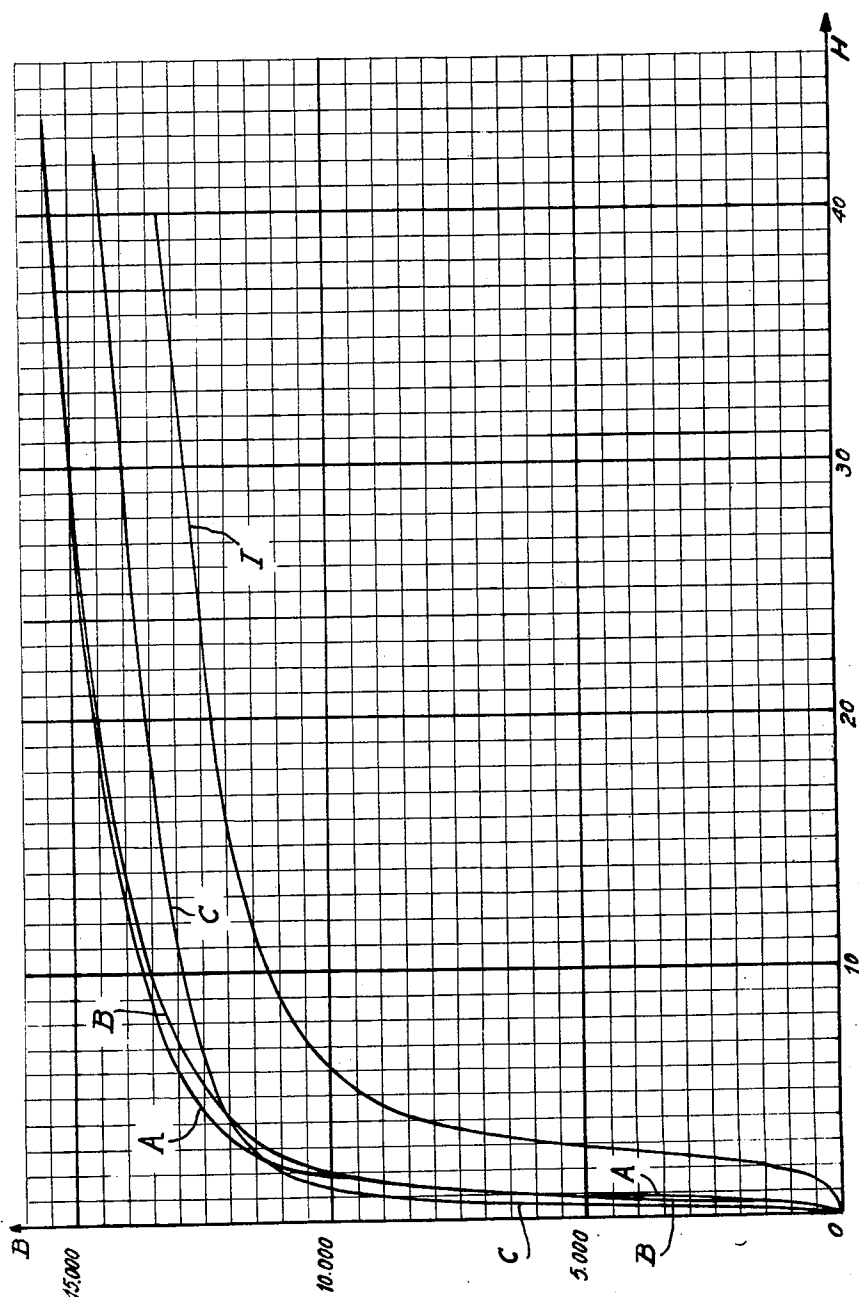


Sept. 4, 1962

E. R. A. JOSSO
METAL COMPOSITION HAVING IMPROVED OXIDATION- AND
CORROSION-RESISTANCE AND MAGNETIC
CHARACTERISTICS, AND METHOD OF
PREPARING SAME
Filed Jan. 27, 1959

3,052,576



Inventor

Emile R.A. Josso

By Stevens Davis Miller & Meader
Attorneys

1

3,052,576

METAL COMPOSITION HAVING IMPROVED OXIDATION- AND CORROSION-RESISTANCE AND MAGNETIC CHARACTERISTICS, AND METHOD OF PREPARING SAME

Emile R. A. Josso, Sauvigny-les-Bois, Nièvre, France, assignor to Societe Metallurgique d'Imphy, Paris, France, a company of France

Filed Jan. 27, 1959, Ser. No. 789,411

Claims priority, application France Feb. 6, 1958

7 Claims. (Cl. 143-120)

This invention relates generally to iron alloy compositions.

In recent years a need has arisen for magnetically "soft," i.e. low-remnance materials, that would be capable of prolonged and unimpaired operation under oxidizing conditions, as in warm moist atmosphere, distilled water, etc., and/or chemically corrosive conditions such as encountered in brine-laden atmosphere, ocean mist and spray, nitrous vapours, and the like. Conventional magnetic alloys are not entirely satisfactory in these respects. Some, such as iron, soft steel, iron-silicon alloys containing about 3 to 4% Si, iron-cobalt alloys, iron-nickel alloys containing less than 60% Ni, have inadequate corrosion resistance. Others, including iron-nickel alloys with more than 60% Ni, do not yield the desired high values of magnetic permeability.

Iron-chrome alloys containing at least 12% Cr are known to have excellent resistance to corrosive agents and have moderately good magnetic characteristics. Thus alloys containing about 17% Cr are frequently used where chemical resistance is an imperative requisite. However the magnetic characteristics of these materials is still poor when compared to those of the usual magnetic alloys. Thus an induced magnetization of about 10,000 to 11,000 gauss may be obtained in an inductor field of 3 oersteds when using an ordinary grade of iron-silicon sheet material. In the same inductor field strength, the commercial Fe—Cr alloy containing 17% Cr mentioned above only yields 2000 to 6000 gauss. The magnetic losses for an induced magnetism of 10,000 gauss and at a frequency of 50 cycles per second, attain values as high as 5 to 12 watts per kilogram, whereas such losses are no more than about 1.3 to 2.6 watts per kilogram in the case of hot-rolled iron-silicon sheet of usual grade. For the above reasons, the use of iron-chrome alloys has been restricted to induced magnetism values of about 10,000 to 11,000 gauss and the efficiency ratio of systems using such materials has been poor.

Materials of the kind just specified are commercially prepared in the presence of atmospheric air, usually in an electric arc furnace or an induction-heated furnace, and it is endeavored during the production process to keep the concentration of impurities low. The refining reactions require the production of slag that will be alternately oxidizing and reducing. However such reactions never proceed to completion. They succeed in lowering the concentration of impurities but not in eliminating them completely. In particular, a non-negligible proportion of oxygen is retained in the liquid bath, and this must be neutralized if a sound material is to be obtained that will be readily convertible into finished products. For this purpose, strong de-oxidants are added to the metal bath, such as calcium, silicon, aluminium, titanium, and the like, which act to fix the oxygen as stable compounds. Part of these compounds is eliminated by a settling process, but the finer particles remain in suspension in the bath and occur in dispersed form throughout the body of the solidified ingot. If an excess amount of deoxidizers is added in an attempt to achieve complete oxygen neutralization, it is found that the avidity of

2

such agents towards the carbon and nitrogen in the bath is such that carbides and nitrides are produced which occur throughout the product material. It is well known that the presence of foreign particles in the midst of a magnetic material increases the magnetic hardness, i.e. remanence, of the material. Hence, the combined effects of oxides, carbides and nitrides all contribute to impairing the magnetic characteristics of the product.

It is an object of this invention to provide a method of producing iron-chrome alloys that will be purer, more resistant chemically and will possess better magnetic characteristics than those heretofore available. The improved materials make it possible to produce values of induced magnetism of the order of 9,000 gauss and more in an inductor field of 3 oersteds and less, with losses, at 10,000 gauss and 50 c.p.s. of about 1 to 2.5 watts per kilogram. While these figures are given simply by way of indication, when compared with the previously mentioned data relating to conventional products of otherwise comparable properties, they illustrate the outstanding differences of the improved products of this invention over conventional iron-chrome alloys of similar chrome content, which latter are so inefficient magnetically that they can only be used in cases where the condition of chemical inalterability is so imperative that considerations of efficiency, space and weight can be sacrificed. The magnetic characteristics of the improved product are comparable to those of hot-rolled iron-silicon sheet of usual grade, over which, of course, the product of the invention has the great advantage of chemical inertness.

The iron alloys to which the method of the invention is applicable are those containing not less than 12% chromium. The chemical inertness of such alloys is the higher in proportion as their chrome content is higher, but the values of magnetic induction that can be attained therewith decrease with chrome content, as indicated by the ensuing table in which the magnetism B_0 is given in gauss for various values of chrome concentration percent.

Cr percent:	B_0 gauss
13	18,000
15	17,400
17	16,900
20	16,100
22	15,600
25	14,800
28	14,000
30	13,400
40	10,000

It is seen that the conditions of optimum chemical inertness and optimum magnetic characteristics are not consistent with each other. In most cases a satisfactory compromise between the two conditions is obtained with a chromium content of about 17%; such composition however is not restrictive and other compositions, both lower and higher in chrome content, have yielded good results. A range of chrome content values usable in accordance with this invention is from about 12 to about 40% Cr. Below 12% Cr chemical inertness is inadequate; above 40% Cr the magnetic flux densities obtainable are insufficient. A composition according to the invention preferably further contains a small proportion of manganese, from 0 to about 2%, with the remainder comprising iron, and possibly any of the usual metallurgical impurities. A narrow preferred range of composition according to the invention can be given as Cr: 13.5-20%, Mn: 0-1%, with the remainder comprising Fe and any minor impurities.

The process of preparing a composition according to the invention broadly involves two steps. The first step

comprises preparation of a high-purity alloy, while the second step is to prepare the final composition from such alloy, in such a manner as to retain, and preferably improve, the high initial purity obtained in the first step.

In the first step of the process the constituents of the alloy are melted together in the proportions specified above, and under such conditions as to minimize or prevent any contamination with air, and one at least of the steps starting with the melting of the constituents and ending with the cooling of the solidified alloy in a mould, being effected under subatmospheric pressure.

The constituents are melted in an electric furnace which may be an induction furnace, a resistance or an arc furnace, within a sealed enclosure having means for selectively reducing the internal pressure and/or introducing a gas atmosphere of selected composition. So-called "vacuum melting furnaces" are well suited for this purpose. While the melting operation may be performed under a highly reduced pressure, it is usually more desirable, in order to prevent excessively violent boiling of the molten metal, to operate under a pressure only slightly less than atmospheric. Preferably the furnace atmosphere comprises a non-oxidizing and non-nitriding medium, such as argon, helium, hydrogen, and the like. Where the metal charge, essentially comprising iron and chromium in the specified proportions and possibly a small amount of carbon, has not been melted under high negative pressure, the pressure is first reduced by means of a vacuum pump when the alloy constituents have been entirely melted, and at a very gradual rate so as to control at all times the degree of boiling in the bath. The manganese usually added may be introduced into the solid charge or it may be added to the liquid bath prior to or during the vacuum pumping.

The reduction in pressure causes a refining of the alloy in two ways:

(a) It promotes the discharge of volatile impurities contained therein in free or combined condition, and

(b) It shifts the equilibrium point of the reaction $C + O \rightleftharpoons CO$ between the carbon and oxygen contained in the molten metal towards the CO side, thereby completely eliminating both the carbon and oxygen impurities, especially the oxygen.

For this purpose high vacuum is not necessary. The reaction $C + O \rightarrow CO$ already is highly active under a pressure of about $\frac{1}{10}$ of atmospheric. However, the degree of refining is increased as the pressure is reduced.

It is found advantageous to adjust the composition of the melt so as to have a slight excess of carbon in it capable of ensuring complete de-oxidation. Any residual carbon that may remain is less objectionable than would be oxygen, since a major part of it can always be removed if desired during subsequent heat treatment steps according to the invention. The excess of carbon can attain as much as 0.20%, but is preferably made not higher than about 0.10%. Since de-oxidation was effected by the action of carbon under reduced pressure, it becomes superfluous to add one or more active de-oxidizers such as calcium, aluminum, titanium, etc., thereby averting the many drawbacks which the formation of compounds of these elements usually entails.

After reduced pressure has been maintained for a suitable time depending on the desired degree of refining, the molten alloy is cast in ingot or other moulds, preferably under sub-atmospheric pressure and where possible in a non-oxidizing and non-nitriding atmosphere.

As regards the second stage of the process, unless the solidified alloy is to be used directly in the form of mouldings, the ingots may be forged or rolled hot, by conventional methods, into suitable shapes such as bars, strips or sheet. The latter may then either be used directly for the production of magnetic parts or they may serve as semi-finished products from which wires may be drawn or strips may be cold-rolled. Such latter operations will usually involve one or more intermediate softening (an-

nealing or tempering) treatments between the successive rolling or wire-drawing stages for eliminating cold-work stresses and permitting further dimensional reduction. In the process of the invention such intermediate annealing steps are carried out in a temperature range of from 600 to 1100° C. substantially in the absence of air in order to avert contaminating the magnetic alloy and preserve its pure condition. By the expression "substantially in the absence of air" it is here meant that the operation should be carried out under such conditions that surface alteration of the kind that would occur if the operation were conducted in free contact with air, is avoided. Thus, annealing within a sealed enclosure, preferably filled, in addition to the treated metal, with inert and/or oxygen- and nitrogen-fixing materials, and hence only containing a small quantity of air prevented from being renewed, is according to the invention considered as being carried out "substantially in the absence of air," since the quantity of air available is insufficient seriously to contaminate the metal. Such annealing procedure therefore enters within the scope of the invention to the same extent as would annealing treatments conducted in neutral or reducing media. Desirably, the cold-rolling or wire-drawing treatments are preceded by removal of the surface film of oxide formed during forging or hot rolling. This step may be performed by pickling, grinding or rectifying, cleaning with emery cloth or by any other well-known mechanical and/or chemical procedure.

The outstanding magnetic characteristics previously mentioned are imparted to the finished product by appropriate heat treatment. In accordance with the invention, such treatment is designed to conserve the high initial purity of the product and if possible to enhance it, and for this purpose it may comprise annealing in a temperature range of from 600 to 1300° C., and preferably from 700 to 1150° C., substantially in the absence of air (this phrase being used in the same sense as above), and possibly followed by a further annealing step also substantially in the absence of air and within a temperature range of from 550 to 950° C., with the temperature in this further annealing treatment being at least 50° C. lower than the temperature used in the first annealing operation. The first annealing treatment is, in principle, sufficient to impart the high magnetic characteristics to the composition of the invention, but the second annealing operation will frequently achieve a substantial additional improvement in the characteristics. The annealing steps should be conducted under non-oxidizing and non-nitriding conditions. As the atmosphere used in the annealing furnace, rare gases such as argon and helium are very satisfactory but are relatively expensive. While a reducing atmosphere comprising a mixture of hydrogen and nitrogen as obtained in ammonia cracking processes may in some cases be used, such an atmosphere is not especially well-suited because of the liability to nitridation due to the presence in the mixture of nitrogen gas and possibly small proportions of incompletely reacted ammonia. Excellent results are obtained where the annealing atmosphere used is pure hydrogen in vacuo. When a high vacuum is used, the resulting metal has a surface finish as clean as and sometimes brighter than it was before treatment. Insufficient vacuum may result in slight oxidation, but this can be minimized and even entirely eliminated by taking care to expell the air from the treating enclosure with a stream of argon, helium, hydrogen, or the like before evacuating the enclosure. In an atmosphere of hydrogen and other suitable media the resulting metal surface will generally be more or less coloured due to the presence of traces of oxygen. However such oxide film may in some cases have a beneficial effect in that it will provide electrical insulation preventing the flow of eddy currents in service and will contribute to reduce power losses in laminated magnetic circuits. In other cases however the oxide film may be undesirable to the extent that it may tend to lower corrosion resistance which property is

influenced by the physical and chemical conditions of the metal surface. In such cases the heat treatment should be followed by a chemical pickling step or the like and possibly a passivating treatment by conventional methods; such latter treatment may likewise be applied alone in some cases where the material does not require pickling.

The ensuing examples are given as illustrations of the invention. The accompanying drawing is a chart showing magnetization (or flux density) in gauss plotted against magnetic field strength (or magnetomotive force) in oersteds, for three alloy compositions prepared according to the invention and for a conventional alloy of generally comparable character.

The attached table indicates the principal magnetic characteristics of the same four alloy compositions. Initial permeability was measured at 400 c.p.s. using an impedance bridge in the case of a toroidal test-piece, while the maximum permeability and magnetomotive field were determined on a toroidal testpiece by means of a dynamic galvanometer. Losses were measured using test strips inserted in the core of a measuring bridge.

Using an induction furnace, three iron-chromium melts were prepared, respectively designated A, B and C. The chrome contents in the three melts were about 15%, 17.5% and 20% respectively, with iron in corresponding proportions. Melt C further contained 0.10% carbon. Each charge thus obtained was first heated in a vacuum higher than 10^{-3} mm. mercury so long as it remained solid, and then was melted in an argon atmosphere at a pressure of 600 mm. mercury. After thorough melting the pressure was reduced and an amount of 0.5% Mn was added when the pressure had dropped to 50 mm. mercury. Evacuation of the furnace was continued until the following limiting pressures were reached:

Melt A: 0.40 mm. mercury

Melt B: 0.35 mm. mercury

Melt C: 0.14 mm. mercury

The alloys were cast in steel ingot moulds in an argon atmosphere at a pressure of 250 mm. mercury. The resulting compositions in percent discounting impurities, were as follows:

	C	Si	Mn	Cr	Fe
Melt A-----	0.02	0.01	0.38	14.44	Complement.
Melt B-----	0.02	0.01	0.48	17.53	Do.
Melt C-----	0.01	traces	0.29	19.69	Do.

The ingots were forged and then hot-rolled into 5 mm. thick strips which were ground on both faces to remove scale to a depth of 0.3 mm., and then cold-rolled to a thickness of 0.3 mm. During the cold rolling the stock was annealed between passes at a temperature of 850° C. in hydrogen. The 0.3 mm. strips were then formed by conventional techniques into magnetic core elements both in toroidal and strip form, which were heat treated as follows:

Stock A: Single annealing treatment at 1000° C. in pure hydrogen;

Stock B: First annealing step at 1000° C. in pure hydrogen followed by a second anneal at 800° C. in pure hydrogen;

Stock C: Single anneal at 1000° C. in a vacuum of about 2.5×10^{-5} mm. Hg.

The accompanying chart shows the magnetic curves for the stock A, B and C and for a convention 17% Cr alloy labelled I. The curves show that for a given magnetomotive force the flux densities obtained are much higher in the alloys of the invention or, in other words, that a given magnetization is obtained with a much weaker field.

The table below relates to the same products and shows that all magnetic characteristics and especially those relating to power losses are considerably improved in the compositions of the invention over the conventional composition.

Reference	Cr, per-cent	Initial permeability	Maximum Permeability	Magnetomotive field for a max. field of 20 oe. (oersteds)	Losses at 10,000 g. at 50 cps. (Watts/kg.)
A-----	14.44	676	5,790	0.80	1.2
B-----	17.53	535	5,870	0.80	1.3
C-----	19.69	712	9,410	0.46	1.4
I-----	17	200	2,000	3	5.6

It is emphasized that the magnetic characteristics given in this table and in the chart do not by any means constitute maximum or optimum figures, but rather should be interpreted as mean values, since in some cases even higher performance was recorded.

Further, various modifications may be made in the details of composition and procedure described without departing from the scope of the invention.

What I claim is:

1. The method of producing shaped magnetic products having a high oxidation and corrosion-resistance and low magnetic remanence, which consists in melting together substantially in the absence of air the constituents of an alloy consisting essentially of 12 to 40% chromium, up to 2% manganese, less than about 0.2% carbon, with the remainder essentially iron and minor impurities, subjecting the melted alloy to a vacuum of at least $\frac{1}{10}$ atmosphere thereby removing free and combined oxygen therefrom to obtain an alloy substantially free of oxygenated compounds, cooling the resultant refined melted alloy under sub-atmospheric pressure at least to its solidification point, forming the solid alloy into a shaped product, annealing said product in an atmosphere substantially free of air in a temperature range of from about 600° C. to 1300° C. to develop high magnetic characteristics therein; and subjecting said shaped and annealed product to a second annealing treatment in an atmosphere substantially free of air in a temperature range of from 550° C. to 950° C. and at a temperature less by at least 50° C. than said first annealing treatment.

2. The method of claim 1 wherein the first and second annealing treatments are effected in a hydrogen atmosphere.

3. The method of claim 1 wherein the first and second annealing treatments are both effected at sub-atmospheric pressure.

4. The method of claim 1 wherein the first and second annealing treatments are effected in a non-nitriding atmosphere.

5. The method of claim 1 wherein the first annealing treatment is effected in a temperature range of from about 700° C. to 1150° C.

6. The method of claim 1 comprising in the shaping operation for the solid alloy at least two cold working operations separated by a softening or annealing treatment, wherein said softening or annealing treatment is effected substantially in an atmosphere substantially free of air and in a temperature range of from 600° C. to 1100° C.

7. In a process of producing shaped magnetic products, having a high oxidation and corrosion-resistance and low magnetic losses, consisting in shaping into a finished product an alloy consisting essentially of from 12 to 40% chromium, up to 2% manganese, less than about 0.2% carbon, with the remainder essentially iron and minor impurities, said alloy being further substantially free of oxygenated compounds in dispersed form

throughout its body, then annealing said product at sub-atmospheric pressure substantially in the absence of air in a temperature range of from about 600° C. to about 1300° C. to develop high magnetic characteristics therein, the improvement consisting in subjecting said product to a second annealing treatment substantially in the absence of air in a temperature range of from 550° C. to 950° C. and at a temperature less by at least 50° C. than said first annealing treatment, for further developing the high magnetic characteristics of the product.

References Cited in the file of this patent**FOREIGN PATENTS**

338,409	Great Britain	Dec. 20, 1929
1,009,214	Germany	May 29, 1957

OTHER REFERENCES

Ham et al.: Pages 35-48 of Vacuum Metallurgy, 1954, Libr. Call No. TN 686 E 45; p. 43 relied upon.

Kinzel et al.: The Alloys of Iron and Chromium, vol. II, 1940, pp. 96-98.