

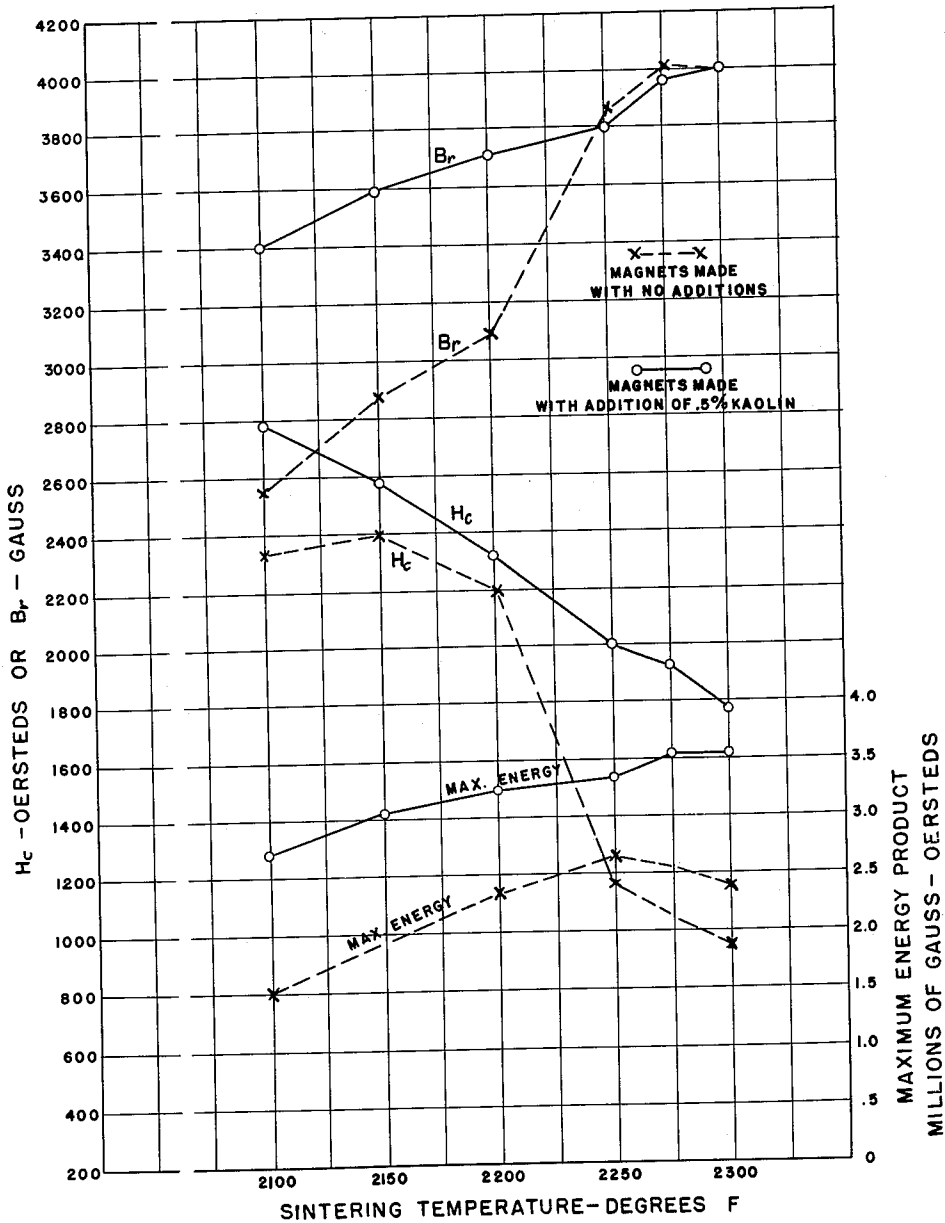
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FERRITE COMPOSITIONS AND METHOD OF MAKING SAME

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**FERRITE COMPOSITIONS AND METHOD OF MAKING SAME**

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The present invention is concerned with a method for improving the magnetic properties of certain magnetic compositions, and to compositions thus produced.

The invention deals specifically with methods for improving the coercive force and the maximum energy product of permanent magnets of the ferrite type represented by the formula  $MO \cdot xFe_2O_3$  wherein M is a bivalent metal and x is an integer. These products are normally prepared by sintering a mixture of iron oxide with one or more metal oxides in powdered form.

For many applications of permanent magnet materials, the best index for the suitability of the composition is its maximum energy product  $(BdHd)_m$ . A typical ferrite composition has a maximum energy product of about  $1 \times 10^6$  gauss oersteds. The maximum energy product of such materials can be improved by including during their manufacture a step which might be called an orienting process. In order to make this process fully effective, the oxide powder has to be brought into a state where every powder particle represents a single crystal. This is usually accomplished by thorough milling of the powdered materials, sintering, and then milling to the desired particle size. When such a powder is oriented and compacted in a magnetic field, its particles orient themselves with a certain crystallographic axis more or less parallel to the applied field. This preferred orientation persists after sintering the sample, giving it a high value of residual induction. In some cases, the maximum energy product can be brought to a value approximating  $3 \times 10^6$  gauss oersteds by the orientation procedure.

One of the difficulties accompanying such increase in maximum energy product, however, is the fact that as the residual induction is increased, it is usually accomplished by a decrease in the coercive force of the material. Thus, raising the sintering temperature of ferrite mixtures usually increases the residual induction while lowering the coercive force due to the increase in apparent density of the specimen due to grain growth. For many applications, a preferable solution would be to provide some means of increasing the coercive force which automatically would increase the maximum energy product, provided the residual induction was kept more or less constant during the process.

Accordingly, an object of the present invention is to provide an improved method for increasing the maximum energy product of ferrite type magnetic compositions.

Another object of the invention is to provide an improved method for increasing the coercive force and the maximum energy product of ferrite type permanent magnet compositions without substantially affecting the residual induction of the material.

A further object of the invention is to provide improved magnetic compositions of the ferrite type having maximum energy products at least as high as, and generally higher than comparable materials presently available.

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Another object of the invention is to provide an improved composition for the manufacture of permanent magnet materials in which the sintering conditions are not so critical as they are presently in the manufacture of ferrite magnets.

The present invention provides a magnetic material of increased maximum energy product comprising a ferrite composition containing a minor amount of a refractory ceramic composition distributed through the ferrite composition. The addition of relatively small amounts of such refractory ceramic materials, particularly combinations of alumina and silica, has been found to increase rather substantially the maximum energy product and the coercive force values of ferrite compositions and, as another advantage, has been found to render the conditions of sintering less critical than previously.

The ferrite compositions usable in the practice of the present invention may be any of a wide variety of ferrites, and preferably consist of those ferrites which have maximum energy products on the order of  $1 \times 10^6$  gauss oersteds or more. A particularly preferred ferrite composition for use in the present invention consists of non-cubic crystals of ferrites in which the ferric oxide lattice is substituted by a metal such as barium, strontium, or lead. Perhaps the best example of a composition of this type is one prepared by combining one molecular proportion of barium oxide with six molecular proportions of ferric oxide to produce materials having high coercive force values and high maximum energy products. The preparation of crystals of this type usually consists in mixing thoroughly a powdery mixture of ferric oxide and an oxide or carbonate of one or more of the other metals, sintering at an elevated temperature and milling the sintered material to the desired particle size. The resulting particles will then represent substantially single crystals. This powder is then compacted while under the influence of a magnetic field and the resulting compact is heated to a temperature in the range from about 2000° to about 2500° F. in a non-reducing atmosphere so that the ferric oxide is not reduced to a lower state of oxidation.

During the mixing or milling operation, the powders are combined with a refractory ceramic powder. All of the following materials have been found to produce the desired effect in varying degrees of effectiveness:

- (1) Silica
- (2) Alumina
- (3) Titania
- (4) Boric oxide

The following mixtures have also been found effective, the mixtures being employed in any proportions, either as a physical mixture or as a chemical combination:

- (5) Alumina-silica
- (6) Calcium oxide-silica
- (7) Calcium oxide-titania
- (8) Alumina-titania
- (9) Boric oxide-silica
- (10) Boric oxide-titania
- (11) Chromic oxide-silica
- (12) Chromic oxide-titania

Where physical mixtures are employed, the two compounds are preferably combined in equal parts by weight.

The preferred material is an alumina-silica combination of the type represented by an aluminum silicate such as a silica-alumina porcelain, kaolin ( $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ ), mullite ( $3Al_2O_3 \cdot 2SiO_2$ ) or other clays or minerals consisting essentially of aluminum silicates and relatively small amounts of other metallic oxides and compounds.

The beneficial effects of the refractory addition are evident even where as little as 0.10% by weight of the

oxide, mixture, or compound is included in the composition. Amounts of the additive in excess of about 2% by weight appear to provide no additional effect insofar as raising the maximum energy product is concerned.

The mechanism by which the refractory additions operate to improve the magnetic properties is not completely understood. It is possible that some form of non-magnetic material is formed around each crystal, thereby causing some slight separation between the crystals and reducing the possibility of domain walls crossing from one crystal to another. The effect of this factor would be to increase the coercive force. It seems clear that the improvement is not a simple mechanical phenomenon because magnets made without the additions have resistivities on the order of a few hundred thousand to a few million ohm-cm, whereas magnets using such additions have resistivities on the order of a few hundred to a few thousand ohm-cm.

The process of the present invention has been used successfully to produce permanent magnet materials having maximum energy products in excess of  $3 \times 10^6$  gauss oersteds. This improvement is obtained by achieving an increased coercive force at a given residual induction. The increase in coercive force is of a considerable importance not only because it is accompanied by an increase in maximum energy product but also because it makes the magnet less susceptible to the demagnetizing influences of stray fields, shocks, and temperature changes.

In the past, some magnet compositions have been prepared with energy products on the order of 3.5 million gauss oersteds, but these were achieved by grinding away the misoriented material on the surfaces of such magnets. Even with this process, entirely inconsistent results were obtained, whereas with the process of the present invention, it is possible to produce consistently magnets with energy products of 3.5 million gauss oersteds without resorting to any grinding whatever.

The attached sheet of drawing illustrates a graph in which the coercive force, remanence, and maximum energy product of two identical materials are compared, the difference being that the curve drawn with the dashed lines represent a barium oxide—ferric oxide (1 to 6 mole ratio) ferrite composition without the addition of the refractory material, while the solid line curve represents the values obtained with the same composition combined with 0.5% of powdered kaolin. As evidenced from these curves, an increase of the sintering temperature very substantially reduces the coercive force of the material without the kaolin addition, while the reduction of coercive force in the preferred sample is much more gradual. It will also be noted that the maximum energy product of the sample with the kaolin addition increases despite an increase in the sintering temperature, whereas the maximum energy product of the material without the addition decreases after sintering temperature of about 2250° F. It will also be noted that the coercive force values for the material with the additive are higher in all instances at the various sintering temperatures and that the remanence characteristics are substantially higher at the lower sintering temperatures for the improved material of the present invention, and substantially the same at the higher sintering temperatures.

The following specific examples illustrate the results achieved in the compositions of the present invention.

#### Example I

A typical example of a barium oxide ferrite containing one molecular proportion of barium oxide and six molecular proportions of ferric oxide had a remanence (Br) of 4035 and a coercive force ( $H_c$ ) of 1260. The maximum energy product ( $BdHd$ )<sub>m</sub> was equal to  $2.83 \times 10^6$  gauss oersteds.

When the identical material was milled with powdered silica-alumina porcelain constituting ¾% by weight of

the mixture, the remanence observed in the final product was 4010, the coercive force was 1900 oersteds and the maximum energy product was  $3.55 \times 10^6$ . Thus, the addition of even a small amount of the refractory material was effective to raise the maximum energy product by about 25%.

#### Example II

The same starting material as in Example I was combined with ¾% of kaolin and ball-milled to produce a very finely divided powder. This material after sintering had a remanence of 3900, a coercive force of 1860 oersteds, and a maximum energy product of  $3.47 \times 10^6$ .

#### Example III

A barium ferrite sample of the type used in the preceding examples was made with the addition of ½% silica. The materials had a remanence of 3940, a coercive force of 1700 oersteds and a maximum energy product of  $3.39 \times 10^6$ .

#### Example IV

A barium ferrite sample of the type used in the preceding examples was made with the addition of ¼% boric acid and ¼% silica. This material had a remanence of 3960, a coercive force of 1520 oersteds, and a maximum energy product of  $3.28 \times 10^6$ .

From the foregoing, it will be apparent that the process of the present invention is effective to increase substantially the maximum energy product of ferrite type magnets and at the same time provides a composition which is more stable towards sintering than ordinary ferrite compositions. It will also be evident that various modifications can be made to the described embodiment without departing from the scope of the present invention.

I claim as my invention:

1. In a method of producing a permanent magnet of the mixed ferrite type having a non-cubic crystalline lattice and an empirical formula  $MO.6Fe_2O_3$  where M is a metal selected from the group consisting of barium, strontium, and lead wherein said magnet is prepared by mixing iron oxide with a source of the oxide MO followed by sintering the mixture at a temperature in the range from 2,000 to 2,500° F. and compacting the mixture while under the influence of a magnetic field, the improvement whereby the maximum energy product is increased which comprises adding to said mixture prior to said compacting from 0.1 to 2.0% by weight of a refractory oxide mixture selected from the group consisting of alumina and silica, calcium oxide and silica, calcium oxide and titania, alumina and titania, boric oxide and silica, boric oxide and titania, chromic oxide and silica, and chromic oxide and titania, the alumina to silica molar ratio being generally between 1 to 2 to 3 to 2, and the other oxides of the remaining mixtures being substantially in equal proportions by weight.

2. In a method of producing a permanent magnet of the mixed ferrite type having a non-cubic crystalline lattice and an empirical formula  $MO.6Fe_2O_3$  where M is a metal selected from the group consisting of barium, strontium, and lead wherein said magnet is prepared by mixing iron oxide with a source of the oxide MO followed by sintering the mixture at a temperature of 2,000 to 2,500° F. and compacting the mixture while under the influence of a magnetic field, the improvement whereby the maximum energy product is increased which comprises adding to said mixture prior to compacting from 0.1 to 2.0% by weight of a mixture of alumina and silica having a molar ratio of from about 1 to 2 to 3 to 2.

3. A permanent magnet material comprising a non-cubic mixed ferrite composition having the empirical formula  $MO.6Fe_2O_3$  where M is a metal selected from a group consisting of barium, strontium, and lead in combination with from 0.1 to 2.0% by weight of a refractory oxide mixture selected from the group consisting of

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alumina and silica, calcium oxide and silica, calcium oxide and titania, alumina and titania, boric oxide and silica, boric oxide and titania, chromic oxide and silica, and chromic oxide and titania, the alumina and silica being in relative molar proportions of between about 1 to 2 to 3 to 2, and the other oxides of the remaining mixtures being substantially in equal proportions by weight.

4. A permanent magnet material comprising a barium ferrite having the empirical formula  $BaO \cdot 6Fe_2O_3$  in combination with from 0.1 to 2.0% by weight of a mixture of silica and alumina having a molar ratio of from about 1 to 2 to 3 to 2, said material having a maximum energy product in excess of  $3 \times 10^6$  gauss oersteds.

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