter tube furnace with an ammonia flow rate of 20 litres per hour the preferred times of nitriding are about 42 hours at 250° C., about 17 hours at 300° C., about 5 hours at 350° C., about 3 hours at 400° C. and about 1 hour or even less at 500° C. or 550° C. It is important when nitriding the carbonyl iron powder that substantially all the particles of the iron are exposed to ammonia during the treatment in order to assure a homogeneous product with respect to the carbon and the nitrogen contents. This is achieved by agitating or mixing the powder during the nitriding process, for example, by tumbling or other means. When carbonyl iron powder is nitrided at a low temperature of 250° C. and in the range of about 250° C. to not exceeding about 300° C., the Q values, while improved, are not as high as the Q values obtained when the nitriding treatment is conducted at temperatures of above 300° C. and up to about 400° C., for example, at about 350° C. When the nitriding process is carried out within the range of about 250° C. to 300° C., markedly improved results are achieved when the process is followed by a high-temperature homogenizing treatment. In other words, a two-stage process may be employed involving a low-temperature stage process in ammonia (at about 250° C. to 300° C.) in which nitrogen is absorbed into the carbonyl iron powder and a high-temperature stage in nitrogen (above 300° C. and up to about 400° C., e. g. 350° C.) in which the nitrogen absorbed during the low-temperature stage is caused to diffuse by heat treatment in the powder to produce a substantially homogenized powder. The second stage is referred to as a homogenizing treatment. When the nitriding process provided by the invention is carried out at or above about 350° C., a separate homogenizing treatment is not necessary as the nitriding temperatures employed are sufficient to homogenize the powder.

As illustrative of the results which are achieved with the two-stage treatment, the following example is given:

A carbonyl iron powder having an average particle size of about 5.3 microns, a nitrogen content of about 0.68% and a carbon content of about 0.64% was employed. This powder had a Q value at 20 megacycles in the untreated condition of about 162 and a value at 50 megacycles of 129. A weight of 50 grams of this powder was treated in a one-inch diameter tube furnace at about 250° C. for a period of 24 hours in anhydrous ammonia flowing at the rate of about 5 litres per hour. The powder after cooling was found to be slightly sintered and was ground. As a result of the low-temperature treatment, the iron powder had an increased nitrogen content of about 4.69% with the carbon content remaining at about 0.64%. The Q value at 20 megacycles improved to 167 while the Q value at 50 megacycles im-

proved to 146. The powder was then again placed in the tube and subjected to a high-temperature homogenizing treatment at about 350° C. for 2 hours in a substantially oxygen-free nitrogen atmosphere. The powder after cooling was found to be slightly sintered and was ground. The powder after the high-temperature homogenizing treatment had the same nitrogen and carbon contents but exhibited markedly improved magnetic properties. The Q value at 20 megacycles was improved to 182 while at 50 megacycles it was improved to 178.

While it has been stated that the ammonia nitriding process may be conducted at temperatures up to about 550° C., it is preferred for consistent results that the temperature not exceed about 450° C. as the ammonia tends to dissociate appreciably in the presence of iron powder into nitrogen and hydrogen. When this occurs, the hydrogen may react with the carbon and remove it as methane unless special precautions are taken. Likewise, the nitrogen originally contained in the powder may also be removed. This was indicated in an experiment involving the nitriding of a stationary bed of carbonyl iron powder containing 0.49% nitrogen and 0.47% carbon at a temperature between 450° C. and 500° C. Ammonia was passed over the stationary bed of the powder for a given length of time sufficient to cause nitriding. During the beginning of the nitriding, the exit gas was found to contain about 6.4% methane, thus indicating carbon removal and hence decarburization of the iron. Upon completion of the test, the powder at the inlet end was found to contain about 5.71% nitrogen and about 0.34% carbon while the powder at the exit end contained a much lower nitrogen content of about 0.09% nitrogen and a lower carbon content of about 0.14%. The nitrogen-enriched powder at the inlet end exhibited a high Q value of about 158 at a frequency of 20 megacycles as compared to a low Q value of only 65 obtained at the same frequency for the nitrogen-poor powder produced at the exit end. When the nitriding process is carried out at a temperature not exceeding 450° C. and preferably below this temperature, e. g., 350° C., this effect is substantially minimized. When a high nitriding temperature in excess of about 450° C. is employed, it is preferred that the bed of iron powder be agitated during the process in order to keep the iron particles in continual contact with substantially undissociated ammonia to insure the production of a uniform product of improved electromagnetic properties. In other words, loss of nitrogen and carbon must be avoided in the product when high nitriding temperatures in excess of 450° C. are employed.

When the nitriding process of the invention is carried out over the temperature range of about 250° to 550° C., the flow rate of ammonia employed should be sufficient to ensure that hydrogen formed during the reaction is quickly swept away so that no particle comes into contact with an atmosphere containing any substantial proportion of hydrogen. The rate of flow required will depend on the dimensions of the apparatus and on the operating conditions. It is desirable that the carbonyl iron powder being treated have an average particle size falling within the range of about 2 microns to about 6 microns. Generally, the finer the particle size of the iron powder, the shorter will be the treating time at a given temperature.

It has been found that in order to achieve the results of the invention, the carbon-containing, nitrided product must fulfill certain requirements with respect to its composition. It is not sufficient that the carbon-containing product merely contain nitrogen per se. It is important that the nitrogen be present in a special form consistent with obtaining the results of the invention. Depending upon the nitrogen content, the nitrided product at ordinary temperatures may be comprised of one or more phases. For nitrogen contents of up to about 8% and up to 11%, the one or more phases which may be present include alpha (α), gamma' (γ') and epsilon (ϵ). It has been found that unless the amounts of these phases are controlled within certain limits, the results of the invention are not achieved. Tests have indicated that in order for the product to exhibit the substantially improved Q values provided by the invention, the product should comprise not more than about 50% of the alpha phase, not more than about 25% or 30% of the epsilon phase, substantially the balance comprising the gamma' phase. It is preferred for consistent results that the product comprises not more than about 20% of the alpha phase, not more than about 10% of the epsilon phase, the balance being substantially all gamma'. For best results, it is most desirable that the product be comprised substantially of the gamma' phase.

The alpha phase referred to hereinbefore is substantially an iron-nitrogen solid solution containing less than about 0.1% nitrogen. This phase has a body-centered cubic structure characteristic of pure alpha iron. The gamma' phase appears to correspond to the iron-nitrogen compound Fe_4N which is comprised of about 94.1% iron and about 5.9% nitrogen and which has an ordered face-centered cubic structure. The nitrogen in the gamma' phase may range approximately from about 5.8% to 6.1%. With regard to the epsilon phase, X-ray diffraction studies have indicated this phase to be based upon the formula Fe_3N (closed-packed hexagonal structure). A stoichiometric composition of Fe_3N corresponds to about 7.7% nitrogen. This phase appears to have a wide range of nitrogen solubility ranging from about 8% to about 11%.

As it has been stated hereinbefore, it is essential that the epsilon phase (Fe_3N) in the nitrided product not exceed about 25% or 30%, otherwise the Q values are detrimentally affected. This is indicated by the data in the following tables:

Table I

Powder	Composition			Structure [1]		
	Percent N	Percent C	Percent Fe	Percent Epsilon (Fe_3N)	Percent Alpha (Fe)	Percent Gamma' (Fe_4N)
A	5.6	0.7	Bal.	50	20–30	Bal.
No. 1	5.6	0.7	Bal.	30	----------	Bal.
No. 2	5.3	0.7	Bal.	20	----------	Bal.
No. 3	5.0	0.6	Bal.	----------	----------	Bal.
No. 4	4.9	0.4	Bal.	----------	10–15	Bal.
No. 5	5.1	0.4	Bal.	----------	----------	Bal.
No. 6	6.1	0.1	Bal.	10	----------	Bal.

[1] Estimated from X-ray diffraction data.

Table II

Powder	Q Values	
	20 Megacycles	30 Megacycles
A	148	160
No. 1	165	187
No. 2	177	187
No. 3	177	196
No. 4	173	192
No. 5	170	190
No. 6	166	187

It will be noted from the tables that powder "A," which was estimated by X-ray diffraction data to contain about 50% of the epsilon phase and about 20% to 30% of the alpha phase and which is outside the scope of the invention, exhibited a lower Q value than powders No. 1 to No. 6 provided by the invention. Powder "A" was nitrided at the low temperature of 250° C. which, as indicated hereinbefore, is not usually sufficient by itself in achieving the results of the invention, unless the low-temperature treatment is followed by a high-temperature homogenizing treatment. Powder No. 1 is powder

"A" subjected to a homogenizing treatment for two hours at 350° C. in an inert atmosphere. It will be noted that the Q values improved because of the homogenizing treatment which resulted in a decrease in the amount of the epsilon phase from 50% to 30%. Powders No. 2 to No. 6 are illustrative of the optimum Q values which can be obtained when the nitriding temperature is at or above 350° C. Powder No. 2, which was nitrided at 350° C., has a still lower epsilon content of about 20%, substantially the balance being all gamma'. Powder No. 3, which was nitrided at 400° C., comprised substantially all gamma'. Powder No. 4, which was nitrided at 470° C., likewise did not indicate the presence of epsilon although it did contain from 10% to 15% of the alpha phase. Powder No. 5, which was nitrided at 500° C., was indicated to be comprised of substantially all gamma'. Powder No. 6, which was nitrided at 550° C., indicated a slight falling off in the Q value as compared to powders No. 3 to No. 5 due to the presence of about 10% epsilon phase, substantially the balance of the powder being gamma'. The data in the foregoing tables confirm that when the epsilon phase in the powder exceeds 30%, the Q values are detrimentally affected. Tests have indicated that peak Q values are obtained when the nitrided carbonyl iron powder is comprised substantially of the gamma' phase. In other words, when the iron powder contains about 5.8% to about 6.1% nitrogen all substantially combined as Fe_4N (gamma'), maximum Q values are obtained. If the alpha iron in the nitrided powder increases up to about 50%, there is a falling off in Q values. Likewise, when the spsilon phase in the powder increases up to 25% or 30%, there is also a falling off in Q values but at a much more rapid rate than when only alpha is present. It is preferred that the nitrogen content of a properly produced nitrided powder should not exceeds 6% so that the epsilon phase may be maintained at a minimum. It is found that in nitrided powders containing a high proportion of carbon, e. g. 0.5% to 0.7% carbon, a 100% gamma' phase may be produced with less than about 6% nitrogen present, e. g. about 5% nitrogen. It is believed that part of the carbon in such powders enters the Fe_4N (gamma') lattice and replaces part of the nitrogen. It is also believed, based on experimental observation, that the amount of carbon that enters the lattice has the same effect in improving Q values as a higher amount of nitrogen. Whatever the theory, tests indicate that carbon appears to have an important effect, together with nitrogen, in improving Q values.

It is also possible by means of the invention to effect a substantial improvement in the Q values at high frequencies of decarburized iron carbonyl powders, e. g. with 0.01% to 0.03% carbon. The products obtained by nitriding such powders are, however, not so satisfactory for the manufacture of magnetic cores for use at high frequencies as those obtained by nitriding powders containing 0.1% to 0.9% carbon and preferably about 0.5% to 0.85% carbon which have not undergone decarburization. The reason for this is that during the decarburization process deleterious effects, for instance distortion from a substantially spherical form due to sintering, are produced on the powder particles, and these effects render the particles less easy to insulate properly.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A magnetic core suitable for use at high frequencies of up to about 50 megacycles and higher and having a high Q value, said core comprising a nitrided carbonyl iron powder which has a carbon content of about 0.1% to 0.9% and which contains such an amount of nitrogen that said nitrided powder is in a form corresponding to substantially all gamma' phase.

2. A magnetic core suitable for use at high frequencies of up to about 50 megacycles and higher and having a high Q value, said core comprising a nitrified carbonyl iron powder which has a carbon content of about 0.5% to 0.85% and which contains such an amount of nitrogen that said nitrided powder is in a form corresponding to substantially all gamma' phase.

3. A magnetic core suitable for use at high frequencies of up to about 50 megacycles and higher and having a high Q value, said core comprising a nitrided carbonyl iron powder which has a carbon content of about 0.1% to 0.9% and which contains such an amount of nitrogen that said nitrided powder is in a form corresponding to alpha phase in amounts not exceeding about 20%, epsilon phase in amounts not exceeding about 10%, with the balance substantially all gamma' phase.

4. A magnetic core suitable for use at high frequencies of up to about 50 megacycles and higher and having a high Q value, said core comprising a nitrided carbonyl iron powder which has a carbon content of about 0.5% to 0.85% and which contains such an amount of nitrogen that said nitrided powder is in a form corresponding to alpha phase in amounts not exceeding about 20%, epsilon phase in amounts not exceeding about 10%, with the balance substantially all gamma' phase.

5. A nitrided carbonyl iron powder characterized by a high Q value at high frequencies of up to about 50 megacycles and higher, said powder comprising about 0.1% to 0.9% carbon and comprising such an amount of nitrogen that said nitrided powder is in a form corresponding to alpha phase in amounts not exceeding about 50%, epsilon phase in amounts not exceeding about 30%, with the balance substantially all gamma' phase.

6. A nitrided carbonyl iron powder characterized by a high Q value at high frequencies of up to about 50 megacycles and higher, said powder comprising about 0.5% to 0.85% carbon and comprising such an amount of nitrogen that said nitrided powder is in a form corresponding to alpha phase in amounts not exceeding about 50%, epsilon phase in amounts not exceeding about 30%, with the balance substantially all gamma' phase.

References Cited in the file of this patent

UNITED STATES PATENTS

2,666,724 Beller ---------- Jan. 19, 1954