

Dec. 31, 1963

P. HOKKELING ETAL

3,116,181

PERMANENT MAGNETS

Filed Jan. 12, 1960

2 Sheets-Sheet 1

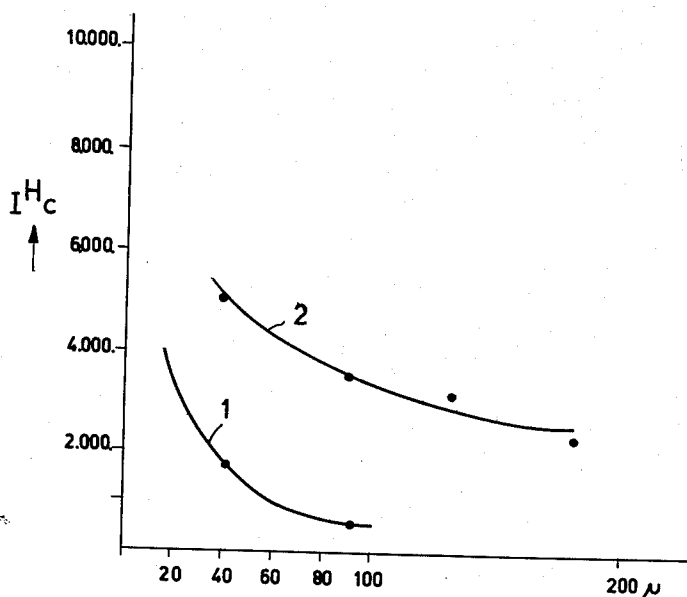


FIG. 1

INVENTORS

C. P. MARKS
H. ZIJLSTRA
K. J. DE VOS
A. J. J. KOCH
P. HOKKELING
M. G. VAN DER STEEG

BY

Paul R. Lefort
AGENT

Dec. 31, 1963

P. HOKKELING ETAL

3,116,181

PERMANENT MAGNETS

Filed Jan. 12. 1960

2 Sheets-Sheet 2

FIG.2

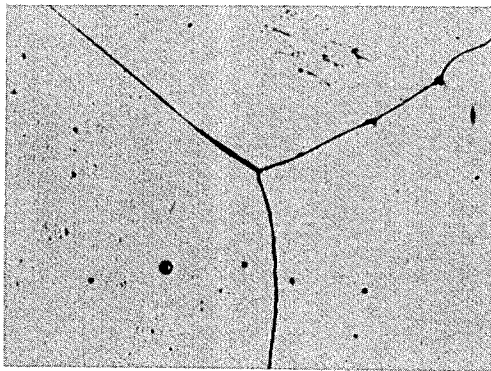


FIG.3

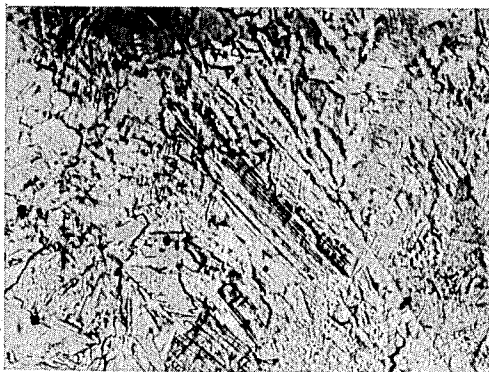
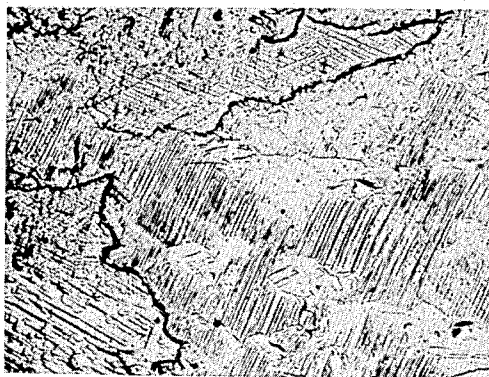


FIG.4



1

3,116,181

PERMANENT MAGNETS

Pieter Hokkeling, Adolf Jehannus Jacobus Koch, Christiaan Philip Marks, Michael Gottfried van der Steeg, Krijn Jacobus de Vos and Hinne Zijlstra, Eindhoven, Netherlands, assignors to North American Philips Company, Inc., New York, N.Y., a corporation of Delaware

Filed Jan. 12, 1960, Ser. No. 2,028

Claims priority, application Netherlands Sept. 30, 1958
18 Claims. (Cl. 148—31.57)

Our invention relates to permanent magnets and to methods of making the same.

This application is a continuation-in-part of our pending U.S. patent application Serial No. 842,729, filed September 28, 1959, now abandoned.

Claims to the method are being presented in our copending U.S. patent application Serial No. 277,062, filed June 20, 1963.

An object of the invention is to produce permanent magnets of advantageous magnetic properties in a simple and inexpensive manner.

A more specific object is to produce permanent magnets which have a particularly high resistance to demagnetization.

A further object is to provide a permanent magnet which has a saturation magnetization at least substantially equal to that of the MnBi materials, while at the same time using less expensive and readily-available starting materials.

Another object is to provide a permanent magnet in which a relatively large quantity of impurities may be present without deleteriously affecting the permanent magnet properties.

A further object is to provide permanent magnets of a particle size which may be advantageously formed, with or without a binder, into permanent magnets, particularly anisotropic magnets, of larger size and of various shapes.

Another object of our invention is to improve the magnetic anisotropic properties of such magnets.

A still further object is to produce anisotropic permanent magnets having a high $(BH)_{\max}$ value, for instance 3.5×10^6 gauss oersteds, while at the same time keeping the cost of the magnets low.

A more specific object is to provide particle-size permanent magnets which are particularly adapted for forming magnetic seals.

Further advantages will appear as the specification progresses.

We have discovered that the above objects are attained with permanent magnets of materials which comprise, as the "essential constituent," a phase which contains at least 60%, preferably at least 65%, by weight of manganese and which exhibits a tetragonal crystal structure with an axes ratio (c/a) of more than 1 and less than $\sqrt{2}$, the "range of existence" of this phase being integral with that of the phase occurring in the binary Mn—Al alloys and having an Mn—Al atom ratio of approximately 5:4, which phase, according to X-ray or neutron powder diagrams, may be described as having a tetragonal crystal structure with an axes ratio (c/a) of about 1.3 and occupation of the lattice points 0, 0, 0, and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, with preference of the Mn atoms for one of these lattice points.

The term "tetragonal phase" as used herein is to be understood to mean the above-described tetragonal crystal structure which hitherto unknown phase we have found to be the constituent which imparts advantageous properties to permanent magnets of such materials, and thus this phase should be considered as the above-

2

mentioned "essential constituent." This tetragonal phase is not a phase of equilibrium, but has the nature of the metastable phase, and therefore can be obtained only by a special thermal treatment according to the invention.

The term "range of existence" as used herein is to be understood to mean a range of concentration in which identical structure can be fully realized 100% in a continuous sequence of alloys, with or without a thermal treatment.

The term "permanent magnet" as used herein is to be understood to mean a body having permanent magnet properties and to include not only cast bodies, but also crushed or pulverized bodies of small size, particularly particles with a grain size less than about 100 microns, and bodies of larger size and various shapes which have been formed, with or without a binder or by sintering, from a large number of the smaller-size bodies.

Generally the amount of the tetragonal phase amounts at least 10% by weight, preferably at least 50%, of the magnet body.

According to a further aspect to the invention, the "essential constituent" is the tetragonal phase of the binary Mn—Al alloy which may contain the usual impurities and small amounts of additional elements. This tetragonal phase is particularly prevalent in alloys consisting essentially of about 68% to 75% by weight of manganese and the remainder aluminum. The usual impurities as well as certain additions may be present, provided they are in such amounts that do not deleteriously affect the formation of the tetragonal phase. Especially good results have been obtained when using 70.5% to 72.5% of manganese. The Curie point of such alloys lies between about 350° C. and 400° C.

In accordance with the method of our invention, the tetragonal phase is obtained by subjecting the alloy to a thermal treatment at a temperature below about 1000° C., preferably below 825° C., for a period of time long enough to produce the tetragonal phase (see FIGS. 3 and 4). Generally this treatment will be carried out above about 300° C.

We are aware that the magnetic properties of several prior art alloys depend upon the presence of manganese, but such alloys have phases whose structure is quite different than the structure of the tetragonal phase of the present invention. For example, the Heusler alloys, for instance Cu_2MnAl , contain relatively small amounts of manganese, but have a body-centered cubic crystal structure. The U.S. Patent No. 2,797,995 describes materials with a ferromagnetic phase which contains not less than 60% manganese and 2 to 5.5% carbon and one or more of the additional metals, aluminum, indium, zinc and tin, but such materials have a face-centered cubic structure in which the manganese and the additional metal atoms occupy cube-corners and face-center positions, whereas carbon occurs in the body-center position.

In accordance with an embodiment of the invention, we impart magnetic anisotropic properties to the Al—Mn permanent magnets having the tetragonal phase by means of mechanical deformation.

It is known that in general deformation of crystal substances can only take place by sliding along the crystal planes or by twinning. Our investigation of alloys of the above type has indicated that the mechanism of the deformation according to the invention is based mainly on twinning.

In order that our invention may be clearly understood and readily carried into effect, we will now describe the same in more detail with reference to a number of examples according to the invention and, for comparison, a number of examples not utilizing the invention, and with reference to the accompanying drawing in which

FIG. 1 is a graph showing the relationship between intrinsic coercive force and particle size,

FIG. 2 is a photomicrograph with enlargement of 500 \times of an Mn—Al alloy with non-magnetic phase,

FIG. 3 is a photomicrograph with an enlargement of 500 \times of a permanent magnet material according to the invention which has not been subjected to mechanical deformation, and

FIG. 4 is a photomicrograph with an enlargement of 500 \times of a permanent magnet material according to the invention which has been subjected to mechanical deformation.

The invention is particularly advantageous in connection with permanent magnets, particularly of the magnetically anisotropic type, which are formed of a large number of separate particles. These particles, or small permanent magnets, exhibit per se permanent magnetic properties and include the tetragonal phase. These particles preferably have a grain size less than about 100 microns, especially less than about 50 microns, but we have found that satisfactory permanent magnets may be obtained when using particles of larger size, for instance about 1 mm.

The graph shown in FIGURE 1 shows the relationship between intrinsic coercive (H_C) in oersted and particle size in microns. Curve 1 shows this relationship for intermetallic compounds MnBi, whereas curve 2 shows this relationship for particles of an alloy according to the invention with the tetragonal phase and having a composition of about 72% manganese and 28% aluminium (atom ratio Mn:Al of about 5:4). From this graph it is seen that the particles having the new tetragonal phase have a particularly high resistance to demagnetization.

In forming such composite permanent magnets the particles may be molded and then sintered, or they may be mixed with a suitable plastic or compressed with or without a known binder, and the particles oriented by applying a magnetic field either prior to and/or during the compression. If desired the bodies can then be sintered.

As a rule technically-pure raw materials will be utilized for the manufacture of the alloys according to the invention, and thus certain impurities will be introduced. In addition certain impurities may be introduced during the manufacture, for example due to reaction with a crucible. However, the presence of such impurities, as well as the presence of certain additions, such as cobalt, titanium, carbon, silver, and bismuth, do not deleteriously affect the properties of the permanent magnets according to the invention provided they are not present in amounts, for instance, not more than 10%, preferably not more than 5%, which would prevent the formation of the tetragonal crystal structure.

In accordance with the method of the invention the tetragonal phase is formed by subjecting the alloy to a thermal treatment consisting of heating the same in a temperature range below about 1000° C., preferably below 825° C. to about 300° C., preferably about 375° C., for a period of time long enough to produce the tetragonal phase. This thermal treatment may be effected in various ways, for example by heating the alloy in said range at a temperature which is as constant as possible, i.e. isothermally. On the other hand, the thermal treatment may consist of subjecting the alloy to one or more sequences of cooling operations which may or may not be followed by a heating process. The periods of time to which the alloys are subjected to the thermal treatment vary with the temperature or the temperature cycle and will, as a rule, be shorter when the average temperature is higher.

According to one type of thermal treatment according to the invention, the alloy is cooled from a temperature of about 825° C. to a temperature of about 600° C. at an average cooling rate of about 0.5° C. to 100° C. per second, preferably between about 2.0° C. and 30° C. per second. According to another type of thermal treat-

ment the alloy is quenched, for instance in water of different temperatures, compressed air or suitable other fluids such as oil, tetra-chloromethane and the like, from a temperature from about 1000° C. to a temperature below about 825° C., preferably below about 700° C., for instance 300° C., at an average cooling rate of more than 100° C. per second, whereby a non-magnetic hexagonal crystal structure is obtained. The alloy is then heat treated at a temperature between about 825° C., preferably about 700° C., and about 300° C., for a period of time sufficient to produce the desired tetragonal phase.

It is generally advisable to subject the alloys, prior to the thermal treatment necessary to form the tetragonal phase, to a homogenizing treatment consisting of maintaining the alloy at a high temperature for some time, for instance at a temperature of about 1150° C. for about one hour.

The particle-size permanent magnets may be produced by a method according to the invention in which they are obtained by diffusion in the solid state from powders of the metals concerned, and/or powders of preliminary alloys of these metals, and are then subjected to one of the above-mentioned thermal treatments to produce the tetragonal phase. When using binary Mn—Al alloys we use manganese powder and aluminum powder, or one or both of these powders, in conjunction with a preliminary manganese-aluminum alloy, after which one of the above-mentioned thermal treatments is used to produce the tetragonal phase.

The particle-size permanent magnets used to form large-size permanent magnets may be obtained by pulverizing a cast or sintered body, and a thermal treatment to produce the tetragonal phase being applied either to the body or to the pulverized material. For example, a cast or sintered body of an alloy consisting of 68% to 75% manganese, preferably 70.5% to 72.5% manganese, and the remainder essentially aluminium was subjected to one of above-described thermal treatments to obtain the tetragonal phase. The body was then ground to a powder which was then annealed at a temperature between about 200° C. and 600° C. This annealing, although not necessary, has a favorable effect on the magnetic properties.

Instead of pulverizing a body in which the tetragonal phase exists, it is also possible, in accordance with the invention, to pulverize a body which does not contain the tetragonal phase and to produce such phase subsequently. For example, a body of the binary MnAl alloy was cooled from a temperature above 825° C. to a temperature less than 300° C. at an average cooling rate of more than 100° C. per second, and the resulting body was pulverized to a powder, for example by grinding. The resulting powder was then subjected to one of the thermal treatments described above to thereby produce the tetragonal phase. Another method of producing the particles is to maintain a body of the binary MnAl alloy at a temperature below about 825° C. for such a long time that the cubic β -Mn structure is at least partly formed. The resulting body, which is more brittle than if it had been subjected to the cooling at a rate of more than 100° C., is then pulverized into the particles which are subjected to one of the above-mentioned thermal treatments to thereby produce the tetragonal structure. A particularly advantageous method of producing the particle-size permanent magnets is to cool the Mn—Al body at an average cooling rate of less than about 0.5° C. per second from a temperature of about 825° C. to about 600° C. and then pulverizing the same into particles which are subjected to one of the above-mentioned thermal treatments to produce the tetragonal phase. We have found that it is advantageous to carry out the pulverizing at a low temperature, for instance below about 0° C., because at such low temperatures the body is more brittle and thus more readily pulverized.

Permanent magnets according to the invention may have

5

intrinsic coercive force values (H_C) exceeding 1000 oersteds, for instance values as high as about 6000 oersteds have been obtained. In addition, they may have BH_{\max} values more than 0.5×10^6 , particularly more than 1.5×10^6 , values as high as about 1.9×10^6 having been obtained with the magnetically-anisotropic type.

When using mechanical deformation (BH) $_{\max}$ values as high as 3.5×10^6 have been obtained.

Example 1

An alloy consisting by analysis of 68.5% manganese, 30.6% aluminum and the remainder impurities, was subjected to a homogenizing treatment consisting of heating the same at a temperature of 1150°C . for about one hour in a suitable furnace. The alloy was then cooled to room temperature, for instance in air, during which it was, according to the invention, subjected to a thermal treatment to obtain a tetragonal structure, which treatment consisted of cooling at an average cooling rate of about 25°C . per second in the temperature range of 825°C . to 600°C . A body of this alloy was magnetized in a field of about 12,000 oersteds and had a value $4\pi I_r$ of 710 gauss and an intrinsic coercive force (H_C) of 560 oersteds. X-ray powder diagrams of this material showed that a tetragonal phase existed at the side of other phases.

As used herein the term " $4\pi I_{5000}$ " is to be understood to mean $4\pi I$ gauss with a field H of 5,000 oersteds.

Example 2

A body was cast from an alloy consisting by analysis of 69.5% manganese, 30.1% aluminum and the remainder impurities. The body was cooled to room temperature immediately after casting in air. During this cooling it was subjected to a thermal treatment according to the invention by cooling it at an average cooling rate of about 18°C . per second in the temperature range from 825°C . to 600°C . After being magnetized the body was found to have a value $4\pi I_{5000}$ of 2540 gauss, a value $4\pi I_r$ of 1370 gauss and intrinsic coercive force (H_C) of 1060 oersteds. X-ray powder diagrams of this material showed that it contained a larger quantity of the tetragonal phase than did the material of Example 1.

Example 3

An alloy consisting by analysis of 71.8% manganese, 27.5% aluminum and the remainder impurities was subjected to a homogenizing treatment by heating the same at a temperature of 1150°C . for about one hour in a suitable furnace. The alloy was then cooled to room temperature during which cooling it was subjected to a thermal treatment according to the invention by cooling at an average cooling rate of 23°C . per second in a temperature range of 725°C . to 600°C . A body of this alloy was subjected to the magnetizing field of Example 1 and was found to have a value $4\pi I_{5000}$ of 4190 gauss, a value $4\pi I_r$ of 2000 gauss and a value H_C of 580 oersteds. This alloy was found to consist completely of the tetragonal phase and had a manganese-aluminum atom ratio of approximately 5:4.

Example 4

An alloy consisting by analysis of 72.5% manganese, 26.6% aluminum and the remainder impurities was subjected to a homogenizing treatment by heating the same in a furnace at a temperature of 1100°C . for about one hour. The alloy was then cooled to room temperature.

During the cooling the alloy was given a thermal treatment according to the invention by cooling it at an average cooling rate of about 23°C . per second in the temperature range from 825°C . to 600°C . After a body of this alloy was subjected to the magnetizing field of Example 1 it was found to have a value $4\pi I_r$ of 1150 gauss and a value H_C of 910 oersteds. This material was found to contain the tetragonal phase as well as other phases.

6

Alloys consisting of 73.5% and 74.5% manganese respectively and the remainder aluminium treated in the same way as stated above yielded about the same magnetic values. However, it is to be remarked that at increasing values of the percentage of manganese the quantity of the tetragonal phase decreases. In consequence thereof the value of $4\pi I_{5000}$ will be lower and amounts at a percentage of 74.5 manganese about 500 gauss.

Example 5

An alloy of the composition given in Example 3 was subjected to a homogenizing treatment consisting of heating the same in a furnace at a temperature of 1100°C . for about one hour and was then annealed at a temperature of about 830°C . for another hour. The alloy was then subjected to a thermal treatment required to obtain the tetragonal phase by cooling the same from about 830°C . to 600°C . at an average cooling rate of about 20°C . per second. After a body of this alloy was subjected to the magnetizing field of Example 1 it was found to have a value $4\pi I_{5000}$ of 3680 gauss, a value $4\pi I_r$ of 1790 gauss and a value H_C of 600 oersteds. This alloy, similarly to the alloy subjected to the treatment of Example 3, consisted completely of the tetragonal phase.

Example 6

An alloy consisting of 71.3% manganese, 27.7% aluminium and 1% cobalt was subjected to the process described in Example 1. After being magnetized with a field of 10,000 oersteds, a body of this alloy was found to have a value $4\pi I_{5000}$ of 4090 gauss, a value of $4\pi I_r$ of 1720 gauss and a value H_C of 500 oersteds. From X-ray powder diagrams it appeared that this material contained the tetragonal phase.

Example 7

An alloy consisting of 69.8% manganese, 27.2% aluminium and 3% cobalt was treated in the manner described in Example 3. A body of such alloy was subjected to a magnetizing field of 10,000 oersteds and was found to have a value $4\pi I_{5000}$ of 3740 gauss, a value $4\pi I_r$ of 1700 gauss and a value H_C of 530 oersteds. X-ray powder diagrams showed the existence of the tetragonal phase.

Example 8

An alloy consisting of 66.5% manganese, 28.5% aluminium and 5% cobalt was treated in the manner described in Example 3 and after being subjected to a magnetizing field of 10,000 oersteds was found to have a value $4\pi I_{5000}$ of 4020 gauss, a value $4\pi I_r$ of 1480 gauss and a value H_C of 260 oersteds. X-ray powder diagrams showed the presence of the tetragonal phase.

Example 9

An alloy consisting of 71.8% manganese, 28.0% aluminium and 0.2% titanium was subjected to a thermal treatment consisting of cooling the same at an average cooling rate of 15°C . per second in the range of about 850°C . to 600°C . A body of the alloy was then subjected to a magnetizing field of 10,000 oersteds and was found to have a value $4\pi I_{5000}$ of 3490 gauss, a value $4\pi I_r$ of 1790 gauss and a value H_C of 950 oersteds. X-ray powder diagrams showed that this alloy contained the tetragonal phase in addition to other phases.

Example 10

An alloy consisting of 71.8% manganese, 28.0% aluminium and 0.2% titanium was subjected to a thermal treatment consisting of cooling from 900°C . to 600°C . at an average rate of 20°C . per second. After being subjected to magnetizing field of 10,000 oersteds the alloy was found to have a value $4\pi I_{5000}$ of 1695 gauss, a value $4\pi I_r$ of 790 gauss and a value H_C of 1080 oersteds. Similarly to the alloy of Example 9, this alloy was found to contain the tetragonal phase in addition to other phases.

Example 11

An alloy consisting of 71.7% manganese, 27.8% aluminum and 0.5% bismuth was subjected to a homogenizing treatment at 1150° C. for about one hour. The alloy was then cooled, whereby it was subjected, in accordance with the invention, to a thermal treatment consisting of cooling at an average cooling rate of about 25° C. per second in the temperature range from 825° C. to 600° C. A body of this alloy was subjected to a magnetizing field of 10,000 oersteds whereupon it was found to have a value $4\pi I_{5000}$ of 3955 gauss, a value $4\pi I_r$ of 1790 gauss and a value I_{HC} of 555 oersteds. X-ray powder diagrams showed that the major part of the alloy consisted of the tetragonal phase.

Example 12

An alloy consisting of 71.8% manganese, 28.0% aluminum and 0.2 silver was subjected to a homogenizing treatment by being heated for about one hour at a temperature of 1150° C. The alloy was then cooled, whereby it received a thermal treatment consisting of cooling at an average cooling rate of about 20° C. per second in the temperature range from 850° C. to 600° C. A body of the alloy was subjected to a magnetizing field of 10,000 oersteds whereupon measurements showed that it had a value $4\pi I_{5000}$ of 4030 gauss, a value $4\pi I_r$ of 1750 gauss and a value I_{HC} 510 oersteds. The existence of the tetragonal phase in this material was shown by X-ray powder diagrams thereof.

Example 13

An alloy consisting of 71.7% manganese, 27.8% aluminum and 0.5% carbon was subjected to homogenizing treatment consisting of heating the alloy for about one hour at 1150° C. whereupon the alloy was cooled in air. Thereafter the alloy received a thermal treatment, according to the invention consisting of cooling at an average rate of about 13° C. per second in the temperature range from 850° C. to 600° C. The body of the alloy subjected to a magnetizing field of 10,000 oersteds was found to have a value $4\pi I_{5000}$ of 3440 gauss, a value of $4\pi I_r$ of 1670 gauss and a value I_{HC} of 900 oersteds.

Example 14

An alloy consisting of 70.9% manganese, 27.6% aluminum and 1.5% carbon was heated for about one hour at a temperature of about 1100° C. whereupon it was cooled in air. Thereafter the alloy received a thermal treatment necessary for the production of the tetragonal phase by being cooled at an average cooling rate of about 0.5° C. per second in the temperature range of 900° C. to 600° C. A body of such alloy, after being magnetized with a field of 10,000 oersteds, was found to have a value $4\pi I_{5000}$ of 3550 gauss, a value $4\pi I_r$ of 2050 gauss and a value I_{HC} of 860 oersteds.

Example 15

An alloy consisting of 70.2% manganese, 27.3% aluminum and 2.5% carbon was subjected to a homogenizing treatment consisting of heating at about 1100° C. for about one hour. The alloy was then cooled during which it was subjected to a thermal treatment consisting of cooling at an average cooling rate of about 0.25° C. per second from 880° C. to 600° C. A body of the alloy magnetized with a field of 10,000 oersteds was found to have a value $4\pi I_{5000}$ of 3115 gauss, a value $4\pi I_r$ of 1840 gauss and a value I_{HC} of 1010 oersteds.

Example 16

An alloy consisting of 69.8% manganese, 27.2% aluminum 3.0% carbon was homogenized by heating at a temperature of about 1100° C. for about one hour whereupon it was subjected to a thermal treatment consisting, according to the invention of cooling at an average cooling rate of 1° C. per second from about 825° C. A body of the alloy was magnetized with a field of 10,000 oersteds

and was found to have a value $4\pi I_{5000}$ of 2020 gauss, a value $4\pi I_r$ of 1100 gauss and a value I_{HC} of 1020 oersteds. This alloy, as well as the alloys of Examples 13 to 15, were found to contain the tetragonal phase, with or without other phases.

Example 17

An alloy consisting of the composition similar to that of Example 3, i.e. about 72% manganese and 28% aluminum, was heated for about one hour at 1100° C. and was then quenched in tetra-chloromethane at an average cooling rate of about 100° C. per second. It was found that this alloy was not magnetic and did not contain the tetragonal phase. A body of the alloy was then subjected, in accordance with the invention, to an isothermal treatment to produce the tetragonal phase, i.e. was heated for about two hours at a temperature of 400° C. The alloy was then magnetized in a field of 10,000 oersteds and was found to have a value $4\pi I_{8000}$ of 1400 gauss, a value $4\pi I_r$ of 740 gauss and a value I_{HC} of 1160 oersteds.

When the above alloy was treated in the above manner, except that the isothermal treatment at 400° C. continued for six hours instead of two hours, it was found to have a value $4\pi I_{8000}$ of 3300 gauss, $4\pi I_r$ of 1720 gauss and a value I_{HC} of 1320 oersteds.

From X-ray powder diagrams it was found that the above two alloys which were subjected to the isothermal treatments contained the tetragonal phase.

Example 18

An alloy of the composition given in Example 3, i.e. about 72% manganese and 28% aluminum, was heated for about one hour at 1100° C., after which it was quenched in water of 100° C. to room temperature at an average cooling rate of more than 100° C. per second. The material was then given a thermal treatment of about 450° C. for 15 minutes and after being magnetized in a field of 10,000 oersteds was found to have a value $4\pi I_{8000}$ of 3800 gauss, a value $4\pi I_r$ and a value I_{HC} of 1300 oersteds. When the isothermal treatment at 450° C. was carried out for three hours, instead of 15 minutes, the resulting alloy had a value $4\pi I_{8000}$ of 3960 gauss, a value of $4\pi I_r$ of 1920 gauss and a value I_{HC} of 1120 oersteds.

From X-ray powder diagrams it was found that the above two alloys contained the tetragonal phase.

Example 19

An alloy of the composition given in Example 3, i.e. about 72% manganese and 28% aluminum, was quenched to room temperature at an average cooling rate of more than 100° C. per second. The alloy was subjected to a thermal treatment at a temperature of about 500° C. for three minutes. It was found that the alloy had a value $4\pi I_{8000}$ of 4050 gauss, a value $4\pi I_r$ of 2130 gauss and a value I_{HC} of 1280 oersteds.

When the alloy was given a thermal treatment at 500° C. for one and one-half hours, instead of three minutes, it was found that it had a value $4\pi I_{8000}$ of 4160 gauss, a value $4\pi I_r$ of 2090 gauss and a value I_{HC} of 850 oersteds.

From X-ray powder diagrams it was found that the above two alloys contained the tetragonal phase.

Example 20

An alloy consisting of approximately 70% manganese and 30% aluminum was homogenized by subjecting it to a temperature of about 1150° C. for one hour after which it was cooled to room temperature during which it was subjected to the thermal treatment necessary for the formation of the tetragonal phase by being cooled at an average cooling rate of 20° C. per second in the temperature range between 825° C. and 600° C. The resulting body was then pulverized in a crushing mortar whereupon particles of a size less than about 40 microns were sifted out. These particles were then compressed

into a magnet body which was magnetized. It was found that the body had the following magnetic properties:

$4\pi I_{10,000}$ -----	2700 gauss.
$4\pi I_r$ -----	1700 gauss.
I_{H_C} -----	3050 oersteds.
I_{H_C} -----	1250 oersteds.
$(BH)_{max}$ -----	0.62×10^6 gauss oersteds.

Example 21

An alloy consisting of approximately 72% manganese and 28% aluminium was homogenized by being heated for about one hour at a temperature of about 1100° C., after which it was cooled. During the cooling the alloy was given the thermal treatment necessary for the production of the tetragonal phase by being cooled at an average cooling rate of about 23° C. per second in the temperature range between 825° C. and 600° C. The resulting body, which had permanent magnetic properties, i.e. a value I_{H_C} of 615 oersteds, was then pulverized in a crushing mortar after which particles having a grain size less than about 30 microns were sifted out. These particles were then annealed by subjecting the same to a temperature of 300° C. for about 17 hours after which they were compressed into a body while applying a magnetizing field. The resulting permanent magnet body was anisotropic and had the following magnetic properties in the preferential direction: a value $4\pi I_r$ of 3050 gauss, a value I_{H_C} of 5450 oersteds, a value I_{H_C} of 2390 oersteds, and a $(BH)_{max}$ value of 1.85×10^6 gauss-oersteds. The photomicrograph of this material is shown in FIG. 3.

Example 22

The magnet body produced in the manner described in Example 6 was pulverized and particles of a grain size less than about 40 microns were sifted out. These particles which were of course small permanent magnet bodies, were found to have a I_{H_C} of about 2210 oersteds.

It was found that large permanent magnet bodies of any desired shape can be made by compressing the above particles and will have a I_{H_C} value of substantially the amount given above.

Example 23

A body produced in the manner described in Example 7 was pulverized whereupon particles of a grain size less than about 50 microns were sifted out. It was found that material formed of such particles had a I_{H_C} of about 1500 oersteds.

It was found that larger permanent magnet bodies made by compressing the above particles will have I_{H_C} values of the amount given above.

Example 24

A body made by the method described in Example 8 was pulverized whereupon particles of a grain size less than about 50 microns were sifted out. Such particles were found to have a I_{H_C} value of about 1125 oersteds.

It was found that larger permanent magnet bodies made by compressing the above particles will have I_{H_C} values of the amount given above.

Example 25

A body formed of an alloy consisting of about 72% manganese and 28% aluminium was cooled from 900° C. to room temperature at an average cooling rate of about 0.3° C. It was found that this body had a β -Mn structure and was not magnetic. The body was then pulverized in a crushing mortar to particles of a grain size of less than about 40 microns. These particles were then heated at about 900° C. in an atmosphere of a protective gas, after which they were quenched at an average cooling rate greater than 100° C. per second. The so-treated particles were then subjected to a thermal treatment to produce the tetragonal structure by isothermally heating

them at 500° C. for 15 minutes. It was found that particles subjected to the above treatment exhibit the tetragonal phase and were well adapted to be formed into permanent magnet bodies of larger size and of various shapes.

Example 26

An alloy consisting of about 72% manganese and 28% aluminium was homogenized for about one hour at 1000° C. after which it was quenched in water at an average cooling rate of more than 100° C. per second. The resulting alloy was non-magnetic and did not contain the tetragonal phase. A body of this alloy was then ground into a powder from which particles of a grain size less than 40 microns were sifted out. These particles were then subjected to an isothermal treatment at a temperature of 450° C. for 30 minutes in a protective atmosphere. The so-treated particles were found to contain the tetragonal structure and to be suitable for the formation of permanent magnet bodies of larger size and various shapes, such as bodies of plastic material in which the particles are distributed.

Example 27

A body produced by the method described in Example 4 was pulverized and particles of a grain size less than about 150 microns were sifted out, and it was found that these particles had a I_{H_C} of about 1560 oersteds.

Example 28

A body formed of an alloy consisting of 70.2% manganese, 27.3% aluminium and 2.4% carbon was homogenized at a temperature of about 1100° C. for about one hour after which it was cooled to room temperature. During the cooling the body was subjected to a thermal treatment necessary for the formation of the tetragonal phase by being cooled at an average cooling rate of about 0.5° C. per second in the temperature range between 900° C. and 600° C. It was found that the so-treated body, after being magnetized in a field of about 10,000 oersteds, had a I_{H_C} of about 920 oersteds. The body was then pulverized whereupon particles of a grain size less than about 150 microns were sifted out and were found to have an I_{H_C} value of about 1270 oersteds.

Example 29

An alloy consisting of about 72% manganese and 28% aluminium was heated for about one hour at 1100° C. after it was quenched at an average rate of more than 100° C. per second to room temperature. It was found that the so-treated alloy did not exhibit magnetic properties nor did it contain the tetragonal phase. The alloy was then subjected to a thermal treatment to form the tetragonal phase by being isothermally heated at a temperature of about 650° C. for 5 minutes. It was found that the alloy, after being magnetized in a field of about 10,000 oersteds, then had a value $4\pi I_{5000}$ of 4050 gauss, a value $4\pi I_r$ of 1925 gauss, and a value I_{H_C} of 730 oersteds.

According to an embodiment of the invention we mechanically deform Mn—Al alloys which have a tetragonal phase obtained by heat treatment to thereby produce magnetic anisotropic properties therein. More particularly, we subject Mn—Al bodies having the tetragonal crystal structure to a mechanical deformation process, such as rolling, hammering, pressing, extrusion, explosion and the like. The amount of the anisotropy produced by the deformation depends upon the amount of the deformation, and the deformation may be carried out at various temperatures, for instance at room temperature or temperatures above room temperature, provided the tetragonal phase is present at the temperature used.

Magnets which have been deformed according to the invention will have directions of preferred magnetization which are approximately parallel to the direction of the deformation force or forces, or at approximately right

angles thereto. It is possible to produce permanent magnets having various directions of preferred magnetization, for example to make cylindrical or annular anisotropic permanent magnets, for instance by pressing, in which the directions of preferred magnetization are radially symmetric, i.e. extending in all radial directions.

Mn—Al alloys having tetragonal crystal structure generally have a low resistance to mechanical shock. Thus, when using mechanical deformation involving impact, such as hammering, it is desirable to enclose the magnet in a jacket of a suitable deformable material to thereby prevent the body from disintegrating during the deformation.

According to a particular advantageous embodiment of the invention, we first mechanically deform particle-size permanent magnets of Mn—Al alloy having the tetragonal phase to produce directions of preferred magnetization and then form said particles into a large-size magnet while mainly orienting said directions by the application of a magnetic field. These particle magnets may be held together by a suitable binder or may be sintered. We prefer to use a binder when the particles are of a comparatively large size, for example 500 μ . When using particles of smaller size, about 40 μ , we prefer to compress the particles into a body and then sinter the same.

It is also possible to compress the Mn—Al particles having the tetragonal phase into a body, with or without the presence of a magnetic field, and then mechanically deform the resulting body to produce the anisotropy.

We have found that the magnetic properties of magnets which have been made anisotropic by mechanical deformation are improved by re-annealing them at a temperature between about 200° C. and 800° C. Instead of annealing the large-size magnets it is also possible to anneal the deformed particle magnets before they are packed together and formed into the larger-size magnet.

The following examples are illustrative of methods of making permanent magnets in which, according to our invention, the magnetic anisotropy is produced by mechanical deformation.

Example 30

A rod about 3 mms. in diameter, about 70 mms. long and formed of an alloy of about 72% Mn and 28% Al was homogenized at 1150° C. for about an hour. The rod was then cooled at an average rate of about 25° C. per second over a range of 825° C. to 600° C. to thereby produce the tetragonal phase. The rod was jacketed in a tube of 25—20 Cr—Ni steel which was then hammered at room temperature to reduce the cross-sectional area of the rod to about 1 sq. mm. The resulting rod-shaped magnet had the following magnetic properties in the axial direction, which was also the direction of preferred magnetization.

$4\pi I_{5000}$	4400 gauss.
$4\pi I_2$	3700 gauss.
I_{HC}	4000 oersteds.
B_{HC}	2400 oersteds.
$(BH)_{max}$	2.6×10^6 gauss-oersteds.

The photomicrograph of the material made by the method described in this example is shown in FIG. 4.

Example 31

Thirty-six rods 3 mms. in diameter, 100 mms. long and formed of an alloy of 72% Mn and 28% Al were homogenized at 1150° C. for one hour after which they were cooled at an average cooling rate of 25° C. per second over a temperature range of about 825° C. to 600° C. to thereby produce the tetragonal phase. The rods were then arranged side-by-side in a 25—20 Cr—Ni steel tube having an inside diameter of 20 mms. and an outside diameter of 24 mms. The tube was then hammered until its inside diameter was reduced to about 12 mms. The resulting body had the following magnetic

properties in its axial direction which was also a preferred direction of magnetization.

$4\pi I_{2500}$	4150 gauss.
$4\pi I_2$	2800 gauss.
I_{HC}	1960 oersteds.
B_{HC}	1400 oersteds.
$(BH)_{max}$	1.2×10^6 gauss-oersteds.

Example 32

Nine rods 3 mms. in diameter, 100 mms. long and formed of an alloy of about 72% Mn and 28% Al were homogenized at 1150° C. for one hour after which they were cooled at an average cooling rate of about 25° C. per second over a temperature range of 825° C. to 600° C. to thereby produce the tetragonal phase. The rods were then arranged side-by-side within a 25—20 Cr—Ni steel tube having an inside diameter of 10 mms. and an outside diameter of 14 mms. The tube was then hammered at room temperature to reduce its inside diameter to a value at which the cross-sectional area of the deformed material was about 15 sq. mms.

The resulting rod had the following magnetic properties in its axial direction which was also a preferred direction of magnetization.

$4\pi I_2$	3100 gauss.
I_{HC}	2000 oersteds.
B_{HC}	1300 oersteds.
$(BH)_{max}$	1.35×10^6 gauss oersteds.

Example 33

A rod-shaped magnet was produced in the manner described in Example 32 except that the hammering was continued until the cross-sectional area was reduced to about 5 sq. mms. This magnet had the following magnetic properties in the axial direction.

$4\pi I_{5000}$	4070 gauss.
$4\pi I_2$	3470 gauss.
I_{HC}	4320 oersteds.
B_{HC}	2250 oersteds.
$(BH)_{max}$	2.2×10^6 gauss oersteds.

Example 34

A rod-shaped magnet was produced in the manner described in Example 33 after which it was reannealed for about four hours at a temperature of about 300° C. and was found to have the following magnetic properties in the axial direction.

$4\pi I_{5000}$	4370 gauss.
$4\pi I_2$	3620 gauss.
I_{HC}	4100 oersteds.
B_{HC}	2275 oersteds.
$(BH)_{max}$	2.4×10^6 gauss oersteds.

Comparison of Examples 33 and 34 shows the advantageous results obtained by reannealing, and the following Examples 36, 37 and 38 show the improvement in these results due to additional annealing.

Example 35

The rod-shaped magnet produced in the manner described in Example 34 was given an additional annealing at a temperature of about 350° C. for about four hours and then had the following improved magnetic properties in an axial direction.

$4\pi I_{5000}$	4615 gauss.
$4\pi I_2$	3870 gauss.
I_{HC}	3880 oersteds.
B_{HC}	2290 oersteds.
$(BH)_{max}$	2.6×10^6 gauss oersteds.

Example 36

A magnet produced by the method described in Example 35 was given an additional annealing at a temperature of about 400° C. for about four hours. This

13

magnet had the following further improved magnetic properties in the axial direction from which it will be noted that even a $(BH)_{\max}$ of 3.5×10^6 was achieved.

$4\pi I_{5000}$ -----	4860 gauss.
$4\pi I_2$ -----	4280 gauss.
I_{HC} -----	4650 oersteds.
B_{HC} -----	2700 oersteds.
$(BH)_{\max}$ -----	3.5×10^6 gauss oersteds.

Example 37

A portion of a rod-shaped magnet produced in the manner described in Example 33 was annealed after the second hammering operation for about four hours at a temperature of 400°C . and was found to have the following magnetic properties in the axial direction.

$4\pi I_{5000}$ -----	5085 gauss.
$4\pi I_2$ -----	4250 gauss.
I_{HC} -----	3560 oersteds.
B_{HC} -----	2330 oersteds.
$(BH)_{\max}$ -----	3.3×10^6 gauss oersteds.

Example 38

A rod having a cross-sectional area of about 6.2 sq. mms. of an alloy of about 72% Mn and 28% Al which had the tetragonal phase was placed in a Cr—Ni steel tube which was hammered at a temperature of about 500°C . to produce a cross-sectional area of about 5.6 sq. mms. Prior to the hammering the rod-shaped magnet had a value $4\pi I_{8000}$ of about 3810 gauss and an I_{HC} value of about 1210 oersteds, whereas after the hammering the I_{HC} value was increased to about 1620 oersteds. The magnet was subjected to additional hammering at a temperature of 500°C . to reduce the cross-sectional area to about 4.9 sq. mms. The magnet then had the following magnetic properties in its axial direction which at the same time was the direction of preferred magnetization.

$4\pi I_{8000}$ -----	5280 gauss.
$4\pi I_2$ -----	4500 gauss.
I_{HC} -----	1520 oersteds.
B_{HC} -----	1170 oersteds.
$(BH)_{\max}$ -----	1.9×10^6 gauss oersteds.

Example 39

A rod-shaped magnet formed of about 72% Mn and 28% Al and having the tetragonal phase was mechanically deformed by rolling the same in a rolling mill having shaped rollers whereby the rod was made magnetically anisotropic with the direction of preferred magnetization extending in longitudinal or axial direction of the rod. In this direction the magnet had a $4\pi I_{8000}$ of 4200 gauss and an I_{HC} of 1940 oersteds, whereas at right angles to this axial direction it had a value $4\pi I_{8000}$ of 3910 gauss and a value I_{HC} of about 2450 oersteds. Thus, it is seen that magnets having a desired cross-sectional shape may be obtained by rolling which at the same time deforms the body to produce the anisotropy.

Example 40

A rod shaped magnet having a diameter of about 3 mms. a length of about 50 mms. and formed of an alloy of about 72% Mn and 28% Al was subjected to one of the above-described heat treatments in order to produce the tetragonal phase. This magnet was then jacketed in a brass tube having a wall thickness of about 0.5 mm. and, after being placed in a matrix, was subjected to axial compression by applying a compressive force of about 30 tons. As a result of this compression, the magnet became magnetically anisotropic with a direction of preferred magnetization extending at right angles to the direction in which the compressive force had been applied, i.e. in radial directions. This magnet exhibit radial symmetry, i.e. had preferred orientation in all radial directions, which is shown by the following:

14

(a) Magnetic properties in directions parallel to the direction of the compressive force:

$4\pi I_{5000}$ -----	gauss--	3770
I_{HC} -----	oersteds--	1500

(b) Magnetic properties one given direction at right angles to the compressive force:

$4\pi I_{5000}$ -----	gauss--	4220
I_{HC} -----	oersteds--	1400

(c) Magnetic properties in a second given direction at right angles to the compression force:

$4\pi I_{5000}$ -----	gauss--	4250
I_{HC} -----	oersteds--	1380

For a comparison this rod-shaped magnet had the following magnetic properties when it was in the isotropic state:

$4\pi I_{5000}$ -----	gauss--	3700
I_{HC} -----	oersteds--	780

Example 41

A rod was subjected to the same treatment as described in Example 40 above but was compressed axially by means of a greater force, i.e. about 45 tons. The resulting magnet had, in the axial direction, a value $4\pi I_{8000}$ of about 2950 gauss and a value I_{HC} of about 3100 oersteds. In directions at right angles to the axis of the rod (radial symmetry) the rod had a value $4\pi I_{8000}$ of about 3900 gauss and a value I_{HC} of 2260 oersteds.

Example 42

In accordance with one of the methods described above we produced a quantity of particles having grain size of about 1 to 2 mms., formed of an alloy of about 72% Mn and 28% Al and having the tetragonal phase. A 25—20 Cr—Ni steel tube with an inside diameter of about 20 mms. was filled with these grains, and the tube then closed at the ends. The tube was then hammered to reduce the inside diameter to approximately 10 mms. whereby the particles were made magnetically anisotropic. The anisotropic particles were then removed from the tube and compressed into a magnet body while being oriented in a magnetic field. The resulting magnet had the following magnetic properties in the direction of preferred magnetization.

$4\pi I_2$ -----	3600 gauss.
B_{HC} -----	2040 oersteds.
$(BH)_{\max}$ -----	2.8×10^6 gauss oersteds.

It is to be understood that the several specific compositions and methods described herein are examples illustrative of the invention and that obviously many modifications and varieties of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A permanent magnet of an alloy of about 65% to 75% by weight of manganese and the remainder aluminum and less than about 10% by weight of impurities and additions which do not prevent the formation of the tetragonal phase, at least 10% by weight of said alloy being in the tetragonal phase.
2. A permanent magnet of an alloy of about 68% to 75% by weight of manganese and the remainder aluminum and less than about 10% by weight of impurities and additions which do not prevent the formation of the tetragonal phase, at least 10% by weight of said alloy being in the tetragonal phase.
3. A permanent magnet of an alloy of about 70.5% to 72.5% by weight of manganese and the remainder aluminum and less than about 10% by weight of impurities and additions which do not prevent the formation of the

tetragonal phase, at least about 10% by weight of said alloy being in the tetragonal phase.

4. A magnetically-anisotropic permanent magnet of an alloy of about 65% to 75% by weight of manganese and the remainder aluminum and less than about 10% by weight of impurities and additions which do not prevent the formation of the tetragonal phase, at least about 10% by weight of said alloy being in the tetragonal phase, said alloy being mechanically-deformed to make the same magnetically-anisotropic.

5. A magnetically-anisotropic permanent magnet of an alloy of about 70.5% to 72.5% by weight of manganese and the remainder aluminum and less than about 10% by weight of impurities and additions which do not prevent the formation of the tetragonal phase, at least about 10% by weight of said alloy being in the tetragonal phase, said alloy being mechanically-deformed to make the same magnetically-anisotropic.

6. A permanent magnet comprising a plurality of particle-size permanent magnets each consisting of an alloy of about 65% to 75% by weight of manganese and the remainder aluminum and less than about 10% by weight of impurities and additions which do not prevent the formation of the tetragonal phase, at least about 10% by weight of said alloy being in the tetragonal phase.

7. A permanent magnet comprising a plurality of particle-size permanent magnets each consisting of an alloy of about 68% to 75% by weight of manganese and the remainder aluminum and less than about 10% by weight of impurities and additions which do not prevent the formation of the tetragonal phase, at least about 10% by weight of said alloy being in the tetragonal phase.

8. A magnetically-anisotropic permanent magnet comprising a plurality of particle-size permanent magnets each consisting of an alloy of about 65% to 75% by weight of manganese and the remainder aluminum and less than about 10% by weight of impurities and additions which do not prevent the formation of the tetragonal phase, at least about 10% by weight of said alloy being in the tetragonal phase, each of said particle-size magnets being mechanically-deformed with a preferred direction of magnetization and being oriented with said directions extending substantially in the same direction.

9. A magnetically-anisotropic permanent magnet comprising a plurality of particle-size permanent magnets each consisting of an alloy of about 70.5% to 72.5% by weight of manganese and the remainder aluminum and less than about 10% by weight of impurities and additions which do not prevent the formation of the tetragonal phase, at least about 10% by weight of said alloy being in the tetragonal phase, each of said particle-size magnets being mechanically-deformed with a preferred direction of magnetization and being oriented with said directions extending substantially in the same direction.

10. A magnetically-anisotropic permanent magnet comprising a plurality of particle-size permanent magnets each consisting of an alloy of about 65% to 75% by weight of manganese and the remainder aluminum and less than about 10% by weight of impurities and additions which do not prevent the formation of the tetragonal phase, at least about 10% by weight of said alloy being in the tetragonal phase, each of said particle-size

magnets being mechanically-deformed with a preferred direction of magnetization and being oriented with said directions extending substantially in the same direction, and a binder holding said particle-size magnets together.

11. A magnetically-anisotropic permanent magnet comprising a plurality of particle-size permanent magnets each consisting of an alloy of about 65% to 75% by weight of manganese and the remainder aluminum and less than about 10% by weight of impurities and additions which do not prevent the formation of the tetragonal phase, at least about 10% by weight of said alloy being in the tetragonal phase, each of said particle-size magnets being mechanically-deformed with a preferred direction of magnetization and being sintered together with said directions extending substantially in the same direction.

12. A permanent magnet comprising as the essential constituent a phase which contains about 65% to 75% by weight of manganese and the remainder aluminum and less than about 10% by weight of impurities and additions which do not prevent the formation of the tetragonal phase, said phase forming at least 10% by weight of the magnet and exhibiting a tetragonal crystal structure with an axes ratio (c/a) between more than 1 and less than $\sqrt{2}$, the range of existence of said phase being integral with that of the phase occurring in the binary Mn—Al alloys and having an Mn—Al atom ratio of approximately 5:4, said phase, according to X-ray or neutron powder diagrams, may be described as having a tetragonal crystal structure with an axes ratio (c/a) of about 1.3 and occupation of the lattice points 0, 0, 0, and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, with reference of the Mn atoms for one of these lattice points.

13. A magnet as defined in claim 1 in which at least 50% by weight of the alloy is in the tetragonal phase.

14. A magnet as defined in claim 2 in which at least about 50% by weight of the alloy is in the tetragonal phase.

15. A magnet as claimed in claim 3 in which at least about 50% of the alloy is in the tetragonal phase.

16. A magnet as defined in claim 4 in which the manganese is present in an amount between about 68% to 75% by weight and at least 50% by weight of the alloy is in the tetragonal phase.

17. A magnet as defined in claim 5 in which at least 50% of the alloy is in the tetragonal phase.

18. A magnet as defined in claim 7 in which at least about 50% by weight of the alloy is in the tetragonal phase.

References Cited in the file of this patent

UNITED STATES PATENTS

2,196,824	Dahl et al.	Apr. 9, 1940
2,285,406	Bieber	June 9, 1942
2,489,520	Camras et al.	Nov. 29, 1949
2,534,178	Marquaire	Dec. 12, 1950
2,797,995	Morgan	July 2, 1957

OTHER REFERENCES

Journal of Metals, September 1954, pages 983-988, "Ferromagnetism of Certain Manganese-Rich Alloys," by E. R. Morgan.