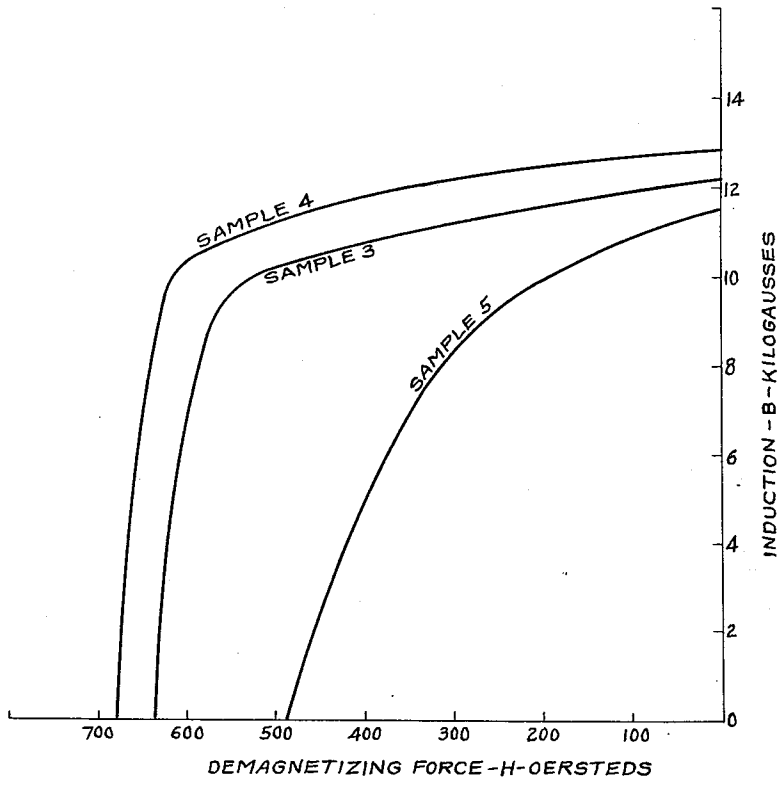
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SINTERED HIGH ENERGY PERMANENT MAGNETS

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Inventors:
Robert J. Studders,
Dolph G. Ebeling,
by
Their Attorney.

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SINTERED HIGH ENERGY PERMANENT MAGNETS

Robert J. Studders, Schenectady, and Dolph G. Ebeling, Troy, N. Y., assignors to General Electric Company, a corporation of New York

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The present invention relates to sintered high energy Alnico magnets prepared by powder metallurgy methods. It is more particularly concerned with sintered high energy permanent magnets characterized by a massive crystalline structure and a BH max. value equal to or higher than the BH max. values of the best cast anisotropic Alnico magnets.

Both cast and sintered Alnico magnets of various compositions but essentially containing aluminum, nickel, cobalt, and iron, have been on the market for same years. As compared with the cast products, the sintered magnets, prepared, for example, in accordance with the teachings of Howe Patents 2,192,743 and 2,192,744 have been characterized by the fine grain structure normally found in sintered products made by the usual powder metallurgy techniques. The sintered products have also been characterized by somewhat lower magnetic properties than the corresponding cast alloys due to the impracticability of obtaining maximum physical density in the sintered alloys.

While most of the Alnico magnets have been magnetically isotropic, an outstanding exception are the cast anisotropic magnets prepared in accordance with the teachings of the Jonas Patent 2,295,082. The cast magnet alloys which are described in the Jonas patent as iron base alloys having a cobalt content of 16 to 30 per cent, a nickel content of 12 to 20 per cent and an aluminum content of 6 to 11 per cent with or without other additions such as up to 7% copper, are rendered anisotropic by heat treatment (cooling) in a magnetic field. The heat treated products exhibit BH max. values in one direction at least 50 per cent, and generally over 100 per cent, higher than those of the same alloy which has not been so heat treated. Representative of these cast anisotropic magnets is the commercially available magnet known as Alnico 5. This magnet alloy consists of about 8 per cent aluminum, 14 per cent nickel, 24 per cent cobalt, 3 per cent copper, balance substantially iron, and exhibits the following magnetic properties:

Peak H	oersteds	2,000
Peak B	gauss	15,700
Coercive force H_c	oersteds	575
Residual B_r	gauss	12,000
BH max	gauss-oersteds	4.5×10^6

Heretofore, it has not been found possible to prepared sintered anisotropic Alnico magnets comparable with the cast anisotropic magnets by the simple duplication in the sintered product

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of the chemical composition of the cast magnet. This indicates that factors other than chemical composition influence the effectiveness of the magnetic field treatment in imparting superior available energy products to the alloy.

The present invention has as a primary object the preparation of sintered anisotropic Alnico magnets having BH max. values as high or higher than those of a cast magnet of the same composition.

Another object of the invention is to provide a high energy sintered Alnico magnet characterized by a massive crystalline structure.

These, and other objects which will become apparent from the following description taken in connection with the accompanying drawing in which the single figure includes demagnetization curves of magnets prepared in accordance with the present invention.

The invention will best be understood after first considering the practices heretofore employed in the manufacture of sintered magnets, which practices are more fully described in the above-mentioned Howe patents.

In accordance with those practices, whereby dense, fine-grained alloys of superior strength could be produced to close tolerances, oxidation of the aluminum is prevented by adding this element as a pre-alloy of aluminum and iron, cobalt or nickel. A pre-alloy of 50 per cent aluminum and 50 per cent iron is generally used because it is brittle and easily disintegrated by ball-milling. The finely-divided aluminum alloy is mixed with the remaining elements in powder form and the mixture pressed to the desired form or shape. The pressed products are sintered in a hydrogen atmosphere at a temperature below but close to the melting point of the alloy. To obtain the desired consolidation by interdiffusion of the powdered metals, the sintering has been carried out at a temperature above the melting point of the aluminum alloy (aluminum-iron) component.

The advisability of using aluminum-nickel alloys or aluminum-iron alloys other than the 50:50 alloy has also been investigated, the conclusion being that for acceptable results the pre-alloy should have a melting point below but close to that of the final alloy. For example, G. Ritzan, Wiss. Veroff aus den Siemens-Werken, Werkstoff Sonderheft 37 (1940), concludes that such other pre-alloys as may be used should be those which give a liquid phase at the sintering temperature and which are not characterized by a maximum melting point. The same con-

clusions are presented by S. J. Garvin in his article entitled "Sintered Permanent Magnets," in "Engineering" June 6, 1947.

The commercial sintered Alnico products and those obtained by following the teachings of these investigators have been characterized by a fine-grained structure with a grain size the order of the size of the metal particles employed in making the products.

In accordance with the present invention, there has been provided sintered Alnico magnets differing from the prior art products in having a massive, and in some cases, a single crystal structure. In addition, the anisotropic magnets of the present invention are characterized by energy values in a principal direction substantially higher than those of cast anisotropic magnets of the same composition.

These results are obtained by a sintering process which primarily differs from the prior art processes in that it includes the introduction of the low melting point constituents, particularly the oxidizable low melting constituent, i. e., the aluminum, in the form of a master alloy or pre-alloy having a melting point at or above, rather than below, the sintering temperatures.

While the invention is not limited thereto, it will be particularly described with reference to the preparation of sintered anisotropic magnets of the composition given in the above-mentioned Jonas patent, specifically a sintered anisotropic magnet of the same chemical composition as Alnico 5.

In preparing the sintered products of the present invention, the powdered metal constituents are mixed in the required proportions with the aluminum constituent being added in the form of a high melting point alloy of cobalt, nickel or iron. If desired, the copper which also melts below the sintering temperature (1200 to 1400° C.) may also be added in the form of a high melting point alloy with one of the remaining metals. However, when the total quantity of copper is low, e. g., about 3–5%, this procedure is not necessary, probably due to the fact that during sintering the unalloyed copper may be continuously consumed in the formation of a high melting point alloy so that the net result is in fact the formation of a copper alloy having the melting point requirements specified hereinbefore.

Except for the introduction of the low melting point metals, such as, the aluminum in the form of an alloy having no molten phase below the sintering temperature, the products of the present invention are prepared in substantially the same manner as that usually employed in making sintered Alnico magnets in accordance with the above-mentioned Howe patents. The finely divided aluminum alloy is mixed with the other finely divided metal ingredients to provide a mixture of the intended composition and the mixture pressed into the desired shape. The pressed products are sintered in a hydrogen atmosphere at temperatures of from about 1200° to 1400° C., preferably below but close to the melting point of the alloy. The time required for the sintering action will, of course, depend upon the size of the furnace load and size of the pressed pieces. Ordinarily, the sintering time will be from about two to five hours. The sintered material, which will now be characterized by a crystal structure which is a ten to twenty thousand fold increase in the crystal size over the starting material, i. e., the metal powder, can then be subjected to the magnetic field treatment described in the Jonas patent to obtain an anisotropic magnetic product. The heat treatment in the magnetic field is preferably carried out by withdrawing the material from the sintering zone of the furnace at a temperature of about 1250° C. and controlling its cooling cycle in a magnetic field of proper field strength. Further low temperature treatments may be applied as described by Jonas.

This process, insofar as the production of a massive crystal structure is concerned, is better than any known process for the commercial production of large crystals by casting of the molten alloy. The benefits of the massive type crystal structure, which often is a single crystal, are readily apparent from the test results set forth in the following table.

MASSIVE CRYSTAL SPECIMENS

No.	B_r	H_c	BH max.	At B
1	12,500	655	5.64×10^6	10,400
2	12,550	670	5.96×10^6	10,450
3	12,050	635	5.18×10^6	9,600
4	12,700	690	6.36×10^6	10,200

FINE GRAINED MATERIAL MADE WITH LOW MELTING MASTER ALLOY

5	11,600	480	2.5×10^6	8,000

In the above table, the specimens 1–4 inclusive had the same composition as Alnico 5 and were prepared in accordance with the present invention using a pre-alloy of 25 per cent aluminum, balance cobalt. Specimen 5 was a fine-grained sintered product of the same composition prepared by use of the low melting 50:50 Fe-Al pre-alloy. The demagnetization curves of specimens 3, 4 and 5 are shown in the accompanying drawing, from which it will be seen that there is a tremendous increase in BH max. in the transition from the fine-grained structure of specimen 5 to a massive crystal structure of specimens 3 and 4. It is to be noted also that the BH max. values for specimens 1–4 inclusive are all higher than the BH max. value of cast Alnico (Alnico 5) of the same composition.

The aluminum pre-alloys employed in the practice of this invention include those which can be selected, for example, from the phase diagrams of the binary Fe-Al, Co-Al, and Ni-Al alloys as having no molten phase below the sintering temperatures. The useful alloys include the aluminum-cobalt alloys containing from about 67 to 85 per cent by weight of cobalt, the aluminum-nickel alloys containing about 64 to 80 per cent by weight nickel and the aluminum-iron alloys containing up to 18 per cent aluminum. All of these designated alloys are characterized by freedom from a molten phase below 1400° C. For practical reasons, the aluminum-cobalt alloys are preferred.

The advantages of the present method in which the aluminum is added to the powdered mixture in the form of a high melting point alloy are very pronounced. In addition to the higher BH max. values of the anisotropic products along the 100 crystallographic face, all of the products have a surface which is comparable with the best surface obtainable by precision casting methods. In addition, the products have a physical density which is higher than that of the sintered materials obtained by adding the aluminum in the form of a low melting point alloy. Although the specific gravity is about 5–6% lower than that of

a cast magnet of the same composition, the magnetic properties are comparable with the best cast magnet and are much superior to the magnetic properties of the usual commercial cast Alnico magnets.

It has also been noted that there is an improvement in the physical strength of the sintered materials prepared as described herein, possibly because, in the absence of a molten phase, there is less tendency for the aluminum to oxidize so that the impurities are more restrained in their movement and are not expelled to the grain boundaries. This result is to be compared with the usual cast or sintered Alnicos in which the molten phases allow the impurities to congregate and form grained boundaries which can act as restrictions against further growth of the crystals.

It is believed that at least three things contribute to the formation of the massive crystal structure in the present product. First, due to the condition of the aluminum master alloy surface, oxidation of the powder is at a minimum. Secondly, a somewhat longer sintering time of at least two hours and the use of a sintering temperature which approaches within 15–50° of the melting point of the entire composition appears to effect the growth of the massive crystal structure under conditions which do not favor the congregation of impurities. Thirdly, the absence of any molten aluminum-bearing phase greatly reduces any tendency toward oxidation of the aluminum during sintering.

The following experiment illustrates the difference in the results obtained by employing a high melting point aluminum-cobalt alloy as compared with a lower melting point aluminum-cobalt alloy. In this experiment, two mixes were made up of identical compositions, one employing a 50:50 aluminum-cobalt master alloy and the second a 25:75 aluminum-cobalt master alloy. Both alloys were reduced to a minus 200 mesh powder under conditions which were designed to prevent any significant oxidation of aluminum components thereof.

These binary alloys were then made into powder mixes of the Alnico 5 composition. Test bars were pressed from the mixes. One bar from each mix was placed in a sintering boat with the bars placed side by side. These boats were then passed through a sintering furnace at a rate of 10 inches per 2.25 hours at a temperature of 1380–1385° C.

Upon examination of the sintered products, it was found that the bars from the mix containing lower melting 50:50 aluminum-cobalt alloy were severely distorted, melted, and were full of holes. The bars from the 25:75 aluminum-cobalt mix had a very smooth surface with practically no distortion. Upon fracturing the bars, it was found that each of the bars from the 25:75 aluminum-cobalt mix was characterized by a massive crystal structure, while every bar from the 50:50 aluminum-cobalt mix was essentially fine-grained and comparable in this respect to the previously known sintered Alnico magnet alloys. The massive crystal structure products possessed BH max. values of the order of specimens 1–4, as set forth in the foregoing table, whereas the 50:50 aluminum-cobalt products possessed BH max. values comparable with the BH max. value of specimen 5.

A further aspect of the present invention comprises a modification of the process whereby the massive crystalline structure can be obtained

with an orientation of the crystal in the direction most favorable to the influence of the directionalizing magnetic field applied during the heat treatment in the preparation of anisotropic products.

Alnico compositions of the type with which the present invention is concerned have been found to possess a body centered cubic crystal lattice and the most desirable orientation is with the edges of the cube either parallel or perpendicular to the direction of the magnetic field applied during the heat treatment. In order to obtain a high percentage of products in which the massive crystal is so oriented, a seed crystal is planted close to one end of the bar during pressing. These seeds are so placed with respect to the well defined 100 crystal plane of the crystal that upon growth thereof, there is obtained a massive crystal of the proper orientation. The seeded bars are then cycled through the sintering furnace as described hereinbefore with the seeded end of the bar preferably entering the furnace first. After sintering, it is found that in at least 75% of the products, there is obtained a favorable crystal orientation so that the resultant products have a BH max. value approaching the maximum theoretical value.

The seeding crystals employed in this process can be obtained, for example, by fracturing the sintered massive crystal products of the present invention. The specimens appear to fracture along the 100 crystallographic face and the seed crystals are placed in the compacts with this face properly oriented.

While the invention has been particularly described with reference to specific Alnico compositions, it is to be understood that it is not limited thereto. Any of the various compositions coming within the teachings of the above-mentioned Jonas patent can be employed, provided the aluminum and, if necessary, any other low melting point component which is present in a substantial amount, is employed in the form of an alloy melting above the sintering temperatures and provided further that the pressed powder is sintered at a temperature approaching, but below, the melting point of the entire composition. It is further to be understood that the invention is not limited to binary aluminum pre-alloys but includes the addition of the aluminum in the form of any high melting point alloy having no molten phase at sintering temperatures and consisting of two or more of the metal constituents of the Alnico compositions.

We claim:

1. The method of making a sintered anisotropic permanent magnet having a massive crystalline structure which comprises compacting a mixture of powdered metals including iron, nickel, cobalt and aluminum, the aluminum being present in the form of an alloy with an iron group metal having no molten phase at the sintering temperature of the mixture, said aluminum alloy being selected from the group consisting of aluminum-cobalt alloys containing from about 67 to 85 percent by weight cobalt, aluminum-nickel alloys containing from about 64 to 80 percent by weight nickel, and aluminum-iron alloys containing up to 18 percent by weight aluminum, and sintering the compact at a temperature of from 1200 to 1400° C., which temperature is below that at which any molten phase is formed in said mixture.

2. The method of making a sintered anisotropic magnet having a massive crystalline structure and a BH max. of at least about 5×10^6 which com-

prises forming a mixture of powdered iron, nickel, aluminum, cobalt and copper in which the aluminum is present in the form of an aluminum-cobalt alloy containing from 67 to about 85 percent by weight of cobalt and sintering the formed mixture at a temperature of from 1200 to 1400° C., said mixture containing from 16 to 30 percent cobalt, 12 to 20 percent nickel, 6 to 11 percent aluminum, up to 3 percent copper, and balance substantially all iron.

3. The method of claim 2 in which the aluminum-cobalt alloy contains about 25 percent aluminum, balance substantially cobalt and the sintering temperature is 1380 to 1385° C.

4. The method of making a sintered anisotropic magnet alloy which comprises mixing a plurality of metal powders essentially including iron, nickel and aluminum, the aluminum being in the form of an alloy with an iron group metal which alloy contains no molten phase at the sintering temperature, compacting the mixture with a seed crystal within said compact at a temperature of 1200 to 1400° C. and oriented in the desired direction and sintering the compact to obtain a product containing massive crystals of the same orientation as the seed crystal.

5. The method of claim 4 in which the sintered alloy consists essentially of 6 to 11 percent aluminum, 16 to 30 percent cobalt, 12 to 20 percent nickel and about 3 percent copper, balance iron, and the aluminum is employed in the form of an aluminum-cobalt alloy.

6. The method of claim 4 in which the sintered alloy consists essentially of about 8.5 percent aluminum, 14 percent nickel, 25 percent cobalt, 3 percent copper, balance iron except for incidental impurities, and the aluminum is in the form of a powdered aluminum-cobalt alloy containing about 25 percent aluminum and 75 percent cobalt.

7. The method of making a sintered anisotropic magnet having a massive crystalline structure

and a BH max. of at least about 5×10^6 which comprises forming a mixture of powdered iron, nickel, aluminum, cobalt and copper in which the aluminum is present in the form of an alloy of aluminum and an iron group metal having no molten phase below 1400° C., said aluminum alloy being selected from the group consisting of aluminum-cobalt alloys containing from about 67 to 85 percent by weight cobalt, aluminum-nickel alloys containing from about 64 to 80 percent by weight nickel, and aluminum-iron alloys containing up to 18 percent by weight aluminum, and sintering the formed mixture at a temperature of from 1200° to 1400° C., said mixture containing from 16 to 30 percent cobalt, 12 to 20 percent nickel, 6 to 11 percent aluminum, up to 3 percent copper, and balance substantially all iron.

ROBERT J. STUDDERS.
DOLPH G. EBELING.

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