

Substitute magnetic materials

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MAGNETIC materials are classified into two main groups: soft magnetic materials and permanent magnets. Soft magnetic materials are used on tonnage scale as cores of transformers and armatures of dynamos and motors and principally work in a.c. circuits. Permanent magnets can deliver a constant amount of energy in a given air gap with or without any external aid and are used in a wide variety of electrical and electronic instruments such as electricity meters, ammeters, voltmeters, loud speakers, telephones, teleprinters, motors, generators, televisions, lifting devices, etc. The manufacture of soft and permanent magnet materials presents a number of problems. They either contain metals like nickel and cobalt which do not occur in India or require high grade starting materials which are not manufactured at present or offer processing difficulties. To find suitable solutions of these problems and to develop suitable substitute materials a programme of research on the development of magnetic materials was initiated at the National Metallurgical Laboratory sometime back and results are reported in this paper together with a review of the existing magnetic materials to bring out their technical and economic merits and demerits.

Material requirements

The special requirements of soft magnetic materials of the transformer core type for use in a.c. applications is two-fold viz. low core loss and high permeability. The core loss represents losses due to eddy currents and magnetic hysteresis. The eddy current loss is related to the characteristics of the core material used and operating conditions and can be reduced by raising the electrical resistance of the core laminations or their effect can be reduced by making the lamination thinner. The electrical resistance is related primarily to the chemical composition of the core material, which in turn is related to the magnetic properties. For a certain chemical composition of the alloy the most effective method for reducing the eddy current losses would, therefore, be to use thinner laminations. The importance of the economic and ready workability of the core materials can thus be readily appreciated.

The hysteresis loss arises from the lag of the magnetic

induction behind the magnetising field and can be quantitatively judged from the value of coercive force of the material, the smaller the coercive force the smaller being the hysteresis loss. Both the coercive force and the permeability are structure sensitive properties and are influenced by metallurgical factors like interstitial impurities, grain size, lattice imperfection, crystal anisotropy and magnetostriction. Any treatment or condition, which leads to a strain-free lattice and the lowest value of magnetostriction and crystal anisotropy, will lead to the lowest values of coercive force and highest permeabilities.

In short, low coercive force, high permeability, high electrical resistance and excellent rollability are some of the important factors which make a suitable soft magnetic material. The cost of the melting, rolling and annealing, to achieve the best magnetic properties may however, overshadow the cost of raw materials in some cases.

In contrast to soft magnetic materials the permanent magnets must possess the highest possible value of hysteresis loss and therefore high values of coercive force and remanence so that the magnets will not demagnetize under its own demagnetization field. The magnet, therefore, should possess the highest degree of strains, high crystal anisotropy and high magnetostriction in permanent magnets. The magnetization proceeds by the rotation of magnetization vectors from their easy direction of magnetization and force required to magnetize them is quite large. The corresponding force to demagnetize the magnet is also therefore very large. Fine particles of a ferromagnetic material having dimensions of a single domain where the magnetization necessarily proceeds by the above process have very large values of coercive force.

A. Soft magnetic materials

Although iron is the best magnetic material, it does not find application in alternating current machinery due to its poor electrical resistivity and its use is generally limited to d.c. applications only. Additions of various metals to iron give rise to a number of alloys having a wide range of properties which are used in innumerable ways. These alloys can be classified into four chief groups as follows :

- (i) High permeability materials,
- (ii) Constant permeability materials,
- (iii) High saturation value materials
- (iv) High resistivity sintered oxides.

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High permeability materials

Iron-silicon and iron-nickel alloys almost entirely constitute this group of materials. In silicon-iron, silicon not only increases the electrical resistance of iron appreciably but by virtue of its being a powerful deoxidizer and graphitizer, also helps iron to get rid of unwanted impurities and makes it suitable for use in a.c. machine. Low silicon alloys are easily workable but comparatively poor in magnetic and electrical properties and therefore are used in dynamos and motors where such properties can be tolerated. High silicon alloys are comparatively difficult to work but have excellent magnetic and electrical properties. These alloys invariably contain 4 to 4.5% silicon and can be hot-rolled only. For obvious reasons the stacking capacity of such sheets is poor. The coercive force of the hot-rolled sheets ~ 0.6 oersted and maximum permeability ~ 7000 . Cold rolling of silicon irons is limited to 3% silicon as the alloy becomes brittle when silicon content is increased further. The cold-rolled sheets develop textures after heat treatment which are associated with very high maximum permeabilities and are invariably greater than 20 000. Aluminium is similar to silicon in regard to its effect upon electrical and magnetic properties of iron but little work has been reported in literature on these alloys and seem to be promising due to their better cold workability.

Iron-nickel alloys, with nickel content more than 45%, have very high permeabilities and low losses. They are comparatively costly and their use is limited to special types of transformers. These alloys, depending upon the nickel content, are known under various trade names like hipernik, permalloy, mu metal 1040 alloy, etc. In addition to nickel they contain small percentages of chromium, molybdenum, copper, manganese, etc. One of the best alloys in the series is supermalloy containing 79%Ni, 15%Fe, 5%Mo and 0.5%Mn. In the form of 0.014% sheets, it has an initial permeability of 50 000 to 150 000 and a maximum permeability of 600 000 to 1 200 000. Aluminium-iron alloys having aluminium content from 10 to 16% have been reported to show high values of permeabilities and have been compared with nickel alloys in this respect.²

Constant permeability materials

Constant permeability materials are employed as magnetic cores of inductances which are required to maintain a constant inductance value with variation of the magnetizing current. These materials are generally alloys of either iron, cobalt and nickel or iron, nickel and copper. Constant permeability is also shown by some powders made from iron or permalloy when bonded suitably. These metal powder cores are generally used for filter coils in radio and telephone transmission lines for the faithful reproduction of sound.

High saturation value materials

Cobalt is the only element which increases the saturation value of iron and the maximum increase occurs at about 34.5% cobalt. These alloys are, however, asso-

ciated with low value of resistivity and small amounts of vanadium are frequently added to overcome this shortcoming. These alloys are very costly and are used in special cases where saving in space or weight and use of the highest flux density are important.

High resistivity sintered oxides

These oxides are derived from ferrites, which are mixed oxides derived from ferrous ferrite $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ by substituting ferrous oxide by the oxide of a divalent metal like zinc, magnesium, copper, manganese, nickel, etc. The mixed crystals containing zinc ferrite have higher permeabilities than the rest. Consequently the properties of mixed crystal of copper, magnesium, manganese and nickel ferrites with zinc ferrite have been investigated. The initial permeabilities generally vary from 700–4 000. Their electrical resistivity is of the order of 10^6 microhms-cm. As the losses are very low at high frequencies, they are used in coils operating at carrier and radio frequencies. Some of these ferrites also possess high values of Q and are used as antenna rods at medium frequencies.

B. Permanent magnet materials³

Permanent magnet materials can be broadly divided into the following four groups:

1. Magnet steels
2. Dispersion hardening alloys—hard and brittle.
3. Dispersion hardening alloys—ductile and malleable.
4. Sintered metal oxides and metal powders.

Magnet steels

These alloys contain carbon and carbide forming alloying elements as their important ingredients and range from the high carbon steels to chromium and cobalt steels. The carbon content of these alloys is generally about 1% and the alloy contents vary from about 2%Cr to about 35% cobalt. The martensite produced on rapid cooling as well as the high internal stresses set up on the precipitation of the alloy carbides, are responsible for the magnetic hardness of these steels. They have coercive force ranging from about 40 oersteds in the case of plain carbon steels to about 250 oersteds in the case of 35% cobalt steels, but have high values of remanence about 10 000 gauss. The steels are the older types of permanent magnet materials and are now being replaced increasingly by the more powerful alloys mentioned below. The alloy steels have, however, the advantage that they can be produced as castings or forgings and can be machined, drilled and worked with relative ease.

Dispersion hardening alloys (hard and brittle)

This group of permanent magnet materials includes the wellknown AlNi, Alnico and Alcomax type alloys which contain about 23–27% nickel, 0–6% copper, 0–24%

cobalt, 50-60% iron and 8-14% aluminium with or without addition of small quantities of titanium, niobium. These alloys have much higher coercive force than the steel magnets and may range from about 400 to 700 oersteds, remanence which may range from about 6000 to 12000 gauss. Alloys containing iron, nickel and aluminium only constitute the AlNi type of permanent magnets, while those containing cobalt and copper in addition to the above elements constitute the Alnicos. Alloys with Co 24%, Al 8-9% with other constituents as nickel, copper and iron in the usual proportion are amenable to heat treatment in a magnetic field due to their high curie point and form the so called Alcomax group of permanent magnets. All these develop a high coercive force only after suitable heat treatment, which generally consists in heating relatively to high temperatures and cooling at optimum rates. After heat treatment, tempering of these alloys is usually carried out and results in overall improvement in the magnetic properties. A controlled cooling rate is essential to impart the best magnetic hardness in these alloys, as it prevents the complete precipitation of an intermetallic phase from the matrix and retains the lattice in an immensely strained condition. The Alnico group of permanent magnet materials is extremely hard and brittle, cannot be machined or drilled and has to be cast and ground only before use.

Dispersion hardening alloys (malleable and ductile)

This group of alloys also attains magnetic hardness by a dispersion hardening process but the alloys are malleable and ductile. These alloys have comparatively low remanence ~4000 gauss but the coercive force is quite high about 500 oersteds. Typical commercial alloys are Cunife and Cunico, whose names themselves indicate the nature of the alloys. These alloys are quite ductile and malleable and develop best magnetic properties after cold working.

Sintered metal oxides

Kato and Takei² discovered that a powder compact made from equal number of mols of iron and cobalt oxides after sintering at 1000°C and cooling in a magnetic field from 300°C developed a remanence about 4000 gauss and a coercivity of about 600 oersteds. In spite of the low mechanical strength of such compacts, the advantages of lightness and relative ease of manufacture, involving no melting equipment, have led to the wide use of this group of materials especially in air craft instruments. Much higher properties are developed in oxides of hexagonal structures prepared from iron oxide and one of the alkaline earth oxides like CaO, BaO and SrO.⁴ In case of oxide magnets prepared from barium and iron oxides, coercive force 1500 oersted and remanence 2000 gauss have been obtained in commercial specimens and these are now displacing Alnico magnets from a number of applications, like cycle, dynamos, loud speakers, television tubes, hysteresis motors, door latches and a variety of toys.

Metal powders

The theory of coercive force predicts that fine elongated particles of domain size (diameter 200Å) of ferromagnetic materials should exhibit an energy product of 40 mega-gauss oersted.⁵ Such particles have been made on commercial scale from iron and iron cobalt alloy by electrodeposition and magnets of all sizes and shapes are being produced under the name of Iodex. The magnetic properties achieved are on average as good as commercial grade cast Alnicos.

Development work at the National Metallurgical Laboratory

From the review given in the preceding pages it is clear that a number of alloys are of interest to this country which do not require strategic raw materials like nickel and cobalt for their production and can easily be prepared from the indigenous raw materials with satisfactory properties. As stated in the introduction such examples are iron-aluminium alloys, soft and hard ferrites, intermetallic compounds of manganese and elongated particles of ferromagnetic materials. Work carried on some of these as well as conventional materials is detailed in the following pages.

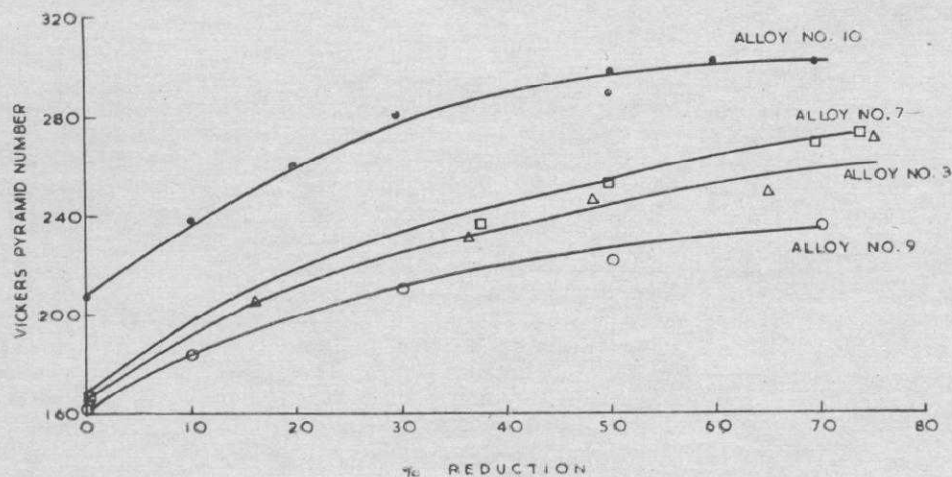
Iron-aluminium alloys

Alloys were made in the composition range 2 to 16% aluminium with or without addition of manganese using pure raw materials. The compositions of the alloys studied are shown in Table I.

TABLE I Chemical composition of the alloys

Alloy No.	%Mn	%Al	%C	%S	%P	%Si	%Ni
I	0.7	2.86	0.03	0.03	—	—	—
II	1.83	2.95	0.02	0.04	0.025	—	0.004
III	3.43	2.95	0.04	0.019	0.06	—	0.004
IV	4.1	2.95	0.04	0.015	0.014	—	0.006
V	2.48	3.19	0.04	0.022	0.007	—	0.003
VI	1.9	2.34	0.055	0.047	—	—	—
VII	3.13	3.78	0.06	—	—	—	0.003
VIII	1.46	3.83	0.04	0.015	—	—	—
IX	2.6	4.39	0.02	0.017	—	—	0.007
X	1.5	5.72	0.04	0.02	—	—	—

The metals were melted in a magnesite lined induction furnace and killed with ferro-silicon, calcium silicide and in some cases with calcium-aluminium master



1 Work-hardening behaviour of some iron-aluminium alloys

alloy containing 50% calcium and chill cast into ingots of 2" x 2" cross section. The ingots were forged and hot-rolled at 1100°C to 0.1" thick sheets, finishing the rolling at about 750°C. The hot-rolled pickled sheets were cold-rolled in a four high rolling mill to 0.005 in thickness. The sheets were then annealed at 1150°C for various durations and tested ballistically.

Cold rolling and work hardening capacity of the iron-aluminium alloys

The sheets made from all the alloys studied could be cold-rolled from 0.1 in to 0.005 in thickness without showing any edge cracks. Hardness values of the sheets were determined after various reductions and are shown in Fig. 1. It is observed that the alloys do not work-harden appreciably. The figure also shows that work-hardening capacity of different steels is almost equal in spite of the fact that manganese and carbon contents differed significantly from alloy to alloy. These steels however, could be cold-rolled only if they were normalized from above 650°C. The annealed steels showed catastrophic cracking on cold rolling. The phenomenon is perhaps related to temper brittleness of low alloy steels when they are annealed at or about 600°C. This brittleness was more conspicuous in steels having higher manganese contents.

The steels containing 10% aluminium could not be cold-rolled due to their excessive coarse grained structure. These steels however could be rolled if they were first sufficiently warm-worked at about 500°C to break the brittle structure.

On account of the excellent cold-rollability of the aluminium steels they are likely to have good stacking factor and therefore low eddy current loss.

Magnetic properties

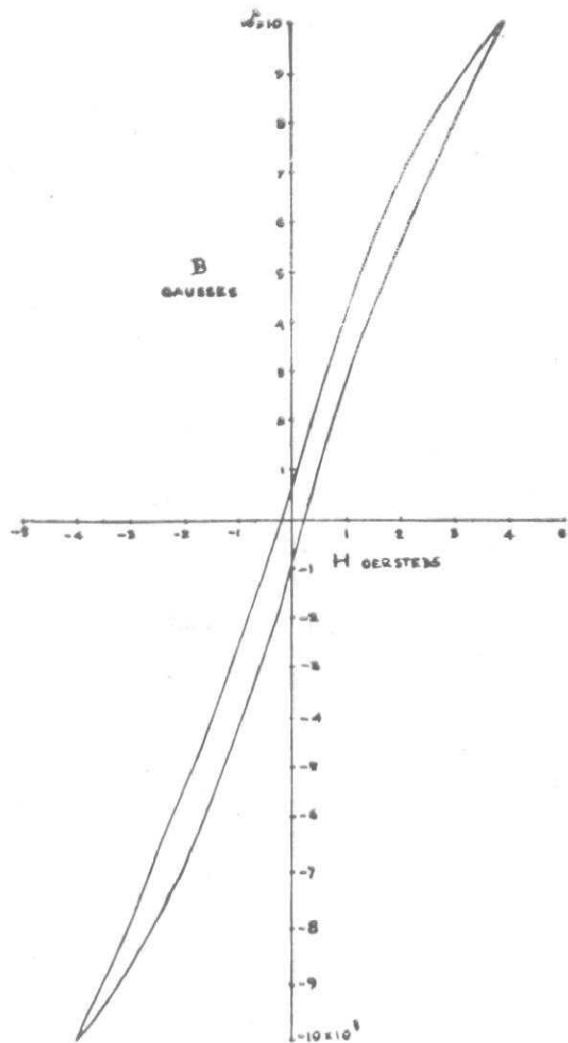
The rolled sheets were vacuum annealed at 1150°C and tested ballistically for their magnetization and B-H curves. The results are shown in Table II. It is observed

TABLE II Electrical and magnetic properties of some iron-aluminium alloys

Alloy No.	Hc for B=10000-gauss oersteds	Hc for B=13000-gauss oersteds	Br gauss	Maximum permeability B/H
I	—	0.5	—	3100
II	0.45	0.7	—	—
III	0.40	—	3000	2900
IV	0.35	—	2600	—
V	0.25	—	850	2700
VI	0.60	—	—	—
VII	0.40	—	3000	2900
VIII	0.40	0.5	—	7000
IX	0.15	0.4	770	2000
X	0.3	3.35	—	11000

Alloys No. VIII and X annealed at 1150°C for 90 hours in vacuum. The rest of the alloys were annealed for 5 hours only.

that iron-aluminium alloys are associated with extremely low coercive force values. The values of maximum permeability varied greatly from specimen to specimen. It is, however, seen from the table that high values of permeability are obtained in steels annealed for very long durations, and having high aluminium and low manganese contents. No relationship however could be observed between coercive force/permeability and chemical composition. These properties were, however, more dependent upon the state of deoxidation of the metal and annealing conditions. The steels which were deoxi-



2 Hysteresis loop of 2.48 Mn, 3.19 Al alloy showing low value of remanence

dized with Ca-Al master alloy at the end gave lower values of coercive force and high values of permeability (alloy No. 8 and 10 particularly) extremely low values of coercive force were, however, obtained in steels No. 5 and 9 which have high manganese contents. These steels also had very low values of remanence 800 gauss, Fig. 2. Due to abnormally low values of remanence these steels can be effectively used for relays where low residual induction will minimize or eliminate the air gap.

The best magnetic properties were obtained in case of steel No. 10 having 5.7% aluminium after annealing at 1150°C for 90 hours. The maximum permeability was 11000 and coercive force for $B=13000$ was 0.35 oersted, Fig. 3. These properties are far superior to those of 4% silicon sheets. It is, however, not clear why other alloys in the series showed smaller values of maximum permeability though they had shown very small values of coercive force. One difference between steel No. 8 and 10 and the remaining steels was that they were

annealed for 90 hours and the latter for five hours only at 1150°C. The microstructure of the differently treated steels was almost identical. They all had dispersed particles of alumina distributed throughout the grains. Due to extremely low coercive force values the aluminium steels seem to have great potentialities of being developed as transformer core material if their permeabilities can be improved by producing cleaner steels free from alumina inclusions. Their excellent cold-rollability can be exploited to induce grain orientation so that easy direction of magnetization of grains lies in the direction of rolling. The first problem is related to the deoxidation of the steel and second one with the secondary recrystallization. These aspects of the problem are now being vigorously pursued at the National Metallurgical Laboratory.

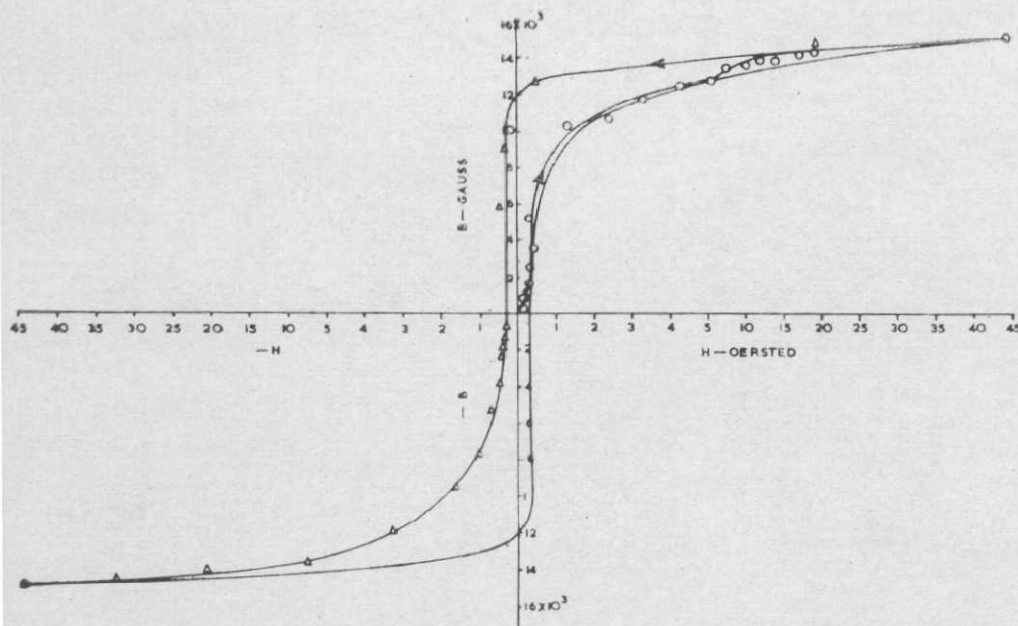
High aluminium alloys particularly with aluminium content ~10% are difficult to work. They required to be warmed to about 500°C before they could be cold reduced. An air-melted alloy containing 10% aluminium was hot-rolled to 0.1% thick strips which were reduced to 0.01" thick sheets through warm working. The alloy was finally annealed at 1100°C and showed a coercive force of about 0.4 to 0.5 oersted for $B=14000$ gauss. Iron aluminium alloys containing 12-16% aluminium undergo order-disorder changes and their coercive force is directed by the heat-treatment given to them. The alloys are still under detailed investigation vis-a-vis ternary alloying additions to improve their working heat treatment and properties.

Ferrite

The object of the investigation was to prepare soft and hard ferrites employing commercial grade iron oxide occurring in nature in this country and to find out the possibility of replacing Alnicos which are generally used in the preparation of such materials magnets by ferrite magnets in many applications.

Soft ferrites

The soft ferrites which are also known as ferroxcubes were prepared by reaction of iron oxide with zinc and Ni/Mn oxides in a wide range of molar proportions of each. The reacted mass was ground to fine powder and extruded into rods of 10-12 in. length and 0.2 in diameter with the help of suitable clayey type plasticizers and extruding dies developed at the National Metallurgical Laboratory. The plasticizers used also increased room temperature strength of the rods for their subsequent easy handling. The rods were then dried at low temperatures in the range of 100 to 300°C and sintered in the temperature range 1200 to 1280°C for 2 to 4 hours. The heating and cooling cycle was, however, spread over 24 to 36 hours. The rod specimens underwent considerable shrinkage during sintering. The sintered rods showed an electrical resistance in the range of 10^5 to 10^8 micro-ohm centimeter and Q values similar to those shown by imported rods in the frequency range 200 to 300 kilo cycles in a comparative test designed for the purpose as given below.



3 Magnetization curve and hysteresis loop of $1.5 \times \text{Mn } 5.72\% \text{ Al}$ alloys after annealing at 1150°C for 90 hours

Q values at 200 to 300 Kc/sec.

N.M.L. rods	imported rods (Philips)
145	170
205	

The magnetic hysteresis curve of the rods was also similar to that of imported one. These ferrite rods can thus be used with advantage as antenna rods in radios operating at medium frequencies.

Hard ferrites

Hard ferrites also known as ceramic magnets are characterised by very high values of coercive force and can be used in preference to Alnico magnets in a number of applications due to their higher resistance to demagnetization. The ferrite magnets are made by reaction of iron oxide and one or more of the oxides of calcium, barium, strontium and lead in molar proportion of about 1:6. The oxides used in this investigation were principally barium and commercial grade iron oxide containing 2 to 4% of impurities. BaO was also substituted by lead oxide in various proportions. The ingredients were first thoroughly mixed and then calcined in the temperature range $900\text{--}1100^\circ\text{C}$ for sufficient duration to complete the reaction. The calcined mass was then ground to fine powder of not less than 300 mesh. The powder was then pressed into suitable shapes with the help of lubricants and binders like starch, stearic acid and sintered in the temperature range 1100°C to 1300°C for duration up to eight hours. The sintered compacts underwent volume shrinkage of 10–35% depending upon the chemical composition of the ferrite magnets and sintering time and

temperature employed. Further most of the sintering was completed during first half of an hour at any sintering temperature. The heating and cooling cycle of the sintering compacts was important due to the marked anisotropy of expansion and contraction of hexagonal structure possessed by these oxides and had to be at low rates in the range of 2 to 6°C min. The sintered magnets were tested ballistically under a field at 14000 gauss. The best magnetic properties were obtained after sintering for about two hours around 1200°C . The magnets showed coercive force values ranging from 1200–1600 oersteds, remanence ranging from 1800–2400 gauss and energy product ranging from 0.7–1.0 m.g.o. The properties of some compositions are shown in Table III.

TABLE III Magnetic properties of some barium ferrite magnets after sintering for two hours at 1176°C

	1Ba 0.6 Fe_2O_3	0.2Pb 0.8BaO 0.6 Fe_2O_3	0.4Pb 0.6Ba 0.6 Fe_2O_3
Coercive force (oersted)	1200	1425	1455
Remanence (Gauss)	1900	2385	2078
BH max. (m.g.o.)	0.66	1.0	0.83

The demagnetization curve of one of the best compositions is shown in Fig. 4.

Commercial aspects of the problem were completely worked out, and after carrying out trial experiments on fairly large scale to prove the feasibility of the process, the technical know-how of the manufacture of ceramic magnets based upon the composition and technical details worked at the National Metallurgical Laboratory was licensed to a few parties for their manufacture.

The flow sheets of the process is given below :

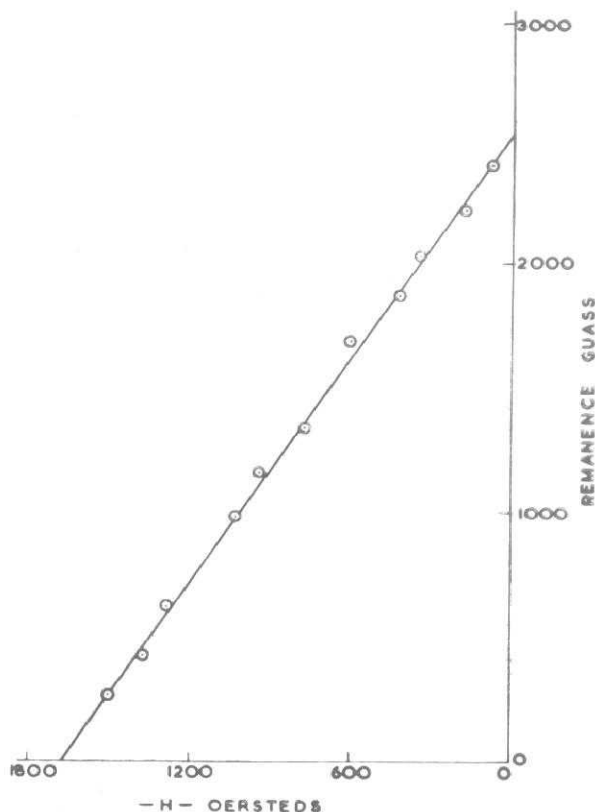
Flow sheet of the process



It is clear from the flow sheet that the machinery required for setting up a plant for the manufacture of barium ferrite magnets, is quite simple and can easily be fabricated to specifications. The raw materials are in abundant occurrence in the country. In contrast the Alnico magnets required raw materials and machinery to be imported.

Manganese-aluminium intermetallic compounds

Manganese metal is paramagnetic in nature but becomes strongly ferromagnetic when alloyed with other elements like nitrogen, bismuth and aluminium. Manganese-aluminium alloys⁶ having coercive force ~2000 oersteds are of a special interest in this country due to abundant occurrence of these metals. Experiments have been carried out at the NML to introduce ferromagnetism in these alloys in the composition range 65 to 72% manganese balance aluminium. The experiments showed that if these



4 Demagnetization curve of a barium-ferrite magnet

alloys are cooled from 1100°C at a rate of about 20-30°C/sec. they exhibit strong ferromagnetism. The X-ray diffraction studies of the critically cooled specimens showed that their ferromagnetism is associated with formation of a non-equilibrium phase having a tetragonal structure. The preparation of the alloys, however, presents difficulties. The casting methods give brittle structures which are difficult to handle while powder metallurgical techniques introduce serious oxidation problems. These are being tackled at present in the laboratory.

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