

May 28, 1935.

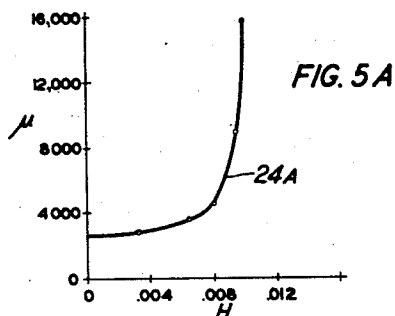
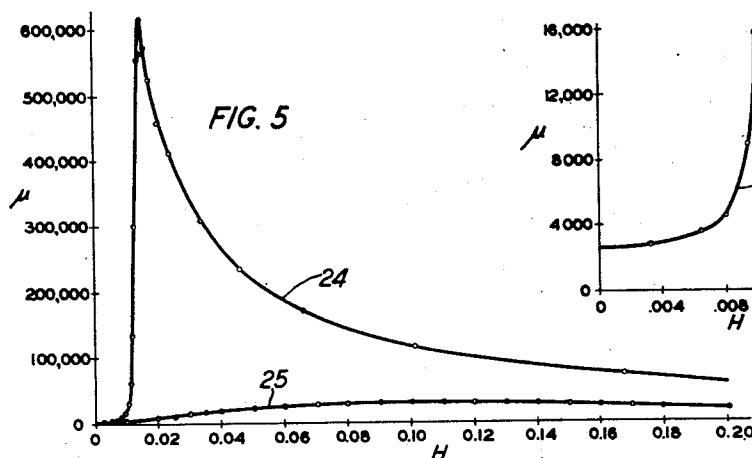
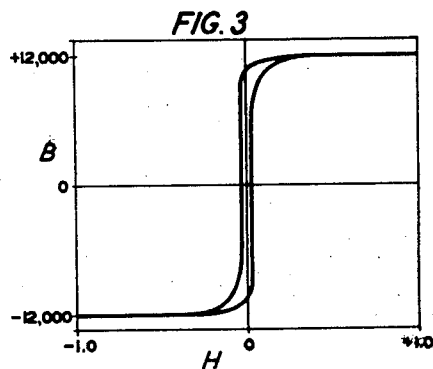
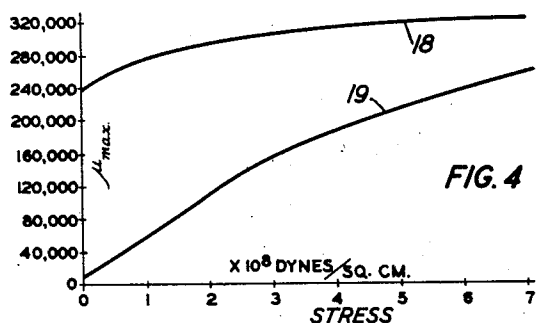
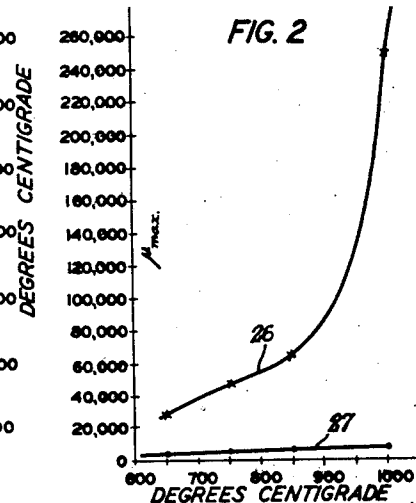
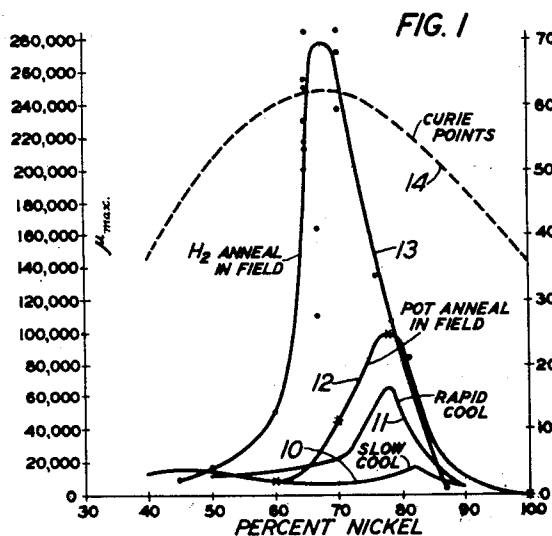
R. M. BOZORTH ET AL

2,002,689

MAGNETIC MATERIAL AND METHOD OF TREATING MAGNETIC MATERIALS

Filed March 2, 1934

2 Sheets-Sheet 1



INVENTORS R. M. BOZORTH
J. F. DILLINGER
BY *g H Schmied*
ATTORNEY

May 28, 1935.

R. M. BOZORTH ET AL

2,002,689

MAGNETIC MATERIAL AND METHOD OF TREATING MAGNETIC MATERIALS

Filed March 2, 1934

2 Sheets-Sheet 2

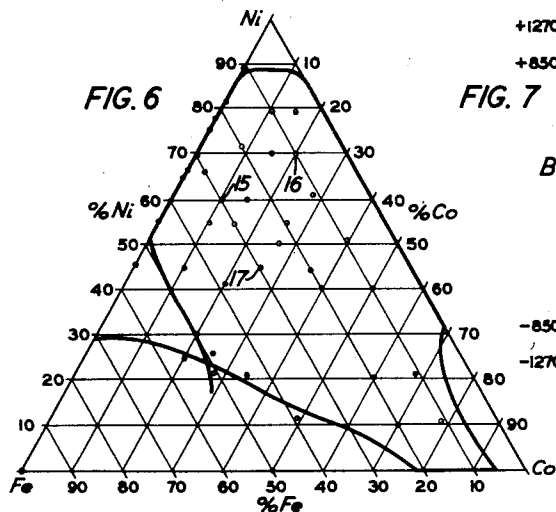


FIG. 7

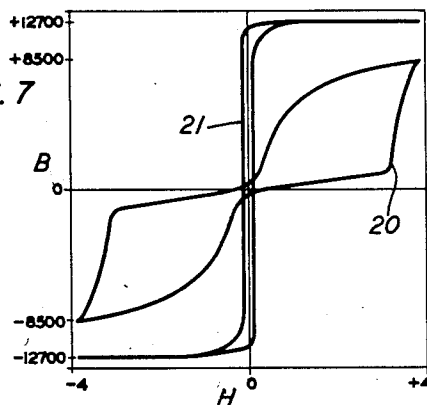


FIG. 9

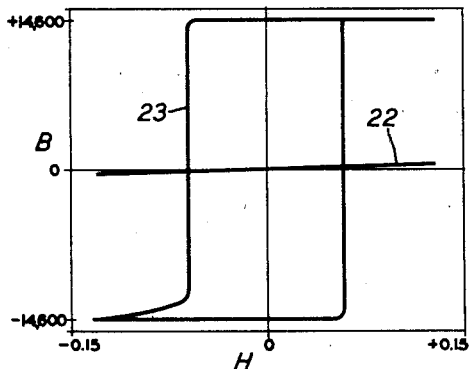
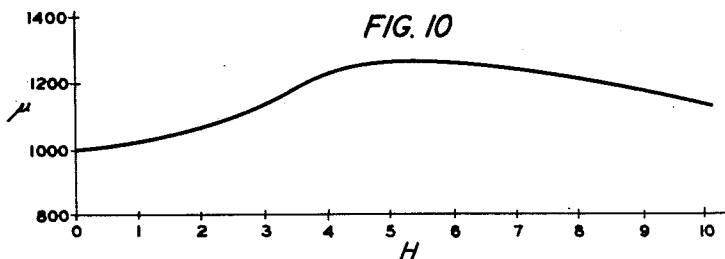
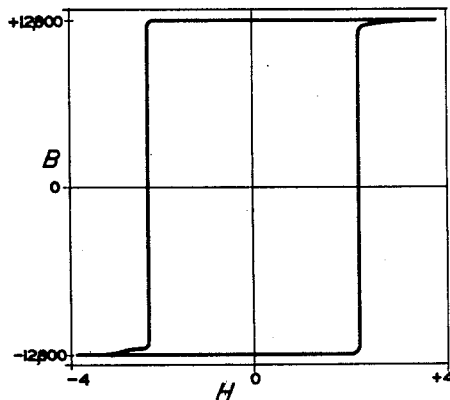


FIG. 8



INVENTORS **R. M. BOZORTH**
J. F. DILLINGER
BY *J. W. Schumacher*
ATTORNEY

UNITED STATES PATENT OFFICE

2,002,689

MAGNETIC MATERIAL AND METHOD OF
TREATING MAGNETIC MATERIALS

Richard M. Bozorth, Short Hills, and Joy F. Dillinger, East Orange, N. J., assignors to Bell Telephone Laboratories, Incorporated, New York, N. Y., a corporation of New York

Application March 2, 1934, Serial No. 713,674

15 Claims. (Cl. 175-21)

This invention relates to improvements in magnetic materials and more particularly to a new method of heat treating ferro-magnetic materials to improve their magnetic properties.

5 As disclosed in U. S. patent to P. P. Cioffi, 1,708,936, April 16, 1929 and a patent application of G. A. Kelsall, Serial No. 697,576, filed November 11, 1933, magnetic properties of ferro-magnetic material may be improved by heat treating
10 them in a magnetic field. U. S. patent to P. P. Cioffi, 1,866,925, July 12, 1932 and an application of P. P. Cioffi, Serial No. 629,507, filed August 19, 1932 show that the magnetic properties of the ferro-magnetic materials may be improved by
15 heat treating them in a hydrogenous atmosphere.

A feature of this invention resides in the discovery that the combination of these heat treatments produce a further unexpected improvement in the magnetic properties of these materials.

20 U. S. patents to G. W. Elmen, 1,586,883, June 1, 1926, G. W. Elmen, 1,586,884, June 1, 1926 and G. W. Elmen, 1,768,237, June 24 1930, disclose nickel-iron alloys in which the optimum composition for high maximum permeability and low
25 hysteresis loss is 78½ per cent nickel and 21½ per cent iron when they are rapidly cooled from a temperature above the non-magnetic temperature of the material.

30 A further feature of this invention resides in the discovery that the optimum composition for high maximum permeability and low hysteresis loss is 65 to 70 per cent nickel and the balance mostly iron when heat treated in both a hydrogenous atmosphere and in a magnetic field.

35 According to the present invention the heat treatment consists in heating the material to a high temperature between say 500° C. and 1500° C. in an atmosphere of hydrogen and maintaining it at this temperature in this atmosphere for
40 a period of time that is say from one hour or less to twenty-four hours or longer. The material may then be cooled to room temperature after which it is reheated to about the non-magnetic temperature in a magnetic field and preferably
45 in an atmosphere of hydrogen and maintained under these conditions for some time, that is for, say, an hour or longer after which it is slowly cooled to room temperature while subjected to
50 the magnetic field.

The treatment may be made continuous with the same result, if desired, by cooling the material from the high temperature to room temperature in a magnetic field and a hydrogenous atmosphere or it may be cooled to a temperature near the non-magnetic temperature in an atmosphere of hydrogen and a magnetic field applied to it at about this temperature after which it may be maintained near the non-magnetic temperature in the magnetic field for a period of time and then cooled to room temperature in the magnetic field. Experimental evidence and theoretical considerations indicate a range of equivalents including most of the magnetic materials of relatively high permeability or which may be given high permeability by methods set forth in the prior art and which have a non-magnetic temperature above approximately 400° C. Thus in the nickel-iron series those compositions are included in which the ratio of nickel to iron is equal to or greater than 40 per cent nickel and including many of the known compositions containing 1 to 12 per cent of added elements or two or more added elements such as Mo, Cr, Mn, Cu, Va, Ti, Si and Al.

In the iron-nickel-cobalt series all those alloys which have a non-magnetic temperature above about 400° C. are included together with those including 1 to 12 per cent of the same added elements. Most but not all of these which consist of iron-nickel-cobalt alone are within the curved boundary line of Fig. 6.

In the iron-cobalt series those alloys having an iron content of 25 per cent or higher the balance chiefly cobalt with or without small amounts of added elements are of particular interest.

In order that the invention may be more fully understood several specific examples of it will now be described with reference to the attached drawings of which:

40 Fig. 1 shows several curves which illustrate the relationship between the maximum permeability and the percentage nickel for the various manners of heat treating nickel-iron-alloys;

45 Fig. 2 shows the change in permeability of an alloy of 65 per cent nickel and 35 per cent iron when treated in accordance with this invention;

Fig. 3 shows the hysteresis loop of a nickel-iron alloy comprising about 65 per cent nickel and heat treated in accordance with this invention;

Fig. 4 shows curves which illustrate the relationship between the maximum permeability and the strain to which a specimen is subjected both for a specimen heat treated in accordance with this invention and a specimen which has been heat treated in the usual manner;

Figs. 5 and 5a show curves which illustrate the relationship between the permeability and the applied field for a nickel-iron alloy comprising 65 per cent nickel and the remainder iron when heat treated in accordance with this invention;

Fig. 6 illustrates in diagrammatic form the composition of a few of the various alloys which have been investigated;

Fig. 7 shows a hysteresis loop for a nickel-iron-cobalt alloy heat treated in a normal manner and one for a similar alloy heat treated in accordance with this invention;

Fig. 8 illustrates the hysteresis loop of a nickel-iron-cobalt alloy of different composition which has been heat treated in accordance with this invention;

Fig. 9 shows the hysteresis loops of samples of a nickel-iron-cobalt alloy which have been heat treated in accordance with this invention. In one case the magnetic field applied during heat treatment is in the same direction as that used to obtain the hysteresis loop, while in the other case the magnetic field applied during the heat treatment is at right angles to the field used during the measurement;

Fig. 10 illustrates the relationship between the permeability and the applied field strength for a nickel-iron-cobalt alloy which has been heat treated in accordance with this invention in which the magnetic field applied during heat treatment is at right angles to the magnetic field employed to secure these measurements.

In obtaining the curves shown in Fig. 1, specimens of the various compositions were obtained in the form of rings approximately three inches in diameter made from one turn of .006" x .125" tape that overlapped about one-eighth of an inch at the ends where it was spot welded at several points. These samples were then heated in an atmosphere of hydrogen to about 1000° C. and maintained at this temperature in the hydrogen for approximately one hour after which they were cooled in the furnace at a maximum rate of about 300° C. per hour. These rings were then placed in a toroidal box and a toroidal winding applied to the box and then again reheated to a temperature which was from 30° to 50° above the temperature at which the particular material became non-magnetic. The specimens were maintained at this temperature for one hour, during which time a current of sufficient size to produce a field strength of approximately 16 oersteds at the ring was passed through the winding. A much smaller field was usually sufficient but the larger field did no harm. The sample was then slowly cooled that is at a maximum rate of about 200° C. per hour, while subjected to this magnetic field. These rings were then placed in other toroidal winding boxes to which windings were applied and measurements made to determine the magnetic characteristics including the maximum permeability and hysteresis loss. The maximum permeability vs. the percent nickel was then plotted to form curve 13 as illustrated in Fig. 1.

In order to compare this manner of heat treatment with other known methods of heat treating magnetic material, similar samples were heat treated at a temperature of approximately 1000°

and then slowly cooled to room temperature and the magnetic characteristics including the maximum permeability measured. The maximum permeability vs. the per cent nickel in the alloy was then plotted to the same scale and curve 10 drawn through the points. Other samples were similarly heat treated and then heated to above the non-magnetic temperature and rapidly cooled by quenching or being placed upon a copper plate at room temperature. The magnetic properties including the maximum permeability were then measured and curve 11 plotted in accordance with the maximum permeability. In still other samples, the material was heated to a high temperature and slowly cooled in a magnetic field in a neutral atmosphere, and curve 12 plotted in accordance with the maximum permeability of these samples.

From these curves it is evident that the slowly cooled specimen, the rapidly cooled specimens and the specimens slowly cooled in the magnetic field which had not been subjected to hydrogen have an optimum nickel content of around 78½ per cent nickel, whereas alloys which are heat treated both in a magnetic field and in a hydrogenous atmosphere at an elevated temperature have optimum nickel content of approximately 65 to 70 per cent nickel. In addition curve 14 which shows the temperature at which these various alloys become non-magnetic has been included and would tend to indicate that the maximum permeability occurs for those samples which have the maximum or highest non-magnetic temperature. From this it appears that the treatment near the non-magnetic temperature in the magnetic field tends to relieve the magnetostrictive strains within the material. Then when the material is cooled and the field removed other magnetostrictive strains appear which tend to aid magnetization and thus produce a high permeability in the material. In addition the higher the non-magnetic temperature the more easily, quickly and completely the magnetostrictive strains may be removed during the heat treatment near the non-magnetic temperature. It has been found that if the non-magnetic temperature is below say 400° C. it is almost impossible to remove these strains in any reasonable time.

In obtaining the data for curve 26 specimens of an alloy of 65 per cent nickel and 35 per cent iron were heated in a hydrogenous atmosphere to different temperatures for an hour and then cooled to room temperature. During this treatment they were subjected to a magnetic field of about 15 oersteds. The permeability of the cooled specimens was then measured and plotted as ordinates against the temperature to which the specimen was heated during the treatment. The data for curve 27 were obtained in a similar manner with the exception that no magnetic field was applied during the treatment. By comparing the permeabilities of curves 13 and 26 of Figs. 1 and 2, respectively, it may be noted that the single treatment produces substantially the same maximum permeability as the double treatment and may therefore be considered substantially equivalent to it. In addition, it may be noted that a marked improvement results from a single heat treatment in a magnetic field and in a hydrogenous atmosphere for comparatively low temperatures as shown by curve 26 of Fig. 2.

For the curves in Figs. 3, 5 and 5a the specimens were heated in a hydrogenous atmosphere at a temperature of about 1400° C. for approxi-

mately eighteen hours and slowly cooled to room temperature and the winding applied after which they were again heated to above the non-magnetic temperatures. The magnetic field was

then applied to the specimen by connecting the winding to a source of electromotive force so that a current flowed through it. The specimen was maintained in this field at this temperature for approximately one hour after which time it was slowly cooled in the magnetic field. The curve in Fig. 3 illustrates the shape of the hysteresis loop for a maximum induction of 10,000 gauss when this material is heat treated in this manner. The area of this loop indicates an energy loss of approximately 50 ergs per cubic centimeter per cycle at this maximum induction which is the smallest known hysteresis loss for any material for a maximum induction above 10,000 gauss. Curves 24 and 24a of Figs. 5 and 5a respectively show the relationship between the permeability and the magnetic field strength for this material when heat treated as described above. It should be noted that the maximum permeability rises to well over 600,000 which is in excess of the permeability of any other material known today. This material also has a coercive force of only .012 oersteds for a maximum induction of 10,000 gauss. In order to illustrate the effect of the second heat treatment in which a magnetic field is applied, curve 25 has been drawn in Fig. 5 to the same scale for the same material which has only been subjected to the high temperature heat treatment in a hydrogenous atmosphere. In these tests specimens in the form of solid rings having a cross section $\frac{3}{8}$ " x $\frac{1}{4}$ " were employed.

In general the longer the period of time during which the material is maintained in the hydrogenous atmosphere, the higher the temperature below the melting point during this hydrogen treatment, and the longer the time the material is maintained in a magnetic field at a temperature near the nonmagnetic temperature the higher the maximum permeability and the lower the hysteresis loss. After treatments for eighteen to twenty-four hours very little additional improvement can be obtained by applying the treatment for additional periods while treatments of a half an hour or less in accordance with this invention produces a marked improvement of these magnetic properties.

It was noted that the hysteresis loops of these materials were approximately rectangular in form as illustrated in Fig. 3. This is similar to the form of the hysteresis loop of magnetic materials which are subjected to mechanical strain. It was accordingly believed that these magnetic materials when treated in accordance with this invention would be less affected by strain than magnetic materials treated in other manners. The results of tests which showed this to be so are illustrated in Fig. 4, in which curve 18 shows the variation in maximum permeability with the tensile stress in dynes per square centimeter times 10^8 applied to the material of an alloy comprising 65 per cent nickel which has been heat treated both in a hydrogenous atmosphere and in a magnetic field, while for curve 19 of Fig. 4, the same material was treated only in the hydrogenous atmosphere.

Fig. 6 illustrates in graphic form a few of the various compositions of alloys tested. For example, point 15 represents an alloy having 60 per cent nickel, 30 per cent iron and 10 per cent cobalt, while point 18 represents an alloy having 70 per cent nickel, 10 per cent iron and 20 per cent

cobalt. Similarly, point 17 represents an alloy comprising 45 per cent nickel, 30 per cent iron and 25 per cent cobalt.

In addition the following table shows the coercive force H_c and remanence B_r for numerous of these alloys when heat treated in accordance with this invention.

Composition			Results for Fe, Co, Ni alloys	
Percent Fe	Percent Co	Percent Ni	H_c	B_r
10	10	80	0.20	6700
10	20	70	0.28	7400
11	28	61	0.89	8700
10	39	51	0.69	9200
11	49	40	1.42	10400
11	59	30	2.28	12300
11	68	21	1.25	10900
11	78	11	2.54	11500
30	10	60	0.11	11200
25	15	60	0.17	11200
30	25	45	0.09	11700
24	21	50	0.12	9700
20	40	40	0.07	11200
45	10	45	0.44	10800
39	20	41	2.00	12200
40	29	31	0.26	12400
30	44	26	0.74	12200
20	60	20	1.57	12300
20	70	10	2.21	12700

It should be noted that the maximum permeability for these materials is approximately equal to the quotient obtained by B_r divided by H_c , since the form of the hysteresis loop is substantially rectangular.

A magnetic alloy comprising 45 per cent nickel, 30 per cent iron and 25 per cent cobalt was used to obtain the magnetic properties illustrated in Figs. 7, 8 and 10, while a magnetic alloy comprising 10 per cent nickel, 20 per cent iron and 70 per cent cobalt was used to secure the hysteresis curve shown in Fig. 8.

It should be noted that the width of the hysteresis loop in Fig. 8 is very wide and very much wider than that shown in Figs. 3, 7 and 9. This is probably due to the high cobalt content of this alloy.

Curve 20 of Fig. 7 shows the hysteresis loop for an alloy comprising 45 per cent nickel, 30 per cent iron and 25 per cent cobalt which has been slowly cooled from a high temperature and shows the characteristic form of this material heat treated in this manner. Curve 21 shows the hysteresis loop of the same material when heat treated in accordance with this invention by subjecting it to a high temperature in a hydrogenous atmosphere and then subjecting it to a lower temperature in a magnetic field. It is to be noted that the sides of the loop of curve 21 are very nearly vertical and they are very close together so that the permeability is very much higher than that for the material illustrated by curve 20.

In obtaining the data for the curves of Figs. 9 and 10 a seamless tube having an outside diameter of $\frac{1}{8}$ inch, a wall thickness of .010 inch and a length of 24 inches was employed. This tube was heated to over 1000° C. in a hydrogenous atmosphere and slowly cooled after which it was again heated to over 650° C. in a strong magnetic field applied parallel to the axis of the tube and in which the tube was slowly cooled. Measurements were then made by winding a search coil through the ends of the tube along the axis and back on the outside as well as by a coil wound circularly around the outside of the tube. By using these two windings it was possible to take magnetic measurements of the magnetic properties in directions at right angles to each other

The hysteresis loop shown by curve 23 of Fig. 9 was obtained when magnetic field employed during the heat treatment was in the same direction as the magnetic field used during the measurement, while curve 22 of Fig. 9 shows the form of the hysteresis loop when the two fields were at right angles to each other. The curve in Fig. 10 shows the relationship between the permeability and the magnetizing force of the material when the two fields are at right angles to each other. From curve in Fig. 10 it may easily be seen that the permeability starts at a rather high figure and remains very nearly constant over the entire range of field strengths shown.

In addition, it has been found that for the materials having a rectangular hysteresis loop the time required for the flux to change may be very long, say, three minutes, when the applied field is just sufficient to cause the change of flux to start.

The above descriptions of several specific embodiments of the invention are for the purpose of illustrating the features of this invention, but do not limit its scope as defined in the following claims.

What is claimed is:

1. A ferro-magnetic material which has been heat treated in a hydrogen atmosphere and in a magnetic field and has a permeability in excess of 450,000.
2. An iron-nickel alloy which has been heat treated in a hydrogen atmosphere and in a magnetic field, and has a permeability in excess of 450,000.
3. An iron-nickel-cobalt alloy which has been heat treated in a hydrogenous atmosphere and in a magnetic field to improve its magnetic properties.
4. A nickel-iron alloy consisting of 65 per cent to 70 per cent nickel and the remainder chiefly iron and having a maximum permeability of over 450,000.
5. A method of heat treating nickel-iron alloys which comprises heating the alloy to a temperature above about 1000° C. in an atmosphere of hydrogen for some time, slowly cooling the alloy to room temperature, reheating it to a temperature near the non-magnetic temperature of the alloy in a magnetic field, maintaining the alloy in said magnetic field for a time and then cooling the alloy in the magnetic field to room temperature.
6. A nickel-iron alloy which has been subjected to a temperature in excess of about 1000° C. in a hydrogenous atmosphere slowly cooled to room temperature and reheated in a magnetic field to a temperature near the non-magnetic temperature of the alloy and then cooled in said magnetic field.
7. A nickel-iron-cobalt alloy which has been heat treated in a hydrogenous atmosphere at a temperature above 1000° C. slowly cooled to room

temperature and then reheated to a temperature near non-magnetic temperature of the alloy in a magnetic field, and then again slowly cooled to room temperature in said magnetic field.

8. A nickel-iron alloy consisting of approximately 65 per cent to 70 per cent nickel and the remainder iron which has been subjected to a temperature in excess of 1400° C. in a hydrogenous atmosphere, slowly cooled to room temperature, reheated to about the non-magnetic temperature in a hydrogenous atmosphere, maintained at this temperature in said hydrogenous atmosphere for a period of time and then slowly cooled to room temperature while subjected to a magnetic field.

9. A ferro-magnetic material which has been heat treated in a hydrogen atmosphere and in a magnetic field directed in the same direction in the material as the magnetic field in which the material is to be used and has a permeability in excess of 500,000.

10. A ferro-magnetic material which has been heat treated in a hydrogenous atmosphere and in a magnetic field directed in a direction in the material at right angles to the magnetic field in which the material is to be used.

11. A method of improving the magnetic characteristics of magnetic materials which comprises subjecting the material to a temperature in excess of 1000° C. in a hydrogenous atmosphere for some time, slowly cooling the material to room temperature, reheating it to a temperature near the non-magnetic temperature of the material in a reducing atmosphere and in a magnetic field, maintaining the material at said temperature in said magnetic field and reducing atmosphere for a short time and then slowly cooling the material in said magnetic field and said atmosphere to room temperature.

12. A nickel-iron alloy comprising approximately 65 per cent to 70 per cent nickel and the remainder chiefly iron which has been heat treated in a hydrogenous atmosphere and in a magnetic field and has a hysteresis loss less than 100 ergs per cubic centimeter per cycle at an induction of in excess of 10,000 gauss.

13. A ferro-magnetic material which has a hysteresis loss less than 100 ergs per cubic centimeter per cycle at an induction of in excess of 10,000 gauss.

14. A nickel-iron alloy which has a hysteresis loss less than 100 ergs per cubic centimeter per cycle at an induction greater than 10,000 gauss.

15. A method of improving the magnetic properties of nickel-iron alloys which comprises heating the alloy in a hydrogenous atmosphere to a temperature near the non-magnetic temperature of the alloy and then cooling the alloy to room temperature, characterized in that a magnetic field is applied during this treatment.

RICHARD M. BOZORTH.
JOY F. DILLINGER.