

Feb. 20, 1940.

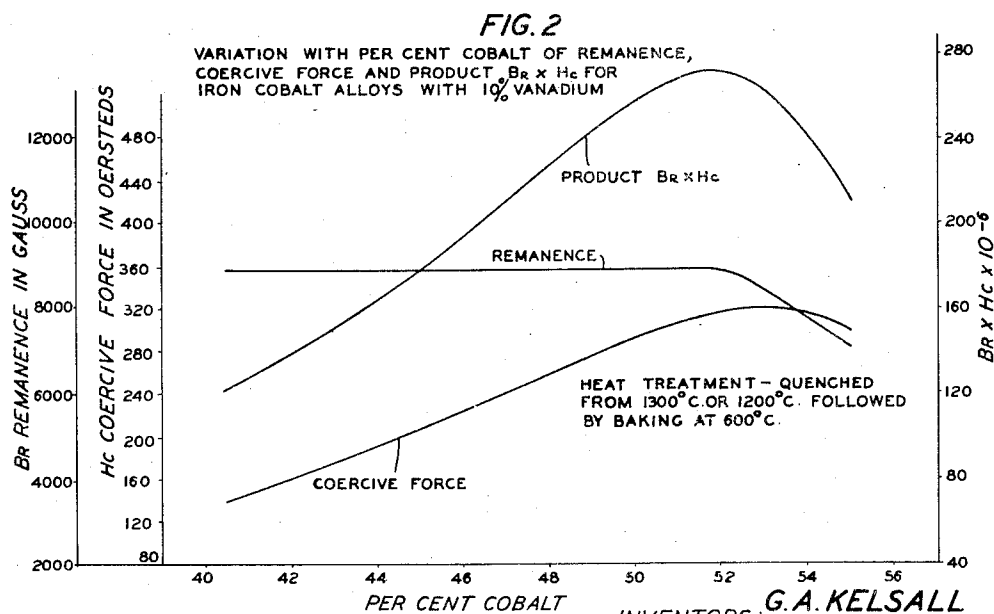
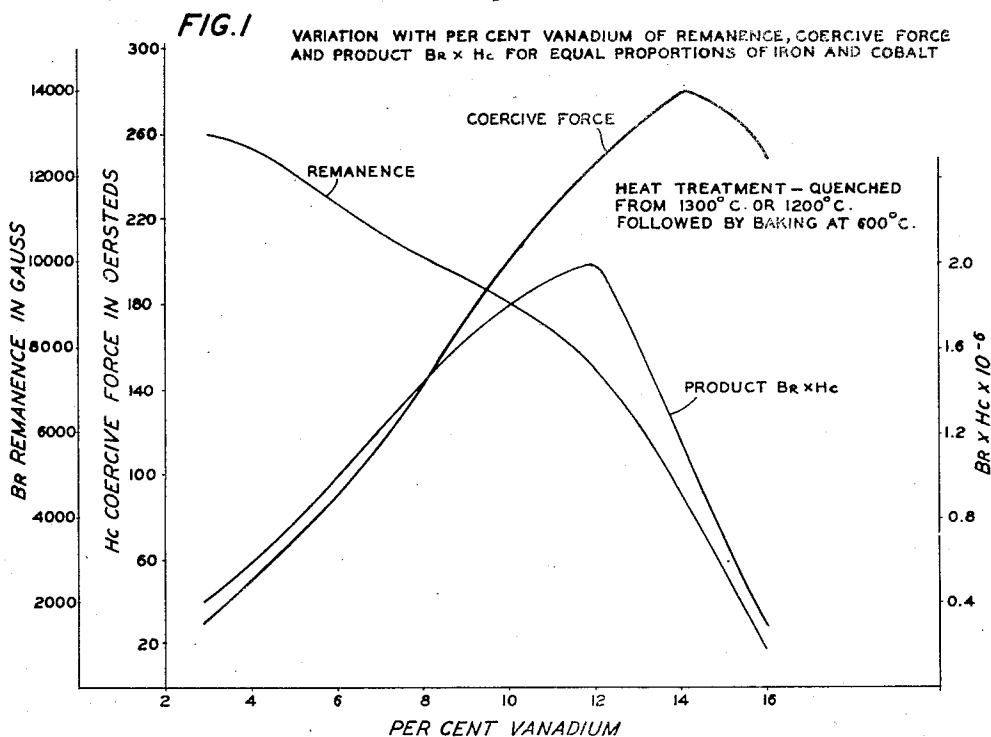
G. A. KELSALL ET AL

2,190,667

PERMANENT MAGNET ALLOY

Filed April 9, 1938

3 Sheets-Sheet 1



INVENTORS: G. A. KELSALL
E. A. NESBITT
BY *J. W. Schmied*
ATTORNEY

Feb. 20, 1940.

G. A. KELSALL ET AL

2,190,667

PERMANENT MAGNET ALLOY

Filed April 9, 1938

3 Sheets-Sheet 2

FIG. 3

VARIATION WITH QUENCHING TEMPERATURE OF REMANENCE, COERCIVE FORCE, AND B AT A LARGE MAGNETISING FORCE FOR VANADIUM-IRON-COBALT ALLOY.

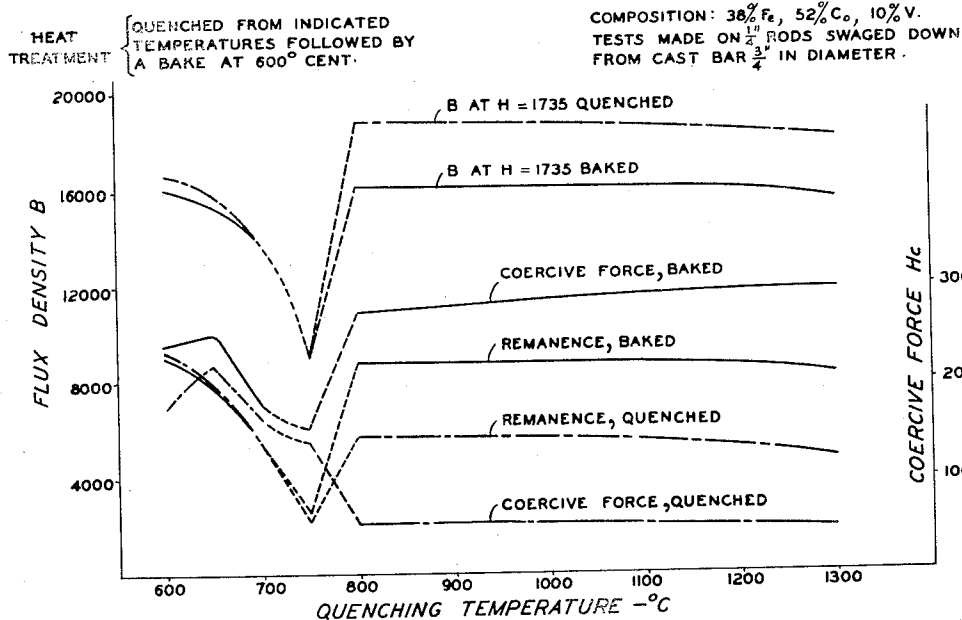
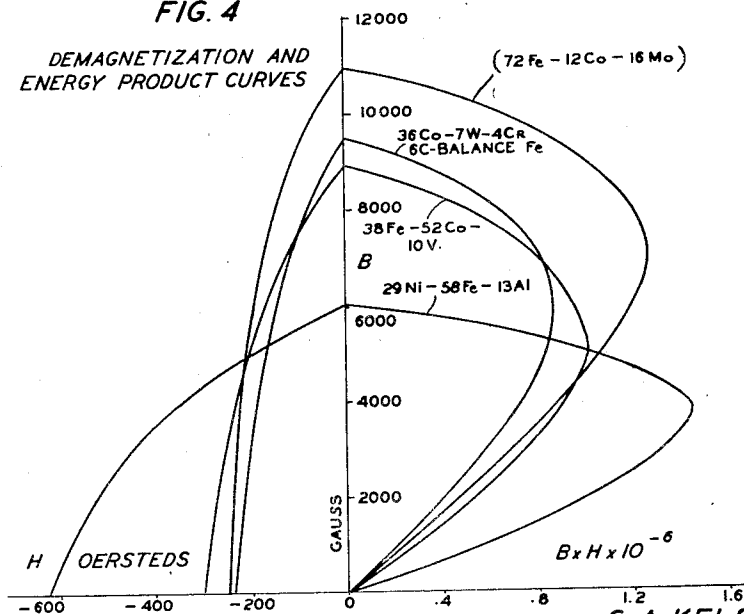


FIG. 4

DEMAGNETIZATION AND ENERGY PRODUCT CURVES



INVENTORS: G. A. KELSALL
E. A. NESBITT
BY J. W. Schmied
ATTORNEY

Feb. 20, 1940.

G. A. KELSALL ET AL

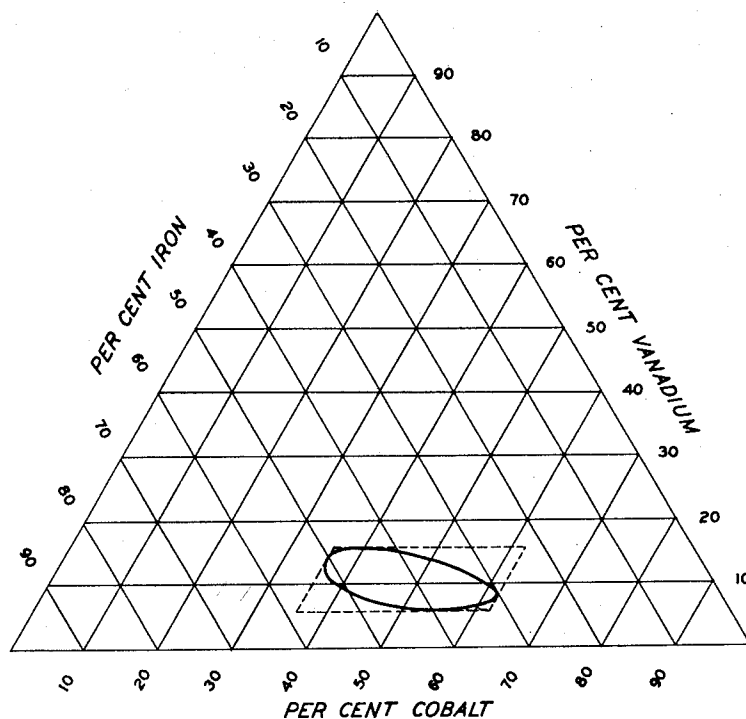
2,190,667

PERMANENT MAGNET ALLOY

Filed April 9, 1938

3 Sheets-Sheet 3

FIG. 5



INVENTORS: G. A. KELSALL
E. A. NESBITT
BY *J. W. Schmied*
ATTORNEY

UNITED STATES PATENT OFFICE

2,190,667

PERMANENT MAGNET ALLOY

George A. Kelsall, Belleville, N. J., and Ethan A. Nesbitt, Brooklyn, N. Y., assignors to Bell Telephone Laboratories, Incorporated, New York, N. Y., a corporation of New York

Application April 9, 1938, Serial No. 201,058

5 Claims. (Cl. 148—13)

The invention relates to iron and cobalt alloys for use as strong permanent magnets and methods of producing the same.

An object of the invention is to achieve a permanent magnet composition which possesses in a high degree the combination of properties, first, ability to function as a permanent magnet equal or better than the best materials heretofore available in the art and, second, workability to a degree previously unattained in a permanent magnet material in the first class as a permanent magnet.

In order to achieve the main object of the invention, that is, to produce permanent magnet properties in iron-cobalt alloys, an investigation was made, of the alloys among others of the iron-cobalt group with vanadium. As a result of this investigation it was found that alloys of iron, cobalt and vanadium in quantities varying within definite percentage ranges and with definite heat treatments produced materials of high permanent magnet properties. These materials have unusual mechanical advantages; before hardening for permanent magnet properties, a one-quarter inch round bar may be swaged down from a three-quarter inch cast bar; may be bent cold without fracture; sheet forms may be rolled down to one-thousandth of an inch by one and a quarter inches wide without difficulty; the material thus produced has also been drawn into fine wire. Specimens after quenching are easily drilled, tapped and machined. A round one-quarter inch rod after quenching from 800° C. had a Rockwell hardness (scale C) of 25, about equal to that of soft steel. Final permanent magnet properties obtained for the alloy by the present process are substantially the same for both cast and worked material. These alloys thus have unequalled advantages in workability and machineability over permanent magnet materials heretofore known. Also they possess definite advantages from a heat treating standpoint in that it is not necessary to use temperatures over 800° C.

It was discovered that the alloys that proved advantageous from the standpoint of both permanent magnetic properties and machineability should have as their component elements 30 to 52 per cent iron, 36 to 62 per cent cobalt and 6 to 16 per cent vanadium. The preferred composition

discovered contains approximately 38 per cent iron, 52 per cent cobalt and 10 per cent vanadium and has a remanence of 9000 gauss, a coercive force of 300 oersteds and an energy product ($B \times H$) of 1.02×10^6 . Its heat treatment is not critical. For optimum permanent magnet properties, it is not necessary to use temperatures above 800° C. In other words, it may be subjected to either one or two heat treatments and after either treatment, it may be quenched rapidly or slowly without affecting its permanent magnet properties. A subsequent baking treatment at 600° to 800° C. is an essential feature of the heat treatment necessary to achieve the best results.

The above described and other objects and features of the invention will be apparent from the following detailed description taken in connection with the accompanying drawings, in which:

Fig. 1 is a curve chart showing the results obtained with iron-cobalt in equal proportions containing vanadium in quantities varying from 7.4 per cent to 16 per cent;

Fig. 2 is a curve chart showing the results obtained from alloys in which the quantity of vanadium employed was 10 per cent and the proportions of iron and cobalt vary;

Fig. 3 is a curve chart showing the variations of remanence, coercive force and flux density B at a large magnetizing force for the optimum composition for different quenching temperatures;

Fig. 4 is a curve chart showing a comparison between the optimum composition of the applicants' alloy and other permanent magnet materials; and

Fig. 5 is a composition triangle diagram showing the range of elements employed in the applicants' alloys having highly desired magnetic properties.

These alloys are in the same class magnetically as Honda steel (36 per cent Co, 7 per cent W, 4 per cent Cr, 0.67 per cent C, bal. Fe) and remallo (72 per cent Fe, 12 per cent Co, and 16 per cent Mo). An outstanding difference of the new alloys from other permanent magnet materials is their mechanical properties; before they are age-hardened they can be cold drawn and cold rolled almost as readily as soft steel.

The range of compositions comprising the sub-

ject of the present invention is indicated by the elliptical area on the triangular diagram shown in Fig. 5. The extreme limits of this area are 30 and 52 per cent iron, 36 and 52 per cent cobalt and 6 and 16 per cent vanadium. The preferred composition, as stated above, so far has been found to be 38 per cent iron, 52 per cent cobalt and 10 per cent vanadium, which has a remanence of 9000 gauss and a coercive force of 300 oersteds with a maximum energy product ($B \times H$) of 1.02×10^6 . The maximum energy product is usually taken as a figure of merit for permanent magnet material and a discussion of the maximum energy product may be had by referring to Chapter II of "Applied Magnetism" by T. F. Wall. The maximum ($B \times H$) product is not usually determined because of the labor involved. Usually, the practice is to merely obtain the remanence B_r and coercive force H_c . The product of $B_r \times H_c$ is higher than the maximum $B \times H$, but is roughly proportional to it. Generally, for the same $B_r \times H_c$ of two materials, the one with the higher B_r is preferred. Hereinafter the product $B_r H_c$ is used as an index of the figure of merit.

Before hardening for permanent magnet properties, the new alloys are more workable and more easily fabricated than any other permanent magnet material heretofore known with comparable permanent magnet properties. They are easily machined, drilled or cut and can be bent cold. The alloys have either in the worked or cast condition about the same final permanent magnet properties after heat treatment so that they can be used either cast or worked, whichever suits the purpose in mind. These materials, if merely baked at 600° C. after being worked, have very good permanent magnet properties. In one case the sample had about 10,315 gauss for remanence and 215 oersteds for coercive force. While this product ($B_r \times H_c$) is not as high as for a complete heat treatment, namely a quench or an anneal followed by a bake, the remanence is high and the net result is very good for such a simple heat treatment which does not require going above 600° C. The so-called baking treatment need not be given at a temperature above 600° C. but may be at a higher temperature up to about 800° C., the extreme limits of said ranges varying a little, but not much, with variations in the composition. Moreover, as the temperature goes up the time may be shortened until just below the critical point the time may be quite short but in no case should the temperature exceed a critical point around or just below 800° C. In preparing strip material such as, for example, recording tape, it is a well known fact that a convenient and desirable method of heat treatment of strip material is given by using a continuous furnace through which the material is drawn. The fact that the material needs only a short time baking, if the temperature is right, is therefore a noteworthy advantage. A baking treatment applied to a cast specimen without an intermediate quench does not have so high a product, but with a complete treatment as stated above, the cast and worked materials are about equal. However, in the most general case the initial alloying of the material followed by casting and cooling at any convenient rate may fulfill the requirements of an initial heat treatment at 800° C. to 1300° C. as set forth hereinafter in which case no further treatment other than the baking treatment at 600° to 800° C. need be given.

Furthermore, in connection with this baking treatment, the dimension of the mass of material must be taken into consideration. Very thin specimens reach a uniform temperature throughout the mass almost instantly while larger bodies require more time. For this reason an exceedingly short treatment of a massive body at a higher temperature cannot be practically accomplished.

On account of this workability, it is particularly applicable for unusual shapes of magnets, for magnets requiring mechanical precision and for purposes requiring material in thin or laminated forms. A commercial application for this material is for magnetic recording tape.

In many cases, permanent magnet structures are terminated by magnetic material of relatively higher permeability and larger flux carrying capacity than the permanent magnet in order to concentrate the flux from the permanent magnet across an air-gap. These new alloys are particularly adaptable as regards the heat treatment requirement of such terminating parts. In other words, the terminating parts may be welded to the permanent magnet and the whole assembly heat treated together. For example, if the permanent magnet has pole-pieces of iron, the whole assembly may be pot annealed at 900° or 1000° C. which is a proper heat treatment for both the iron and the vanadium-iron-cobalt alloy. The second heat treatment in this case will be a bake at 600° C. from which temperature the whole assembly is cooled slowly. The second heat treatment makes the vanadium-iron-cobalt alloy a permanent magnet and is not harmful to the iron. These same remarks apply if an alloy of 45 per cent nickel, the balance iron, is used instead of the iron. If the terminating parts are an alloy of 78½ per cent nickel, the balance iron, the whole assembly for the second heat treatment may be quenched from 600° C. after baking instead of cooled slowly. This produces the desired high permeability in the alloy of 78½ per cent nickel, the balance iron, and a rapid cooling from 600° C. is equally as good as slow cooling for the permanent magnet. The heat treatment of the assembly can also be adapted for pole-pieces composed of alloys of equal parts of iron and cobalt. This adaptability is unique. It is often necessary with other permanent magnet materials that parts have to be welded on the permanent magnet structure after heat treatment for the permanent magnet is partly or wholly completed because the heat treatment of the permanent magnet is harmful to the magnetic properties of the terminating parts. In some cases this is only a partial remedy as the welding process still does a certain amount of harm to the magnetic properties of the terminating parts or the permanent magnets or both.

In the first period of this investigation vanadium-iron-cobalt alloys of equal proportions of iron and cobalt with varying vanadium contents up to 16 per cent were used. The samples tested included round cast bars three-quarter inch in diameter and rods one-quarter inch in diameter worked down from the three-quarter inch rods. Results of the same order were obtained for the same composition for both the worked and cast specimens. The specimens were first quenched in oil from 1200 to 1300° C. and then baked at 600° C. The magnetic results for this series of alloys are shown by curves in Fig. 1. The remanence, as seen from this curve chart

decreases almost linearly with the percentage of vanadium, while the coercive force is almost proportional to the vanadium content up to a maximum of 280 oersteds at 14 per cent vanadium.

- 5 A curve showing the variation of the product of remanence times coercive force ($B_r H_c$) is also shown. The product ($B_r H_c$) is roughly proportional to the maximum energy product (BH).
 10 The product curve has its maximum value of 1.845×10^6 at 12 per cent vanadium corresponding to a remanence of 7500 gauss and a coercive force of 246 oersteds. This diagram is conclusive evidence of a critical region of compositions.

- 15 The effect of varying the proportions of iron and cobalt was also investigated. Accordingly, six additional alloys were cast into three-quarter inch bars. The compositions of these alloys, their heat treatment and their magnetic properties for the cast specimens are given below in Table I.

Table I

Percent Fe	Percent Co	Percent V	B _r	H _c	B _r H _c × 10 ⁶	Heat treatment
41	51	8	9570	200	1.91	1300° C., 20 min., oil quench; baked 600° C., 18 hrs., in hydrogen.
51	41	8	8750	71	.62	1300° C., 20 min., oil quench; baked 600° C., 8 hrs., in hydrogen.
40.5	49.5	10	8850	282	2.50	1300° C., 20 min., oil quench; baked 600° C., 12 hrs., in hydrogen.
49.5	40.5	10	8960	136	1.22	1300° C., 20 min., oil quench; baked 600° C., 13 hrs., in hydrogen.
40	48	12	7350	318	2.34	1300° C., 20 min., oil quench; baked 600° C., 12 hrs., in hydrogen.
48	40	12	7820	209	1.64	1300° C., 20 min., oil quench; baked 600° C., 8 hrs., in hydrogen.

The results in the above table show that in the range covered for a given vanadium content the alloy with the larger amount of cobalt gave the best values. The alloy with a composition of 40.5 iron, 49.5 cobalt and 10 per cent vanadium had a ($B_r H_c$) of 2.5×10^6 . This is the largest product for these six alloys.

- As the next step in searching for an optimum composition for permanent magnet properties, a number of alloys were made in which the vanadium was held constant at 10 per cent and the proportions of iron and cobalt varied. The variations with per cent cobalt of remanence, coercive force, and ($B_r H_c$) products for these alloys are shown in Fig. 2. For the range of cobalt shown the remanence remains substantially constant at 9000 gauss with increase in cobalt up to 52 per cent. With further increase in cobalt the remanence decreases in value. The coercive force increases almost linearly with increase in cobalt up to a maximum of 320 oersteds for 53 per cent cobalt. The maximum ($B_r H_c$) product is obtained for the alloy containing 52 per cent cobalt, 38 per cent iron and 10 per cent vanadium. The remanence is 9000 gauss and the coercive force 300 oersteds.

- The heat treatment of the composition thus selected as an optimum was investigated more fully. Swaged specimens one-quarter inch in diameter were quenched from the following temperatures 600, 650, 700, 750, 800, 900, 1000, 1100, 1200 and 1300° C. These specimens were tested magnetically and then baked at 600° C. for various lengths of time before the second test. The results of these experiments are shown on Fig. 3. The variations with quenching temperatures of maximum flux density, remanence and coercive force corresponding to a maximum magnetizing force of 1735 oersteds, is shown for the specimens in both the quenched and baked conditions. For the baked condition the values of B_r and H_c associated with the highest ($B_r H_c$) product are given. A survey of the curves shown in Fig. 3 show the magnetic characteristics substantially constant for a wide range of quenching tempera-

tures from 800° C. to 1300° C. With the specimens in a quenched condition the maximum flux density and remanence are 18,800 and 5800 gauss, respectively, for a quenching temperature of 800° C. and remain practically constant for quenching temperatures up to 1100° C., and decrease slightly when quenched from 1200 and 1300° C. The coercive force is substantially constant at about 50 oersteds. For the baked condition the maximum flux density and remanence are 16,200 and 9000 gauss, respectively, for quenching temperatures up to 1100° C. and fall off slightly with further decrease in temperature. The coercive force has a value of 275 oersteds when quenched from 800° C. and increases with quenching temperatures to 295 oersteds for 1300° C. It is thus seen that ($B_r H_c$) is nearly constant for this range of quenching temperatures.

The results for quenching temperatures below

800° C. are also interesting. With the quenching temperature lowered to 750° C. the behavior of the alloys changed radically. The maximum flux densities and remanences decrease materially and almost coincide for the quenched and baked conditions. The curve for coercive force falls for the baked condition and rises for the specimens quenched so as almost to meet. On the whole there is not much difference in the results of the two heat treatments.

As the quenching temperature is decreased below 750° C., the maximum flux density and remanence increase and the curves for the two heat treatments almost coincide. The resulting values are remarkably good for such low temperature treatments. The coercive force curves are similar in shape, but the values, as quenched, are lower than for the baked condition, the difference increasing as the quenching temperature is decreased.

X-ray examination showed the existence of only one phase in specimens that were quenched or slow-cooled from 800° C. or higher. Two phases appeared in these specimens after a subsequent baking at 750° C. Resistivity measurements on one-quarter inch rods corresponding to these conditions are given in Table II. (F. C. signifies furnace cooled.)

Table II

Heat treatment	Resistivity microm. cm.
Swaged from $\frac{1}{4}$ " bar.....	91.3
Pot annealed, 1000°, 1 hr. F. C.....	90.5 Rod No. 1
Pot annealed, 1000°, 1 hr. F. C.+750°, F. C.....	67.2
Swaged from $\frac{1}{4}$ " bar.....	91.1 Rod No. 2
750°, 1 hr. F. C.....	67.0

The above table shows a material drop in resistivity with the occurrence of the additional phase.

In the course of this investigation other heat treatments than those already recorded were given samples with the compositions selected as an

optimum. The results are shown in Table III. (P. A. signifies pot annealed.)

Table III

Heat treatment	B.	H.	Diameter of specimen
As cast.....	5040	64.5	3/4"
As cast+600° C., 8 hrs., in hydrogen.....	6890	295	3/4"
As cast+pot annealed, 1100° C., 20 hrs. F. C.....	5270	55.9	3/4"
As cast+P. A. 1100° C., 20 hrs. F. C.+600° C., 8 hrs., in hydrogen.....	8630	299	3/4"
Pot annealed, 1,000° C., 1 hr. F. C.....	5035	51.6	1/4"
Swaged from 3/4" diameter+P. A. 1000° C., 1 hr., dropped to 600° C., 4 hrs. F. C.....	5160	58	1/4"
P. A. 1000° C., 1 hr., F. C.+600° C., 8 hrs., in hydrogen.....	8100	290	1/4"
Swaged from 3/4" diameter+600° C., 2 hrs., in hydrogen.....	10350	215	1/4"
Swaged from 3/4" diameter+650° C., 15 min., oil quench.....	8000	220	1/4"
1200° C., 20 min., oil quench+575° C., 31 hrs., in hydrogen.....	8750	305	1/4"

As shown by this table substantial values can be obtained by baking after casting without an immediate quench. This table also shows that results of the same order can be obtained by substituting an anneal for quenching. As shown by the last result in the above table, baking at 575° C. produces about the same magnetic result as from 600° C. but requires about three times as long.

The curves shown in Fig. 4 compare the preferred new alloy with three competing permanent magnet materials, iron-cobalt-molybdenum (72 Fe, 12 Co, 16 Mo), iron-cobalt-tungsten-chromium-carbon (36 Co, 7 W, 4 Cr, 0.6 C, bal. Fe) and a nickel-iron-aluminum alloy (29 per cent Ni, 58 Fe, 13 Al). The new alloy is comparable in magnetic properties with the two alloys just mentioned. The maximum (BH) product for the new alloy lies between that for the former and the latter of the two alloys to which reference has just been made. The iron-cobalt-tungsten-chromium-carbon alloy and the iron-cobalt-molybdenum alloy have remanences of 9500 and 11,000 gauss and a coercive force of 240 and 250 oersteds, respectively, as compared with 9000 gauss and 300 oersteds for the new material. The mechanical properties of this new alloy are better than any existing permanent magnet material with useful magnetic properties.

It was also found that by immersing the alloy, high in vanadium, in liquid air for several hours produced a product having satisfactory permanent magnet properties. For example, a three-quarter inch diameter bar of an alloy consisting of 40.5 per cent iron, 45.5 per cent cobalt and 14 per cent vanadium was heated to 1200° C. for thirty minutes, quenched in oil. It was then immersed in liquid air for several hours and then baked at 600° C. for four hours. The specimen was measured after quenching and measured again after immersion in liquid air, and the increase in its magnetic properties due to the immersion in liquid air was very noticeable. The final results obtained after baking with this specimen were 5200 gauss for remanence, 329 oersteds for coercive force and 10,850 gauss for B at H=1735.

Fig. 5 shows the composition triangular diagram wherein the elliptical area marked thereon shows the ranges of ingredients in percentages that may be used to produce alloys more highly desirable for permanent magnet purposes. By comparing this area with the percentages stated in the specification, the area shown in dotted lines on a chart in accordance with the percentages stated in the specification is trapezoidal

whereas the area of the actually preferred percentages is elliptical. This elliptical area has been drawn upon the basis of experiment but, of course, the utility of border line cases is a matter of judgment. However, because there is no practical manner of defining this elliptical area, it is intended that the appended claims setting forth ranges of compositions be construed to define essentially this elliptical area.

The vanadium, iron and cobalt alloy of the present invention may have small amounts of other elements present without material detriment to the permanent magnet properties of the alloy. Any one of these elements may be present or added in the following quantities: 1 per cent silver, 0.1 per cent carbon, 1 per cent columbium, 2 per cent chromium, 3 per cent copper, 1 per cent manganese, 2 per cent molybdenum, 0.25 per cent phosphorus, 0.5 per cent silicon, and 3 per cent tungsten. Magnets made in accordance with the present invention are tough enough to withstand machining during the manufacturing stages; they are also adequately tough when completed to withstand the usual shock incidental to the handling and usage usually given to permanent magnets; they are perhaps not as tough as some other inferior permanent magnets previously used but on the other hand they are not nearly so brittle as many others which have been subject to breakage upon dropping or similar rough treatment.

The term "swaging" is intended to include reduction in diameter or thickness of the material or a change in shape of the material in one or more operative steps by the application of mechanical force. Machining is intended to include tapping, drilling, cutting, filing or similar operations.

What is claimed is:

1. A process of manufacturing a permanent magnet article of high toughness and a product of coercive force in oersteds and remanence in gauss greater than 10^6 which comprises treating a body of an alloy comprising 30 to 52 per cent iron, 36 to 62 per cent cobalt, and 6 to 16 per cent vanadium, minor constituents not being excluded, at 800° to 1300° C., thereafter cooling said material to considerably below 600° C. and thereafter maintaining said body around 600° C. for a period of hours and thereafter magnetizing the body to the required extent.

2. A process of manufacturing a permanent magnet article of high toughness and a product of coercive force in oersteds and remanence in gauss greater than 10^6 which comprises treating a body of an alloy comprising 38 ± 1 per cent iron, 52 ± 1 per cent cobalt, and 10 ± 1 per cent vanadium, minor constituents not being excluded, at 800° to 1300° C., cooling said material substantially below 600° C., thereafter maintaining said body around 600° C. for a period of hours and thereafter magnetizing the body to the required extent.

3. A tough non-brittle magnetic article of high permanent magnet properties composed of an alloy comprising as essential constituents 30 to 52 per cent iron, 36 to 62 per cent cobalt, and 6 to 16 per cent vanadium produced by heating the alloy to from 800° to 1300° C., cooling substantially below 600° C., thereafter maintaining it at around 600° C. to 800° C. for a period of time from several hours at the lower range to a much shorter time at the higher range and thereafter magnetizing it.

4. A flexible strip of magnetic material of dimensions, mechanical properties and magnetic

quality suitable for magnetic recording comprising iron between 30 and 52 per cent, cobalt between 36 and 62 per cent and vanadium between 6 and 16 per cent, heat treated at some stage of its manufacture at 800° C. to 1300° C., thereafter cooled to considerably below 600° C. and thereafter heated to between 600° C. and 800° C.

5 A composite magnetic structure comprising a permanent magnet portion and a highly permeable magnetic pole-piece of low coercive force welded thereto, said permanent magnet portion
10 comprising iron between 30 and 52 per cent, cobalt between 36 and 62 per cent and vanadium be-

tween 6 and 16 per cent, said structure having been treated as a unit after assembly by heating to between 800° C. and 1300° C., cooled substantially below 600° C., and thereafter maintained for a substantial period of time at around 600° C. whereby said permanent magnet portion is given a high capability of retaining magnetism and said pole-piece is given the desired permeability and low coercive force, and magnetizing the permanent magnet portion.

GEORGE A. KELSALL.
ETHAN A. NESBITT.